

Removal of COD and color loads in bleached kraft pulp effluents using ozone

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ABSTRACT: The efficiency of ozone in removing chemical oxygen demand (COD) and color loads in the effluents of a kraft pulp bleach plant was kinetically investigated. Effluents from the following bleaching stages were tested: 1) the first acidic and second alkaline stages of a chlorine-bleached hardwood kraft pulp line, 2) the sulfuric-acid treatment (A) as well as the first acidic and second alkaline stages in a chlorine-dioxide-based elemental-chlorine-free (ECF) bleached hardwood kraft pulp line, and 3) the first acidic and second alkaline stages in a chlorine-dioxide-based ECF bleached softwood kraft pulp line. To obtain the highest ozonation efficiency, the effluents of the A-stage and the first acid stages of the chlorine and ECF bleaching processes for hardwood kraft pulps should be treated with ozone in their original form. However, the alkaline effluents of these bleaching processes should be neutralized before ozonation. Compared to the hardwood kraft pulp effluents, ozone does not effectively remove COD and color loads from either acidic or alkaline effluents, with or without neutralization, of the ECF bleaching process on softwood kraft pulp. It was also found that, irrespective of wood species (hardwood or softwood) or effluent type (acidic or alkaline), ozonation enhances COD removal in subsequent biological treatment.

Application: This paper could help decision-makers in a kraft pulp bleach plant or an integrated pulp and paper mill to decide whether the use of ozone would be beneficial in treating effluents to meet federal and state environmental regulations.

Treatment of effluents in a pulp and paper mill is typically composed of neutralization, primary clarification, biological treatment, secondary clarification, tertiary clarification, and release into receiving water bodies. Considerable amounts of adsorbable organic halogens (AOX), biological oxygen demand (BOD), chemical oxygen demand (COD), dioxins, toxic chlorinated compounds, and color bodies are normally eliminated in these steps. However, novel technologies such as treatments with ozone and fly ash [1, 2] are still sought after to further abate these environmental contaminants.

In a closed bleaching line (i.e., with countercurrent washing), the acidic and alkaline effluents are those discharged from the first and second stages, respectively, of a multi-stage bleach plant. These effluents are the main source of COD and color loads as confirmed by a United States pulp and paper mill [3]. To comply with increasingly severe environmental laws in different countries, chlorine has been almost completely phased out, replaced by either chlorine dioxide or ozone (so-called elemental-chlorine-free or ECF bleaching). It

should be noted that among the components of the effluents released into receiving waters such as seas, rivers, or lakes, AOX, BOD, and COD are often regulated by legislation. Although color bodies are not strictly governed by law in every country, the image of a company would be very much improved if its effluents discharged into receiving waters were as clear as possible.

Because ozone is expensive compared with other pulp bleaching chemicals such as chlorine dioxide and hydrogen peroxide, it has not so far been used to treat effluent from pulp bleach plants. However, with 25 bleach plants around the world now using ozone to produce ECF and totally-chlorine-free (TCF) bleached chemical pulps [4], there is great potential for the use of ozone to treat bleaching effluents.

Approximately 90% of color bodies in the unbleached effluent of a kraft containerboard mill were removed at an ozone dosage of 92 mg L⁻¹ [5]. The biodegradability of an alkaline effluent from a bleached softwood kraft pulp that was previously ozonated at an ozone dosage of 800 mg L⁻¹ was enhanced by an additional COD reduction

of 21% [6]. Ozonation of effluents collected at the outlets of secondary biological processes at two bleached softwood kraft pulp mills and one recycled corrugated board mill removed 36%–76% of COD loads at ozone consumptions of 400–1583 mg L⁻¹ [7]. These studies did not describe the bleaching processes that produced the effluents used. Other workers have found that ozonation of the whole effluents from hardwood and softwood kraft pulps bleached with chlorine and hypochlorite is more effective in removing color than in removing COD load, and that an ozonation stage would improve COD removal in the subsequent algal treatment [8]. Similar positive effects of ozonation on subsequent biological treatment were observed for the ECF-bleaching effluents of eucalyptus kraft pulp [9]. However, none of these studies dealt with the kinetics of bleaching-effluent ozonation. The efficiency of ozonation therefore remains to be studied.

In light of the above, the objectives of this work were: 1) to investigate, through kinetic investigations, the efficiency of the ozonation of bleach effluents from Cl₂-HBKP (bleached hard-

wood kraft pulp), chlorine-dioxide-based ECF-HBKP, and chlorine-dioxide-based ECF-SBKP (SBKP: bleached softwood kraft pulp), as well as the effluent from the sulfuric-acid-treatment (A) stage, in terms of COD and color loads, 2) to compare the ozone treatability of these effluents, and 3) to investigate the effect of ozonation on subsequent biological treatment.

EXPERIMENTAL

Effluent samples

The sequences of the bleaching processes from which the effluent samples were taken, as well as their COD, color loads, and pH values, are given in **Table I**. The samples (40 L) were withdrawn from the corresponding filtrate chests, cooled overnight to room temperature, filtered through double 150-mesh screens to remove residual pulp fibers and suspended matter, stored at 5°C, and used within one week. The wood-chip specifications, digester conditions, and bleaching conditions used to produce the pulps in the ECF-HBKP and Cl₂-HBKP bleach lines were reported elsewhere [10–12]. The A stage is located in front of the ECF-HBKP line. Descriptions of this stage can be found in the literature [13–15].

Ozonation of effluent, kinetic study, and calculation of oxygen used in the ozonation of COD load

Ozonation was carried out in a gas-washing bottle containing 250 ml of effluent at 37°C–40°C using an SGA-01A-PSA4 laboratory PSA ozonizer (Sumitomo Precision Products Co., Ltd.). The ozone gas was produced at a concentration of 8.1% (w/w) from PSA (pressure-swing adsorption) oxygen. The effluents were ozonated in their original or neutralized form (Table I). Neutralization was performed using either dilute sodium hydroxide or sulfuric acid. Excess ozone gas from the reaction was complete-

ly destroyed by absorption into two consecutive washing bottles containing 500 ml each of 10% potassium iodide solution. Ozonated effluent was analyzed for COD, color, and pH.

In the kinetic computation, C_0 represents the concentration of COD or color in the effluent at the initial time of ozonation, and C_t is the corresponding parameter at reaction time t . We calculated values of $\ln [C_0/(C_0 - C_t)]$ and plotted them against ozonation time, and we investigated the kinetics of the removal of COD and color loads in the bleaching effluents.

The amount of oxygen incorporated into COD was estimated as the decrease of COD load by ozonation and converted into a number of oxygen molecules. We estimated the number of ozone molecules consumed from the amount of ozone consumed and the molecular weight of ozone.

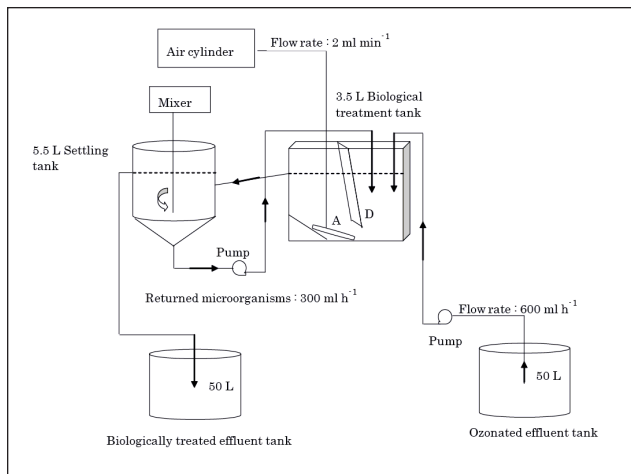
Biological treatment of ozonated effluent

Biological treatment was carried out using large batches (20 L) of ozonated effluents. For these volumes, the ozone input of the 250-ml effluent test described above was used, but the ozonation time was adjusted proportionally to the ratio of the volumes of the two tests. **Figure 1** shows the experimental scheme. The ozonated effluent was neutralized to a pH of approximately 7 and diluted with industrial water to a COD limit of 230 O₂ mg L⁻¹ before being pumped into a reaction tank containing microorganisms taken from the biological treatment basin. This step was performed because the microbial community could not withstand a COD concentration higher than the limiting value. (The “industrial water” was river water that was neutralized, clarified, and filtered through a sand column.) The biological-treatment tank was aerated continuously during each test. The treated liquor was allowed to overflow into a settling tank, and the precipitated microorganisms were pumped back to the reaction tank. Biologically treated liquor

Process ¹⁾	Bleaching sequence ²⁾	Bleaching stage ³⁾	Abbreviation of effluent ²⁾	COD (O ₂ mg L ⁻¹)		Color (C.U.)		pH
				original (O)	neutralized (N)	original (O)	neutralized (N)	
Cl ₂ -HBKP	C/D-Eo-H-D	C/D	ac	1250	1150	955	1735	2.3
		Eo	al	634	587	438	428	7.9
ECF-HBKP	A-D ₀ -Eo-P-D ₁	A	ac	1286	1314	1436	1833	2.1
		D ₀	ac	692	667	193	367	2.2
		Eo	al	1140	1160	3015	2572	10.4
ECF-SBKP	D ₀ -Eo-P-D ₁	D ₀	ac	328	364	307	470	3.1
		Eo	al	560	560	1170	955	11.6

Notes : ¹⁾ Cl₂-HBKP : chlorine bleaching of hardwood kraft pulp; ECF-HBKP : chlorine dioxide-based ECF bleaching of hardwood kraft pulp; ECF-SBKP : chlorine dioxide-based ECF bleaching of softwood kraft pulp.
²⁾ C/D : chlorine with addition of chlorine dioxide; Eo : alkaline extraction reinforced with oxygen, H : hypochlorite; A : sulfuric acid treatment; D : chlorine dioxide; P : hydrogen peroxide
ac : acidic effluent; al : alkaline effluent, O : original effluent; N : neutralized effluent; C.U. : color units.
³⁾ Bleaching stage from which sample of effluent was taken.

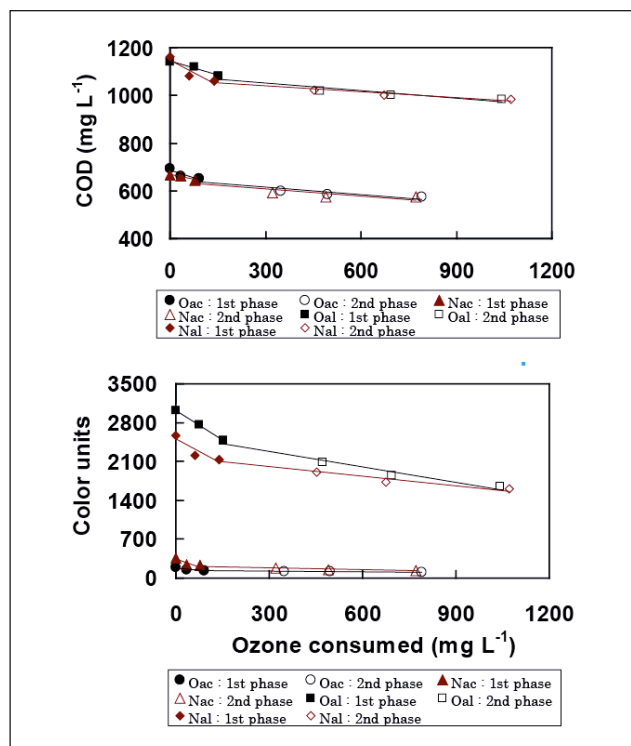
I. Properties of the effluent samples used.



1. Experimental setup for the biological treatment of ozonated bleaching effluents. A: air bubbler, D: divider.

was allowed to overflow into a receiving tank. Each test was run for 48 hours, and samples of the treated liquor were taken at eight-hour intervals and analyzed for COD. The mixed-liquor suspended solids (MLSS) in the biological treatment tank were determined at the start and end of each experiment.

Because the sampling of biologically treated acidic and alkaline hardwood effluents from chlorine and ECF bleaching was accidentally omitted, their color data could not be generated to compare with those from softwood.



2a. COD and color units in ECF-HBKP effluents as functions of ozone consumption. Oac, Nac, Oal, Nal: see footnotes of Table I.

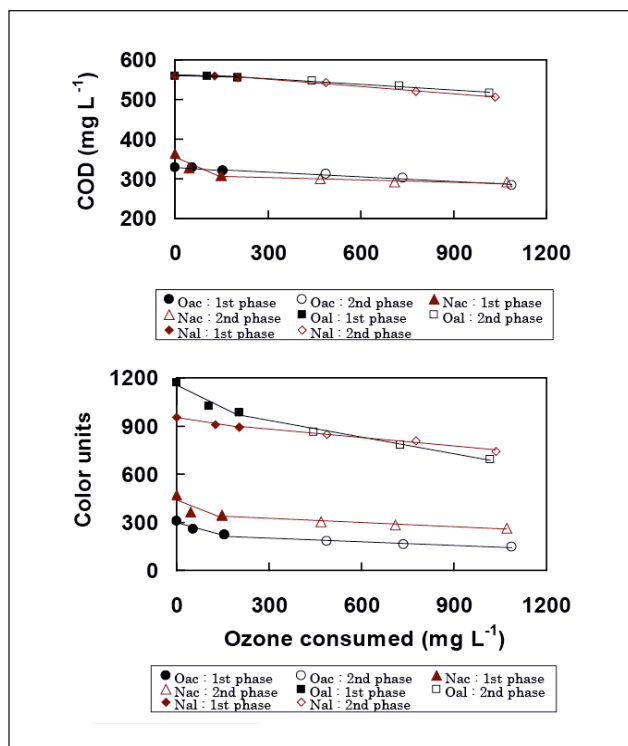
Analytical methods

Effluent color was measured at 465 nm, as indicated in the literature [16]. COD was determined according to the Japanese Industrial Standard (JIS) method K0102:¹⁹⁹⁸, which has been described in detail elsewhere [17]. MLSS was gravitationally determined using 100 ml of the microbial liquors. Reported values of COD, color, MLSS, and pH were the average of two determinations. Initial and residual ozone concentrations were determined by absorption into 10% potassium iodide solutions, acidification with 4N sulfuric acid, and titration against 0.1N sodium thiosulfate.

RESULTS AND DISCUSSION

Effect of neutralization on COD and color loads of raw effluents

Because industrial effluent treatment usually starts with neutralization, the effect of this step on the characteristics of the effluents was examined. Irrespective of bleaching method, neutralization did not have much effect on the COD loads of either acidic or alkaline effluents (Table I). However, neutralization caused a large increase in color bodies (53%–90%) in the original acidic effluents, but reduced marginally (2%–18%) the color loads of the alkaline effluents. This was expected because of the use of sulfuric acid and sodium hydroxide respectively in the neutralization of alkaline and acidic effluents. As for the A-stage acidic effluent, neutralization did not change its initial COD by much, but increased its initial color reading by 28%, a percentage much lower than those



2b. COD and color units in ECF-SBKP effluents as functions of ozone consumption. Oac, Nac, Oal, Nal: see footnotes of Table I.

obtained for acidic effluents generated by bleaching processes. This result indicates a distinct difference between the color substances in the acidic effluents from bleaching processes and from sulfuric acid treatment.

Effect of ozonation on COD reduction

ECF-HBKP and ECF-SBKP are now the most widely produced pulps in the world. Their COD and color loads upon ozonation are shown in **Figs. 2a** and **2b**, respectively. For both pulps, the COD and color loads of the ozonated alkaline effluents were higher than those of the ozonated acidic effluents. Ozonation of bleached kraft pulp effluents followed a two-phase path, of which the first phase was rapid and the second slow. The ozone consumption in each phase varied for different effluents from various bleaching processes. For all the effluents examined, the maximal quantity of molecular oxygen incorporated into COD substances per ozone molecule consumed in the second phase was 0.18, which is rather low, suggesting that ozonation can be ceased at the end of the first phase (**Table II**).

For the acidic effluents of Cl_2 -HBKP and ECF-HBKP, neutralization only degraded the efficacy of COD removal by ozone, because the number of incorporated oxygen molecules in this case was approximately one-half the original number. By contrast, the neutralized alkaline effluents absorbed twice as many oxygen molecules as the corresponding original effluents. Compared to Cl_2 -HBKP, the acidic effluent of ECF-HBKP consumed less ozone and incorporated less oxygen into COD substances, whereas its alkaline effluent digested more ozone, but incorporated less oxygen into COD substances. These results suggest that ozone is suitable to treat COD loads in original acidic and neutralized alkaline effluents of hardwood kraft pulp bleached with either chlorine or ECF processes.

Because almost no oxygen was incorporated into COD substances in the second phase of the ozonated acidic effluent from ECF-SBKP, ozonation can be terminated at the end of the first phase (**Table II**). Furthermore, because the intake of oxygen in both the first and second phases of ozonated alkaline effluent was also almost nil, ozone can be considered unsuitable for reducing COD in ECF-SBKP alkaline effluent.

For both the first and second phases of the ozonation of the A-stage original and neutralized effluents, the number of oxygen molecules incorporated into COD loads per ozone molecule consumed was lower than with the corresponding effluents from Cl_2 -HBKP and ECF-HBKP (**Table II**), suggesting

Effluents	O ₂ molecules incorporated into COD per O ₃ molecules consumed ¹⁾		Color units removed per O ₃ molecules consumed ²⁾		O ₃ consumption for left columns ^{1), 2)} (mg L ⁻¹)	
	1 st phase	2 nd phase	1 st phase	2 nd phase	1 st phase	2 nd phase
Cl ₂ - HBKP						
Oac	1.59		136	12	150	800
Nac	0.76	0.07	198	22	150	800
Oal	1.26		50	0	50	500
Nal	2.01		3	1	50	500
ECF - HBKP						
Oac	0.74	0.16	30	2	100	800
Nac	0.38	0.18	113	6	100	800
Oal	0.59	0.16	169	47	150	1000
Nal	1.18	0.12	167	30	150	1000
ECF - SBKP						
Oac	0.11	0.05	28	5	150	1000
Nac	0.89	0.03	46	6	150	1000
Oal	0.02	0.05	50	16	150	1000
Nal	0.02	0.07	15	8	150	1000
A stage						
Oac	0.19	0.16	90	12	500	1200
Nac	0.79	0.13	123	10	500	1200

Oac, Oal, Nac, Nal : see footnotes of Table 1.

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II. Effect of ozone on the behavior of COD and color loads in different bleaching effluents.

that ozone did not react favorably with 2-furoic acid and 5-formyl-2-furoic acid, the main organic acids in the A-stage effluent. These acids come from the hydrolysis of hexenuronic acid groups by sulfuric acid [18], which is formed during the kraft pulping process [19, 20].

It is clear from the above results that the maximum amount of oxygen incorporated into COD substances was two molecules per ozone molecule consumed, suggesting that ozone may not be a cost-effective agent to reduce COD loads in effluents from kraft pulp bleach plants.

Effect of ozonation on the reduction of color bodies

Similarly to COD ozonation, decolorization by ozone is also a two-phase process, with the removal of color occurring mostly in the first phase (**Figs. 2a** and **2b**, **Table II**). Because the number of initial color bodies in all the neutralized acidic effluents (Cl_2 -HBKP, ECF-HBKP, ECF-SBKP, A-stage) was greater than in the corresponding original effluents, the number of color units removed per ozone molecule consumed was greater in the former group.

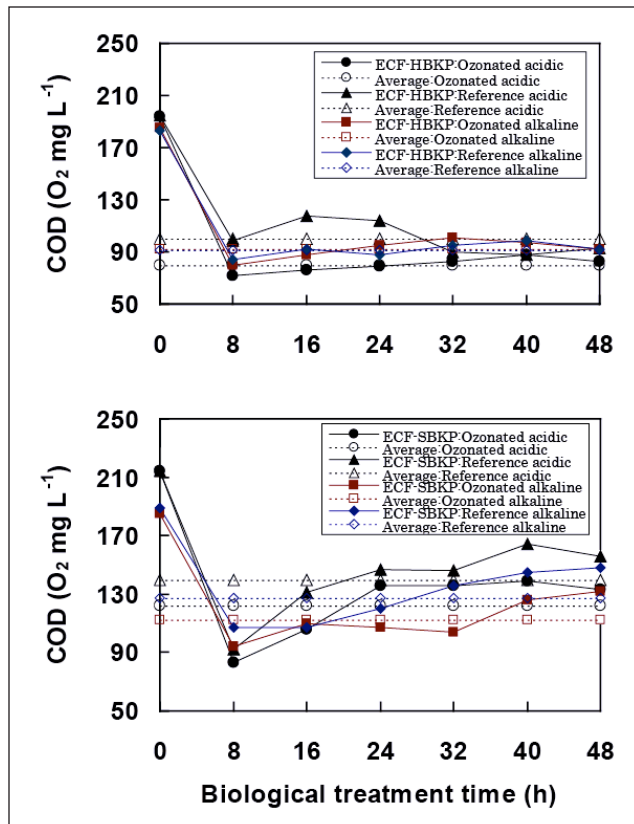
For Cl_2 -HBKP, the decolorization by ozone of both original and neutralized acidic effluents can be terminated at the end of the first phase, because the number of color units removed during the second phase was approximately one-tenth the number removed in the first phase. Although ozone is effective in removing color load from neutralized acidic effluent, the real color value after ozonation of the original acidic effluent was lower than that of the neutralized acidic effluent. Therefore, it is best to treat the acidic effluent with ozone in its original form so that the benefits of reduction of both COD

and color loads can be obtained. On the other hand, ozone was not as effective in decolorizing both original and neutralized alkaline effluents, because the maximal number of color units removed, 50 C.U., was observed only in the first phase of the original alkaline effluent.

Similar to the observations for Cl_2 -HBKP acidic effluent, ozone decolorization of both original and neutralized ECF-HBKP acidic effluent can also be stopped at the end of the first phase. Therefore, it is better to reduce both COD and color loads in the acidic effluent in its original form, because its real color value after ozonation was lower than that of the neutralized effluent, in spite of the lower removal rate in the original effluent. Compared to the original alkaline effluent, the color load of the neutralized effluent was lower and its COD load similar. Therefore, neutralization can be expected to enhance the ozone treatability of ECF-HBKP alkaline effluent. This is probably due to the alkaline-labile color-causing double bonds in these effluents.

Likewise, the decolorization by ozone of both original and neutralized acidic A-stage effluents can also be stopped at the end of the first phase. Furthermore, it is better to reduce the color load in the acidic effluent in its original form, because its real color value after ozonation was lower than that of the neutralized stream.

For ECF-SBKP, the color removal of the acidic effluent was lower compared to the corresponding Cl_2 -HBKP, ECF-HBKP, and A-stage effluents. Neutralization did not help much because the real color-unit value of the original alkaline effluent was lower than that of the neutralized effluent, in spite of its



3. Decrease of COD loads during the biological treatment of ECF-HBKP and ECF-SBKP ozonated and reference effluents. Upper figure: ECF-HBKP; lower figure: ECF-SBKP.

Bleaching method and effluent	Status	Volume used (L)	Ozone consumed (g L ⁻¹)	COD (O ₂ mg L ⁻¹)						MLSS (ppm)		
				before dilution	after dilution	after biological treatment		reduction	0 h	48 hrs	loss	
						average	sigma	r (%)	(%)			(%)
Cl ₂ - HBKP									17.7			
1)Acidic effluent	Ozonated	9	0.66	1080	210	95	14.9	19.2	54.8	4500	3257	27.6
	Reference	8	-----	1275	215	112	19.0	12.4	47.9	4500	3105	31.0
2)Alkaline effluent	Ozonated	14	0.58	967	220	82	9.0	8.7	62.7	4600	3558	22.7
	Reference	10	-----	1189	217	90	6.9		58.5	4600	3305	28.2
ECF - HBKP												
1)Acidic effluent	Ozonated	15	0.62	472	194	80	5.7	8.1	58.8	4300	2800	34.9
	Reference	12	-----	720	195	100	12.8	14.5	48.7	4300	2800	34.9
2)Alkaline effluent	Ozonated	10	0.62	940	185	92	7.4	9.1	50.3	6500	4589	29.4
	Reference	8	-----	1156	183	92	5.2	6.4	49.7	6500	4485	31.0
ECF - SBKP												
1)Acidic effluent	Ozonated	25	0.69	363	214	122	22.7	21	43.0	4500	3100	31.1
	Reference	30	-----	267	214	139	25.7	20.9	35.0	4500	2900	35.6
2)Alkaline effluent	Ozonated	17	0.50	389	185	112	14.2	14.3	39.5	4900	1944	60.3
	Reference	16	-----	489	189	127	18.4	16.4	32.8	4900	1708	65.1
A stage												
1)Acidic effluent	Ozonated	15	0.83	700	210	90	7.4	9.3	57.1	4500	3144	30.1
	Reference	8	-----	1178	225	114	19.5	19.3	49.3	4500	3053	32.2
Note : r is the % repeatability according to the Tappi method T 1206 rp-91.												

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III. Further COD reduction during the biological treatment.

lower ozonation efficiency (Table II). However, the decolorization of the alkaline effluent was comparable to that of Cl_2 -HBKP effluents. Moreover, the neutralization step did not affect the COD and color loads because these values were almost the same for both reference and ozonated alkaline effluents. Therefore, it seems that ozone is not particularly effective in reducing COD and color loads in acidic and alkaline ECF-SBKP effluents.

Effect of ozonation on subsequent biological treatment

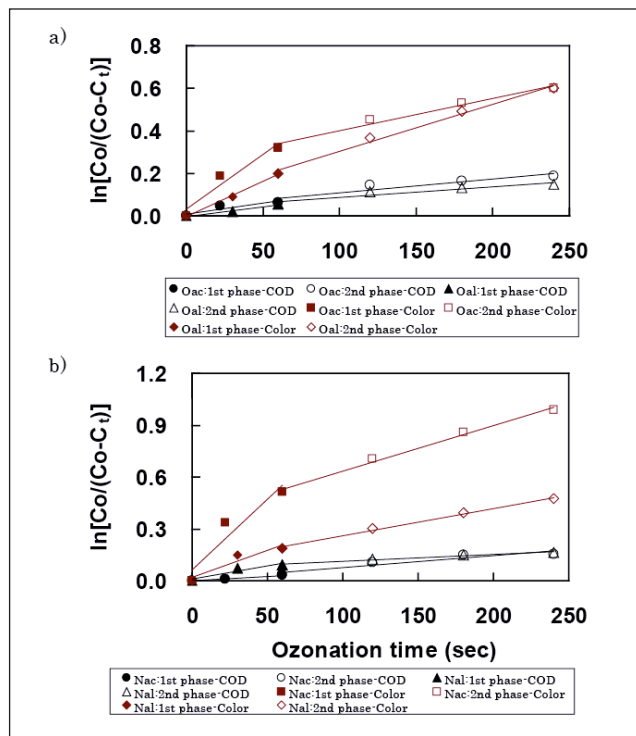
Figure 3 shows that the COD values of both ozonated and reference bleaching effluents were relatively stable during the remaining 40 hours of the biological treatment. This indicates that the activity of the bacterial community took place mainly during the first eight hours of treatment. The COD reduction of ozonated effluents by biological treatment is greater than that of the reference effluents, irrespective of wood species and bleaching method. Whereas the average improvement for ozonated acidic effluents, including A-stage effluents, is 8.2 percentage points, that for ozonated alkaline effluents is 3.8 percentage points, which indicates the lesser degree of biological degradation of the latter. The final average COD values for the biologically treated softwood effluents are higher than those for hardwood effluents, suggesting that, with or without ozonation, biological treatment is not effective in removing COD load from softwood effluents. Another characteristic of the ozonated effluents is that their MLSS losses during biological treatment were less than those of reference effluents, suggesting that substances toxic to the bacterial community were partially removed during the ozonation process (Table III).

The limited data available show that for softwood kraft effluents, the color bodies in the ozonated effluents are harder to biodegrade than those in reference effluents, 19.3% vs. 48.7% for acidic effluents and 59.9% vs. 69.8% for alkaline effluents. Moreover, the degree of biological decolorization of the acidic effluent is less than that of the alkaline effluent. It seems that COD and color loads in ECF-SBKP effluents exhibit opposite trends in biological treatment.

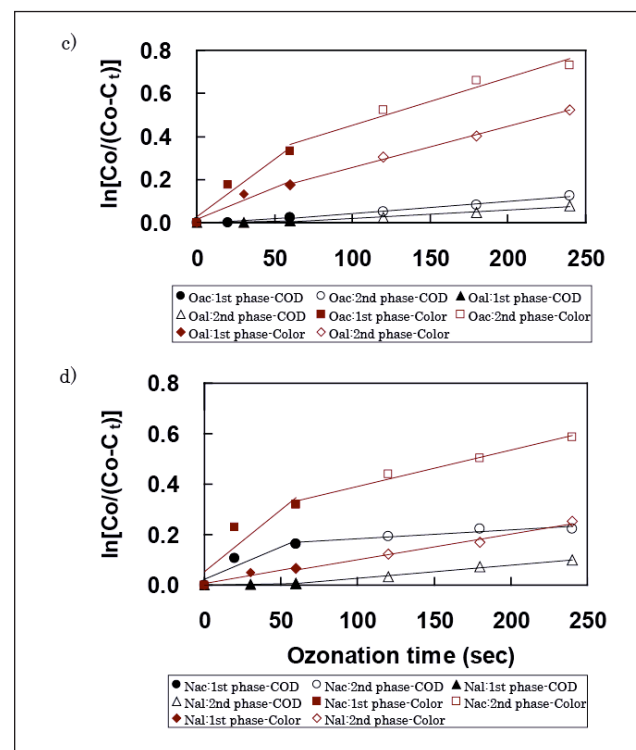
Assuming that: 1) all the spent ozone gas is completely recovered to be used to ozonate the effluents of a bleach plant containing an acid-treatment stage and producing both hardwood and softwood kraft pulps, 2) the highest ozone consumption is 500 mg L^{-1} (Table II), and 3) the effluent-treatment facilities consist of neutralization, clarification, ozonation, neutralization, clarification, and biological treatment, it is estimated that the ozone charge would be in the range of 4–5 kg ADMT⁻¹ (ADMT: air-dry metric ton) and that the final COD load would be approximately 18% lower than that of the effluents without ozonation.

Kinetics of ozonation of bleach effluents

Figures 4a (ECF-HBKP) and **4b** (ECF-SBKP) show that the ozonation of bleaching effluents follows first-order kinetics and that there are two distinct phases with different slopes. In gen-



4a. Plot of $\ln[C_0 / (C_0 - C_t)]$ against ozonation time for different ECF-HBKP bleaching effluents. C_0 : COD or color units at the start of ozonation; C_t : the corresponding parameter at reaction time t . Upper figure: original effluents; lower figure: neutralized effluents.



4b. Plot of $\ln[C_0 / (C_0 - C_t)]$ against ozonation time for different ECF-SBKP bleaching effluents. C_0 : COD or color units at the start of ozonation; C_t : the corresponding parameter at reaction time t . Upper figure: original effluents; lower figure: neutralized effluents.

Bleaching method and effluent		Rate constant (sec ⁻¹ 10 ⁻⁴)	
		1st phase	2nd phase
Cl ₂ -HBKP			
COD	Oac	12	
	Nac	10	2
	Oal	25	
	Nal	39	
Color	Oac	71	34
	Nac	70	45
	Oal	79	
	Nal	3	1
ECF-HBKP			
COD	Oac	10	7
	Nac	5	7
	Oal	9	5
	Nal	15	4
Color	Oac	51	15
	Nac	81	26
	Oal	33	22
	Nal	31	16
ECF-SBKP			
COD	Oac	4	5
	Nac	25	4
	Oal	1	4
	Nal	1	5
Color	Oac	53	22
	Nac	49	14
	Oal	29	19
	Nal	11	10
A stage			
COD	Oac	7	6
	Nac	21	11
Color	Oac	107	30
	Nac	94	48

Oac, Oal, Nac, Nal : see footnotes of Table 1.

IV. Rate constants of the removal of COD and color loads in bleaching effluents by ozone.

eral, the rate constant of the first phase is higher than that of the second phase. Thus, even from the kinetic standpoint, effluent ozonation can be terminated at the end of the first phase.

However, for some cases, such as neutralized alkaline Cl₂-HBKP effluent, the neutralized acidic ECF-HBKP effluent, the original acidic and alkaline effluents as well as the neutralized alkaline effluent from ECF-SBKP, and the original acidic A-stage effluent, both the first and second phases of the ozonation of COD or color loads can be grouped into one phase because the rate constants of both phases are similar and small (**Table IV**). Therefore, ozone may not be a suitable oxidant for these effluents.

Both the incorporation of oxygen molecules into COD substances (Table II) and the high ozonation rate constants (Table IV) of the first phase suggest that ozonation of bleached kraft pulp effluents is not a complete mineralization to carbon dioxide and water, but rather a partial oxidation process in which oxygen is incorporated into the carbonaceous sites

within the reaction product molecules, which are usually resistant to further ozonation [21]. Furthermore, because all COD and color substances in the effluents examined were consistently removed, albeit only slightly for some effluents, from the start of the ozonation and without any initial lag phase, it can be concluded that ozonation of bleaching effluents is not a free-radical-induced chemical-oxidation process. Usually a lag phase is observed in free-radical reactions because a certain concentration of radicals is required to initiate and promote the oxidation reaction [22].

CONCLUSIONS

The estimates of the number of oxygen molecules incorporated into COD load per ozone molecule consumed suggest that, to obtain the best ozonation efficiency, the acidic effluents from the Cl₂-HBKP, ECF-HBKP, and A stages should be treated in their original form. However, the alkaline effluents of Cl₂-HBKP and ECF-HBKP stages should be neutralized before ozonation. It seems that ozone is not particularly effective in removing COD and color loads from either acidic or alkaline ECF-SBKP effluents, with or without neutralization, compared to hardwood kraft pulp effluents.

Irrespective of wood species (hardwood or softwood) or effluent type (acidic or alkaline), COD removal in the biological treatment of previously ozonated effluents is enhanced, suggesting that toxic substances in the effluents may be partially removed during ozonation.

The maximum of two oxygen molecules incorporated into COD substances per ozone molecule consumed and the small rate constants of the ozonation reaction suggest that ozonation of kraft pulp bleaching effluents is a partial and not a

INSIGHTS FROM THE AUTHOR

This study is an attempt to increase the capacity of effluent treatment facilities and thereby make it possible to increase pulp production. This study follows on a previous one which examined the capability of bottom ashes from boilers to remove COD from kraft pulp bleach effluent. It was found that ozone was not as efficient as expected in reducing COD when investigated from the kinetic viewpoint.

Mill personnel may find this work useful when considering ways to increase the capacity of effluent treatment facilities. We plan to now focus our work on modifying the bleaching process in decreasing COD in bleach effluent.



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radical-induced oxidation process. Therefore, ozone may not be a suitable oxidant for reducing the COD and color loads of bleached kraft pulp effluents. **TJ**

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