INVESTIGATION INTO
COMBINED OZONE AND BIOLOGICAL TREATMENT
OF PULP BLEACHING EFFLUENT

A thesis submitted in partial fulfillment of the requirements
for the degree of Master of Technology in Environmental Engineering
at Massey University

Yanming Zhang
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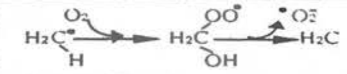
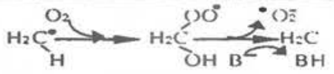
ERRATA SHEET

PART I. EMENDMENTS.

Page	Para	Line	Current Reads	Should be changed to
2	1	7	Donald and McIntosh.,1997	Dell et al., 1997
2	4	7		
3	1	6		
6	Table 2.1	Foot-note	Adsorbalble	Absorbable
8	2, Fig.2.2	3	Johannes and Jurg, 1985	Staehelin and Hoigné, 1985
10	Fig. 2.3			
	Fig. 2.4			
	Fig.2.3			
11	1	5	Johannes and Jurg, 1985	Staehelin and Hoigné, 1985
11	1	5	Hoigne and Bader, 1975	Hoigné and Bader, 1975 (see below).
11	2	7	Kahnmark & Unwin, 1998	Kahmark & Unwin, 1998
12	2	4	oznone	ozone
18	Table 2.3	4	1.5-3 (L/day); 0.037-0.073	3-6 (L/day); 0.073-0.146
21	1	11	removal	the removal of
22	1	8	The AOX total removal was 25%....	The AOX total removal was 49%...
44	Fig. 4.1.1		%color removal at 20 minutes in Fig.4.1.1 is 3% .	% color removal at 20 minutes in Fig.4.1.1 is 16.43%.
45	3	3	...although there was no initial period (20 minutes)	Delete this phrase (see TABLE A2.1 for justification).
55	2	5	The maximum error ... is ± 10%.	The maximum error ......is ± 6%.
69	1	5	removals	removal
69	1	6	......was similar. That was....	....was similar, that was...
70		Table 4.3.2	Ozonation only effluent 796	Ozonation only effluent 769
82	5	4	is	are
91		15	Donald, P.D. and McInstonsh	Dell, P., Donald,R. and McIntosh
91		9	Waste Pollution Control Federation Journal	Journal Water Pollution Control Federation
92		18	Johannes, S & Jurg, H. (1985)	Staehelin.J. and Hoigné, J. (1985)
92		21	Jokeia, J.K. and Salonen, M.S. (1992)	Jokela, J.K. and Salkinoja-Salonen, M. (1992).
92		24	Kahnmark, K.A. & Unwin, J.P.(1997)	Kahmark, K.A. and Unwin, J.P. (1997)
93		1	Kahnmark, K.A. & Unwin, J.P.(1998)	Kahmark, K.A. and Unwin, J.P.(1998)
93		5	Environmental Technology	Environmental Science and Technology
93		14	Möbius, C. & Tolle, M.C.	Möbius,C. and Cordes-Tolle, M.

Emendment for Fig.A1.2: The horizontal scale in Fig.A1.2 is incorrectly represented. It should be as follows:

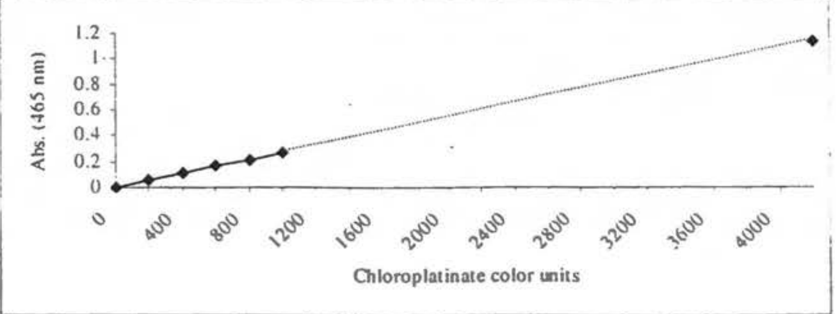


Fig.A1.2
Chloroplatinate
color units standard
curve for
determination of
effluent color.

PART 2. ADDITIONAL RESPONSES TO EXAMINERS' QUESTIONS AND COMMENTS.

Page	Section	Additional Statements
6	Table 2.1 footnote	It was fond that the values for total DC and Eo chlorophenols given in the reference (McFarlane *et al.*, 1991) may be incorrectly calculated. Therefore, the values presented in the Table 2.1 are simple arithmetic sums of components.
25	3.1	The composition of a mixed effluent was chosen in the proportion of 4:1 (Eo:DC) because this gave a mixture with a pH value of approximately 9 and under these alkaline conditions the ozone degradation of lignin was enhanced (see Section 4.1.2. Page 49. para 2. line 1-4).
25	3.1	Prior to ozone treatment, there were no pH-adjustments for the raw bleaching effluents. After ozone treatment, both the ozonated and the non-ozonated raw bleaching effluents were standardized to pH 7.0 for biological treatment (see Section 3.2.1. Page 28. para 4).
30	3.2.2	The anaerobic-aerobic lagoon was evaluated under no pH-control condition and no nutrients were added. While the aerated lagoon was operated under pH control condition and nutrients were added (see page 36. para 2).
53	4.1.3	Ozone treatment was conducted with no pH-adjustment. Both ozonated and non-ozonated raw bleaching effluents were alkaline. However, the subsequent biological treatment required a neutral effluent. Furthermore, the effluent's color is pH dependent. Thus, it is necessary to neutralize the bleaching effluent to pH 7.0 for subsequent biological treatment and standardise the effluent experimental condition (see Page 53. Para 3). The values for pH-adjusted samples are presented in TABLE 4.1.3.
57	4.2.1	In TABLE 4.2.1, the influent's color values for OEo_1 (157 CP.U) and $OMix_1$ (179 CP.U) are transferred from TABLE 4.1.3 and these values are different from those (93 CP.U for OEo_1 and 96 CP.U for $OMix_1$) obtained at the end of ozone treatments (see TABLE A2.1 and A2.3). The differences have not been explained in the thesis because no immediate reasons were identified. However, the ozonated effluent does remain unstable for a period of 12 hours after ozonation. This may explain some of the seeming variations in the ozonated effluent's color. Color values for non-ozonated Eo_1 and Mix_1 effluent given in TABLE 3.1 are raw effluent with no pH adjustment and these given in TABLE 4.1.3 are sample values with pH-adjustment. The color values for Eo_1 and Mix_1 displayed in TABLE 4.2.1 are transferred from TABLE 4.1.3. Thus, the differences of non-ozonated effluent's color (Eo_1 and Mix_1) between TABLE 3.1 and 4.2.1 are due to pH adjustment. Similar explanation can be offered for data in Table 4.2.3.
65	4.2.4	The anaerobic-aerobic lagoon functioned under no-pH control and no nutrient additions. It achieved higher BOD_5 removal and similar COD removal (see Page 65, TABLE 4.2.4) than the aerated lagoon system. This demonstrated that the anaerobic-aerobic lagoon was very effective and favorable for treatment of pulp bleaching effluent.
92		Hoigné, J. and Bader, H. (1975) Ozonation of Water: Role of Hydroxyl Radicals as Oxidizing Intermediates. Science, Vol.190. Pp.782-783.
97	TABLE A1.3	There is no obvious reason for the change in OEo_2 effluent's color from 795 to 914 CP.U within 7 days. A possible explanation is that the acid added for pH control was affecting the analysis of the 39 th and subsequent days (possible error in the strength of acid added).

ABSTRACT

An investigation into combined ozone and biological treatment of pulp bleaching plant effluent was conducted. Treatment efficiencies were evaluated in terms of color, COD and BOD_5 removal. The effectiveness of ozone oxidation and subsequent biological treatment of pulp bleaching effluent were examined separately and the overall color, COD and BOD_5 removal through the two-stage combined treatment were determined.

Ozone pretreatment was carried out in a vertical column batch reactor under a constant ozone flowrate 5 L/min condition. Changes of color, COD and BOD_5 in pulp bleaching effluent during ozonation process were recorded. The subsequent biological treatment was investigated in two lagoon systems. One was an anaerobic-aerobic lagoon system and the other was an aerated lagoon system. The separate contribution made by each zone of the anaerobic-aerobic lagoon to the overall effluent treatment was evaluated. To assess the effect of the ozone pretreatment on the followed biological treatment, the ozonated bleaching effluent and the non-ozonated raw bleaching effluent were parallelly operated in identical biological systems. Comparison of results obtained from treatment of the ozonated and non-ozonated effluent identified the improvement of a two-stage combined treatment over a biological treatment alone.

Results obtained from ozone treatment of two batches of Eo and mixed (Eo and DC) bleaching effluent indicate that ozone was most effective in color removal (up to 74% measured at pH 7), followed by BOD_5 increase (up to 39%) and lesser effective in COD removal (up to 19% only). A color removal formula was developed to model color removal kinetics. The mathematical formula succinctly describes the color removal performance and offers an alternative option to study color removal kinetics during ozone treatment of pulp bleaching effluent.

Because of the ozone pretreatment, the effectiveness of the subsequent biological treatment for COD and BOD_5 removal was improved. However, when the followed biological system included an anaerobic zone, a considerable color increase (98%) in the ozonated effluent was observed during the treatment. If the followed biological treatment was carried out under an aerobic condition only, the color increase in the ozonated effluent was very small (21%). This observation suggests that biological treatment of ozonated effluent should avoid involving an anaerobic condition, otherwise the color removal achieved during the ozone treatment would be lost in the subsequent biological stage. It would obviously be economically infeasible.

The combined ozone oxidation and biological treatment regime improved the overall color removal (34-68%), COD removal (45-51%) and BOD_5 removal (82-95%) over a single stage biological treatment which only achieved up to 17% color removal, 30-35% COD removal and 64-92% BOD_5 removal. For removal of COD and BOD_5, the combined ozone with anaerobic-aerobic lagoon treatment outperformed marginally the combined ozone with aerated lagoon system. However, for color removal, the efficiency of the combined ozone with aerated lagoon treatment was much higher (68%) than that of the combined ozone with anaerobic-aerobic lagoon treatment (43%). The anaerobic zone of the anaerobic-aerobic lagoon was identified as the main sources of color increase and limited the overall color removal for such a combined treatment. In summary, the combined ozone with aerated lagoon system was the better option for treatment of pulp bleaching plant effluent.

ACKNOWLEDGMENTS

I would like to take this opportunity to thank the following people for their help and support in completing my research study:

My supervisor Dr. Graham Manderson for his valuable guidance, patience, assistance and encouragement, it was greatly appreciated.

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Mr. Andy Shilton for his guidance in using the BOD Trak$^{\text{TM}}$ instrument for BOD testing.

Mr. Bart Teekman for the arrangement delivering samples from Tasman Pulp and Paper Company, Wawerau.

Thanks are also expressed to the technical staff in the Microbiology Laboratory, Engineering Laboratory and Environmental Laboratory, namely John Sykes, Ann-Marie Jackson, Michael Sahayam, Don Mclean, Bruce Collins and John Alger for their variety of valuable help with experimental materials and general support.

I would like to thank my husband Ben Cheng for his encouragement and understanding through my research study.

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ABBREVIATIONS AND NOMENCLATURE

AOX:	Adsorbable organic halogen, mg/l.
BOD_5:	Biochemical oxygen demand, mg/l.
C_t:	% color removal at time t during ozone treatment.
C_u:	Ultimate color removal during ozone treatment.
COD:	Chemical oxygen demand, mg/l.
$COD_{Influent}$:	COD value in influent, mg/l.
DC:	Bleaching effluent arising from a chlorine dioxide followed by chlorine bleaching process.
DO:	Dissolved oxygen contained in a liquor during a biological treatment, mg/l.
Eo:	Bleaching effluent arising from an extraction by alkali bleaching stage fortified with oxygen.
F:	Influent flowrate during a biological treatment, L/d.
Fo_3:	O_3 flowrate during ozone treatment, g/hour.
k:	Color removal rate constant, 1/t.
Lc:	COD loading in influent during a biological treatment, kg/m^3d.
n:	Replicate sample number for determination of confidence limits.
R_t:	Retention time during a biological treatment, day.
SD:	Standard deviation for determination of confidence limits.
t:	Ozone treatment time, hours.
t_s:	Student t value for determination of confidence limits.
TOC:	Total organic carbon, mg/l.
V:	treated effluent volume, L.
x_1:	Color, COD and BOD_5 value for influent during a treatment.
x_2:	Color, COD and BOD_5 value for effluent during a treatment.
$\bar{X}$:	Color, COD and BOD_5 removal mean value.

CHAPTER ONE

INTRODUCTION

1.1 Background

Throughout the world pulp production from wood exceeds1,000,000 metric ton per day. From these operations the average effluent generation is 200 m^3/metric ton of pulp (Leuenberger *et al.*, 1985) and the adsorbable organic halogen (AOX) discharge is 2.2 kg/metric ton of bleached pulp (Jokela and Salonen, 1992; Nakamura *et al.*, 1997). In the early 1990s, a variety of harmful responses were reported in fish populations living downstream of bleached kraft pulp mills and included delayed sexual maturity, smaller gonads, changes in fecundity and a depression in secondary sexual characteristics (Kringstad *et al.*, 1983; Munkittrick *et al.*, 1997). Due to heightened public concern about the environmental impact, increasingly stringent government regulations concerning pulp and paper mill effluents are being introduced. Most have focused on chlorinated organic compounds formed during the pulp bleaching process. To meet environmental regulations, two strategies can be adopted for pollutant reduction. These are firstly, internal process modifications such as oxygen delignification and chlorine dioxide substitution and secondly, external effluent treatment such as chemical oxidation, biological system and the combinations of the two processes. Studies continue towards reducing pollutants in the mill effluent as much as possible to enhance the final effluent quality (Onysko, 1993; Hostachy *et al.*, 1997).

New Zealand's roundwood production is 9.1 million m^3/year. The forest resource suitable for processing is predicted to increase to an average of 14 million m^3/year between 1995-2000 and subsequently average 20 million m^3/year between 2000-2005. These developments will be required to take place in a sustainable and environmentally acceptable manner. Elsewhere, the concern over the environmental effect of chlorinated organic compounds has resulted in the development of environmental legislation in Australia. In New Zealand, comprehensive resource management legislation has been enacted (Gifford & McFarlane, 1991) in an attempt to manage the environment in a sustainable manner.

The total annual output for wood pulp products of New Zealand was 1,879,000 tonnes in 1997. There are eight pulp and paper mills in New Zealand. Among them, two are kraft pulp mills. The prime environmental concerns associated with these kraft mills are the receiving waters of the effluents and can be framed in terms of dissolved oxygen, color, toxicity and nutrients. The Tarawera River, which receives the effluent discharged from Tasman Pulp & Paper Co Ltd and CHH Tissue, Kawerau, was investigated by the Bay of Plenty (B.O.P) Regional Council (Donald and McIntosh, 1997).

Major environmental issues concerning the impact of mill effluent on the Tarawera River are dissolved oxygen, color and toxic substances. Parameters that were investigated for the Tarawera River are as follows:

- Dissolved oxygen

Environment B•O•P (Bay of Plenty Regional Council) has adopted the cold water dissolved oxygen standards and imposes limits on the 30-day mean minimum (6.5 g/m^3), 7-day mean-minimum (5 g/m^3) and the absolute minimum oxygen concentration (4.5 g/m^3). The dissolved oxygen concentrations in the lower Tarawera River have frequently fallen below the 7-day mean minimum standard of 5 g/m^3 due to high loads of mill effluent discharged.

- Color

The discharged kraft effluent from the Tasman Pulp and Paper Mill degrades the appearance and visual appeal of the river. A kraft mill effluent is intensely light absorbing and weakly light scattering. The Resource Management Act restricts discharges which cause a conspicuous change in color or visual clarity. Suitable technology to reduce economically pulp mill effluent color is not yet available and discharging large amounts of color will become an illegal activity after the Tarawera River Regional Plan becomes operative (Donald and McIntosh, 1997).

- Toxicity

Although testing demonstrates that there is no apparent chronic and acute toxicity resulting from the mixture of the mill effluent with rivers and streams, analysis of the river biological communities has revealed adverse effects of mill effluents on the Tarawera River ecosystems. The decreased light penetration, additional suspended solids and organic enrichment as well as oxygen depletion are more harmful to the aquatic life than direct toxicity (Donald and McIntosh, 1997).

Innovative treatment processes for reducing pollutant loading in pulp and paper mill effluents have been studied widely. Since mill effluents contain complex organic substances that are influenced by a variety of factors such as raw material, pulping technology, bleaching agents and process designs, effective treatment systems need to be examined case by case to satisfy a particular mill's effluent pollution control strategy.

1.2 Objectives

An effluent arising from a kraft pulp bleaching plant of New Zealand was studied in this paper. A combined ozone pretreatment with a subsequent biological process system was employed to reduce pollutants of the pulp bleaching effluent. The treatment efficiency was identified in terms of color, COD and BOD_5 removal. The objectives of the research described in this thesis were as follows:

1. To investigate changes of color, COD and BOD_5 in a pulp bleaching effluents (Eo[1] & a mixture of Eo and DC[2]) during an ozonation process and to identify whether these changes improved the effluent's characteristics.
2. To establish a mathematical modelling equation to simulate color removal kinetics occurring during ozone treatment of the pulp bleaching effluent.
3. To examine the effect of ozone pretreatment on two subsequent biological effluent treatments including an anaerobic-aerated lagoon system and an aerated lagoon system. The separate contributions made by the anaerobic zone and the aerobic zone of a lagoon to the treatment of the effluent were evaluated.

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[1] Effluent arising from an extraction by alkali bleaching stage fortified with oxygen.

[2] Effluent arising from a chlorine dioxide followed by chlorine bleaching process.

4. To determine the overall color, COD and BOD_5 removal efficiencies using combined ozone with biological process treatment. The most appropriate regime for bleaching effluent treatment was identified through quantitative comparison of results obtained from these processes.

This study was focusing on treatment of New Zealand pulp bleaching plant effluent. The published data on ozone oxidation, biological treatment and ozone-biological combined treatment was a valuable information for design of the experimental process and determination of analysis methodology used in the paper. The ozone treatment was conducted in a vertical column batch reactor and the biological treatment was carried out in a model lagoon system. Efficiency in each treatment stage was examined and the overall color, COD and BOD_5 removal through the combined two-stage treatment was determined.

CHAPTER TWO

LITERATURE REVIEW

Wood pulps are the basic materials for the production of paper. During the wood pulping process, cellulose fibers are separated from other wood components by chemically solubilizing and modifying lignin. Subsequent cellulose fiber bleaching is required to remove condensed lignin compounds from the pulp to meet brightness requirements. Since the principle chemical agent for pulp bleaching is chlorine, the bleaching effluent liberates and forms various chlorinated organic compounds such as resin acids, chlorolignins and chlorophenolic compounds. These substances give a dark coloration to the wastewater and are environmentally persistent and bioaccumulative (Bryant *et al.*, 1987; Onysko, 1993). A variety of mill effluent treatment processes have been developed for the removal of organic compounds from the effluent. Biological treatment is the most common process used for removing readily biodegradable organic materials. But recalcitrant chlorinated organic compounds formed during bleaching processes are usually not removed by the biological process. Chemical oxidation such as ozonation of the wastewaters has been reported as an effective approach for its decolorisation and for changing the structure of these chlorinated organic compounds that are formed in the mill effluent. The combination of ozonation and biological treatment offers an innovative alternative for reducing effluent's color and thus enhancement of final effluent's characteristics (Rodriguez *et al.*, 1998).

2.1 Pulp and Paper Mill Effluent Characteristics

Wood is composed of three main components: lignin, cellulose and hemicellulose (Biermann, 1996). The goal of chemical pulping processes is to separate wood into its constituent fibers (including some of the hemicellulose) by dissolving the lignin from the wood. The pulping process produces a relatively dark-colored pulp that requires bleaching treatment which is achieved through a series of stages. In the first stage, the pulp is dispersed in water and reacts with chlorine (C) and chlorine dioxide (D) that is effective in breaking down lignin. The second stage of the bleaching process is a caustic extraction (E). The caustic solution (NaOH) dissolves most of the modified soluble lignin. In the third stage, further chlorine dioxide is added to the pulp. Any subsequent pulp treatment will depend on the final brightness required (Biermann, 1996).

The components found in the DC and Eo bleaching effluent streams arising from typical bleach plants are tabulated as follows.

TABLE 2.1

Identity, mean yield and yield range of major chlorinated phenolic compounds and AOX[1] in DC[2] and Eo[3] filtrates (McFarlane *et al.*, 1991).

Bleaching Stage	Compounds	Mean Yield (g/tonne of pulp)	Yield Range (g/tonne of pulp)
DC	3.4.5-trichlorocatechol	1.16	0-10.27
	tetrachlorofuranone	0.76	0-3.41
	2.4.6 trichlorophenol	0.43	0-1.44
	tetrachlorocatechol	0.40	0-4.52
	2.4 dichlorophenol	0.28	0-0.64
	4.5-dichlorocatechol	0.24	0-1.33
	Total DC chlorophenols	3.27	0-21.61
	AOX (contained in DC effluent)	880	230-2,050
Eo	6-chlorovanillin	1.75	0-3.49
	4.5-dichlorogualacol	1.66	0-3.76
	5.6-dichlorovanillin	0.43	0-1.03
	3.4.5-trichloroguaiacol	0.27	0-2.13
	2.4.6-trichlorophenol	0.19	0-0.67
	5-chlorovanillin	0.18	0-1.27
	Total Eo chlorphenols	4.48	0-12.35
	AOX (contained in Eo effluent)	539	110-1,130

[1] Adsorbalble organic chlorine.

[2] chlorine dioxide followed by chlorine bleaching stage effluent

[3] Extraction by alkali fortified with oxygen bleaching stage effluent.

TABLE 2.1 indicates that the mean yield of chlorophenolic compounds from the DC stage was 3.27g/tonne and in the Eo stage it was 4.48g/tonne. The AOX yields averaged 880 g/tonne in the DC stage and 539 g/tonne in the Eo stage (McFarlane *et al.*, 1991).

The molecule formulae for some of the phenolic compounds are shown in Fig.2.1.

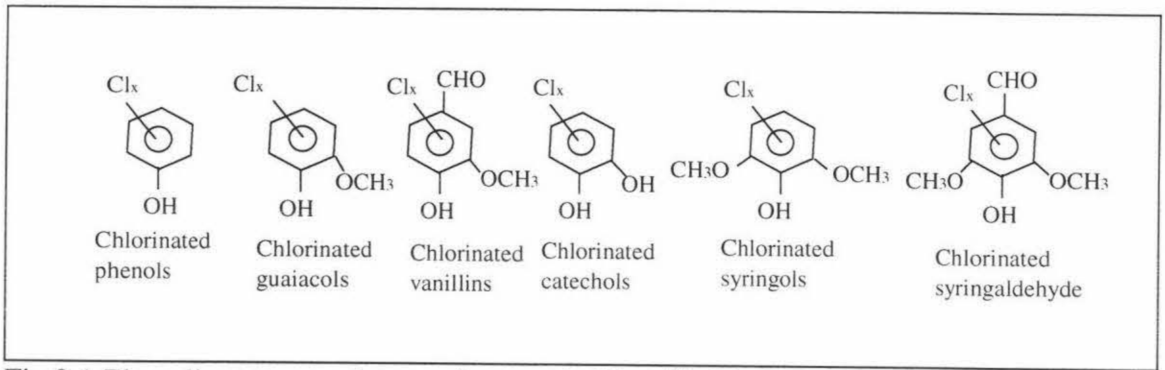

Fig.2.1 Phenolic compounds most frequently identified in bleaching effluent (Kringstad & Lindström, 1984).

Kringstad & Lindström (1984) studied bleaching effluents generated from pulp chlorination and alkali extraction bleaching treatment stages and found that approximately 70% of organically bound chlorine compounds produced during chlorination bleaching process are high molecular weight substances whereas in alkali extraction 95% are high molecular weight compounds. They reported that biological processes are effective in removing low molecular chlorinated organic compounds such as chloroform. However, high molecular weight compounds in the chlorination and extraction effluents are probably biologically inactive because they cannot penetrate cell membranes of living organisms. These non-biodegradable organic compounds, expressed as COD, remain in the biologically treated mill effluent and are responsible for a dark brown color (Möbius & Tolle, 1997). Thus, stringent discharge rules requiring very low COD concentration cannot be met with biological treatment alone. An alternative bleaching effluent treatment to reduce these non-biodegradable organic compounds is the use of ozone and other oxidizing compounds as pre-treatment in combination with a biological treatment stage (Rodriguez *et al.*, 1998).

2.2 Ozone Treatment

Recently, there has been increasing concern about the environmental impact of chemical compounds created in the bleaching process. In particular, the color and chlorinated compounds have been identified as the major source of concern. This is mainly because these compounds are resistant to conventional biological treatment processes and highly toxic in receiving waters. Consequently, various alternative treatment processes have been extensively studied (Heinzle *et al.*, 1992; Rodriguez *et al.*, 1998). Among these processes, ozonation has been demonstrated to be effective in decolorizing pulp mill effluents and oxidizing refractory organic compounds (Tuhkanen *et al.*, 1997). With advances in ozone generating technologies and the development of hybrid ozonation and biological processes, the application of ozonation for bleaching effluent treatment becomes not only technically feasible, but also economically viable (Zhou and Smith, 1997).

2.2.1 Ozonation Mechanisms

Wastewater contains a mixture of various dissolved organic and inorganic substances which play various roles in the ozonation process. Different reaction pathways are responsible for the ozone depletion in the water treatment, see Fig.2.2 (Johannes and Jurg, 1985).

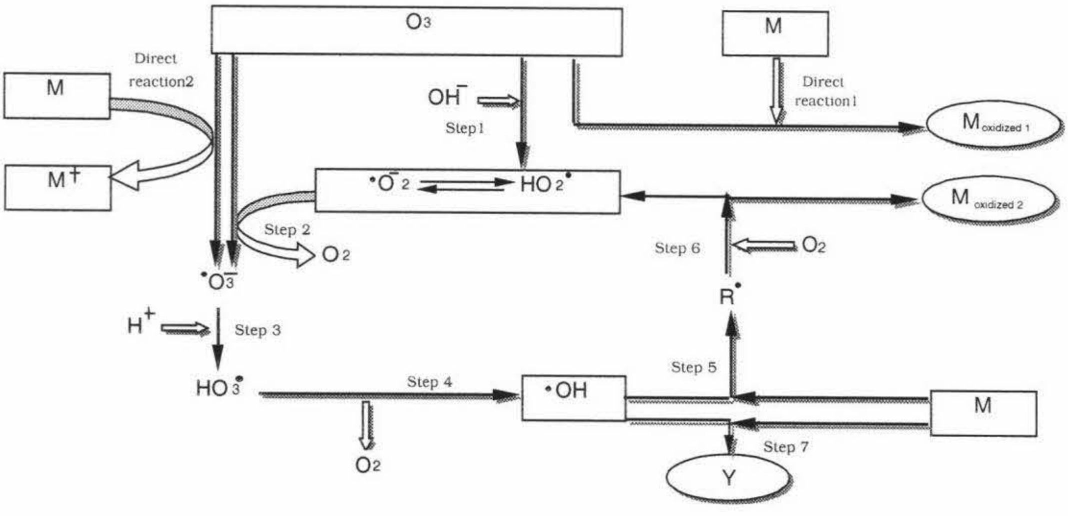

Fig. 2.2 Ozonation model (Johannes and Jurg, 1985)

The mechanism model created by Johannes and Jurg (1985) demonstrates that the ozonation process is comprised of a number of steps.

- *Initiation Step*

Fig.2.2 indicates that ozone reacts with substances (expressed as M in the Fig.2.2) in multiple pathways. It may directly oxidizes some of soluble substances to form either an oxidized substance $M_{oxidized1}$ (see Direct reaction 1) or an ozonide ion radical M^+ by electron transfer (see Direct reaction 2). Also the ozone oxidation of soluble substances present in water is carried out in a radical chain reaction pathway (see reaction chain from step1 to 6). In this chain reaction, ozone initially decomposes into one superoxide anion ($\bullet O_2^-$) and one hydroperoxyl radical ($HO_2\bullet$) by reaction with OH^- involved in the processed liquor. The hydroxide ion (OH^-) is referred as an initiator of the radical chain reaction.

- *Propagation Step*

The superoxide anion ($\bullet O_2^-$) further reacts with ozone (see step 2) to produce an ozonide anion ($\bullet O_3^-$) which decomposes into $\bullet HO$ radical (see step 3 and 4) and then the $\bullet HO$ radical reacts with substances (M) containing organic functional groups immediately. Some substances are oxidized by the $\bullet HO$ radical to form organic radical $R^\bullet$ (see step 5) which adds O_2 to produce oxidized substances ($M_{oxidized2}$) and superoxide anions ($\bullet O_2^-$) (see step 6) that decompose ozone (see step 2) in the chain reaction. These substances promote ozone oxidation and thus are called promoters of the radical chain reaction. A scheme of substances (Formic acid and Methanal) converting $\bullet HO$ radical to $\bullet O_2^-$ is shown in Fig.2.3.

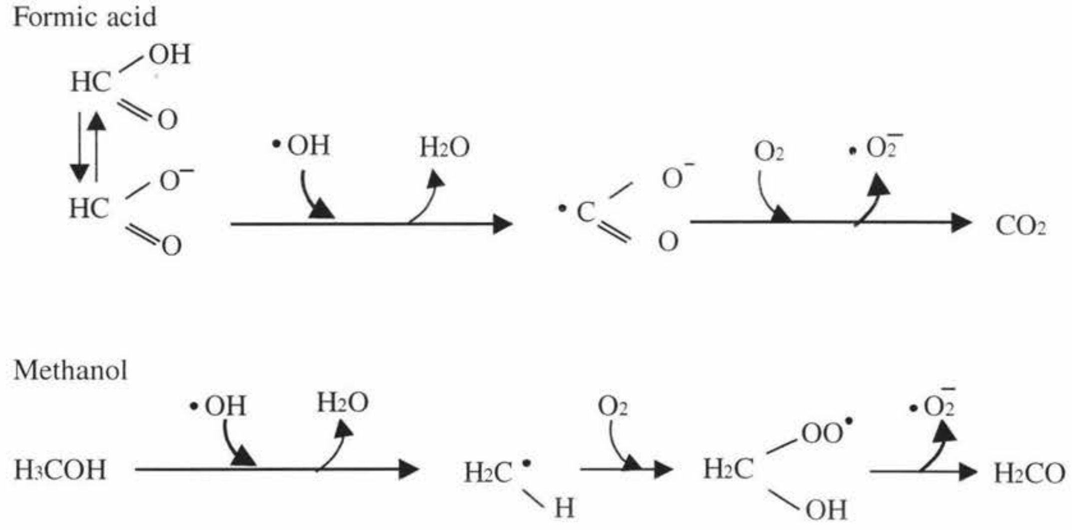

Fig.2.3 Formic acid and Methanol converting •OH radical to •O_2^-(Johannes and Jurg, 1985).

Termination Step

While some of the substances react with the •OH radicals to form radicals (indicated as Y in Fig.2.2) that do not predominately produce •O_2^- (see step 7), these substances terminate the chain reactions and thus are called inhibitors of the radical chain reaction. A scheme of substances (Alky groups and t-Butyl alcohol) consuming •HO radicals is shown in Fig.2.4.

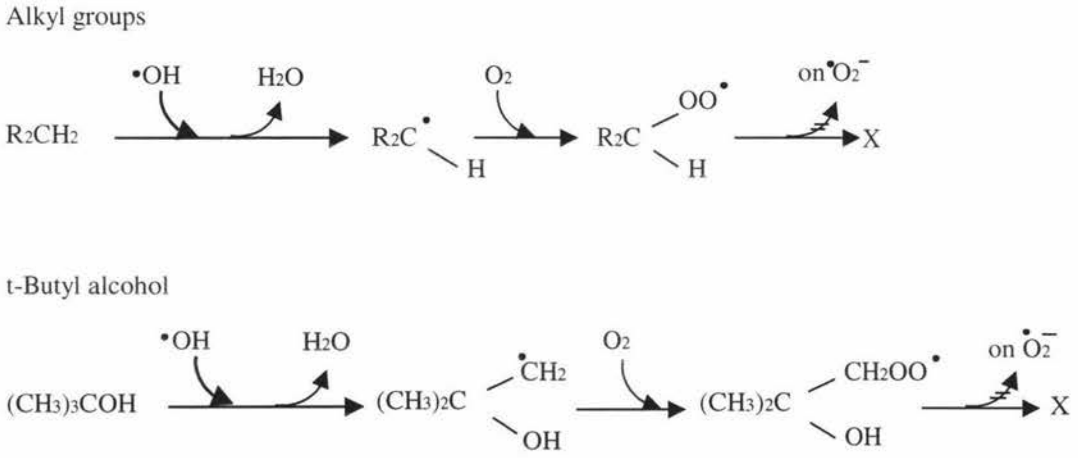

Fig.2.4 Alkyl group and t-Butyl alcohol consuming •HO radical (Johannes and Jurg, 1985) Where X are secondary radicals that do not predominately produce •O_2^- species.

The model indicates that the substances dissolved in water may react either with ozone (direct reaction) or with •OH radical which is initiated by OH^- ions. Some of the soluble substances react with •OH radicals to form $\bullet O_2^-$ species and promote the ozone chain reaction while others consume •OH radicals and contribute little to the formation of $\bullet O_2^-$ species, thus terminate the chain reaction. (Hoigne and Bader, 1975; Johannes and Jurg, 1985).

2.2.2 Ozone Treatment of Kraft Mill Effluent

Kraft bleaching effluent arising from a pulp and paper mill contains various chlorophenolic compounds that are toxic and recalcitrant to the conventional wastewater treatment system and pass through to the receiving surface water. There are a number of alternative ways to treat the bleaching effluent, one of which is the use of ozone. The ozonation of bleaching effluent has been widely investigated and most of the published work shows that ozone treatment breaks down the lignin-like compounds present in the effluent, effectively removes the effluent color and increases the effluent's biodegradability (Kahnmark & Unwin, 1998).

2.2.2.1 Mechanisms for Ozonation of Mill Effluent Components

One of the significant features of ozone action is the preferential attack on firstly, compounds with carbon-carbon double bonds and secondly, functional groups in the mill effluent. The target compounds in bleaching effluents are mainly resin acids, unsaturated fatty acids and chlorinated organic compounds. The dark color in the mill effluent is attributed to lignin degradation products and they too are subject to attack by ozone (Ng *et al.*, 1978).

The ozone reacts with organic compounds in a number of ways. The typical reactions are a direct oxidation by molecular ozone and indirect oxidation by •HO radicals through a chain reaction (see Fig.2.2). The pH value for the ozonation process is a critical parameter which greatly influences the ozonation kinetics. Because both of the ozone and •HO radicals are electrophilic reagents, the oxidation rate rises with the increase in the pH value although under those conditions the ozonation kinetics depend mainly on the •HO radical chain reactions (Boncz *et al.*, 1997). The ozone treatment of mill effluent converts some of the chlorinated organic compounds to dechlorinated oxidation products (Ng *et al.*, 1978), thus leads to a decrease in colorant substances existing in mill effluent and improve the biodegradability.

2.2.2.2 Applications

Arcand and Archibald (1996) reported that ozonation of mill effluents offered 70 % to 80 % of color removal and 15 % of COD removal, depending on the ozonation dose used and the nature of the effluents treated. Conclusions differed about BOD changes (increase or decrease). The authors deducted that the oznone was most susceptible to mill effluent color, followed by BOD. The total organic carbon was slightly reduced by ozone and the toxicity of the effluent was not measurably affected (Arcand and Archibald, 1996).

Other investigations also found that ozonation was particularly effective in removing color from bleaching effluent whereas COD reduction was low and TOC almost unchanged (Hostachy *et al.*,1997; Mőbius and Tolle, 1997; Prat *et al.*, 1989). In the ozonation process pH plays a major role while temperature seems to have no important effect (Heinzle *et al.*,1992; Tuhkanen *et al.*,1997).

TABLE 2.2 shows some of the published data pertaining to the ozone doses used and removal results achieved.

TABLE 2.2

The use of ozone treatment of mill effluent

Effluent Type	Ozone Applied		Effluent Characteristics						Removal %			Publication
	O_3/COD [1]	Ozone charge [2]	Before ozonation			After ozonation						
	(g/g)	(mg/L)	COD	BOD	Color	COD	BOD	Color	COD	BOD	Color	
Bleaching effluent (E stage effluent, soft wood)	0.039	171	4400	~	9930	4180	~	8838	5	~	11	Rodriguez *et al.*, 1998
	0.078	342	4400	~	9930	4000	~	7620	9	~	23	
	0.155	683	4400	~	9930	3870	~	3620	12	~	36	
Whole mill effluent (After aerated lagoon)	0.4	240	607	9.100	1213	~	~	~	18	~	82	Zhou and Smith, 1997
Bleaching effluent (Pine)	0.4	~	2820	750	~	~	~	~	20-40	-35	~	Tuhkanen *et al.*, 1997
Mill effluent (after biological treatment)	0.6	285	500	30	~	~	~	~	31	-104	~	Mobius and Tolle, 1997
Bleaching effluent (Mixing of C and E effluent in the proportion of 2:1)	0.17	300	1750	205	~	1380	175	~	21	15	79	Cecen *et al.*, 1992
	0.34	600	1750	205	~	1210	180	~	31	12	89	
	0.69	1200	1750	205	~	1080	185	~	38	10	96	
	1.030	1800	1750	205	~	967	170	~	45	17	97	

[1] ozone (g) used/Initial COD (g) contained in a raw effluent.

[2] ozone (mg) used/treated effluent (L).

[3] COD & BOD-mg/L and color-CP.U.

Published work indicates that the removal (%) of COD and color increased with an increase in the amount of ozone (g) used per gram COD in the influent. Rodriguez *et al.* (1998) treated an E stage bleaching effluent with a series of ozone doses. When the ozone amount (g) used per 1 gram influent COD increased from 0.039 to 0.155, the COD removal rose from 5 % to 12 % and the color removal increased from 11 % to 36 %. Zhou & Smith (1997) and Tuhkanen *et al.* (1997) employed higher ozone doses in the ozonation process, i.e 0.4 g of ozone per 1 gram of influent COD and obtained greater COD and color removal. Zhou & Smith achieved 18 % COD removal and 82 % color removal while 20 - 40 % of COD removal and 35 % of BOD increase were observed by Tuhkanen *et al.* (1997). Mőbius and Tolle (1997) increased the ozone dose to 0.6 gram ozone per 1 gram influent COD and gained a 31 % COD removal and 104 % BOD increase during the ozonation of a secondary mill effluent. A similar result for COD and color removal was reported by Cecen *et al.* (1992) who studied the ozonation of a mixed bleaching effluent treated with ozone doses ranging from 0.17 to 1.03 gram of ozone per 1 gram of COD in the influent. The COD removal ranged from 21 % to 45 % and color removal ranged from 79 % to 97 %. However, the BOD results noted by these authors were different from those of other authors. Cecen *et at.* (1992) noted that with an increase in the ozone dose the effluent BOD value was decreased from 15 % to 17 %.

Rodriguez *et al.* (1998) adopted a fractional factorial design and multiple linear regression method under experimental conditions to establish color and COD removal equations that can be used to estimate the efficiency of the treatment according to the initial effluent color, AOX, COD and the ozone charge (gram ozone used per liter raw effluent). The model equations are:

$$\begin{aligned}\text{Color Reduction (\%)} = {} & 198.6 - 46.0\,C + 174.1\,AOX - 198.2\,COD + 149.8\,Z + 4.9\,C_2 - 9{,}217.8 \\ & AOX_2 + 57.0\,COD_2 - 148.5\,Z_2 + 105.2\,C{*}\,AOX - 22.9\,C^{*}COD - 11.0 \\ & C{*}Z + 1{,}002.7\,AOX{*}COD + 681.8\,AOX{*}Z \\ & + 17.0\,COD{*}Z \\ & \text{\% of explained variance} = 88\ (95\ \text{\% confidence level})\end{aligned}$$

$$\begin{aligned}\text{COD Reduction (\%)} = {} & 184.6 - 84.1\,C + 1{,}495.7\,AOX - 282.3\,COD + 54.9\,Z + 9.2\,C_2 - 69{,}402.0 \\ & AOX_2 + 103.9\,COD_2 - 24.1\,Z_2 + 2{,}316.6\,C{*}AOX - 106.2\,C{*}COD + 2.8 \\ & C{*}Z + 3{,}468.9\,AOX\,{*}COD - 24.6\,AOX\,{*}Z - 10.2\,COD{*}\,Z \\ & \text{\% of explained variance} = 99\ (99\ \text{\% confidence level})\end{aligned}$$

C = gram initial platinum color/liter effluent; AOX = gram initial adsorbable organic halogen/liter effluent; COD = gram initial chemical oxygen demand /liter effluent; Z = gram ozone used/liter effluent; Subscript 2 = second batch effluent.

2.2.3 Summary

Bleaching effluents arising from pulp and paper mills are problematic because they contain toxic chlorinated derivatives, resin acids and unsaturated fatty acid. Some of these compounds have double bonds and can be preferentially oxidized by ozone. Proposed ozonation mechanisms suggest that the ozone reacts directly or indirectly with oxidizable substances and generates free radicals, which in turn can attack many other substances. The most effective actions of ozonation on mill effluents is decolorization, followed by improvement of biodegradability. However, COD removal is low. The color and COD removal is improved with an increase in the gram ozone used per gram COD contained in the influent effluent. Effluent pH plays a important role in an ozonation of bleaching effluent process. A model is available for estimate the desired color and COD reduction and to understand the kinetics of the ozonation process.

2.3 Biological Treatment

Biological treatment processes offer another means for the removal of mill effluent pollutants. A wide range of chlorinated organic compounds are formed during chlorine bleaching pulp processes and approximately 70 % of the organically bound chlorine compounds present are found as chlorolignin (Häggblom & Salonen, 1991). Aerated lagoons reported by Stuthridge *et al.* (1991) were capable of removing most of the readily biodegradable organic fractions contained in mill effluents. However, some of the high molecular weight compounds such as the chlorolignin remained in the effluent and passed through to the receiving water because of their resistance to biodegradative processes. The sequential anaerobic and aerobic system has been introduced as an innovational process for mill effluent treatment because of the possibility that chlorinated organic compounds can be reduced in this treatment system (Heinzle *et al.*, 1992).

2.3.1 Mechanisms

Aerated lagoons are commonly used in pulp and paper mills for effluent aerobic biological treatment (Welander *et al.*, 1997). An aerated lagoon is a large aerated pond through which the effluent passes in a number of days. Respiratory microorganisms thriving in the lagoon convert biodegradable organic matter in the effluent to carbon dioxide, water and biomass (Welander *et al.*, 1997). In contrast to this, the anaerobic treatment process has been documented to be effective in reducing chlorinated organic compounds in the bleaching effluent (Ferguson and Dalentoft, 1991).

- *Aerated Lagoon Mechanism*

Many pulp and paper mills use aerated lagoons for the removal of BOD, suspended solids and some organic compounds (Bryant *et al.*, 1987). A schematic representation of the removal of conventional pollutants and hypothesized pathways for nonvolatile organic compounds appears in Fig. 2.5.

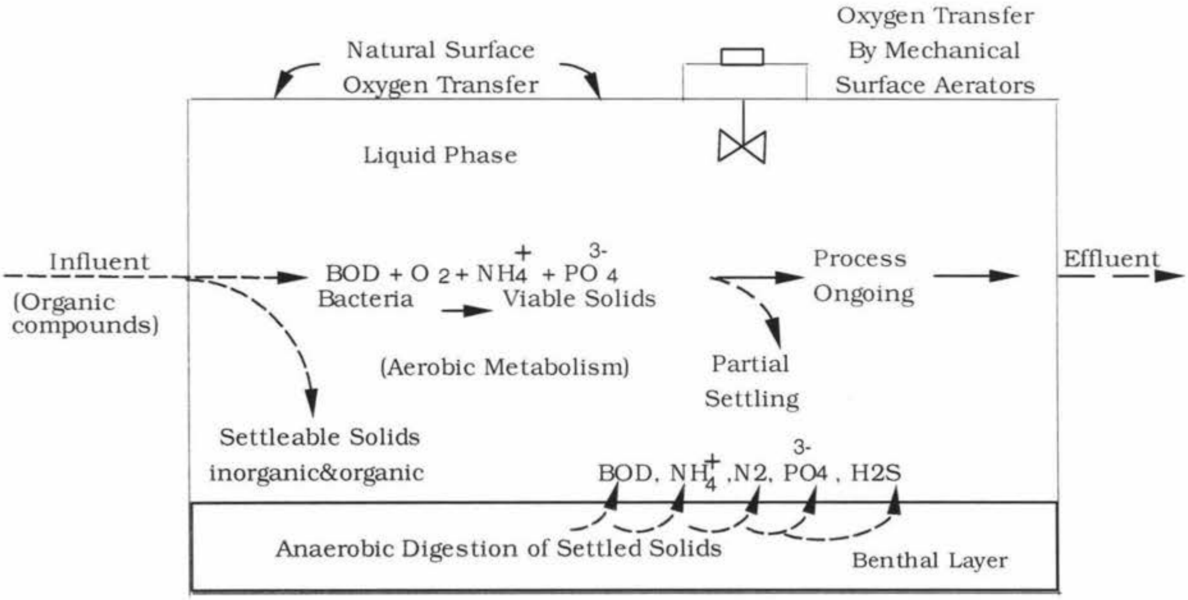

Fig.2.5 Aerated lagoon process for toxic chemical removal (Bryant *et al.*, 1987)

The volatile organic compounds in mill effluents (such as chloroform) are removed from the lagoon via volatilization during aeration. The removal of nonvolatile organic compounds from a lagoon is shown in Fig.2.5. The hypothesized removal mechanisms involved that some of the organic compounds (1) biosorb onto biomass in the lagoon's aerobic zone, (2) then deposit to the benthal layer in the bottom of the lagoon and furthermore, (3) the organic substances degrade in the anaerobic benthal layer (Bryant *et al.*, 1987). Aerated lagoons represent a common treatment system for mill effluent (Welander *et al.*, 1997).

- *Anaerobic Dehalogenation Mechanisms*

Bryant *et al.* (1987) claimed that a major fraction of the adsorbable organic halides (AOX) found in mill effluents were destroyed in the anaerobic benthal layer of the aerated lagoon. Ferguson and Dlenoft (1991) noted that any anaerobic digester sludge could dehalogenate compounds and that the anaerobic microorganisms involved gain energy for their growth from the process. Ferguson and Dlenoft found that the chlorinated organic compounds are highly oxidized and serve as electron accepting compounds in a reducing environment. The dehalogenating anaerobic bacteria obtain energy from the reduction process to support their growth needs. It is emphasized that most of the AOX are high molecular weight compounds that can be fully metabolized only after degradation into small fragments with low molecular weight. Otherwise they can not penetrate into the bacterial cells for biological degradation (Ferguson and Dlenoft, 1991).

2.3.2 Applications

Aerated lagoon systems are usually able to remove 85 % to 90 % of the readily biodegradable organic compounds found in mill effluents. However, they are less effective in removing color, COD and organochlorine compounds (Stuthridge *et al.*, 1991). The authors further reported that with aerated lagoon treatment, only 25 % to 50 % AOX (adsorbable organic chlorine) and 20 % to 60 % chlorinated phenolics were removed from a mill effluent. Saunamäki *et al.* (1991) used an activated sludge system for treating mill effluents and obtained an average of 84 % BOD reduction and 34 % COD reduction. Welander *et al.* (1997) used aerated lagoons to treat a mill effluent and achieved 30 % to 40 % COD removal. Published data concerning process design, influent loading and the removal efficiency associated with bleaching effluent treatment are summarized in TABLE 2.3.

TABLE 2.3

A summary of published data associated with biological treatment of bleaching effluents.

Effluent type	Process design	Facility effective volume	Influent flowrate	Influent COD loading (kg/m^{3}d)	COD removal %	BOD removal %	Authors
Bleaching effluent	Aerated lagoon (retention time 40.5 day.)	430 ML	10.7 ± 1.2 (ML/day)	0.07	36	57.5	Stuthridge *et al.* (1991)
Bleaching effluent (bleaching effluent diluted with tap water to 20 % v/v and with addition of nutrients to give a BOD:N:P ratio of 100:5:1)	Activated sludge	6.7 L	15.5 (L/day)	1.7	54	96	Hall & Randle (1992)
	Facultative stabilization basin	30 L	1.5-3 (L/day)	0.037-0.073	55	96	
	Aerated stabilization basin	15 L	1-3 (L/day)	0.049-0.146	57	96	
Mixed bleaching effluent (adding trace elements once a week)	Anaerobic fluidized bed and then aerobic trickling filter	10 L (anaerobic fluidized bed) 20 L (aerobic trickling filter)	3.2-3.6 (L/day)	0.31-0.35	30-65	60-80	Häggblom& Salonen (1991)

The results reported by Stuthridge *et al.* (1991) were derived from an investigation of one of New Zealand's kraft pulp and paper mill effluent treatment (see TABLE 2.3). The E-stage bleaching effluent passed through an aerated lagoon with a retention time of 40.5 day and this process removed 36 % COD and 57.5 % BOD from the effluent. No significant color removal was observed during the aerated lagoon treatment and it was believed that those chromophores producing the high color content of the bleaching effluent were present as a high molecular weight chlorinated lignin fraction that are not readily removed in the aerated lagoon.

Hall and Randle (1992) established three parallel biological processes, activated sludge, facultative stabilization basin and aerated stabilization basin, to assess the ability of the conventional biotreatments for removing pollutants from the diluted bleaching effluent. They deduced that all three treatment processes eliminated an average of 55 % COD and 96 % BOD from the effluent (see TABLE 2.3).

An anaerobic fluidized bed and then an aerobic trickling filter system was employed by Häggblom & Stalonen (1991) to treat a mixed bleaching effluent generated from chlorination & alkaline extraction bleaching stage and achieved 30 % to 65 % COD removal and 60 % to 80 % BOD removal (see TABLE 2.3). The authors also reported that pulp bleaching effluent could be treated by a sequential anaerobic and then aerobic process. The AOX removal (%) was significant in the anaerobic condition (up to 68%) while the COD and BOD removals mainly occurred in the aerobic condition.

Srinivason (1994) cited that the use of an anaerobic zone before aerobic biological treatment improved the overall COD and color removal from pulp bleaching effluent compared with aerobic treatment alone. Srinivason and Unwin (1995) further noted that the sequential anaerobic and then aerobic treatment removed more than 92% BOD from pulp bleaching effluent.

With respect to nutrient addition, Bryant *et al.* (1987) noted that a pulp mill effluent is normally deficient in nitrogen, thus nitrogen addition was considered important for operating a biological process under optimum conditions.

2.3.3 Summary

Biological processes are effective in removing biodegradable organic compounds. Among them the aerated lagoon is able to eliminate most of readily biodegradable organic compounds and suspended solids. The process mechanism assumption is that the organic compounds adsorb onto the biomass and particulate matter which then settles down to the benthal layer and there undergoes anaerobic digestion.

Dehalogenation has been identified as an energy conversion process whereby the oxidized chlorinated organic compounds are reduced by accepting electrons under the anaerobic condition from hydrogen or other reduced compounds. The anaerobic microorganisms use these reactions to generate energy for growth. However, the anaerobic dehalogenation is limited to those organic compounds with low molecular weights.

A pulp mill effluent contains large quantities of chlorinated organic compounds with both low and high molecular weights. It is mostly the low molecular weight chlorinated organic compounds that are degraded in the aerated lagoon. This leads to a high BOD removal for the treated effluent. However, the high molecular weight chlorinated compounds are very recalcitrant to degradation in an aerated lagoon and remain in the effluent. This results in low COD removal (only 20 %-50 %) and gives the treated effluent a dark color. Other secondary biological treatment processes, such as activated sludge systems, facultative stabilization basins, aerated stabilization basins as well as the sequential anaerobic and aerobic treatment processes have all been used for the treatment of mill effluents. Although these biological treatment processes removed most of the BOD, they all are not effective in color and COD removal. While ozone treatment offers an effective alternative for recalcitrant compound removal. Thus a combine chemical oxidation with ozone and biological treatment system is developed to improve the pulp mill effluent treatment.

2.4 Combination of Ozone and Biological Treatment System

The pulp and paper mill effluent is heavily loaded with organic compounds and brings out serious environmental problems if discharged into surface water without treatment (Munkittrick *et al.*, 1997). Conventional biological processes are capable of eliminating most of readily biodegradable organic compounds contained in the mill effluent, but it is difficult to remove high molecular weight chlorinated organic fractions, especially the chromophoric substances (Heinzle *et al.*, 1992). Ozone oxidation reactions have been shown effective in destroying the chromophoric substances and converting some of the high molecular weight compounds into lower molecular weight compounds, thus leading to improvement of color removal and effluent biodegradability (Zhou & Smith, 1997). The combined ozone oxidation with a biological treatment appears to be an innovative method for removal pollutants from a mill effluent.

2.4.1 Applications

Heinzle *et al.* (1992) established an integrated ozonation-biotreatment process for treating a bleaching plant effluent (see Fig.2.6). The effluent used was collected directly from the chlorine bleaching and subsequent alkaline extraction processes. Two-thirds of the effluent came from chlorine bleaching and the remainder from the alkaline extraction process. Trace elements and mineral nutrients were added as nutritional supplements to the effluent for optimizing treatment conditions.

The bleaching effluent (A) firstly passed through an aerobic biofilm fluidized-bed system. The collected effluent (B) was then subjected to ozonation process (C) and then exposed to an anaerobic followed by an aerobic biotreatment (D, E) using two separate biofilm fluidized-bed systems (see Fig.2.6).

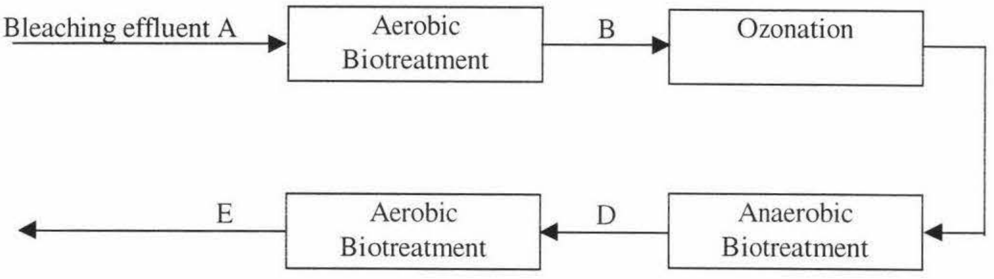

Fig.2.6. A combined ozonation-Biotreatment process for bleaching plant effluent treatment (Heinzle *et al.*, 1992).

The authors conducted three experimental trials which were Control, Case1 and Case2. The control trial was a biological treatment only and for Case1 and Case2 a combined ozonation with biological treatments was used. The ozone dose used was 0.36 gram ozone per gram COD in the influent for Case 1and 0.21 gram ozone per gram COD in the influent for Case 2. The measurement parameters were in terms of COD, AOX and TOC (total organic carbon) removal (%). Results obtained from these experiments indicated that the total COD removal was 31 % for Control process, 56 % for Case1 and 47 % for Case2. The AOX total removal was 25 % for Control process, 70 % for Case1 and 68 % for Case2. The TOC total removal was 24 % for Control process, 37 % for Case1 and 20 % for Case2. An analysis of the data suggests that the integrated ozonation-biotreatment system increased overall COD and AOX removals (47-56% for COD and 68-70% for AOX) compared with the biological treatment alone (only 31% for COD and 25% for AOX). Furthermore, the extent of improvement was associated with ozone dose used. For example, in Case 1 the ozone dose (g/g) was 0.36, 56% COD removal and 70 % AOX removal were observed while in Case 2 the ozone dose (g/g) was 0.21, lesser removal of COD (47%) and AOX (68%) were obtained. However, the integrated treatment system was not effective in improvement of TOC removal (20-37%) over the biological treatment alone (24%) in the used ozone dose range.

Möbius and Tolle (1997) evaluated an ozonation-biofilter process for improving mill effluent biodegradability (see Fig.2.7). The system was run with a biologically treated composite mill effluent. The average ozone dosage used was 0.6 gram ozone per gram COD in the influent.

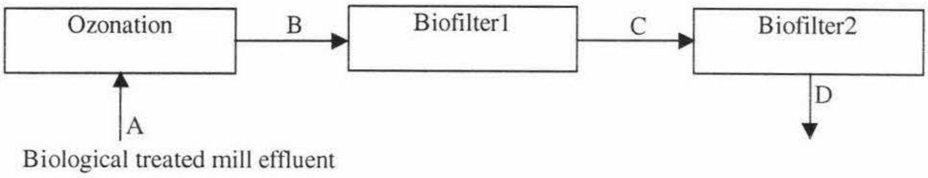

Fig.2.7. A combined ozonation-Biofilter process (Möbius and Tolle,1997).

The total removal was 48 % for the COD, 22 % for the BOD and 72 % for the AOX. The results for the COD and AOX removal were close to those reported by Heinzle *et al.* (1992) who also used an ozonation-biotreatment (biofilms) process for the bleaching plant effluent treatment.

Tuhkanen *et al.* (1997) studied a combined ozonation-activated sludge treatment system. The effluent used was collected from the elemental chlorine free bleaching process. The ozone dosage adopted was 0.4 g ozone for per gram COD in the influent. A simplified process flow chart is shown in Fig.2.8.

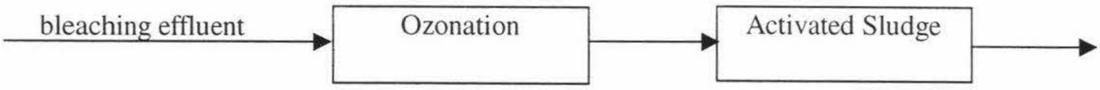

Fig.2.8 A combined ozonation-Activated sludge system as used by Tuhkanen *et al.* (1997).

The overall COD and BOD removals through the ozonation-activated sludge system treatment were 80 % and 91 %, respectively and that obtained in a biological treatment alone without ozone oxidation involved were 60% and 61%, respectively (Tuhkanen *et al.*, 1997). This suggests that the ozone-activated sludge combined system improved COD and BOD removal.

2.4.2 Summary

The combination of an ozone oxidation process with a biological treatment increased the overall COD, AOX and BOD removal rates compared with a biological treatment alone, thus the combined process appears to be an appropriate means for pulp bleaching effluent treatment. The published data showed that removal efficiencies were improved with an increase in the ozone dose used and also influenced by initial effluent characteristics.

These innovative treatment technologies were used to guide this research study. A pulp bleaching plant effluent arising from a New Zealand pulp mill was investigated and combined ozone pretreatment with a subsequent biological treatment process was adopted to eliminate pollutants contained in the effluent. The effectiveness of the treatment was examined in terms of color, COD and BOD removal. A vertical column batch reactor was employed to ozonation of the pulp bleaching plant effluent. An anaerobic zone followed by an aerobic zone biological treatment was designed for biodegradation of the ozone pretreated effluent and an aerated zone alone treatment of ozone pretreated effluent was also evaluated. The separate efficiencies for the ozonation treatment and the biological treatment were identified and then the overall removal rates obtained from the combined system were examined, whereby the best treatment regime for the bleaching effluent studied was selected.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Effluent Samples

Effluents used in experiments were generated from bleaching pulp of *Pinus radiata* at Eo[1] and DC[2] stages of a kraft pulp and paper mill. Two batches of Eo and DC effluent were received during the course of this research. Effluent characteristics for each batch varied with changes in the mill's production (see TABLE 3.1). The Eo and DC bleaching effluents were characterized and a mixed effluent (Mix) prepared from the Eo and the DC effluents (approximate Eo : DC = 4 : 1). The mixture characteristics were evaluated.

TABLE 3.1

Initial effluent characteristics (as received)

Batch No.	Item	Color Units	COD (mg/l)	BOD_5 (mg/l)	pH
1	Eo[1]	633	1250	294	10.4
	Dc[2]	271	1035	180	2.5
	Mix[3]	756	1185	289	9
2	Eo	4142	3000	166.3	10.8
	Dc	407	1185	-	2
	Mix	3310	2415	186	9

[1] Eo stage bleaching effluent
[2] Dc stage bleaching effluent
[3] Mixed with Eo and Dc bleaching effluent (Eo : DC = 4 : 1)

3.2 Experimental Design

A two-stage treatment process was employed to determine the extent of color, COD and BOD_5 removal from the bleaching effluents. The removal efficiency was measured in each stage and the overall removal obtained from two stages was measured.

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[1] E_o = Extraction by alkali bleaching stage fortified with oxygen.

[2] DC = Sequential chlorine dioxide followed by chlorine bleaching.

3.2.1 Ozone Treatment of Effluent

- The Ozonation Reactor

The chemical oxidation with ozone was the first stage of treatment. It was carried out in a vertical column batch reactor with an effective volume of 40L (see Fig.3.1). There are perforated plates (∅ 2 mm holes) in the column to disperse ozone bubbles when the effluent flowed through the column and diffusers were placed at the bottom of the reactor to disperse the ozone gas (Teekman, 1998). Any residual ozone existing in the reactor was destroyed with an activated carbon filter unit before being released to the environment. All of the construction materials for the ozone reactor were ozone stable PVC and stainless steel.

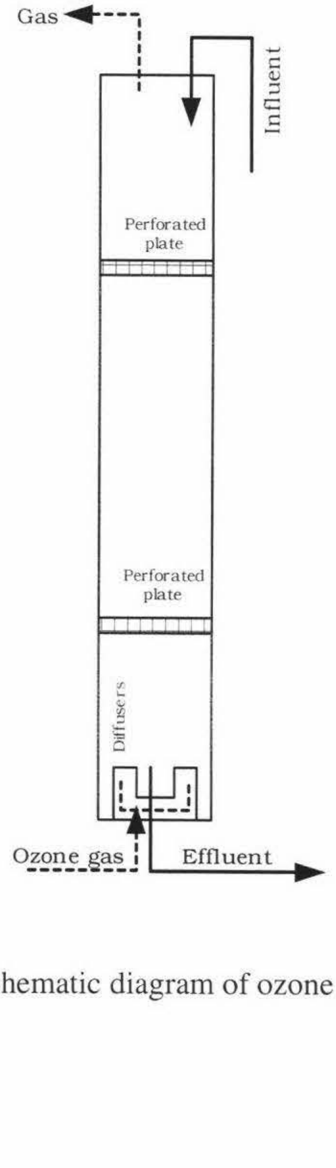


Fig.3.1 Schematic diagram of ozone reactor

- The Ozone Dose Used

The applied ozone dose is expressed as:

$$\text{Applied ozone dose (g ozone/g initial COD)} = (F_{O_3} * t * 1000)/(V * COD_{Influent}) \qquad (3.1)$$

Where F_{O_3} - O_3 flowrate g/hour; t - ozone treatment time (hours); V - treated effluent volume in batch (L); $COD_{Influent}$ - Influent COD concentration (mg/L); g ozone - gram ozone applied during ozonation of the effluent in treatment time t; g initial COD - gram COD involved in the influent effluent tested.

In this case, the O_3 flowrate was constantly controlled at 5L/min that is equivalent to 4.82 gram ozone/hour (Teekman, 1988). The effluent volume and initial COD for a specific batch effluent had been determined. Thus, the ozone dose used only varied with ozone treatment time (t). The ozonation process was terminated when most of the color was removed from the bleaching effluent and additional treatment resulted in little color removal. To reach this stage, the first batch of effluent (Eo_1 & Mix_1) was treated for 3 hours and the second batch of effluent (Eo_2 & Mix_2) was treated for 5 hours. The ozone dose used for each batch of effluent (Eo_1&Mix_1 and Eo_2&Mix_2) according to formula 3.1 was tabulated in TABLE 3.2 (see TABLE 3.1 for influent characteristics).

TABLE 3.2

Ozone Dose used.

Item	O_3 flowrate Fo_3 (g/h)	Treatment time t (h)	Effluent volume[1] L	$COD_{Influent}$ mg/l	Ozone dose g o_3/g COD
Eo_1	4.82	3	60	1250	0.2
Mix_1	4.82	3	60	1185	0.2
Eo_2	4.82	5	60	3000	0.14
Mix_2	4.82	5	60	2415	0.17

[1] Effluent volume = ozone reactor volume (40L) + recycle tank (20L).

- Operation process

The ozonation process flow chart was shown in Fig.3.2. The experiment was started by pumping 70L effluent using a centrifugal pump (supplied by Pump Begley's Industry Ltd., Auckland, NZ) from a storage reservoir into a 150L heating tank in which the effluent was mixed by a stirrer (Janke & Kunkel, GMBH & Co, KG.) to ensure a uniform heating. The effluent's temperature was increased to 70 °C to simulate the on-site bleaching effluent temperature that occurs at the pulp and paper mill. The effluent temperature was controlled by an automatic controller (Philips Electronics, Netherlands) with a sensor in the heating tank. The effluent at 70 °C was then pumped into the 40L ozonation reactor from the top and a 20L recycle tank. When reactor and tank were filled, a pump circulated the effluent between the ozonation reactor (entering from top and exiting from bottom) and the recycle tank to form a circular loop with a flowrate of 4L/min as indicated by an on-site flow-rate meter (supplied by Great Plains Industries Inc, U.S.A). Sample collection was made from the sampling port at the bottom of the reactor.

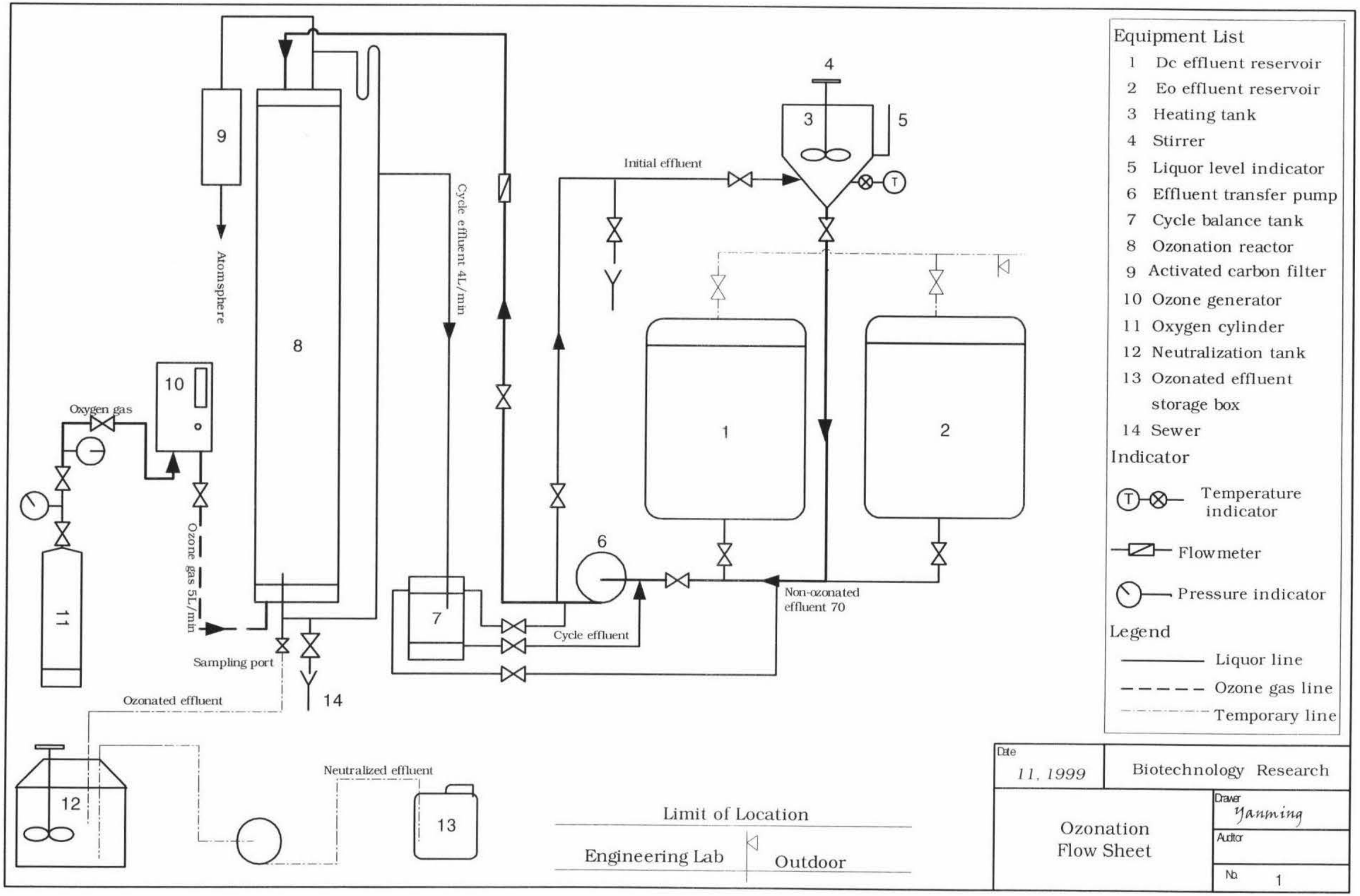
Next, ozone gas was transferred from an ozone generator (Ozone Generator Envirozone brand, model VT-2A, Napier, New Zealand) at a constant flow-rate of 5L/min monitored by a gas flow-rate meter which was incorporated into the equipment. The ozone generator was fed by pure oxygen with a pressure of 50 kPa to overcome the hydrostatic pressure at the bottom of the column.

During experiments, samples were taken at intervals of 20 minutes. The ozonation treatment was terminated when further ozonation produced little additional color removal.

- Ozone Treated Effluent Neutralization and Storage

Two trial ozone treatments for each effluent were carried out and the ozonated effluent generated in the two trials (about 100 liters) was transferred to a container and mixed thoroughly with a mechanical stirrer (Heidolph brand, Supplied by WATSON VICTOR LTD. Wellington, NZ). After being neutralized to a pH value of 7.0 using sodium hydroxide (Laboratory Grade, BDH Ltd., Poole England), the ozonated effluent was distributed into 20-liter boxes and stored in a 4 °C refrigerator room until required for the biological treatment studies. The same neutralization and storage procedure was employed for the non-ozone treated effluent which was also used in the biological treatment experiments. The non-ozonated effluent experiments were used as a control system. Characteristics for both, the ozonated and non-ozonated bleaching effluents in terms of color, COD and BOD_5, were tested under pH 7.0 condition (see CHAPTER Four TABLE 4.1.3).

Fig.3.2 Ozonation process flow sheet



3.2.2 Biological Treatment

Biological treatment was carried out in two systems. One was an anaerobic-aerobic lagoon consisting of an anaerobic zone (see Fig.3.3) and an aerobic zone (see Fig.3.4). The other system was an aerated lagoon only (see Fig.3.4). For each treatment, there were two processing lines, a control line for non-ozonated raw effluent and an experimental line for ozonated effluent biological treatment (see Fig.3.5 & Fig.3.6).

- Anaerobic Zone

The anaerobic zone was a sealed rectangular plastic tank with an effective volume of 10L. It was divided into three equal spaces with two plastic barriers to prevent any effluent flow short cuts (see Fig.3.3). Gas produced during digestion was released from a U shape glass air lock. The influent traveled through the lagoon and run into the bottom of a 1L air lock bottle to prevent air intrusion into the anaerobic zone of the lagoon.

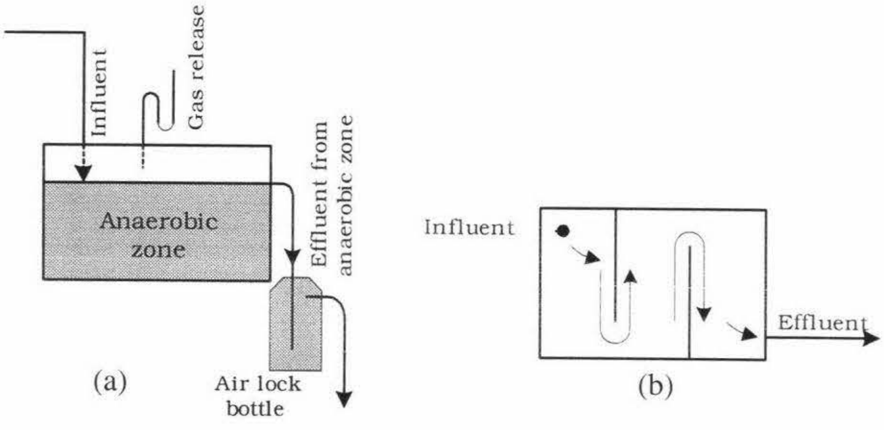
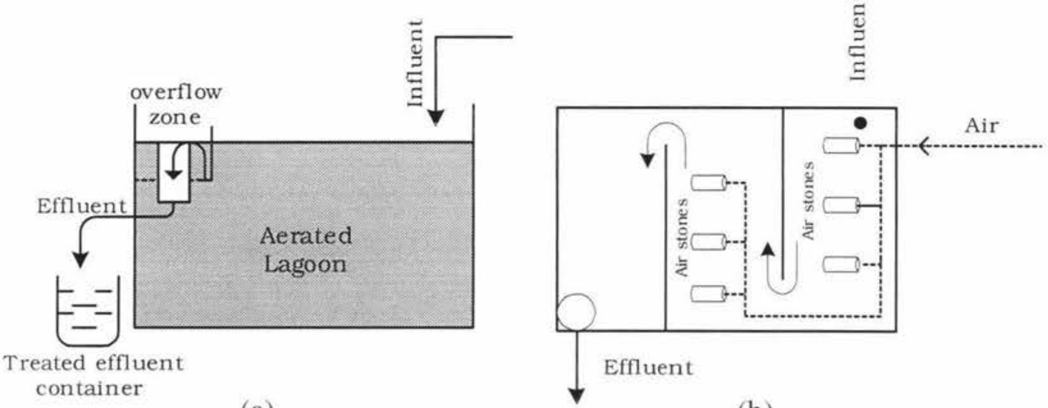


Fig.3.3 Diagrams for an anaerobic zone: (a) Process flow chart, (b) The anaerobic tank horizontal cross section.

- Aerated Lagoon

The aerated lagoon was also a rectangular plastic tank with an effective volume of 17.5L. Two barriers divided the tank into three equal spaces (see Fig.3.4). The first two zones were aerated with air through three air stones for each zone ("Aqua Fizzzz", Malaysia) to ensure that sufficient dissolved oxygen was available for aerobic biodegradation. The third zone was not aerated and suspended solids settled out in this zone before discharge. The influent entered from the first zone and overflowed from the third zone.



(a) (b)

Fig.3.4 Diagram for an aerated lagoon system: (a) Process flow chart
(b) Aerated lagoon (aerobic zone) horizontal cross section.

- Biological Treatment System

In an anaerobic-aerated lagoon system, initial effluent traveled through an anaerobic zone and then entered an aerobic zone, the final treated effluent overflowed into a collection container. The same treatment regime was employed for ozonated effluent and non-ozonated raw effluent (see Fig.3.5)

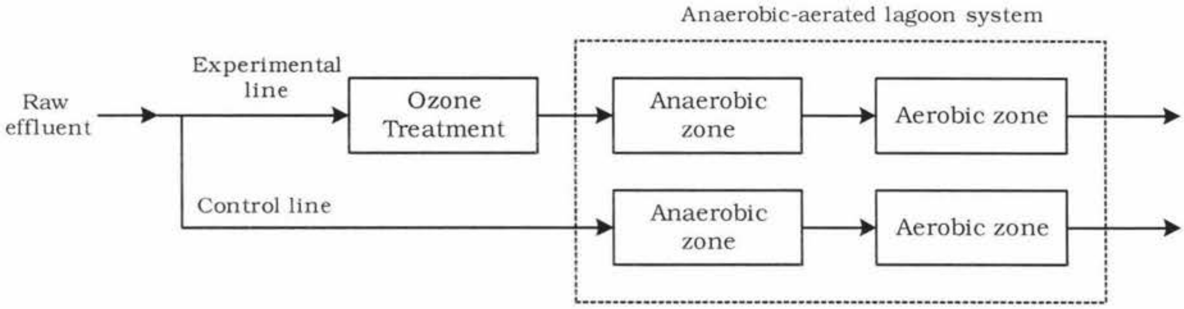


Fig.3.5 Process diagram for the anaerobic-aerated lagoon system for ozonated and non-ozonated effluent biological treatment.

In the aerated lagoon alone treatment system, effluent passed only through an aerated lagoon. Ozonated and non-ozonated effluents were processed in identical procedures (see Fig.3.6)

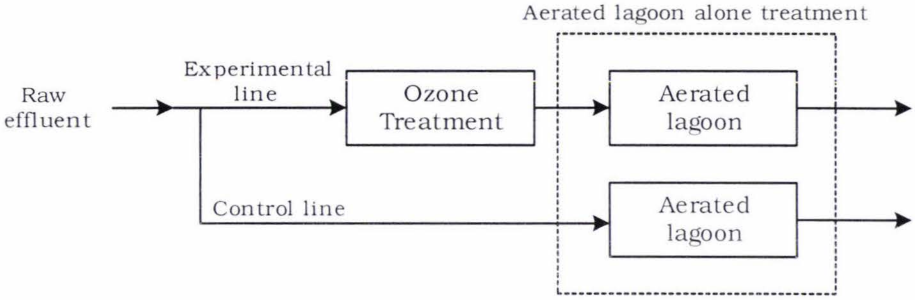


Fig.3.6 Process diagram for the aerated lagoon system for ozonated and non-ozonated effluent biological treatment.

The photograph below (Fig.3.7) shows the aerated lagoon arrangement. Of the four lagoons, lagoon 1 and 2 were used to treat ozonated effluents (experimental lines) and lagoon 3 and 4 for the non-ozonated raw effluents (control lines).

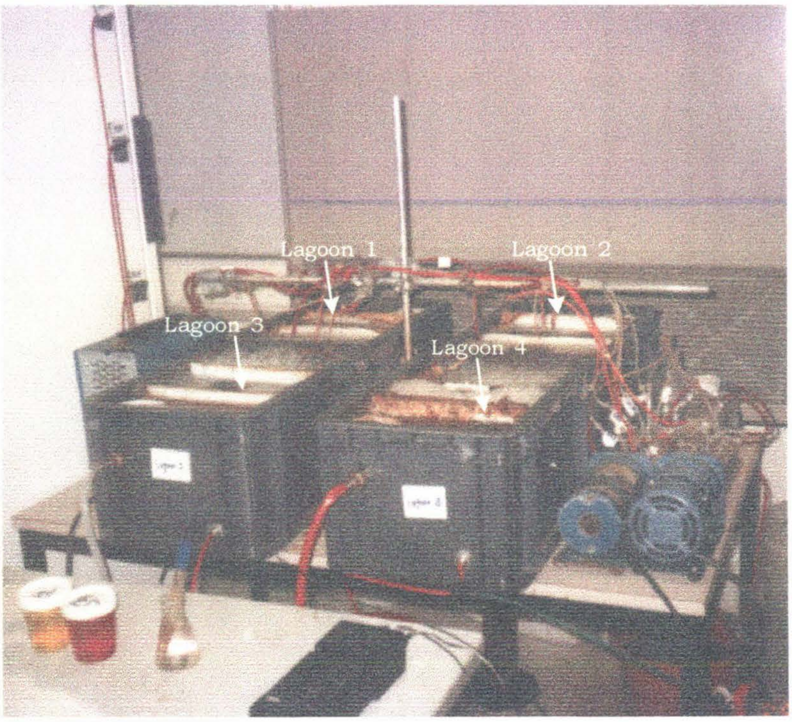


Fig.3.7 Photograph of the aerated lagoon treatment of pulp bleaching effluents.

- Influent Flowrate Determination

The appropriate flowrate was determined by the influent COD loading. According to literature, an influent COD loading to an biological process for a pulp mill effluent treatment usually ranges from 0.07 to 0.15 kg/m^3d (Stuthridge *et al.*, 1991 and Hall & Randle, 1992) and this was the range used for this lagoon studies. The influent flowrate was calculated as follows:

$$F = Lc*V*1000/ COD_{Influent} \tag{3.2}$$

Where F - influent flowrate, L/d; Lc - influent COD loading, kg/m^3d; V - facility effective volume, L; and $COD_{Influent}$ - Influent COD concentration, mg/L.

The influent flowrate was calculated from the COD value of the non-ozonated bleaching effluent. TABLE 3.3 gives the influent flowrate for each effluent (see TABLE 3.1 for initial effluent characteristics).

TABLE 3.3

Influent flowrate

Facilities	Item	Lc (kg/m^3d)	V(L)	So (mg/L)	F (L/d)
Anaerobic-Aerated Lagoon	Eo	0.07-0.15	27.5[1]	1250	1.5-3.3
	Mix	0.07-0.15	27.5	1185	1.6-3.5
Aerated Lagoon	Eo	0.07-0.15	17.5[2]	3000	0.4-0.9
	Mix	0.07-0.15	17.5	2415	0.5-1.0

[1] Effective volume = 10 L (anaerobic zone) + 17.5 L (aerated lagoon).

[2] Effective volume for aerated lagoon.

The optimum influent flowrate for the anaerobic-aerated lagoon was experimentally determined to 2.8 L/d (in the range of 1.5 to 3.5 L/d) and that for the aerated lagoon was set to 0.9 L/d (in the range of 0.4-1.0 L/d).

- Lagoon System Retention Time

The retention time was calculated from the process facility effective volume and influent flowrate:

$$R_t = V/F \tag{3.3}$$

Where R_t - retention time, d; V- facility effective volume, L; F - influent flowrate, L/d.

For the anaerobic-aerated lagoon: V = 27.5 L; F = 2.8 L/d; thus R_t = 10 d.

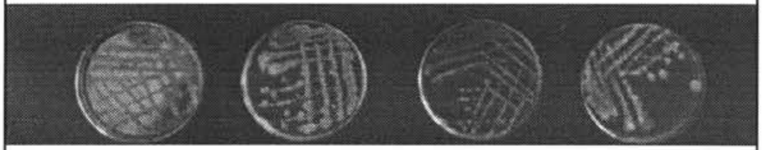
For the aerated lagoon: V = 17.5; F = 0.9 L/d; thus R_t = 20 d.

- Seeding Inocula

Anaerobic bacterial inocula were obtained from the anaerobic section of the wastewater treatment plant in Pamerston North City. Bacterial inocula for the aerobic process were collected from an aerated lagoon of a pulp and paper mill. Experimental processes were started with filling treatment facilities with the bacterial inocula and simultaneously introducing a small amount of pulp bleaching effluent into the process for acclimatization of the inocula. The influent was gradually increased to the normal operation's flowrate.

A microbiological "presence or absence" test for the aerobic process seed was conducted. The seed was carefully streaked onto a pink color "Eosin Methylene Blue" agar plate and a Nutrient Agar plate and then incubated under constant temperature of 30 °C for 48 hours. Results shown in Fig.3.8 suggest that the seed material obtained from the pulp and paper mill lagoon contained a viable population of bacteria including coliforms that would contribute to degradation of color, COD and BOD_5.

"Eosin Methylene Blue" agar plate



Nutrient Agar plate

Fig.3.8 An examination of microbiological colony species present in a pulp bleaching effluent.

- Process Operation

Biological treatment using the lagoon system succeeded the ozonation process. The influent to the lagoon system was pumped (Masterflex Cole-Parmer brand, U.S.A for the pump) from a 20-liter plastic box stored in a 4 °C refrigerator (Fisher and Paykel Ltd, New Zealand). The storage box in the refrigerator was cleaned and refilled periodically with the effluent drawn from the main supply. The effluent characteristics during storage were checked regularly. It was found that the effluent pH value changed slightly from 7.0 to 7.4. The COD and BOD_5 value were also stable.

1. Anaerobic-aerobic lagoon system

Pulp bleaching effluent (batch 1) was passed sequentially through an anaerobic and then an aerobic zone of the lagoon system. This will be referred to the anaerobic-aerated lagoon system in this study. The anaerobic-aerated lagoons were run for 23 days with a retention time of 10 days. The anaerobic zone was initiated with an anaerobic sludge seed and the aerobic zone of the lagoon was started with the pulp mill lagoon seed (see Section 3.2.2, Seeding Inocula). The ozone pretreated effluent (OEo & OMix) was in the "experimental line" and the non-ozone treated effluent (Eo, Mix) was in the "control line". The dissolved oxygen concentration for the aerobic zone was approximately 8 mg/l and therefore, it was assumed that the biological process in the aerobic zone was not oxygen limited. After one retention time the lagoon system was operating at steady state conditions in terms of color, COD and BOD_5 values (see Appendix 1, TABLE A1.2).

2. *Aerated lagoon system*

Pulp bleaching effluent (batch 2) was treated in an aerated lagoon only. The aerated lagoon was run for 61 days with a retention time of 20 days. A nutrient solution was added in a BOD_5 : N : P ratio of 100 : 5 : 1 to favor the process biodegradation. The pH value of the lagoon system was controlled in a range of 6-6.7 by pumping (Masterflex Cole-Parmer pump, U.S.A) 30 ml of 0.06% (v/v) H_2SO_4 per day to the system. The dissolved oxygen concentration for the aerated lagoon was approximately 8 mg/l and therefore, it was assumed that the biological process in the aerated lagoon was not oxygen limited. After 35 days of operation the lagoon system remained in a stable condition in terms of color, COD and BOD_5 (see Appendix 1, TABLE A1.3)

3.3 Methods

Samples were taken from the experiments regularly and characterized in terms of color, COD and BOD_5. The data obtained from these measurements were analyzed quantitatively to identify the treatment efficiencies and assess the success of treatment. The methods used are described below.

3.3.1 Sampling Methods

- Ozonation process

A grab sample was taken from the sample port every 20 minutes at the bottom of the ozonation reactor and into a 60 ml glass beaker. Duplicate samples were taken for each measurement of color, COD and BOD_5.

- Biological systems

Grab samples were taken in duplicate simultaneously from influent and effluent of the biological process and collected into 100 ml glass beakers for color, COD and BOD_5 analysis. These samples were analyzed immediately after sampling.

3.3.2 Measurement Methods

Samples taken from the experimental process were tested for pH, color, COD and BOD_5. Chemicals involved in the measurement were tabulated in Appendix 1 TABLE A1.1.

- *pH value*

The pH value of samples was measured using either a bench pH meter (M82 STANDARD pH METER, supplied by WATSON VICTOR LTD, New Zealand) or a portable pH meter (Model 230A, supplied by WATSON VICTOR LTD, New Zealand). Before measurement the pH meter was calibrated with standard buffer solutions at pH 4.0 or 7.0, depending on situation.

- *Color*

Color was measured using the Visual Comparison Method described in Standard Methods for the Examination of Water and Wastewater (Eaton *et al.*, 1995). The measurement procedures are detailed in Appendix 1, Section A1.3.1.

- *COD*

COD was tested using the closed Reflux Colorimetric Method described in Standard Methods for the Examination of Water and Wastewater (Eaton *et al.*, 1995). The measurement procedures are detailed in Appendix 1, Section A1.3.2.

- *BOD_5*

BOD_5 was analyzed with a BOD Trak^{TM} system (Hach, 1997). The measurement details were illustrated in Appendix 1, Section A1.3.3.

- DO (dissolved oxygen)

The dissolved oxygen concentration in the aerobic zone was measured using a portable oxygen meter (General Purpose Regulator, U.S.A). Before measurement it was calibrated with saturated water under 20 °C.

3.3.3 Data Analysis Methods

- *Comparative methods*

To determine a treatment efficiency, a % change in color, COD and BOD_5 between influent and effluent for a process was calculated:

$$\% \text{ change} = (x_1 - x_2) * 100/x_1 \tag{3.4}$$

Where x stands for color, COD and BOD_5 value; subscript 1 for influent and 2 for effluent. The % change was positive, it suggested that the treatment removed the substance examined from effluent while a negative % change indicated that the process increased the substance loading in the treated effluent.

- *Modelling Method*

Data collected from the ozone treatment stage for color removal was analyzed using a modelling approach. A mathematical formula was derived from experimental data to describe the color removal performance during treatment. The formula, in turn, would be used to predict desired ozonation process time for bleaching effluent.

The color removal modelling was established under the following assumptions:

a) That pulp bleaching effluent was ozonated in a batch mode.
b) That a constant ozone flowrate was supplied to the ozonation process so that the ozone dose applied was dependent only on the ozonation time (i.e ozone dose).

Under these assumptions for a specific pulp bleaching effluent treated in the experimental condition, a general color removal formula is :

$$C_t = C_u (1 - e^{-k*t}) \qquad (3.5)$$

Where C_u is the ultimate % color removal; C_t is the % color removal at time t; t is time (minutes); k is the color removal rate constant 1/t (see Appendix 2, Section A2.1).

3.3.4 Confidence Limits

Replicate experiments for each effluent characteristic in terms of measured color, COD and BOD_5 were carried out for determining the error range. The error was calculated with 95 % confidence limits.

- *Color Removal*

Results for the examined color unit and color removal in 10 replicate experiments are tabulated in TABLE 3.4. Color units shown (2530 to 2545) are in potassium chloroplatinate color unit.

TABLE 3.4

Data for color removal confidence limits

Influent	Effluent		
color unit value (CP.U)	Sample No.	color unit value (CP.U)	% color removal
2930	1	2530	12.8
	2	2545	12.3
	3	2541	12.5
	4	2541	12.5
	5	2541	12.5
	6	2541	12.5
	7	2537	12.6
	8	2541	12.5
	9	2537	12.6
	10	2537	12.6
mean $\bar{X}$			12.5
Standard deviation (SD)			0.14

Sample number (n) = 10; $t_s = 2.25$ (see Appendix 1, Fig.A1.1).

Limits = $\bar{X} \pm SD*t_s / \sqrt{n} = 12.5 \pm 0.14* 2.25 /\sqrt{10} = 12.5 \pm 0.1\%$, thus the color removal error range is ± 0.1%. Where t_s- student t-test value.

- *COD Removal*

Results for COD value and COD removal in 10 replicate experiments are tabulated as follows:

TABLE 3.5

Data for COD removal confidence limits

Influent	Effluent		
COD value (mg/l)	Sample No.	COD value (mg/l)	% COD removal
3000	1	2083	30.6
	2	2083	30.6
	3	2117	29.4
	4	2117	29.4
	5	2133	28.9
	6	2150	28.3
	7	2100	30.0
	8	2100	30.0
	9	2083	30.6
	10	2067	31.1
mean $\bar{X}$			29.9
Standard deviation (SD)			0.86

Sample number (n) = 10; $t_s = 2.25$ (see Appendix 1, Fig.A1.1)

Limits = $\bar{X} \pm SD^{*}t_s / \sqrt{n} = 29.9 \pm 0.86^{*}\ 2.25 / \sqrt{10} = 29.9 \pm 0.6\%$, thus the COD removal error range is ± 0.6%. Where t_s- student t-test value.

- *BOD_5 Removal*

Results for BOD_5 value and BOD_5 removal in 6 replicate experiments are tabulated as follows:

TABLE 3.6

Data for BOD_5 removal confidence limits

Influent	Effluent		
BOD_5 value (mg/l)	Sample No.	BOD_5 value (mg/l)	% BOD_5 removal
166	1	52	68.7
	2	50	69.9
	3	48	71.1
	4	58	65.1
	5	60	63.9
	6	50	69.9
mean $\bar{X}$			68.1
Standard deviation (SD)			2.9

Sample number (n) = 6; $t_s = 2.8$ (see Appendix 1, Fig.A1.1)

Limits = $\bar{X} \pm SD^*t_s / \sqrt{n} = 68.1 \pm 2.9^* 2.8 /\sqrt{6} = 68.1 \pm 3.3\%$, thus the BOD_5 removal error range is ± 3.3%. Where t_s- student t-test value.

CHAPTER FOUR

RESULTS

This chapter presents results obtained when the Eo fraction of a pulp and paper mill bleaching effluent was treated with ozone and then in a model lagoon system. Changes in color, COD & BOD_5 were monitored. Also changes occurring when a mixture of the Eo & DC fractions of the mill's bleaching effluent were treated using the same regime were monitored in terms of above parameters. Flow charts for the processes used are presented in Appendix 2, Fig.A2.1-A2.4.

4.1 Ozone Treatment

Two batches of bleaching effluent were used in this work. As the characteristics of the bleaching effluent varied daily with the production processes, the two batches of effluent received from the mill were very different (see CHAPTER THREE, TABLE 3.1). The ozonation treatment equipment, flowrate and temperature used are given in Section 3.2 Experimental Design for Ozone Treatment of Effluent.

4.1.1 Treatment of Eo Effluent

Using the two batches of Eo effluent, changes in color, COD and BOD_5 during the ozonation process were recorded to determine the success of ozone treatment. Samples were taken from the ozonation reactor every 20 minutes for color and COD measurements. A model was established for each batch of Eo effluent used to quantify the effect of ozone on color removal. COD changes with treatment time were examined using the first batch of Eo effluent whereas the second batch of Eo effluent was only tested for the COD before and after ozone treatment. BOD_5 estimations for both batches of Eo effluent were made at the beginning and end of the ozone treatment.

4.1.1.1 Color Removal

The color removal for the first batch of Eo effluent is displayed in Fig. 4.1.1. It was noted that the maximum color removal was 85% after 180 minutes treatment time.

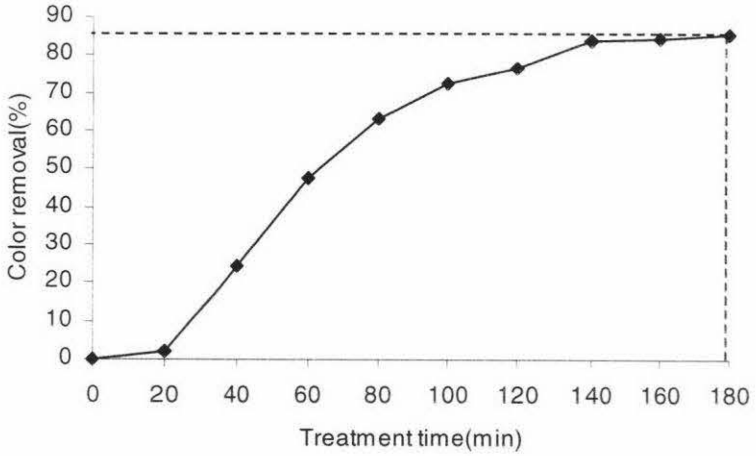


Fig. 4.1.1 Effect of ozone treatment time on color removal from the first batch of Eo effluent.

As shown, there was very little change in the first 20 minutes of treatment after which the color removal occurred rapidly for a further 40 minutes, then slowly decreased. The experiment was terminated at 3 hours of treatment at which time there remained 15% of the original color. Any further increase in ozonation treatment time would be expected to result in little additional color removal.

Ozonation kinetics for a color removal can be expressed by the formula:

$$C_t = C_u\,(1- e^{-k^*t}) \qquad (4.1.1)$$

Where C_u is the ultimate % color removal; C_t is the % color removal at time t; t is time (minutes); k is the color removal rate constant 1/t (see Appendix 2 Section A2.1 for Color Removal Formula Development).

The general formula development is displayed in Appendix 2. In this case, the % color removal C_t at t for the first batch of Eo effluent can be expressed as:

$$C_t = 100\,(1-e^{-0.011^*t}) \qquad (4.1.2)$$

Where $C_u = 100$; $k = 0.011 \pm 0.001$ with a 95% confidence limit (see Appendix 2, TABLE A2.1). Curves for both the model and the observed color removal are shown in the Fig.4.1.2.

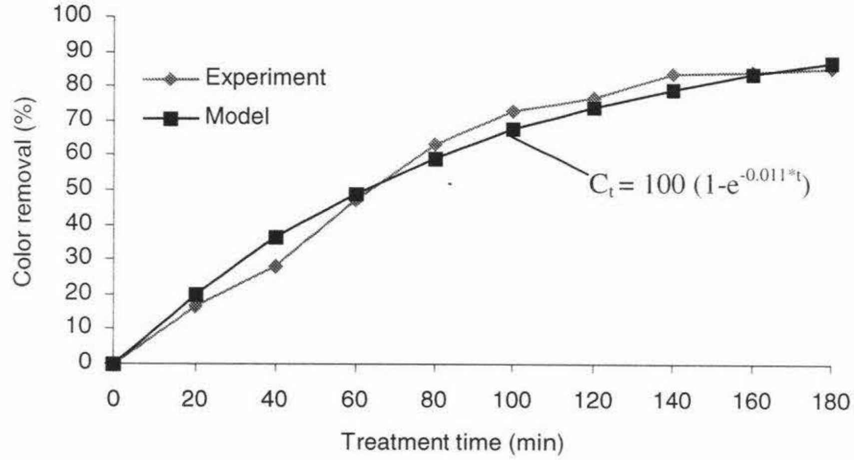


Fig. 4.1.2 Model for the removal of color by ozonation from the first batch of Eo effluent

Fig. 4.1.2 shows that the color removal model for the first batch of Eo effluent simulates reasonably well the experimental data. The maximum error between the theoretical and observed data is 4 % (obtained from estimates of error limits).

Fig. 4.1.3 depicts the results for the decolorisation of the second batch of Eo effluent. The general shape of the color removal curve resembles that of the first batch of Eo effluent tested although there was no initial period (20 minutes) during which negligible decolorization occurred. The maximum color removal achieved was 89% after 300 minutes of treatment.

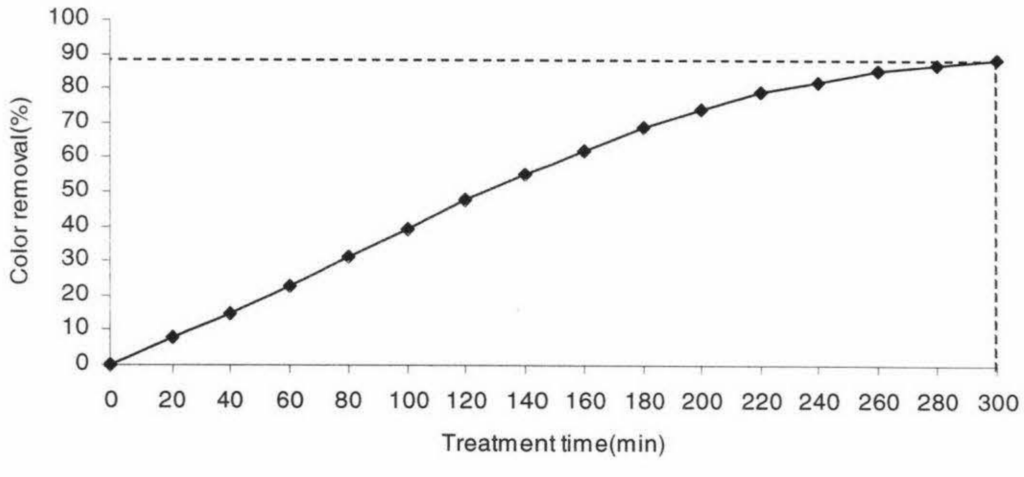


Fig. 4.1.3 Color removal for the second batch of Eo effluent treatment with ozone

A closer examination of the two batches of Eo effluent treatment indicates that the overall color removal achieved was similar, 85% for the first batch Eo effluent and 89% for the second batch of Eo. However, the ozonation time was different, 180 minutes for the former and 300 minutes for the latter. This difference may be related to differences in the initial color. The initial color density for the first batch Eo effluent was 633 CP[1]units while that of the second batch Eo effluent was 4142 CP.units. Furthermore, with this high color density in batch 2 came the possibility that some of the color components were immediately oxidizable by ozone thus allowing decolorization to occur as soon as the reaction was commenced.

The color removal C_t for the second batch of Eo effluent is expressed as:

$$C_t = 100\,(1-e^{-0.006*t}) \qquad (4.1.3)$$

Where $C_u = 100$; $k = 0.006 \pm 0.0007$ with 95% confidence limit (see Appendix 2 TABLE A2.2). Curves for both the model and the observed color removal are shown in the Fig. 4.1.4.

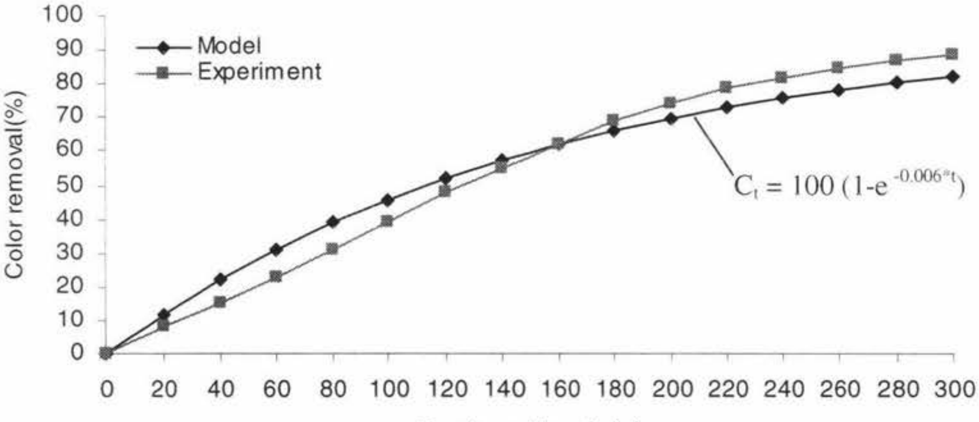


Fig. 4.1.4 Model for the removal of color by ozonation from the second batch of Eo effluent

Fig. 4.1.4 indicates that the model curve fits the collected experimental data reasonably well and tended to overestimate color removal (up to 3 hours). The maximum error between the two curves was ±6%.

---

[1] Chloroplatinate (Units)

These results for color removal demonstrate that ozone was effective and removed 85% to 89% of the color from the Eo effluents. However, empirical observation suggests that the ozonation time depended on the effluent's initial color loading under the constant ozone flowrate condition. These color removal models (formulae 4.1.2 and 4.1.3) can be used to predict the color removal performance during ozone treatment and allow an estimate to be made of the ozonation time needed for the desired color removal with Eo effluents under the experimental conditions used here.

4.1.1.2 COD Removal

The first batch of Eo effluent was used to investigate the COD changes which occurred with ozonation. Fig. 4.1.5 shows the depletion in COD with increased ozone treatment time. The maximum COD removal achieved for the first batch of Eo effluent was 12 % after 180 minutes. The COD value decreased from an initial 1250mg/l to 1100mg/l after the ozonation (see Appendix 2, TABLE A2.5).

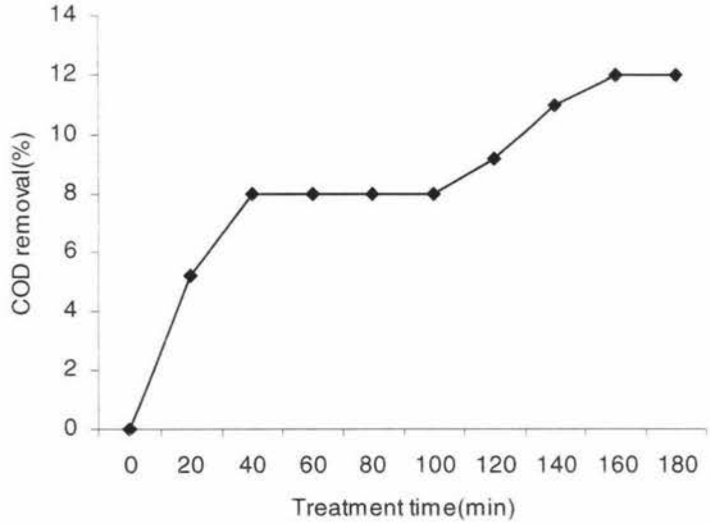


Fig. 4.1.5 COD removal for the first batch Eo effluent treatment with ozone

The COD reduction after 300 minutes was also measured for the second batch of Eo effluent. The COD decreased from an initial of 3000 mg/l to 2500 mg/l after 300 minutes ozonation treatment, that is, 17% (see Appendix 2 TABLE A2.6).

On a percentage removal basis the results for the COD removal were much lower than that observed for the color removal using the two batches of Eo effluent. Therefore, it would seem that although ozone is particularly effective in removing color from the bleaching effluent the removal of COD is less effective.

4.1.1.3 BOD_5 Increase

BOD_5 values for the two batches of Eo effluent were tested before and after the ozone treatment. During ozone treatment the BOD_5 value for the first batch of Eo effluent increased from an initial value of 294 mg/l to 391 mg/l and that for the second batch of Eo effluent increased from an initial value of 166 mg/l to 218 mg/l. That is, the percentage of BOD_5 increase was 33% for the former and 31% for the latter (these values are beyond the BOD_5 change error limit of 3.3%) and suggests that ozone treatment has converted a part of the COD to BOD_5.

The biodegradability of components in effluents can be expressed as the BOD_5/COD ratio. In this case, the BOD_5/COD ratio for the first batch of Eo effluent increased from an initial value of 0.235 to 0.355 and that for the second batch of Eo effluent increased from an initial value of 0.055 to 0.087. Thus, the biodegradability for the former improved 51% and that for the latter improved 58% through the ozone treatment. The biodegradability improvement for the two batches of Eo effluent after ozone treatment averaged 54 %.

These changes induced by ozone are shown in TABLE 4.1.1 (see Appendix 2, TABLE A2.1, A4.2.2, A2.5, A2.6 and A2.7)

TABLE 4.1.1

Effects of ozonation on an Eo bleaching effluent fraction of a pulp and paper mill effluent

Batch No.	% changes			
	Color removal	BOD_5 increase	COD decrease	Biodegradability (BOD_5/COD)
1	85	33	12	51
2	89	31	17	58
Mean	87 ± 0.1	32 ± 3.3	14 ± 0.6	54

In summary, these results suggested that ozone treatment was most effective for color removal and it increased the biodegradability by approximately 54%. The treatment, however, was less effective for COD removal

4.1.2 Treatment of Mixed Effluents

The mixed effluent used in these ozonation trials consisted of approximately 80% (v/v) Eo effluent (alkaline) and 20% (v/v) DC effluent (acidic) and the mixed effluent's pH was approximately 9. Alkaline conditions enhance the ozone degradation of lignin (Kahmark and Unwin, 1997). The same parameters monitored during Eo effluent treatment, which included color removal, COD removal and BOD_5 increase, were again studied in the two batches of mixed effluent prepared from the EO and DC effluents. These will be identified as the Mix_1 & Mix_2 batches.

4.1.2.1 Color Removal

The color removal for the first batch of Mix_1 effluent was measured (see Fig. 4.1.6). The color removal increased with an increase in ozonation treatment time. The maximum color removal was 87% with 180 minutes of treatment. This color removal result was similar to that for the first batch Eo_1 effluent treated (85 % in 180 minutes).

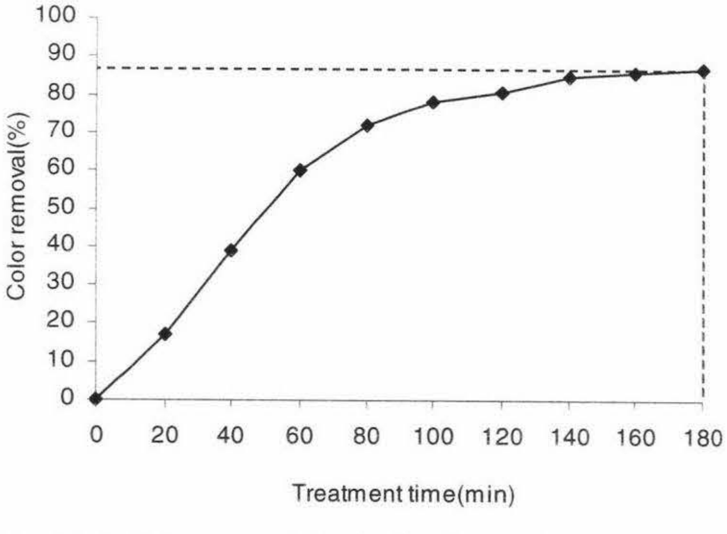


Fig. 4.1.6 Color removal for the first batch of mixed effluent (Mix_1) treated with ozone

From the data obtained for the first batch of mixed effluent a mathematical model was developed. The color removal (% C_t) can be expressed as:

$$C_t = 100\,(1 - e^{-0.013*t}) \qquad (4.1.4)$$

Where $C_u = 100$; $k = 0.013 \pm 0.002$ with a 95% confidence limit (see Appendix 2, TABLE A2.3).

Fig. 4.1.7 shows that the curve developed from this formula simulates the experimental color removal test data and the maximum error is ± 4 %.

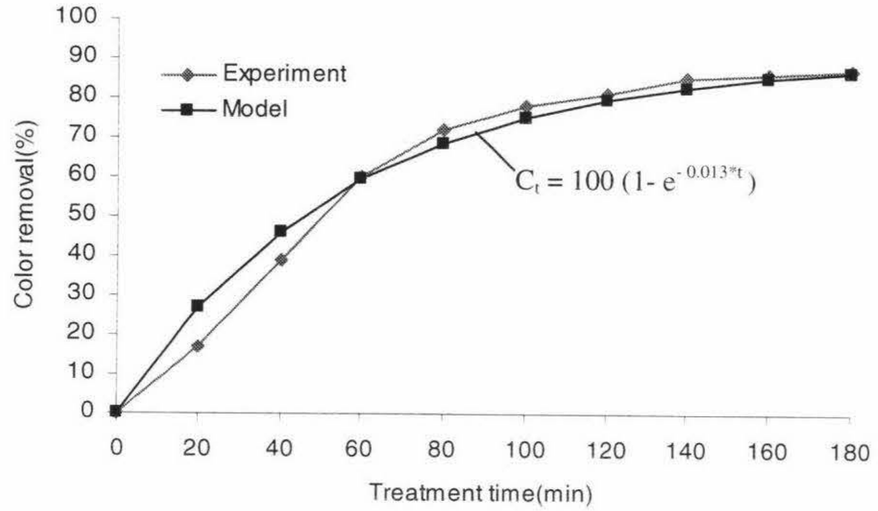


Fig. 4.1.7 Color removal model for the first batch of mixed effluent treated with ozone

The color removal curve for the second batch of mixed effluent treated with ozone is displayed in Fig. 4.1.8. Color removal increased with the ozonation treatment time and the maximum color removal was 88 % after 300 minutes.

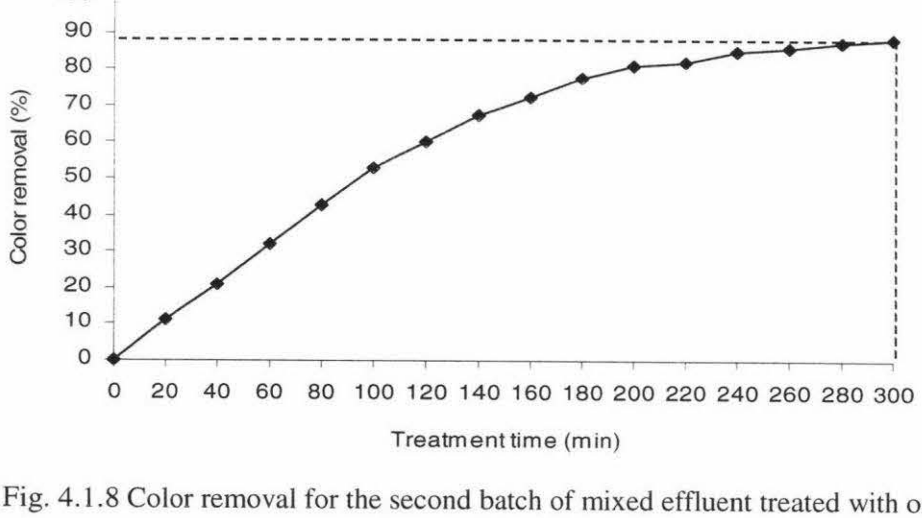


Fig. 4.1.8 Color removal for the second batch of mixed effluent treated with ozone

This second batch of mixed effluent required a considerably longer treatment time than the first experimental batch. This was associated to the greater color intensity of this batch (Section 3.2, TABLE 3.1 for initial effluent characteristics).

A mathematical formula was established from the experimental data. The color removal (%) C_t for the second batch mixed effluent is expressed as:

$$C_t = 100\,(1 - e^{-0.007*t}) \qquad (4.1.5)$$

Where $C_u = 100$; $k = 0.007 \pm 0.0005$ with a 95% confidence limit (see Appendix 2, TABLE A2.4).

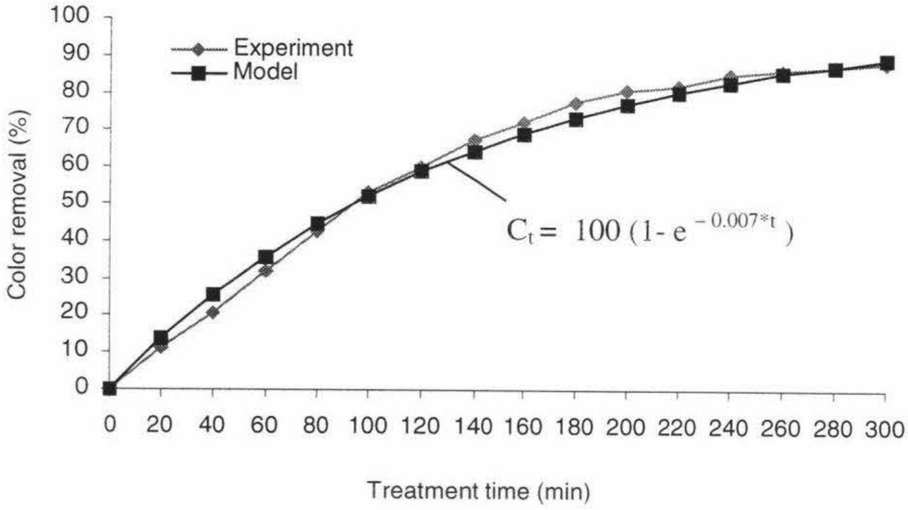


Fig. 4.1.9 Color removal model for the second batch of mixed effluent treated with ozone

A comparison of the experimental color removal curve with the model curve (see Fig. 4.1.9) suggests that the model closely simulates the color removal observed experimentally and the maximum error is ± 2%.

Thus, the results obtained for the ozone treatment of a mixed effluent resembled those obtained in Eo effluent tests. The color removal was 87% for the first batch of mixed effluent and 88% for the second. A model for each of the two batches of mixed effluent was established (see formulae 4.1.4 and 4.1.5). The ozone treatment time related to the initial mixed effluent's characteristics.

4.1.2.2 COD Removal

The first batch of the mixed effluent was treated so that the COD removal with time could be observed. The COD removal improved with increasing ozonation treatment time (see Fig. 4.1.10). The COD decreased from an initial value of 1185 mg/l to 965 mg/l after 180 minutes (see Appendix 2, TABLE A2.5). Thus, the maximum COD removal was 19%.

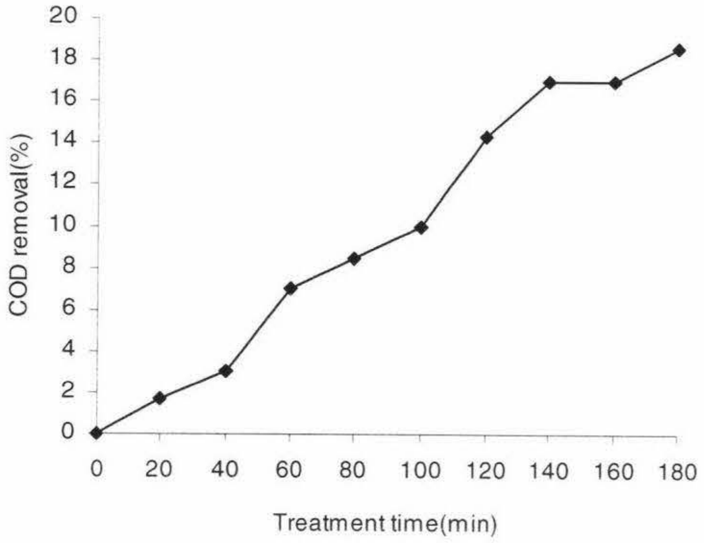


Fig.4.1.10 COD removal for the first batch mixed effluent treated with ozone

The COD values for the second batch of mixed effluent were measured before and after 300 minutes of ozone treatment. The COD decreased from an initial value of 2415 mg/l to 2110 mg/l during treatment which represented a 13% removal (see Appendix 2, TABLE A2.6).

This COD removal in percentage values was much lower than that for color removal in the two batches of mixed effluents but was consistent with the removal rates observed in the Eo effluents.

4.1.2.3 BOD_5 Increase

BOD_5 for each of the two batches of mixed effluent was measured before and after the ozone treatment. The BOD_5 value for the first batch of mixed effluent increased from an initial value of 289 mg/l to 367 mg/l over the 180 minutes treatment time and for the second batch of mixed effluent there was an increase from 186 mg/l to 259 mg/l over 300 minutes of treatment time. Therefore, the percentage of BOD_5 increase for the former was 27% and for the latter was 39%. Consequently, the biodegradability, expressed as the BOD_5/COD ratio, increased from 0.24 to 0.38 for the first batch and from 0.077 to 0.123 for the second batch of mixed effluent. This represented a biodegradability improvement brought about by ozonation of 58% and 60% respectively. These % changes are shown in TABLE 4.1.2 (see Appendix 2, TABLE A2.3-A2.7).

TABLE 4.1.2

Effects of ozonation on a mixed bleaching effluent fraction of a pulp and paper mill effluent

Batch No.	% changes			
	Color removal	BOD_5 increase	COD decrease	Biodegradability (BOD_5/COD)
1	87	27	19	58
2	88	39	13	60
Mean	87.5 ± 0.1	33 ± 3.3	16 ± 0.6	59

In summary, using two batches of mixed effluents the results for color removal, COD removal and BOD_5 increase during ozone treatment exhibited similar patterns of change as observed when Eo effluent was treated.

4.1.3 Ozone Treatment Summary

Two batches of Eo and mixed bleaching plant effluents at the pH value at which they are discharged from the mill were treated with ozone. Because the effluent color is pH dependent, the true color removal for the effluents tested was assessed under conditions in which the pH of all effluents was standardized to 7.0. TABLE 4.1.3 summarized the results obtained for these two batches of bleaching effluents.

These results suggest that for the Eo and mixed bleaching effluents the effectiveness of ozone treatment does not lead to consistent changes in color, COD and BOD$_5$. The % color removal was much higher than COD removal while a BOD$_5$ increase was achieved during treatment. For the Eo and mixed effluents the color removal after pH neutralization to 7.0 ranged from 67% (Eo, batch1) to 74% (Eo, batch2), the COD removal ranged from 12% (Eo, batch1) to 19% (mixed, batch1), the BOD$_5$ increase ranged from 27% (mixed, batch1) to 39% (mixed, batch2) and the ratio BOD$_5$/COD (biodegradability) changed from 51% (Eo, batch1) to 60% (mixed, batch2).

TABLE 4.1.3

Changes in bleaching plant effluent characteristics following treatment with ozone

Batch No.	Item	Color Units	COD (mg/l)	BOD$_5$ (mg/l)	BOD$_5$/COD
1	Eo[1]	470	1250	294	0.235
	OEo[2]	157	1100	391	0.355
	Removal %	67	12	-	-
	Increase %	-	-	33	51
	Mixed[3]	563	1185	289	0.24
	OMix[4]	179	965	367	0.38
	Removal %	68	19	-	-
	Increase %	-	-	27	58
2	Eo	2903	3000	166.3	0.055
	OEo	769	2500	217.7	0.087
	Removal %	74	17	-	-
	Increase %	-	-	31	58
	Mixed[3]	2194	2415	186	0.077
	OMix	619	2110	259	0.123
	Removal %	72	13	-	-
	Increase %	-	-	39	60

[1] Initial Eo stage effluent.
[2] Ozonated Eo effluent.
[3] Initial mixed effluent.
[4] Ozonated mixed effluent.
[5] See Chapter 3, TABLE 3.1 for initial effluent characteristics.
All samples were neutralized to pH 7.0 before analysis for color, COD and BOD$_5$.

The initial characteristics of the effluent influenced the treatment requirements. To achieve the same extent of color removal, the first batch of Eo and mixed bleaching effluent were treated for 180 minutes while the second batch of these effluents required 300 minutes to achieve the same degree of color removal. This was because the initial color intensity of the 2^{nd} batch of Eo effluent was 6 times greater than that of the first while the initial color intensity of the 2^{nd} batch of the mixed effluent was 4 times that of the first.

Mathematical expressions for color removal using ozone treatment were developed for each effluent (see TABLE 4.1.4). These formulae offer a succinct summary of the experimental data. They describe the theoretical color removal behavior of the bleaching effluent during ozone treatment. With these formulae it is possible to calculate the color removal at a selected ozonation treatment time. The maximum error for these estimations of % removal is ± 10%. The general formula for the color removal C_t is expressed as:

$$C_t = C_u\,(1 - e^{-k*t})$$

Where C_u is ultimate % color removal; C_t is % color removal at t time; k is color removal rate constant, t^{-1}; t is time (minutes).

TABLE 4.1.4

Summary of color removal formulae

Batch No.	Item	Initial color units	C_u	k	Formula	Error (%)[3]
1	Eo[1]	633	100	0.011	$C_t = 100\,(1 - e^{-0.011*t})$	4
	mixed[2]	756	100	0.013	$C_t = 100\,(1 - e^{-0.013*t})$	2
2	Eo	4142	100	0.006	$C_t = 100\,(1 - e^{-0.006*t})$	6
	mixed	3310	100	0.007	$C_t = 100\,(1 - e^{-0.007*t})$	2

[1] Initial Eo bleaching effluent with original pH value (no pH neutralization).
[2] Initial mixed bleaching effluent with pH value of 9.0.
[3] Estimated error compared with the experimental color removal curve.

In the formulae, the ultimate color removal C_u and the color removal rate constant k are two important variables. The ozone treatment was very effective for removing color from the Eo and the mixed effluents. Thus the ultimate color removal C_u was assumed to be 100. The color removal rate constant k varied with the initial effluent color. The initial color unit values for the first and second batches of Eo effluents was 633 and 4142 C.P. units respectively. The corresponding k value was 0.011 and 0.006. Likewise, the initial color for the first and second batches of mixed effluents was 756 and 3310 C.P.units, respectively. The corresponding k value was 0.013 and 0.007. It seems, therefore, that the high initial color loading is reflected in the low k value and requires a longer treatment time.

The characteristics for the Eo and mixed effluents are displayed in TABLE 4.1.3. As shown, although the ozone treatment removed most of the color from them, above 80% of the original COD still remained and most of it seemed to be non-biodegradable. Thus ozone oxidation alone dose not offer a complete treatment process and therefore the ozonated effluent was next subjected to biological treatment.

4.2 Biological Treatment

Following ozone treatment of a bleaching plant effluent, a biological treatment process was used to investigate the further removal of COD, BOD_5 and changes in color density. Two lagoon systems were established for this work. One lagoon system consisted of an anaerobic zone followed by an aerobic zone for providing sequential anaerobic and aerobic environments to facilitate biodegradation. The second system consisted of an aerated lagoon only to determine the extent of aerobic biodegradation of the ozonated effluent. To assess the effect of ozone pretreatment on the subsequent biological process, a non-ozonated raw pulp bleaching effluent was passed through those biological processes under identical conditions. For clarity in the diagram (Fig.A2.1-Fig.A2.4), the processing flow line used for the ozonated bleaching effluent is called the "experimental line" while that used for the non-ozonated raw pulp bleaching effluent treated biologically is called the "control line". The characteristics of effluents used in these experiments, including the non-ozonated raw bleaching effluent and the ozonated bleaching effluent, are presented in Section 4.1, TABLE 4.1.3.

4.2.1 Anaerobic-Aerobic Lagoon Treatment

The first batch of bleaching effluents, i.e. non-ozonated (Eo_I & Mix_I) and ozonated (OEo_I & $OMix_I$), were treated in the anaerobic-aerobic lagoon system. Data from these experiments are displayed in TABLE 4.2.1 (see Appendix 2 TABLE A2.8 and Fig.A2.1) and indicate the extent of changes in these effluents that can be associated with the biological activity in the lagoons. Of interest was that the performance of the mixed ($OMix_I$ & Mix_I) effluents resembled that of the Eo (OEo_I & Eo_I) effluents. The results obtained for these effluents showed a similar pattern of changes. There was considerable BOD_5 removal observed and to a lesser extent, COD removal. However, the passage of effluents through the lagoon increased their color content rather than removing it.

TABLE 4.2.1

Comparison of changes brought about by the anaerobic-aerobic lagoon system

Batch 1		Ozonated (OEo_1&$OMix_1$)			Non-ozonated (Eo_1&Mix_1)		
Category	Item	Color *CP.U*	COD *mg/l*	BOD_5 *mg/l*	Color *CP.U*	COD *mg/l*	BOD_5 *mg/l*
Eo_1	Influent	157	1100	391	470	1250	294
	Effluent	310	617	35	597	817	44
	% Removal	-98	44	91	-27	35	85
Mix_1	Influent	179	965	367	563	1185	289
	Effluent	321	617	20	735	767	22
	% Removal	-80	36	95	-31	35	92

Results obtained for the treatment of ozonated (OEo_1) and non-ozonated (Eo_1) effluents (TABLE 4.2.1) indicate that the anaerobic-aerobic lagoon treatment produced a 98% increase in color for the ozonated (OEo_1) effluent and 27% increase in color for the non-ozonated effluent. The BOD_5 removal was 91% for the (OEo_1) effluent and 85% for the Eo_1 effluent. The COD removal was 44% for ozonated (OEo_1) effluent and 35% for the non-ozonated (Eo_1) effluent. The results suggest that although the anaerobic-aerobic lagoon treatment removed slightly more COD and BOD_5 from the ozonated (OEo_1) effluent than the non-ozonated (Eo_1) effluent, it considerably increased color in the OEo_1 effluent compared with Eo_1 effluent. Numerical values for these characteristics are shown in Fig.4.2.1 (see TABLE 4.2.1).

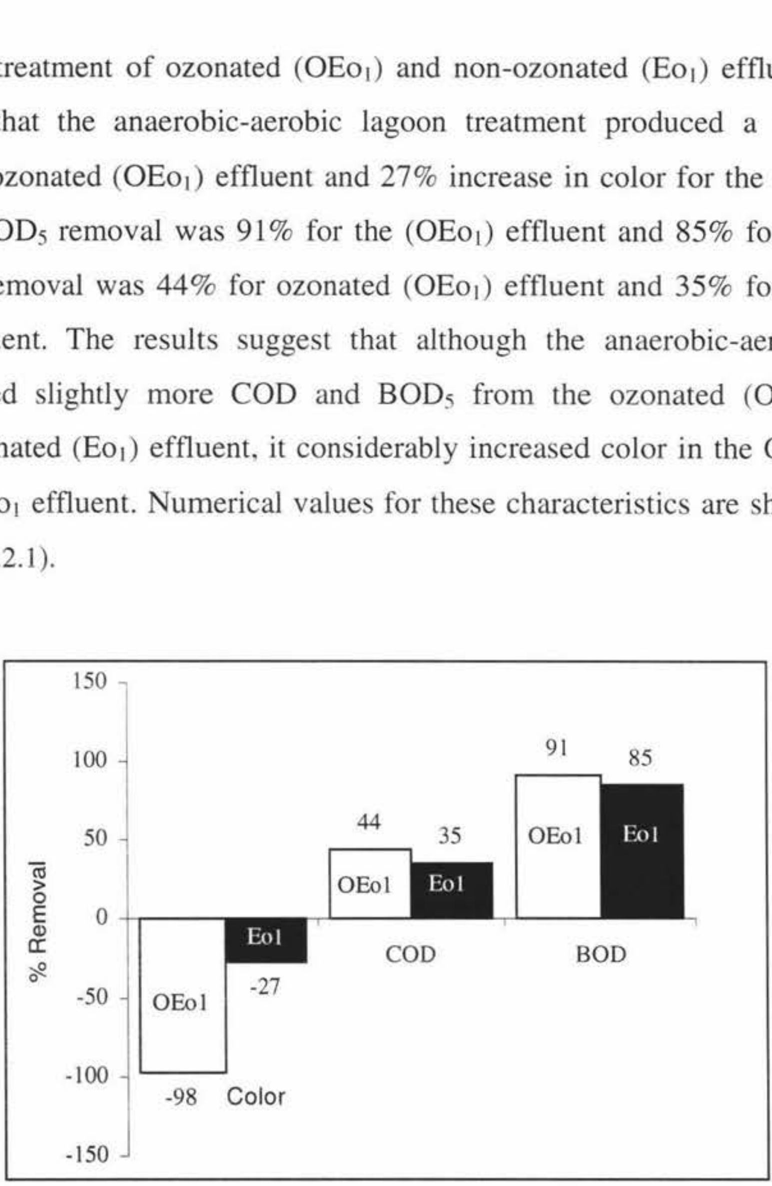


Fig.4.2.1. Changes in color, BOD_5 and COD expressed as percentage of initial value resulting from treatment through anaerobic & aerobic zones of a lagoon for ozonated (OEo_1) and non-ozonated (Eo_1) bleaching effluents.

An analysis of these changes suggests that the anaerobic-aerobic lagoon treatment of ozonated effluent in particular was counter-productive since it increased the color by 98% although it improved COD and BOD_5 removal marginally.

Results obtained for the treatment of ozonated ($OMix_1$) and non-ozonated (Mix_1) effluents are shown in TABLE 4.2.1 and indicate that during the effluent's sequential passage through anaerobic then aerobic zones in the lagoon, BOD_5 was removed and to a lesser extent, COD. Color was increased and the enhancement was greatest (80%) in the ozonated ($OMix_1$) effluent and weaker (31%) in the non-ozonated (Mix_1) effluent. The BOD_5 removal was 95% for the $OMix_1$ effluent and 92% for the Mix_1 effluent. The COD removal was 36% for the $OMix_1$ effluent and 35% for the Mix_1 effluent. Therefore, although the anaerobic-aerobic lagoon treatment removed a similar amount of COD and BOD_5 from ozonated and non-ozonated effluents, it significantly increased color in the ozonated effluent compared with non-ozonated effluent. The % changes are shown in Fig.4.2.2.

Fig.4.2.2. Changes in color, BOD_5 and COD expressed as percentage of initial value resulting from treatment through anaerobic & aerobic zones of a lagoon for ozonated ($OMix_1$) and non-ozonated (Mix_1) bleaching effluents.

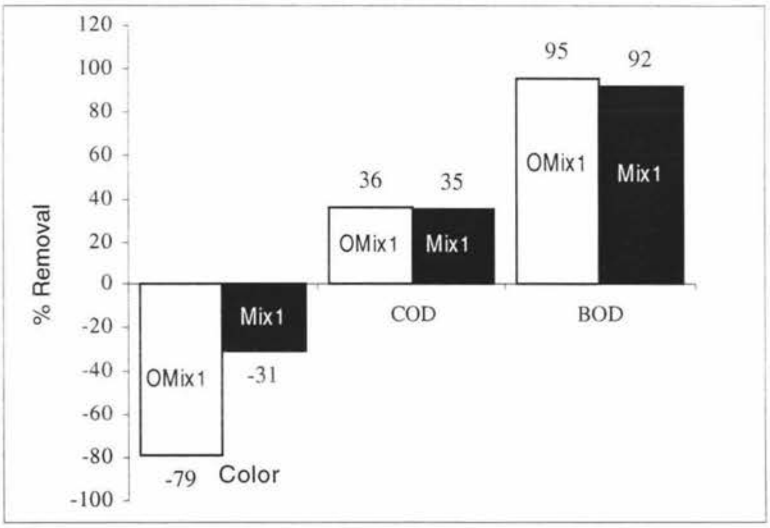


Fig.4.2.2 indicates that the increase in color with the anaerobic-aerobic lagoon treatment is quite noticeable while the extent of BOD_5 & COD changes is similar to that observed from the Eo trial (see Fig.4.2.1).

4.2.2 Anaerobic-Aerobic Lagoon Treatment: Analysis

The separate contributions made to the changes in color, BOD_5 and COD by the anaerobic zone then the aerobic zone, i.e. the overall performance of the lagoon, were analyzed. The analysis for the Eo_1 and Mix_1 effluents is presented in TABLE 4.2.2 (see Appendix 2, TABLE A2.8 and Fig.A2.1 & Fig.A2.3).

TABLE 4.2.2

Changes brought about to a bleaching plant effluent by the anaerobic-aerobic lagoon system.

Batch 1		Ozonated (OEo_1& $OMix_1$)			Non-ozonated (Eo_1& Mix_1)		
Category	Item	Color(R)[1] *CP.U*	COD(R) *mg/l*	BOD_5(R) *mg/l*	Color(R) *CP.U*	COD(R) *mg/l*	BOD_5(R) *mg/l*
Eo_1	Influent[2]	157	1100	391	470	1250	294
	Anaerobic[3]	373(-*138*)	883 (20)	120 (69)	474(-1)	1050(16)	125(58)
	Aerobic[4]	310(40)	617 (24)	35 (22)	597(-26)	817 (19)	44 (27)
	% Removal[5]	-98	44	91	-27	35	85
Mix_1	Influent	179	965	367	563	1185	289
	Anaerobic	429(-140)	820(15)	141(62)	608(-8)	1067(10)	138(52)
	Aerobic	321(60)	617(21)	20(33)	735(-23)	767(25)	22(40)
	% Removal	-80	36	95	-31	35	92

[1] %Partial removal (R) from zone, such as (-138)=(157-373)*100/157 and (40)=(373-310)*100/373

[2] Influent to the anaerobic zone.

[3] Effluent from anaerobic zone.

[4] Effluent from aerobic zone

[5] % removal from the anaerobic & aerobic system

4.2.2.1 The Eo Effluent

Data from the Eo effluent treatment indicates that the ozonated (OEo_1) effluent's color increased 138% in the anaerobic zone and then decreased 40% in the aerobic zone to give a total color increase 98% in the anaerobic-aerobic lagoon. In contrast, the non-ozonated (Eo_1) effluent's color increased only 1% in the anaerobic zone and increased a further 26 % in the aerobic zone, giving a total color increase of 27% in the entire system. Of the total BOD_5 removal for the OEo_1 effluent (i.e., 91%) during biological treatment, 69% was removed in the anaerobic zone and 22% in the aerobic zone. Similarly, of the total BOD_5 removal for the Eo_1 effluent (85%), 58 % removal was achieved in the anaerobic zone and 27 % in the aerobic zone. The COD removal for the OEo_1 effluent was 20 % and 24 % in the anaerobic and aerobic zones respectively. The COD removal for the Eo_1 effluent was 16% and 19% in the anaerobic and aerobic zones respectively. Thus, the total COD removal was 44 % and 35 % for the OEo_1 and Eo_1 effluent respectively. For clarity, the % change values are illustrated as the histograms of Fig.4.2.3.

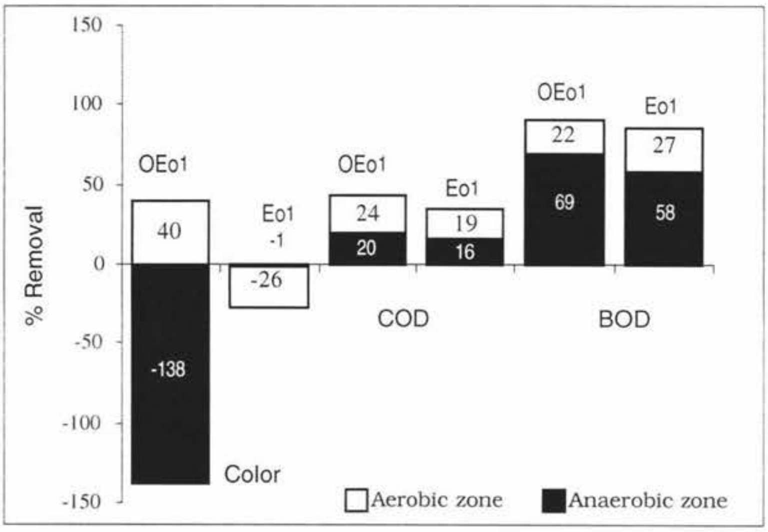


Fig.4.2.3. Changes in color, BOD_5 and COD expressed as percentage of initial value resulting from treatment through anaerobic & aerobic zones of a lagoon for ozonated (OEo_1) and non-ozonated (Eo_1) bleaching effluents of batch 1.

The chart suggests that a similar amount of COD is removed from each of the anaerobic and aerobic zones. BOD_5 is removed mostly in the anaerobic zone. However, anaerobic treatment markedly increases the color of the ozonated effluent. This increase also occurred, but to a lesser extent in the non-ozonated effluent.

4.2.2.2 The Mixed Effluent

Results for the mixed effluent treatment studies indicate that the ozonated ($OMix_1$) effluent's color increased 140% in the anaerobic zone and then decreased by 60% in the subsequent aerobic zone to give an overall color increase of 80% in the anaerobic-aerobic lagoon. In contrast, the non-ozonated (Mix_1) effluent's color increased only 8% in the anaerobic zone and a further 23 % in the aerobic zone, giving a total color increase of 31% in the entire system. Of the total BOD_5 removal for the $OMix_1$ effluent (95 %) in the aerobic-aerobic lagoon, 62% removal occurred in the anaerobic zone and 33% was observed in the aerobic zone. Similarly, of the total BOD_5 removal for the Mix_1 effluent (92%), 52% was achieved in the anaerobic zone and 40% in the aerobic zone. The COD removal for the $OMix_1$ effluent was 15% and 21% in the anaerobic and aerobic zones respectively. The COD removal for the Mix_1 effluent was 10% and 25% in the anaerobic and aerobic zones respectively. Thus, the total COD removal was 36% and 35% for the $OMix_1$ and Mix_1 effluents respectively. For clarity, the % change values are illustrated as the histograms of Fig.4.2.4.

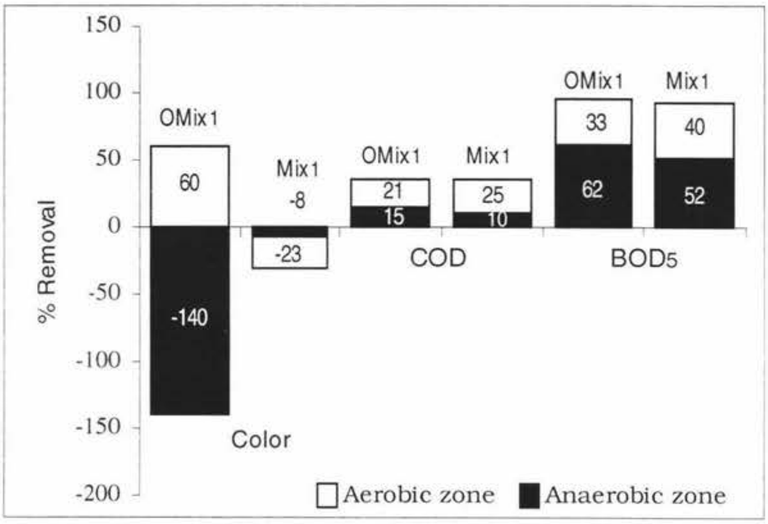


Fig.4.2.4. Changes in color, BOD_5 and COD expressed as percentage of initial value resulting from treatment through anaerobic & aerobic zones of a lagoon for ozonated ($OMix_1$) and non-ozonated (Mix_1) bleaching effluents of batch 1.

Fig.4.2.4 indicates that the COD removal achieved in the aerobic zone was slightly more than that in the anaerobic zone while BOD_5 is removed mostly in the anaerobic zone. However, anaerobic treatment markedly increases the color of the ozonated effluent. An increase also occurred, but to a lesser extent in the non-ozonated effluent.

4.2.3 Aerated Lagoon Treatment

A further batch of pulp bleaching plant effluents (Eo & mixed) was used to identify the contribution of the aerobic zone to effluent treatment. An aerated lagoon was operated under conditions described in Section 3.2, Experimental Design. TABLE 4.2.3 (see Appendix 2, TABLE A2.9 and Fig. A2.2 & A2.4) exhibits the results obtained for this second batch of Eo and Mix effluents treated in the aerated lagoon.

TABLE 4.2.3

Comparison of changes brought about to bleaching plant effluent by aerated lagoon treatment

Batch 2		Ozonated (OEo_2&$OMix_2$)			Non-ozonated (Eo_2&Mix_2)		
Category	Item	Color *CP.U*	COD *mg/l*	BOD_5 *mg/l*	Color *CP.U*	COD *mg/l*	BOD_5 *mg/l*
Eo_2	Influent	769	2500	217.7	2903	3000	166.3
	Effluent	933	1650	39	2537	2110	59.1
	% Removal	-21	34	82	13	30	64
Mix_2	Influent	619	2110	259	2194	2415	186
	Effluent	716	1310	28	1828	1650	46.6
	% Removal	-16	38	89	17	32	75

4.2.3.1 The Eo Effluent

Data in TABLE 4.2.3 illustrates the extent of change occurring in the ozonated (OEo_2) and non-ozonated (Eo_2) pulp bleaching effluents that can be associated with the biological activity in the aerated lagoons. Of interest was that BOD_5 was removed by 82% for the OEo_2 effluent and 64% for the Eo_2 effluent, but the COD removal was only 34% for the OEo_2 effluent and 30% for the Eo_2 effluent. However, the passage of ozonated (OEo_2) effluent through the aerated lagoon darkened the color by 21% whereas for the non-ozonated (Eo_2) effluent 13% of initial color was removed. The % changes are shown in the histograms of Fig.4.2.5.

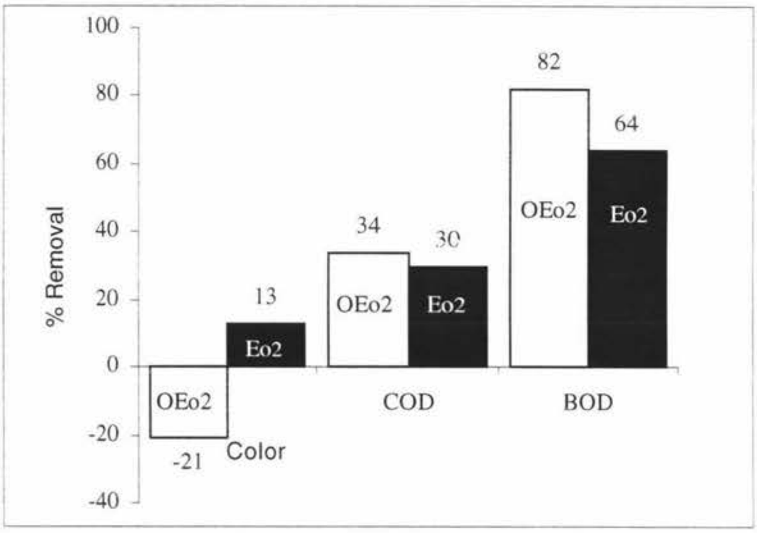


Fig.4.2.5. Changes in color, BOD_5 and COD expressed as percentage of initial value resulting from treatment through the aerated lagoon for ozonated (OEo_2) and non-ozonated (Eo_2) bleaching plant effluents.

These results suggest that the aerated lagoon treatment resulted in a smaller color increase for the ozonated (OEo_2) effluent compared to the anaerobic-aerated system and it reduced the non-ozonated (Eo_2) effluent's color. The aerated lagoon also achieved more BOD_5 removal for the OEo_2 effluent than that for the Eo_2 effluent and improved the COD removal marginally for the ozonated (OEo_2) effluent over that for the non-ozonated (Eo_2) effluent.

4.2.3.2 The Mixed effluent

The same process regimes used for OEo_2 and Eo_2 effluents were employed for treatment of the ozonated mixed ($OMix_2$) and non-ozonated mixed (Mix_2) bleaching effluents. A similar result pattern found with the OEo_2 and Eo_2 effluents was observed with the $OMix_2$ and Mix_2 effluent treatments.

Results obtained for the mixed effluent are shown in TABLE 4.2.3 and demonstrate that with an aerated lagoon treatment, the $OMix_2$ effluent's color increased 16 % whereas the Mix_2 effluent's color decreased 17 %. The BOD_5 was removed by 89 % for the $OMix_2$ effluent and 76 % for the Mix_2 effluent. The COD diminished by 38 % for the $OMix_2$ effluent and 32 % for the Mix_2 effluent. These results suggest that the aerated lagoon caused a lesser extent of color increase in the ozonated $OMix_2$ effluent compared with the anaerobic-aerobic lagoon while the Mix_2 effluent's color was removed in the aerated lagoon. Also there was better BOD_5 reduction for the $OMix_2$ effluent relative to the Mix_2 effluent. Lastly, the COD removal for ozonated $OMix_2$ effluent was improved marginally over the non-ozonated Mix_2 effluent.

The % change values are illustrated as histograms in Fig.4.2.6.

Fig.4.2.6. Changes in color, BOD_5 and COD expressed as percentage of initial value resulting from treatment through the aerobic lagoon for ozonated ($OMix_1$) and non-ozonated (Mix_1) bleaching effluents.

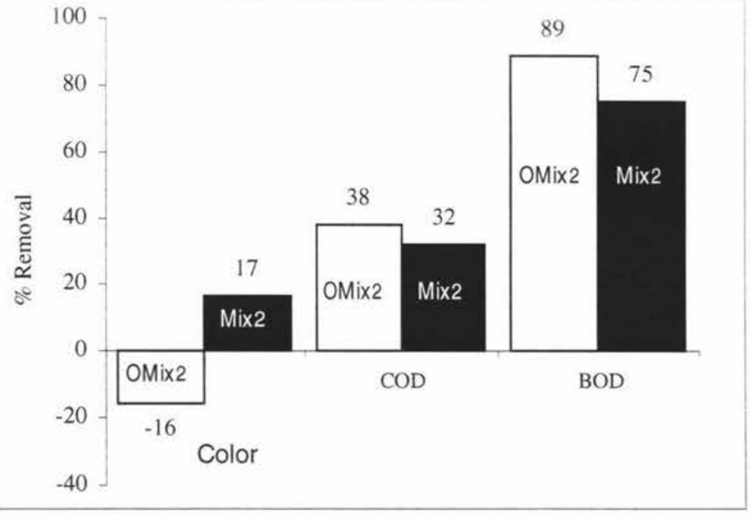


Fig.4.2.6 indicates that with the aerated lagoon treatment BOD_5 decreased and to a lesser extent, so did COD. The color for $OMix_2$ effluent increased, although the extent of this increase was much lesser than that occurring in an anaerobic-aerated lagoon. Aerobic treatment decreased the non-ozonated (Mix_2) effluent's color.

4.2.4 Comparison of Anaerobic-Aerobic lagoon and Aerated Lagoon Treatment

The two lagoon systems under study were the anaerobic-aerobic lagoon and the aerated lagoon. This section of the research was to identify the better biological treatment process of the two systems used. The effects of each of these treatment systems on ozonated and non-ozonated pulp bleaching effluents are shown in TABLE 4.2.4 (see TABLE 4.2.1 and TABLE 4.2.3)

Although the characteristics of the two batches of effluents (as received from the mill) were quite different, the COD loading (kg/m^{3}d) into each lagoon system for the two batches of effluents tested were similar, but not identical (see Appendix 2 TABLE A2.10). Approximately 0.11 COD kg/m^{3}d ± 18% was passed into the lagoon system for the ozonated effluents (OEo$_1$, OEo$_2$, OMix$_1$ and OMix$_2$) and 0.13 COD kg/m^{3}d ± 15% was treated through the lagoon system for the non-ozonated effluents (Eo$_1$, Eo$_2$, Mix$_1$ and Mix$_2$). However, to achieve this, the retention time used in each batch experiment was not the same. Changes in color, BOD$_5$ and COD were observed for all treatment lines. Data (see TABLE 4.2.4) suggests that the anaerobic-aerobic lagoon was able to eliminate more BOD$_5$ from both ozonated and non-ozonated effluents than the aerated lagoon alone, but that the % color increase in the anaerobic-aerated lagoon was considerably higher, especially for ozonated effluents.

TABLE 4.2.4

% Removal brought about by biological lagoon treatment of non-ozonated and ozonated bleaching effluents

		Non-ozonated		Ozonated	
Anaerobic-Aerated		Eo$_1$	Mix$_1$	OEo$_1$	OMix$_1$
	Color	-27	-31	-98	-80
(Batch1)	COD	35	35	44	36
	BOD$_5$	85	92	91	95
Aerated		Eo$_2$	Mix$_2$	OEo$_2$	OMix$_2$
	Color	13	17	-21	-16
(Batch2)	COD	30	32	34	38
	BOD$_5$	64	75	82	89

Results for ozonated (OEo$_1$ & OEo$_2$) effluents (see TABLE 4.2.4) revealed that the anaerobic-aerobic lagoon system removed more COD and BOD$_5$ than the aerated lagoon, 44% of COD & 91% of BOD$_5$ for the OEo$_1$ effluent in the anaerobic-aerated system and

34% of COD & 82% of BOD_5 for the OEo_2 effluent in the aerated lagoon. However, the anaerobic-aerobic system darkened the ozonated (OEo_1) effluent color considerably (98%) while the aerated lagoon produced much less color increase (21%). Because color removal was one of the main objectives in this study, the increased color in the ozonated effluent was obviously unacceptable. Thus, an anaerobic-aerated system was unsuitable for use with an ozone pretreated (OEo) bleaching effluent.

Data for non-ozonated (Eo_1 & Eo_2) bleaching effluent treatment (see TABLE 4.2.4) show that the two lagoon systems removed COD equally well from these (Eo_1 & Eo_2) effluents, (35% for the Eo_1 effluent in the anaerobic-aerated system and 30% for the Eo_2 effluent in the aerated lagoon). The main difference in the treatment of non-ozonated effluents was that the anaerobic-aerobic system eliminated more BOD_5 (85%) from Eo_1 effluent than did the aerated lagoon 64% from the Eo_2 effluent. However, the anaerobic-aerated lagoon caused a color increase (27%) for the Eo_1 effluent while the aerated lagoon removed color (13%) from the Eo_2 effluent. Therefore, for the treatment of non-ozonated effluents an anaerobic-aerated lagoon offers little advantage over an aerated lagoon. The removal of BOD_5 (85%) is offset by the increase in final effluent color (up 27%).

TABLE 4.2.4 indicats that in both, the anaerobic-aerated lagoon and the aerated lagoon, similar amounts of COD and BOD_5 were removed from the ozonated ($OMix_1$&$OMix_2$) effluents; 36% of COD & 95% of BOD_5 was lost from the $OMix_1$ effluent in the anaerobic-aerated system and 38% of COD & 89% of BOD_5 was removed from the $OMix_2$ effluent in the aerated lagoon. However, the anaerobic-aerobic system increased the color by 80% for the ozonated ($OMix_1$) effluent. In contrast, the aerated lagoon (receiving $OMix_2$) only enhanced the color by 16% for this effluent. This suggests that the anaerobic-aerated lagoon was not a practical option for biological treatment of the ozonated (OMix) effluent.

These changes in color, COD and BOD_5 were considered in parallel with the changes brought about in biological treatment lagoons receiving non-ozonated bleaching effluents (see TABLE 4.2.4). The results for the non-ozonated (Mix_1 & Mix_2) effluent treatment resembled those for the non-ozonated (Eo_1 & Eo_2) effluents. The two biological systems studied lowered the COD. There was 35% COD removal from the Mix_1 effluent during anaerobic-aerobic lagoon treatment and 32% COD removal from the Mix_2 effluent in the aerated lagoon process. The anaerobic-aerobic system eliminated more BOD_5 (92%) from the Mix_1 effluent than did the aerated lagoon (75%) from the Mix_2 effluent. However, the anaerobic-aerobic lagoon produced a color increase (31%) for the Mix_1 effluent while the aerated lagoon treatment removed color (17%) from the Mix_2 effluent. Thus, the results suggest that for the treatment of non-ozonated effluents an anaerobic-aerated system offers little advantage over an aerated lagoon. The removal of BOD_5 (92%) is offset by increase in final effluent color (up 31%).

An analysis of data obtained from the biological treatment of ozonated and non-ozonated bleaching effluents indicates that an aerated lagoon is the preferred option for the treatment. With an aerated lagoon treatment the ozonated (OEo and OMix) effluents showed the lowest color increase compared with the increase noted in the anaerobic-aerobic lagoon system although the extent of COD and BOD_5 removal was higher with the anaerobic-aerobic lagoon treatment than the aerated lagoon process.

4.2.5 Biological Treatment Summary

The effect of lagoon treatment can be summarized as follows. Where no ozone was used in the pretreatment of pulp bleaching effluent (i.e. Eo_1& Eo_2 and Mix_1 & Mix_2, see TABLE 4.2.4), COD was removed equally well in both the anaerobic-aerated and aerated lagoons (30-35% COD removal). However, BOD_5 removal appeared to be favored in the anaerobic-aerated lagoon (up to 92% removal) whereas in the aerated lagoon BOD_5 removal was lower (64 to 75%). The anaerobic-aerated system contributed color (27 to 31% of color increase) to the final treated effluent while the aerated lagoon removed the color (13 to 17%) during treatment.

Where the effluent entering the two lagoon systems was pretreated with ozone (i.e. OEo_1 & OEo_2 and $OMix_1$ & $OMix_2$), the responses to COD & BOD_5 removal in the two systems were similar. However, the color increase in the anaerobic-aerated system was considerably higher (80 to 98%) in contrast to the aerated lagoon which contributed less color (16 to 21%) to the final discharged effluent.

4.3 Combined Ozone -Biological Treatment

As noted above pulp bleaching effluent was treated by passage through an ozonation reactor and then through biological processes for removal of color, BOD_5 and COD to improve the final effluent's characteristics. The advantages of the combined treatment over a biological treatment alone were realized when a comparison of the results was made. This section examines the removal of the above mentioned attributes during biological treatment alone and also during ozone pretreatment alone. Then, the overall removal data from the combined process are presented to identify the improvements that are associated with ozone pretreatment. The combined process considered the changes in the final effluent in relation to the raw bleaching plant effluent (as received) with the pH adjusted to 7.0.

4.3.1 Eo Effluents

Eo effluents were tested in two batches. They were all oxidized with ozone as the pretreatment and then subjected to either an anaerobic-aerated lagoon treatment (first batch) or an aerated lagoon treatment (second batch).

4.3.1.1 Combined Ozone and Anaerobic-Aerobic Lagoon Treatment for Eo_1 Effluent

A sample of pulp bleaching effluent (Eo_1) was pretreated with ozone and then it and the non-ozonated (Eo_1) raw effluent sample were processed through an anaerobic-aerobic lagoon system. Results obtained are shown in TABLE 4.3.1 (see Appendix 2, Fig. A2.1). The combined process improved the overall COD and color removal. Thus, the final discharged effluent quality produced by the combined process was enhanced.

TABLE 4.3.1

Comparison of changes brought about by an anaerobic-aerated lagoon alone, combined process and ozone treatment for Eo$_1$ effluent.

Treatment	Category Item	Color *CP.U*	COD *mg/l*	BOD$_5$ *mg/l*
Anaerobic-Aerated lagoon alone (Eo$_1$)	Influent	470	1250	294
	Effluent	597	817	44
	%Removal	-27	35	85
Combined ozonation and anaeobic-aerated lagoon	Influent	470	1250	294
	Effluent	310	617	35
	% Removal	34	51	88
Ozonation alone	Influent	470	1250	294
	Effluent	157	1100	391
	% Removal	67	12	-33

Data in TABLE 4.3.1 indicates that the combined process decreased the color by 34%, since ozone treatment alone removed 67% while the anaerobic-aerated lagoon treatment alone increased the color by 27%. Furthermore, the combined process increased COD removal (51%) over the single anaerobic-aerobic lagoon treatment (35%) and the additional COD removal observed was obtained during the ozone pretreatment (12%). The BOD$_5$ removals in the two treatment regimes was similar. That was an overall of 88% for the combined process and 85% for the anaerobic-aerated lagoon alone. The increased BOD$_5$ (33%) converted from COD during ozone pretreatment was biodegraded in the subsequent biological stage of the combined treatment. For clarity, the % changes in three stages (color, COD and BOD$_5$) for each treatment is exhibited in Fig.4.3.1.

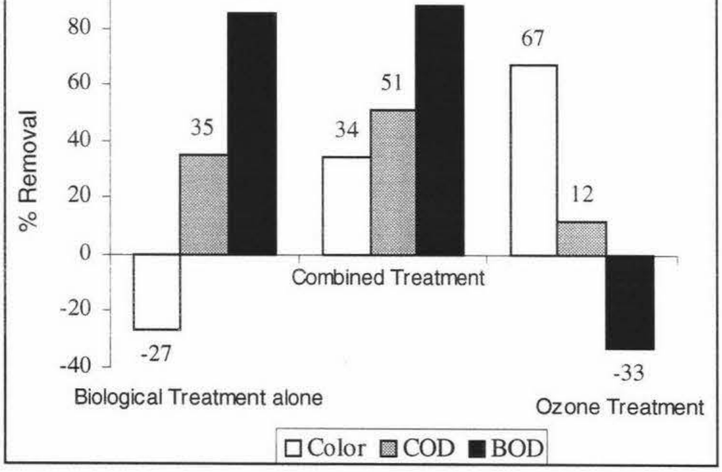


Fig.4.3.1 Changes in color, COD and BOD$_5$ expressed as percentage of initial value resulting from the anaerobic-aerated lagoon alone, combined process and ozone alone treatment for the Eo$_1$ effluent.

Fig.4.3.1 suggests that the combined treatment improved the color removal and observably increased the COD removal as well as achieved high BOD_5 removal including base BOD_5 removal and additional BOD_5 removal that was initially produced during ozone treatment. These particular improvements are also associated with ozone pretreatment alone.

4.3.1.2 Combined Ozone and Aerated Lagoon Treatment for Eo_2 Effluent

Pulp bleaching effluent (Eo_2) was also pretreated with ozone and then passed through an aerated lagoon instead of the anaerobic-aerated lagoon to investigate the effect of aerobic treatment. Data in TABLE 4.3.2 (see Appendix 2, Fig.A2.2) collected from the aerated lagoon treatment alone, the combined process and the ozone only pretreatment suggests that the combined process improved the removal of color, COD & BOD_5 and thus improved the final effluent's characteristics.

TABLE 4.3.2

Comparison of changes brought about by an aerated lagoon alone, a combined process and ozone treatment only for Eo_2 effluent

Treatment	Category Item	Color *CP.U*	COD *mg/l*	BOD_5 *mg/l*
Aerated lagoon alone (Eo_2)	Influent	2903	3000	166
	Effluent	2537	2110	59
	% Removal	13	30	64
Combined ozonation and aerated lagoon	Influent	2903	3000	166
	Effluent	933	1650	39
	% Removal	68	45	77
Ozonation only	Influent	2903	3000	166
	Effluent	796	2500	218
	% Removal	74	17	-31

As shown in TABLE 4.3.2, the combined process removed overall 68% of color, of which 74% had been removed before biological treatment by ozonation. In contrast, the aerated lagoon treatment alone removed only a small amount of color (13%). Also, the combined process increased the overall COD removal by 45% whereas the single aerated lagoon treatment only removed 30% of the COD. The extra COD reduction observed was produced from the ozone treatment (17%). The BOD_5 removal was improved using the combined process (77%) as compared with treatment in the aerated lagoon (64%). The BOD_5 increase (31%) produced during ozonation was then removed in the followed biological process of the combined system. The % changes in color, COD and BOD_5 during these treatments are summarized in Fig.4.3.2.

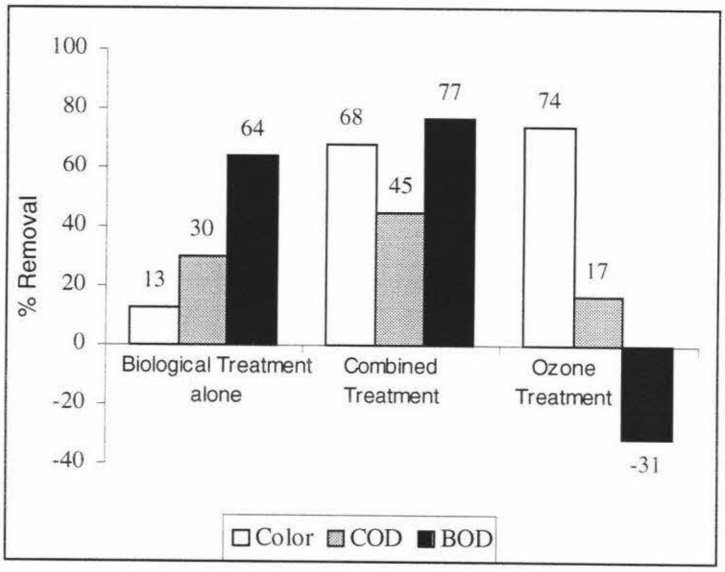


Fig.4.3.2 Changes in color, COD and BOD_5 expressed as percentage of initial value resulting from a single aerated lagoon, combined process and ozone treatment for the Eo_2 effluent.

The histograms indicate that the combined process greatly increased color removal, improved COD reduction and achieved more BOD_5 removal compared to the aerated lagoon alone. It would seem that these improvements are initiated during the chemical oxidation of effluent components with ozone.

The Eo effluents (Eo_1 & Eo_2) were treated using two combined processes, these were ozone combined with an anaerobic-aerobic lagoon and ozone combined with an aerated lagoon. Although the COD and BOD_5 removal obtained from the ozone & an anaerobic-aerobic lagoon treatment (51% of COD & 88% of BOD_5) were slightly higher than did through the ozone & an aerated lagoon process (45% of COD & 77% of BOD_5), the color removal (34%) observed in the ozone & anaerobic-aerobic lagoon system was only half of that (68%) achieved in the ozone & aerated lagoon system (see TABLES 4.3.1 and 4.3.2). Thus, the combined process of ozone & aerated lagoon treatment seemed to offer the best treatment regime for the Eo bleaching effluent.

4.3.2 Mixed Effluents

A mixed pulp bleaching effluent was made from approximately 20% of DC and 80% of Eo stage pulp bleaching effluent (see Section 3.2 TABLE 3.1 for mixed effluent characteristics). This experiment was undertaken in an attempt to evaluate the mixed effluent's performance when passed through the same treatment regime as used with the Eo effluent. Two batches of mixed effluents were processed.

4.3.2.1 Combined Ozone and Anaerobic-Aerobic Lagoon Treatment for Mix_1 Effluent

The effluent sample (Mix_1) was pretreated with ozone and then it and the non-ozonated (Mix_1) raw effluent sample were processed separately through an anaerobic-aerobic lagoon system. Results obtained are shown in TABLE 4.3.3 (see Appendix 2, Fig.A2.3). The combined process increased the overall COD and color removal. Thus, the final discharged effluent quality produced by the combined process was improved.

TABLE 4.3.3

Comparison of changes brought about by an anaerobic-aerated lagoon alone, a combined process and ozone treatment only for the Mix_1 effluent.

Treatment	Category Item	Color *CP.U*	COD *mg/l*	BOD_5 *mg/l*
Anaerobic-Aerated lagoon alone (Mix_1)	Influent	563	1185	289
	Effluent	735	767	22
	%Removal	-31	35	92
Combined ozonation and anaeobic-aerated lagoon	Influent	563	1185	289
	Effluent	321	617	20
	% Removal	43	48	93
Ozonation alone	Influent	563	1185	289
	Effluent	179	965	367
	% Removal	68	19	-27

Results show that the combined process removed overall 43% of the color although 68% was initially removed during the ozone treatment. In contrast, a single step anaerobic-aerobic lagoon system increased the color by 31%. Furthermore, the combined process produced a 48% COD removal while the anaerobic-aerobic lagoon treatment alone removed 35% COD. Ozonation treatment alone removed 19% of the initial COD. The overall BOD_5 removals in the two treatment regimes were similar. For the combined process there was a 93% removal and for the single step treatment (anaerobic-aerobic lagoon) a 92% removal. The BOD_5 generated during the ozonation process (-27%) was removed by the subsequent biological treatment. For clarity, the % changes in the three measured characteristics (color, COD and BOD_5) are exhibited in Fig.4.3.3.

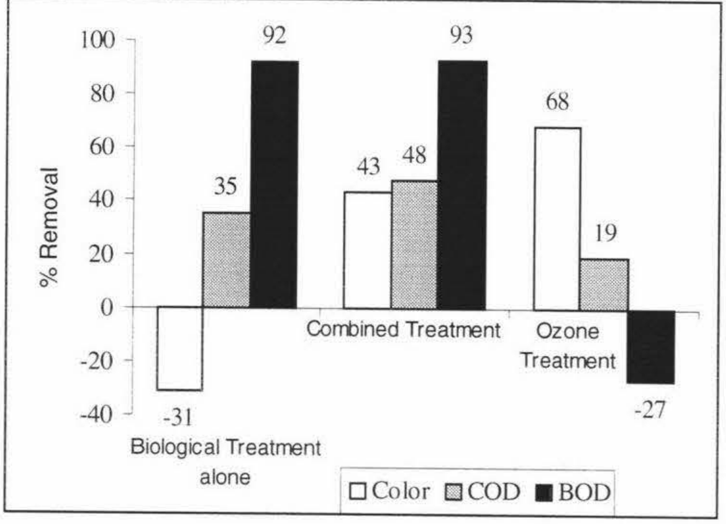


Fig.4.3.3 Changes in color, COD and BOD_5 expressed as percentage of initial value resulting from a single anaerobic & aerated lagoon, combined process and ozone treatment only for Mix_1 effluent.

The histograms suggest that the combined process removed color, COD and BOD_5 from the bleaching effluent (Mix_1). Compared with the anaerobic-aerobic lagoon treatment alone the combined treatment mostly improved the color removal and achieved an observably increased COD removal as well as removing the initial BOD_5 plus the BOD_5 generated during ozone treatment. These improvements were possibly derived from the ozonation process.

4.3.2.2 Combined Ozone and Aerated Lagoon Treatment for Mix_2 Effluent

The mixed pulp bleaching effluent (Mix_2) was examined using the combined treatment process as previously employed for the Eo_2 effluent, i.e., the ozone pretreatment combined with an aerated lagoon treatment regime. TABLE 4.3.4 (see Appendix 2, Fig.A2.4) indicates that with the combined treatment the extent of color, COD and BOD_5 removal was improved as compared with the removal characteristics obtained when the aerated lagoon alone was used.

TABLE 4.3.4

Comparison of changes brought about by an aerated lagoon alone, a combined process and ozone only treatment for the Mix_2 effluent

Treatment	Category Item	Color *CP.U*	COD *mg/l*	BOD_5 *mg/l*
Aerated lagoon lagoon alone (Mix_2)	Influent	2194	2415	186
	Effluent	1828	1650	47
	% Removal	17	32	75
Combined ozonation and aerated lagoon	Influent	2194	2415	186
	Effluent	716	1310	28
	% Removal	68	46	85
Ozonation alone	Influent	2194	2415	186
	Effluent	619	2110	259
	% Removal	72	13	-39

Results shown in TABLE 4.3.4 suggest that the combined process removed most of the color i.e. 68%, of which 72% was initiated during ozone treatment. In contrast to this, the aerated lagoon treatment alone removed only a small amount of color (17%) from the raw Mix_2 effluent. The combined process achieved an overall COD removal of 46% whereas the single aerated lagoon treatment produced a lower COD removal of 32%. The extra COD removal observed in the combined system could be attributed to the ozone treatment (13%). The BOD_5 removal was improved using the combined process (85%) as compared with treatment in the aerated lagoon (75%). The increased BOD_5 (39%) produced during ozonation treatment was subsequently removed in the biological process of the combined system. The % changes in color, COD and BOD_5 during these treatments are summarized in Fig.4.3.4.

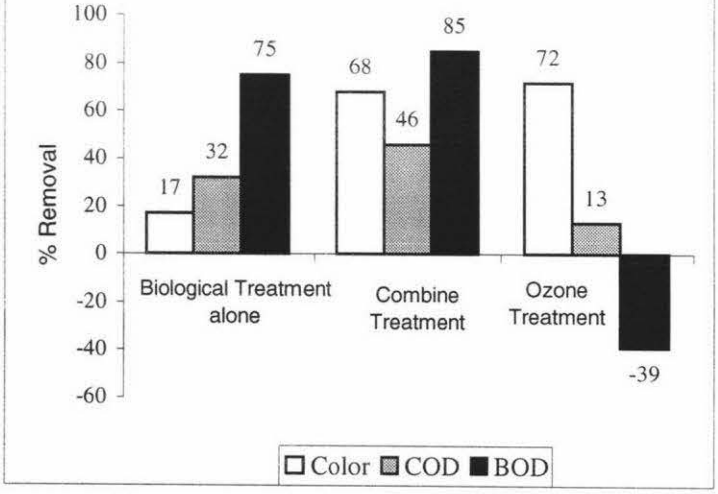


Fig.4.3.4 Changes in color, COD and BOD_5 expressed as percentage of initial value resulting from a single aerated lagoon, combined process and ozone alone treatment for the Mix_2 effluent.

The histogram displayed in Fig.4.3.4 depicts the improvements in color, COD and BOD_5 when a combined treatment process was used. The color removal was slightly better with ozone treatment alone while both COD and BOD_5 removal increased with the combined treatment.

By comparing the results of the study of the Mix_1 and Mix_2 pulp bleaching effluents with those for the Eo_1 and Eo_2 effluents, it is suggested that the behavior during treatment of the mixture of Eo and DC effluents was dominated by the Eo fraction. This observation is based on the similarity of color, COD and BOD_5 removal characteristics obtained from the Mix and Eo effluents during treatment. A comparison of the combined ozone & anaerobic-aerated lagoon and the combined ozone & aerated lagoon treatment data for the mixed effluents suggests that although the former achieved slightly higher COD and BOD_5 removal (48% of COD and 93% of BOD_5) than did the latter (46% of COD and 85% of BOD_5), the former produced a much lower color removal (43%) compared with the latter (68%) (see TABLE 4.3.3 and 4.3.4). Thus, ozonation in combination with an aerated lagoon treatment regime was considered as the most appropriate process for a mixed effluent treatment.

4.3.3 Summary

A study of pulp bleaching effluent was conducted using the Eo and a mixed bleaching effluent treated with chemical & biological methods. Initial characteristics of the effluents used varied according to the batches received. These variations depend on the production activities at the pulp and paper mill (see Section 3.2, TABLE 3.1 for initial effluent characteristics). The ozone pretreatment system produced clear advantages over a one-stage biological system in terms of color, COD and BOD_5 removal (see TABLE 4.3.5).

TABLE 4.3.5

A summary of the % removal data brought about by a combined ozone-biological process and a single biological treatment

Treatment	Biological system alone		Combined process	
Category Item	Eo_1	Eo_2	Eo_1	Eo_2
Color	-27	13	34	68
COD	35	30	51	45
BOD_5	85	64	91	82
Category Item	Mix_1	Mix_2	Mix_1	Mix_2
Color	-31	17	43	68
COD	35	32	48	46
BOD_5	92	75	95	89

Results shown in TABLE 4.3.5 (see TABLE 4.3.1 to 4.3.4) indicate that during treatment the mixed effluents behave similarly to the Eo effluents in terms of color, COD and BOD_5 changes. Although the biological system alone removed most of the BOD_5, the COD removal was low and the color became either worse or only a small reduction was observed. Thus, further processing was necessary. Ozone pretreatment combined with a biological process improved the pulp bleaching effluent treatment in terms of color, COD and BOD_5 removal, but a complete removal of the color, COD and BOD_5 was never achieved. When a combined process using ozone pretreatment with a biological system contained an anaerobic zone, the effluent's color was darkened during the anaerobic treatment stage and thus limited the overall color removal for such a combined process. However, combining ozone pretreatment with aerobic processing improved the overall removal of color, COD and BOD_5 and always gave a better result than a single stage biological treatment.

4.3.4 Comments on COD Changes

Differences were observed between the % removal values obtained with a combined treatment system and the simple arithmetic sum of the two separate process i.e. ozonation and biological treatment. For example, the COD changes noted in TABLE 4.3.1 can be summarized as follows.

COD changes due to ozonation alone, 12%. COD changes due to anaerobic-aerobic lagoon alone, 35%. Therefore the simple arithmetic total change might be 47%. However, the combined process change in COD was 51%.

Taking into account the error range in the COD estimation, i.e. ± 0.6%. The sum of the separate process is (12 ± 0.6%) + (35 ± 0.6%) = 47 ± 0.6% while the combined process is 51 ± 0.6%. Thus, the differences between the data from the sum of the separate process and that from the combined process are slightly in excess of the COD error range of ± 0.6%. This is probably associated with operation variations in the different lagoon systems. Comments on color and BOD_5 changes are made in Appendix 2, TABLE A2.11.

CHAPTER FIVE

DISCUSSION

A pulp bleaching effluent was treated using combined ozone with biological treatment process in this study. Results obtained from the ozone oxidation of the pulp bleaching effluent and the subsequent biological treatment in terms of color, COD and BOD_5 removal are presented in CHAPTER FOUR. In this section a comparison of these results with published data is conducted and a possible explanation is made.

5.1 Ozone Treatment

Color, COD and BOD_5 changes in Eo (Eo_1 & Eo_2) and mixed (Mix_1 & Mix_2) pulp bleaching effluents during ozone treatment were evaluated in the study. Ozone oxidation of these effluents with an ozone dose in a range of 0.14 (batch 2) to 0.2 (batch 1) gram ozone per gram COD in influent (see Section 3.2, for The Ozone Dose Used) removed color & COD and increased BOD_5. The results obtained from the ozone treatment are summarized in TABLE 4.1.3 which indicates that the color removal ranged from 67 % to 74% measured under pH 7.0 condition, the COD removal ranged from 12% to 19% and the BOD_5 increase range from 27% to 39%. These results were well matched with the data reported by Cecen *et at.* (1992) who treated a mixed bleaching effluent with a ozone dose of 0.17 gram ozone per gram COD in influent and removed 79% of color & 21% of COD. Also the color and COD removal obtained in this study resembled those observed by Zhou and Smith (1997) who investigated an ozone oxidation of a pulp mill effluent and achieved 82% color removal & 18% COD removal although the ozone dose (0.4) used by Zhou and Smith was much higher than that (0.14 to 0.2) used in this study. The BOD_5 increase achieved in the experiment agreed with the observation of 35% BOD_5 increase obtained during ozonation of a pulp bleaching effluent noted by Tuhkanen *et al.* (1997), but disagreed with the result that 15% BOD_5 removal was achieved during ozone oxidation of a mixed bleaching effluent reported by Cecen *et at.* (1992).

Results obtained from the experiments suggest that ozonation of a pulp bleaching effluent was most effective in removing color, followed by BOD_5 change and the COD removal was low. This observation was confirmed by Prat *et al.* 1989; Arcand and Archibald 1996 and Hostachy *et al.* 1997.

The explanation of the results is probably that the color in pulp mill effluent is predominantly caused by conjugated carbon-carbon (C-C) double bonds in lignin or lignin derived compounds while ozone is well known for oxidizing compounds with carbon-carbon double bonds found in the mill effluent (Ng *et al.*,1978). During the chemical reaction, ozone breaks down the carbon-carbon double bonds and the products are no longer capable for absorbing light in the visual light range, thus effectively removes color from the effluent (Ng et al., 1978 and Kahnmark & Unwin, 1998). However, ozone does not completely oxidize the color causing organic compounds into smaller molecules or CO_2, but forms intermediate radicals which still contribute to COD although a lesser extent of color is observed (Johannes and Jurg, 1985). Thus, rather moderate COD removal was achieved during the experiments (12% to 19%). This low COD removal indicates that the final stage of the ozone reaction process, during which the carbon-carbon (C-C) bonds in lignin or lignin derived compounds were thoroughly fractured, resulting in substantial COD decrease and large BOD_5 increase, does not occur. The BOD_5 increase (27% to 39%) observed during the ozone treatment suggests that ozonation of pulp bleach plant effluent converts some of the non readily biodegradable substances into biodegradable compounds (Zhou and Smith, 1997).

A color removal formula was developed under the assumption of application in a batch mode and a constant ozone flowrate. (see Appendix 2.1 for Color Removal Formula Development). This mathematical formula succinctly describes the color removal performance and indicates that the color removal rate during ozone treatment of pulp bleaching effluent is an exponential function of the ozone treatment time used. This formula can be further developed to predict a color removal at a selected ozonation treatment time. Compared with the color removal equation summarized by Rodrigues *et al.*(1998), it offers an additional option to study color removal kinetics for ozone treatment of pulp bleaching effluent.

5.2 Biological Treatment

Two biological treatment regimes were examined in terms of color, COD and BOD_5 removal from a pulp bleaching effluent. One was the anaerobic-aerobic lagoon system in which the first batch of bleaching effluents (Eo_1 & OEo_1 and Mix_1 & $OMix_1$) was treated for biological degradation, the other was the aerated lagoon in which the second batch of bleaching effluents (Eo_2 & OEo_2 and Mix_2 & $OMix_2$) was processed for biological decomposition. Results obtained from these processes are presented in Section 4.2. The published data relevant to biological treatment of a pulp mill effluent are only found for the non-ozonated effluent while there is no reported data found for separate biological treatment of an ozonated pulp mill effluent. Thus the experiment results for biological treatment of ozonated bleaching effluent discussed here, involved in Anaerobic-Aerobic Lagoon Treatment (Section 5.2.1), Aerated Lagoon Treatment (Section 5.2.2) and Comparison of Anaerobic-Aerobic Lagoon and Aerated Lagoon Treatment (Section 5.2.3), are new findings presented in the study.

5.2.1 Anaerobic-Aerobic Lagoon Treatment

A sequential anaerobic and then aerobic biological treatment was investigated using the anaerobic-aerobic lagoon system with the first batch of bleaching effluent (Eo_1 & OEo_1 and Mix_1 & $OMix_1$). It was found that for the non-ozonated bleaching effluent, 35% COD removal and 85%-92% BOD_5 removal were observed during the treatment (see TABLE 4.2.1). The COD removal was similar to the results reported by Häggblom & Salonen (1991) while the BOD_5 removal was slightly higher than that noted by those authors who employed an anaerobic fluidized bed and then an aerobic trickling filter system to treat a mixed bleaching effluent and achieved 30-65% COD removal and 60-80% BOD_5 removal.

Because there is no published data found for the separate treatment of an ozonated bleaching effluent, the results obtained from the anaerobic-aerobic lagoon treatment of the ozonated bleaching effluent are new finds (see TABLE 4.2.1). The data shown in TABLE 4.2.1 indicates that although the anaerobic-aerobic lagoon treatment removed more COD (up to 44%) and BOD_5 (up to 95) from the ozonated effluent than the non-ozonated effluent, this sequential biological treatment increased considerable color in the ozonated effluent (up to 98%). The color increase also occurred, but to a lesser extent in the non-ozonated effluent (27% only). A further analysis of the contribution made by each zone of the anaerobic-aerobic lagoon to the overall color, COD and BOD_5 removal suggests that the color increase in the ozonated effluent was mainly attributed to the anaerobic zone treatment (138% color increase) of the anaerobic-aerobic lagoon treatment (98% overall color increase) although the anaerobic zone seems to be favorable the BOD_5 removal. The COD removal achieved in each zone of the anaerobic-aerobic lagoon treatment was similar.

The explanation for the color increase in the ozonated bleaching effluent observed during an anaerobic zone treatment is probably that during ozone treatment the color removal was carried out by (1) ozone oxidation of substances to produce oxidized products, (2) ozonation of substances to form ozonide ion radicals and (3) •HO radical reaction with substances to bring out organic radical $R^{\bullet}$ (Johannes and Jurg, 1985). These intermediate organic compounds produced during ozone treatment are highly oxidized and would serve as electron acceptors under a reducing environmental condition. The colorant compounds would be formed when these intermediate substances were reduced. Therefore, when an ozonated bleaching effluent was subjected to the anaerobic zone, these intermediate oxidized compounds contained in the ozonated bleaching effluent were reduced by accepting electrons under the anaerobic condition from hydrogen or other reduced compounds, thus the color increase in the bleaching effluent occurred.

Results displayed in TABLE 4.2.1 also indicate that the performances of the mixed bleaching effluent resembled those of the Eo bleaching effluent during an anaerobic-aerobic lagoon treatment because the experiment results for the mixed (Mix_I & $OMix_I$) bleaching effluent were always similar to those for the Eo (Eo_I & OEo_I) bleaching effluent. There is no reported data found specially for studying the performances of the Eo (Eo & OEo) and mixed (Mix & OMix) bleaching effluent during biological treatment under identical conditions.

The explanation for the observations is possibly that due to most of the extracted organic compounds formed during pulp bleaching processes were dissolved in the Eo bleaching effluent compared with the DC bleaching effluent (Kringstad & Lindström, 1984), when a portion (approximately 20%) of DC bleaching effluent was mixed into Eo effluent, the performance of the mixture was still dominated by the Eo bleaching effluent during the treatment.

5.2.2 Aerated Lagoon Treatment

The effect of an aerobic zone alone on the pulp bleaching effluent treatment was evaluated using an aerated lagoon with the second batch of bleaching effluent (Eo_2 & OEo_2 and Mix_2 & $OMix_2$). It was found that when the non-ozonated bleaching effluent passed through the aerated lagoon, 30%-32% COD and 64%-75% BOD_5 were removed (see TABLE 4.2.3). The results were similar to the data noted by Stuthridge *et al.* (1991) who treated a pulp bleaching effluent using an aerated lagoon and obtained 36% COD removal and 57.5% BOD_5 removal.

Because there is no published data found for the separate treatment of the ozonated bleaching effluent, the results obtained for the ozonated bleaching effluent during the aerated lagoon treatment are new observations (see TABLE 4.2.3). The results for the ozonated bleaching effluent (see TABLE 4.2.3) indicate that the aerated lagoon treatment removed more BOD_5 (82%-89%) and COD (34%-38%) from the ozonated bleaching effluent than the non-ozonated bleaching effluent. Furthermore, the aerated lagoon treatment resulted in a small amount of color increase (up to 21% only) in the ozonated bleaching effluent compared with the anaerobic-aerated lagoon treatment (98%).

The explanation for the observations could be probably that the aerobic treatment offered an oxygen oxidizing environment, in which there was little chance for highly oxidized intermediate compounds contained in the ozonated bleaching effluent to be reduced back to the colorant compounds. Thus, the color increase in the ozonated bleaching effluent was very small during the aerated lagoon treatment.

Again, the results for the mixed bleaching effluent resembled those for the Eo bleaching effluent during the aerated lagoon treatment (see TABLE 4.2.3). This suggests that the behaviors of the Eo and mixed bleaching effluent are similar during an aerated lagoon treatment. The explanation are probably that due to the Eo bleaching effluent contains most of the extracted organic compounds generated during pulp bleaching processes, when a portion of DC (20%) bleaching effluent with a lower substance loading mixed into the Eo effluent, the performance of the mixture would still depend on the Eo bleaching effluent. Thus, the results for the mixed bleaching effluent was similar to those for the Eo bleaching effluent during treatment.

5.2.3 Comparison of Anaerobic-Aerobic Lagoon and Aerated Lagoon Treatment

Srinivason (1994) compared an anaerobic-aerobic system with an aerobic system alone for treatment of a pulp bleaching plant effluent (raw effluent) and suggested that the use of a sequential anaerobic zone and then aerobic zone treatment resulted in an improvement of COD and color removal over an aerobic treatment alone. Srinivason and Unwin (1995) further noted that the anaerobic-aerobic biological treatment removed in excess of 92% BOD from a pulp bleaching effluent (raw effluent). In the present study, results obtained from the anaerobic-aerobic lagoon treatment and the aerated lagoon treatment for the non-ozonated bleaching effluent confirmed the reported observations for the COD and BOD removal. Results achieved from treatment of the non-ozonated bleaching effluent (see TABLE 4.2.4) show that the sequential anaerobic and then aerobic lagoon treatment enhanced COD removal (35%) slightly and improved BOD_5 removal (85%-92%) over the aerated lagoon treatment alone (30%-32% COD removal and 64%-75% BOD_5 removal observed). However, the results for color removal observed during the treatment disagreed with the reported observation by Srinivason (1994). The data for color removal indicate that the anaerobic-aerobic lagoon treatment darkened non-ozonated effluent's color by 27% rather than removed it. In contrast, the aerated lagoon treatment decreased the non-ozonated effluent's color by 13% (see TABLE 4.2.4).

The explanation could be that an anaerobic treatment provided a favorable condition for biodegradation of chlorinated organic compounds and resulted in the improvement of the BOD_5 removal (Ferguson and Dlenoft, 1991). However, the anaerobic treatment also offered a reducing environment. During pulp bleaching processes, the colorant lignin organic compounds remained in the pulp are oxidized into lignin derivative substances and dissolve into the pulp bleaching effluent (Biermann, 1996). These oxidized organic compounds contained in the bleaching effluent can be reduced to dehalogenated substances under an anaerobic environment (Ferguson and Dlenoft, 1991) and to form colorant compounds. Thus, when the pulp bleaching effluent passed through the anaerobic-aerobic lagoon treatment, the BOD_5 removal was favored, but the effluent's color was increased.

However, there is no publication found for comparison of a sequential anaerobic-aerobic system with an aerobic system alone for treatment of ozonated bleaching effluent. In this study, the data obtained from treatment of ozonated bleaching effluent suggest that the anaerobic-aerobic lagoon treatment improved the COD and BOD_5 removal marginally over the aerated lagoon treatment alone (see TABLE 4.2.4). However, the anaerobic-aerobic lagoon treatment increased significant color in the ozonated bleaching effluent (98%) while to a much lesser extent, the color increase (21%) occurred during the aerated lagoon treatment alone (see TABLE 4.2.4). This observation suggests that the effective color removal achieved during the ozone treatment can be greatly offset by a subsequent biological treatment contained an anaerobic zone.

The data shown in TABLE 4.2.4 also indicates that the ozonated effluent's color was sensitive to a biological process, even under an aerobic condition during which a 21% color increase was observed although it was not a large extent. This is probably due to that the intermediate compounds produced during ozone treatment presented a strong oxidizing character and acted as electron acceptors even in an aerobic environment.

5.3 Combined Ozone-Biological Treatment

Rodriguez *et al.*1998 reported that ozone pretreatment of a pulp bleaching effluent was very effective in decolorization and therefore, resulted in an overall color removal improvement during a combined ozone oxidation with a subsequent biological treatment. In this paper, results obtained from the combined ozone and an anaerobic-aerobic lagoon treatment and the combined ozone and an aerated lagoon treatment confirmed the observations by Rodriguez *et al.*1998. Data for the two combined treatment regimes (see TABLE 4.3.5) indicate that the ozone pretreatment improved the overall color removal (up to 68%) compared with the biological treatment alone (up to 17% only). A further comparison of the color removal data obtained from the two combined treatment regimes suggests that the % color removal achieved during the combined ozone and aerated lagoon treatment (up to 68%) was greatly higher than those observed during the combined ozone and anaerobic-aerobic lagoon treatment (up to 43% only). This observation demonstrates that when the ozone pretreatment was followed by a biological treatment included an anaerobic zone, the overall color removal was reduced significantly.

The explanation for the color removal obtained from the combined treatment is possibly that during the combined treatment, most of the colorant substances contained in the bleaching effluent was removed effectively at the ozone pretreatment stage because the ozone was particularly preferential attack on colorant organic compounds (Ng *et al,* 1978). Therefore, the overall color removal achieved during the combined treatment was improved compared with those observed during biological treatment alone. However, the highly oxidized substances contained in the ozonated bleaching effluent could be reduced under an anaerobic environment to form colorant compounds again. Therefore, when the ozonated bleaching effluent passed through a biological system included an anaerobic zone, the color density was increased in the treated ozonated bleaching effluent. This was limited the overall color removal in such a combine treatment.

Heinzle *et al.*, (1992) established a combined ozonation-biotreatment process for treatment of a pulp bleaching plant effluent and achieved 47% COD removal through the combined treatment. In contrast, only 31% COD removal was observed through the biotreatment process alone. In this study, the results for COD removal observed from the two combined treatments agreed with the reported data by Heinzle *et al.* (1992). The results for COD removal (see TABLE 4.3.5) indicate that the combined treatment removed more COD (up to 51%) from the bleaching effluent than the biological treatment only (up to 35%). A further comparison of the COD removal data obtained from the two combined treatments suggests that the combined ozone and anaerobic-aerobic lagoon treatment removed slightly more COD (up to 51%) than the combine ozone and aerated lagoon treatment (up to 46%) from the pulp bleaching effluent.

The explanation for the COD removal observed during the combined treatment is probably that during the combined treatment, the ozone pretreatment oxidized the chlorinated organic compounds and removed some of the COD existed in the bleaching effluent. The subsequent biological treatment further removed COD contained in the ozonated bleaching effluent through biodegradation of organic compounds, thus the combined treatment regime removed more COD from the bleaching effluent tested than the biological treatment alone.

Tuhkanen *et al.* (1997) employed a combined ozonation-activated sludge system to treat a pulp bleaching effluent and obtained 91% BOD removal with the combined treatment. However, with the activated biological treatment alone, only 61% BOD removal was achieved. In this case (see TABLE 4.3.5), the BOD_5 removal observed during the combined ozone and aerated lagoon treatment resembled the data reported by Tuhkanen *et al.* (1997). The combined treatment removed up to 89% BOD_5, while the aerated lagoon treatment only removed up to 75% BOD_5. However, the BOD_5 removal obtained from the combined ozone and anaerobic-aerobic lagoon treatment was different from that noted by the author. The BOD_5 removal achieved during the sequential biological treatment alone (up to 92%) was almost equally high compared with that observed during the combine ozone and anaerobic-aerobic lagoon treatment (95%). This demonstrates that the sequential anaerobic-aerobic lagoon treatment was very effective in BOD removal, even for the non-ozonated bleaching effluent.

The explanation for the BOD_5 removal observed during the combined treatment is possibly that for the combined ozone and aerated lagoon treatment, the ozonation treatment broke down the lignin-like organic compounds present in the bleaching effluent, converted some of the chlorinated materials to dechlorinated oxidation products and effectively increased effluent's biodegradability (Kahnmark & Uniwin, 1998). Because the ozone pretreatment improved the effluent biological activities, the BOD_5 removal was enhanced during the combined treatment compared with the aerated lagoon treatment only. For the combined ozone and anaerobic-aerobic lagoon treatment, the sequential anaerobic-aerobic lagoon treatment provided firstly, an anaerobic environment for destroying chlorinated organic compounds and dehalogenating lignin derivative substances contained in the bleaching effluent (Bryant *et al.,* 1987; Ferguson and Dlenoft, 1991) and secondly, an aerobic condition for further digesting organic compounds in the presence of oxygen. Such a sequential biological treatment was very effective for biodegradation of pulp mill effluent, thus achieved equally well BOD_5 removal compared with the combined treatment.

Again, similar performances to the Eo effluent in color, COD and BOD_5 removal were observed during the combined ozone and biological treatment of the mixed bleaching effluents (see TABLE 4.3.5). This demonstrates that when a portion (20%) DC effluent was mixed into the Eo effluent, the behavior of the mixture was still controlled by the Eo effluent during the combined ozone and biological treatment. There is no publication found for this observation.

In summary, during the present study the pulp bleaching plant effluent was pretreated with ozone and achieved substantial color removal, noticeable BOD_5 increase and some of the COD removal. Because of the ozone pretreatment, the effectiveness in COD and BOD_5 removal observed during the subsequent biological treatment was improved. However, when the subsequent biological treatment consisting of an anaerobic zone, it significantly increased color in the ozonated effluent. However, when the subsequent biological treatment carried out under aerobic condition the color increase in the ozonated effluent was very small.

The combined ozone oxidation with biological treatment improved the overall color, COD and BOD_5 removal from a pulp bleaching effluent. For elimination of COD and BOD_5, the combined ozone with anaerobic-aerobic lagoon treatment outperformed the combined ozone with aerated lagoon treatment marginally. However, for color removal, the efficiency of the combined ozone and aerated lagoon treatment (68%) was much higher than that of the combined ozone with anaerobic-aerobic lagoon treatment (43%). The anaerobic zone of the anaerobic-aerobic lagoon was identified as the main color producing source and limited the overall color removal for such a combined treatment. In contrast to this, the combined ozone with aerated lagoon system was a better option for a pulp bleaching plant treatment.

CHAPTER SIX

CONCLUSIONS

A pulp bleaching plant effluent was studied through the combined ozone and subsequent biological treatment. The effectiveness of the ozone oxidation and the subsequent biological treatment were examined separately and the overall color, COD and BOD_5 removal during the two-stage combined treatment were determined. The experiment results that are presented in CHAPTER FOUR and then discussed in CHAPTER FIVE are concluded as follows:

1. Ozone oxidation of pulp bleaching plant effluent (Eo & Mix) in ozone dose range from 0.14 to 0.2 (g/g) removed color (up to 74% measured at pH 7), COD (up to 19%) and increased BOD_5 (up to 39), thus improved the effluent biodegradability. Ozone treatment was most effective in color removal, followed by BOD_5 increase and lesser effective in COD removal.

2. A mathematical color removal equation was established under assumption conditions. It described color removal kinetics and indicates that the % color removal was an exponential function of the ozone treatment time. This equation can be developed to predict the color removal performance at a selected ozone treatment time in the experimental conditions.

3. The performance of the mixed bleaching effluent resembled that of the Eo bleaching effluent during both ozone pretreatment and followed biological treatment. Results for the mixed and Eo bleach effluent in terms of color COD and BOD_5 removal were always similar.

4. Ozone pretreatment of pulp bleaching effluent improved the effluent biodegradability, thus the ozonated bleaching effluent achieved more COD and BOD_5 removal than the non-ozonated bleaching effluent during a biological treatment. However, the subsequent biological treatment darkened the ozonated bleaching effluent's color. When the biological treatment contained an anaerobic zone, the color increase in the

ozonated bleaching effluent was considerably high (up to 98%). This color increase also occurred, but to a lesser extent (21%), during an aerated lagoon treatment.

5. An analysis of the contribution made by each zone of the anaerobic-aerobic lagoon to the overall color, COD and BOD_5 removal suggests that the color increase in the ozonated effluent was attributed to the anaerobic zone treatment although it seemed to be favorable for BOD_5 removal. The COD removal achieved in each zone of the anaerobic-aerobic lagoon was similar. This observation indicates that biological treatment of ozonated bleaching effluent should avoid involving an anaerobic condition, otherwise the color removal achieved during the ozone treatment would be lost in the subsequent biological stage. It obviously would be economically infeasible.

6. Comparison of anaerobic-aerobic lagoon and aerated lagoon treatment suggests that for the non-ozonated bleaching effluent, the anaerobic-aerobic lagoon treatment improved the BOD_5 removal (92%) markedly over the aerated lagoon treatment (75%). However, it increased the non-ozonated effluent's color (up to 31%), while the aerated lagoon removed non-ozonated effluent's color (up to 17%). The COD removal observed during the two biological treatments was similar. For the ozonated bleaching effluent, the anaerobic-aerobic lagoon treatment enhanced the BOD_5 removal (95%) marginally over the aerated lagoon treatment (89%). However, it increased significant color (98%) in the ozonated effluent, while the aerated lagoon treatment increased only a small amount of color (21%) in the ozonated effluent. The COD removal obtained from the two biological treatments was similar.

7. The combined ozone and subsequent biological treatment demonstrated clearly advantages over a biological treatment alone. Ozone pretreatment improved overall color (34%-68%), COD (45%-51%) and BOD_5 (82%-95%) removal from a pulp bleaching effluent compared with the biological treatment only (up to 17% color removal, 30%-35% COD removal and 64%-92% BOD_5 removal).

9. Comparison of the combined ozone with anaerobic-aerobic lagoon treatment and the combined ozone with aerated lagoon treatment suggests that for COD and BOD_5 removal, the combined ozone with anaerobic-aerobic lagoon treatment was slightly superior to the combined ozone with aerated lagoon treatment. However, for color

removal, the efficiency of the combined ozone with aerated lagoon treatment was much higher (68%) than that of the combined ozone with anaerobic-aerobic lagoon treatment (43%). The anaerobic zone of the anaerobic-aerobic lagoon was identified as the main sources of color increase and limited the overall color removal for such a combined treatment. In summary, the combined ozone with aerated lagoon treatment was a better option for treatment of pulp bleaching plant effluent.

The main experiment results obtained from the study are concluded above. For further investigating the performances of pulp bleaching effluent during combined treatment, a pilot test is recommended for evaluating the ozone oxidation and followed biological treatment under practical production condition. This would allow determining technical and economic feasibility for a potential full-scale treatment regime.

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APPENDICES

A1. Data & Information associated with Materials and Methods

A1.1 Data Concerning Chemical Reagents Used and Figure for Determination of Student "t_s" Value.

TABLE A1.1

Chemical Reagents used in experiments

Name	Brand	Formula	Supplier
Ozone	Generated on site	O_3	Envirozone Co. Ltd. Napier, New Zealand
Sulphuric Acid	BDH	H_2SO_4	Poole, England
Sodium Hydroxide	BDH	NaOH	Poole, England
Ammonium Chloride	AJAX Chemicals	NH_4Cl	Sydney, Australia
Potassium Hydrogen Orthophosphate	AJAX Chemicals	K_2HPO_4	Sydney,Australia
Lithium Hydroxide Power	HACH	LiOH	Loveland, U.S.A
BOD Nutrient Buffer	HACH	-	Loveland, U.S.A
Potassium chloroplatinate	Laboratory Grade	$K_2P_tCl_6$	St. Louis, U.S.A

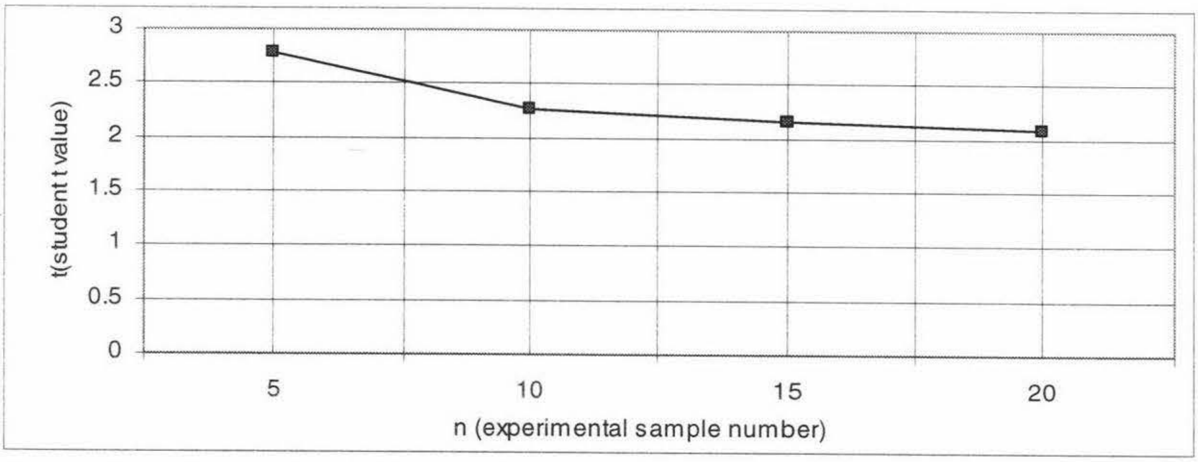

Fig.A1.1 Change in student t factor (t_s) with varying experimental sample number (n)

A1.2 Data Concerning the Stabilization of Biological Treatment Lagoon

TABLE A1.2

Anaerobic-aerobic lagoon stabilization data

Time	COD (mg/l)				BOD5 (mg/l)			
Day	Eo1	OEo1	Mix1	OMix1	OEo1	OEo1	Mix1	OMix1
0	1250	1100	1185	965	294	391	289	367
10	700	550	633	550	69	50	42	35
16	783	583	734	583	56	33	24	20
21	800	617	733	583	40	30	30	25
23	817	617	767	617	44	35	22	20
Color Unit (CPU)								
Day	Eo1		OEo1		Mix1		OMix1	
0	470		157		563		179	
10	493		246		604		220	
16	560		269		690		272	
21	578		295		709		321	
23	597		310		735		321	

TABLE A1.3

Aerated lagoon stabilization data

Time	COD (mg/l)				BOD5 (mg/l)			
Day	Eo2	OEo2	Mix2	OMix2	Eo2	OEo2	Mix2	OMix2
0	3000	2500	2415	2110	166	218	186	259
13	2400	1925	1920	1600	110	90	115	155
21	2910	2200	1900	1650	~	~	~	~
35	2200	1850	1650	1500	~	~	~	~
39	2200	1850	1650	1400	~	~	~	~
46	2200	1675	1650	1310	~	~	~	~
54	2200	1850	1650	1310	57	44	57	35
61	2110	1650	1650	1310	59	39	47	28
Color Unit (CPU)								
Day	Eo2		OEo2		Mix2		OMix2	
0	2903		769		2194		619	
13	2515		784		1907		668	
21	3168		821		2373		709	
35	2690		813		1981		681	
39	2601		795		1925		672	
46	2586		914		1828		716	
54	2608		933		1847		713	
61	2537		933		1828		716	

A1.3 Data & Information for Method Procedure

A1.3.1 Color Measurements

Sample effluent color was measured with the Visual Comparison Method described in Part 2120B of Standard Method for the Examination of Water and Wastewater (Eaton *et al.*, 1995). The maximum color for the bleaching effluent was 4142 CPU. However, the standard solution used in the Standard Methods for the Examination of Water and Wastewater (Eaton *et al.* 1995) uses a standard solution up to 500 CPU. Furthermore, the concentration of the standard solution can not be increased beyond 1000 color units, since it is limited by chemical solubility of the potassium chloroplatinate. Thus, the standard solution used in this study was 1000 CPU and was prepared using double the potassium chloroplatinate, crystallized cobaltous chloride and conc. HCl concentrations described in the Standard Method for the Examination of Water and Wastewater preparing 500 CPU of standard solution (Eaton *et al.*, 1995).

Preparation of the color standard curve

a) The standard solution was prepared by dissolving 2.492 gram potassium chloroplatinate ($K_2P_tCl_6$, Laboratory Grade, supplied by SIGMA CHEMICAL Co. St. Louis, U.S.A.) and 2.00 gram crystallized cobaltous chloride ($CoCl_2{\bullet}6H_2O$, Laboratory Grade, supplied by THE BRITISH DRUG HOUSES LTD, Poole, England) in distilled water, adding 200 ml conc. HCl (Laboratory Grade, supplied by BDH LTD, Poole, England) and then diluted the chemical solution stock to 1000 ml with distilled water. This is the standard solution with 1000 chloroplatinate color units. This standard solution was double strength.
b) The standard solution was then diluted with distilled water to give concentrations of 100, 200, 400, 600, 800 and 1000 CP. color units. The corresponding color absorbance of each solution was measured with a spectrophotometer (HITACHI brand and U-2000 type. Tokyo, Japan) at a wavelength of 465 nm.
c) The standard curve of the color absorbance vs chloroplatinate color units was plotted from the collected data (see the solid line section in Fig.A1.2). However, the bleaching effluent's color was 4142 CPU while the concentration of the standard solution was limited by potassium chloroplatinate solubility. Therefore, the curve for determination

of bleaching effluent's color was prepared by extending the standard curve from 1000 CP.color units to 4200 CP. color units (see dash line in Fig.A1.2) to accommodate the color density of the bleaching plant effluent.

Preparation of filtrate sample

The filtrate sample was obtained by filtering the experimental sample through a MILLIPORE (supplied by Millipore Corporation. Bedford MA, U.S.A.) membrane filter with a pore size of 0.45 μm. The filtered sample absorbance was measured with a spectrophotometer (HITACHI brand and U-2000 type. Tokyo, Japan) at a wavelength of 465 nm.

Determination of effluent color

Sample effluent color was expressed as chloroplatinate units (CPU) which was determined by converting the absorbance values noted in the test to color units using the standard curve of the absorbance vs CP color units.

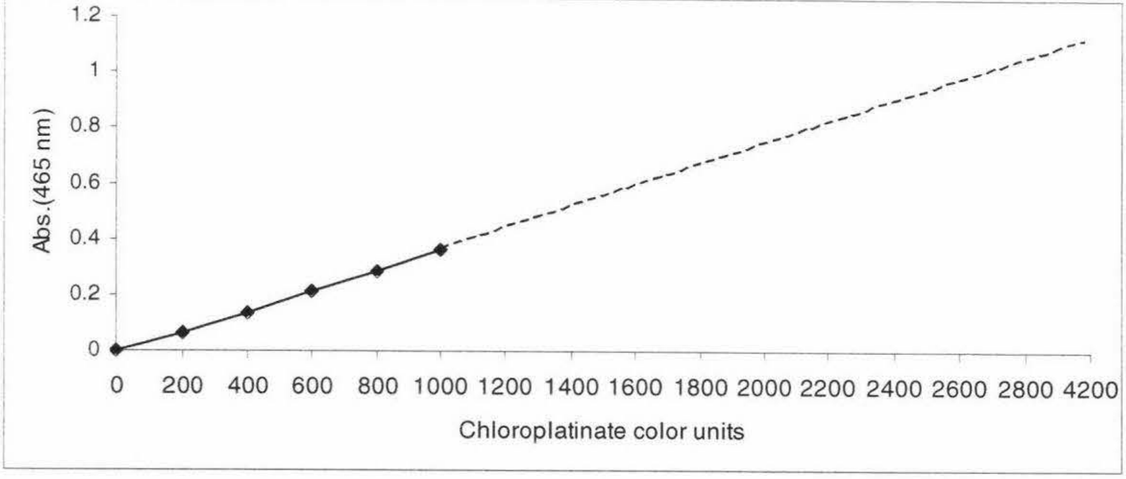

Fig.A1.2 Chloroplatinate color units standard curve for determination of effluent color.

A1.3.2 COD Measurements

Sample effluent COD was tested using closed Reflux Colorimetric Method described in Part 5220D of Standard Methods (Eaton *et al.* 1995). The maximum COD value of the bleaching effluent as received was greater then the upper limits of the COD standard curve, according to Standard Methods (Eaton *et al.* 1995). Therefore, the COD samples for analysis were diluted 5 times before testing and the result was corrected accordingly.

COD test procedure

A sample of 2.5 ml was transferred to a 16×100 mm test tube and 1.5 ml digestion solution and 3.5 ml sulphuric acid was added. The tube was tightly capped and inverted several times to mix completely. Then, it was placed in the COD reactor block (HACH brand, supplied by HACH company U.S.A.) that had been preheated to 150 °C and refluxed 2 hr. After cooling to room temperature the color absorbance was measured with a spectrophotometer (UV-1201 model, made in Japan) at a wavelength of 600 nm. Before the color aborbance measurement, the spectrophotomer was calibrated with a blank sample prepared using distilled water through the same procedure.

Preparation of COD standard curve

A standard solution of *Potassium hydrogen phthalate (KHP)* (see TABLE A1.1) was prepared according to Part 5220B of Standard Methods (Eaton *et al.*, 1995).

a) The standard solution was prepared by dissolving 425 mg of dry potassium hydrogen phthalate in distilled water and then diluting to 1000 ml. This solution has a theoretical COD of 500 μg O_2/mL.

b) The standard solution was then diluted with distilled water to give COD values of 0 (distilled water), 100, 200, 300, 400 and 500 μg O_2/mL. The absorbance of each COD value was measured using the same procedure as for samples with a spectrophotometer (UV-1201 model, made in Japan) at a wavelength of 600 nm.

c) The absorbance vs COD value was plotted using the COD value of the standard solution and absorbance measured (see Fig.A1.3)

Determination of effluent COD values

The COD values were determined with the absorbance value noted in the test and the COD standard curve of the absorbance vs COD value and then 5 times the reading data obtained from the curve. Because of the 5 times dilution made initially, the COD value obtained from the cure was corrected using a factor of 5.

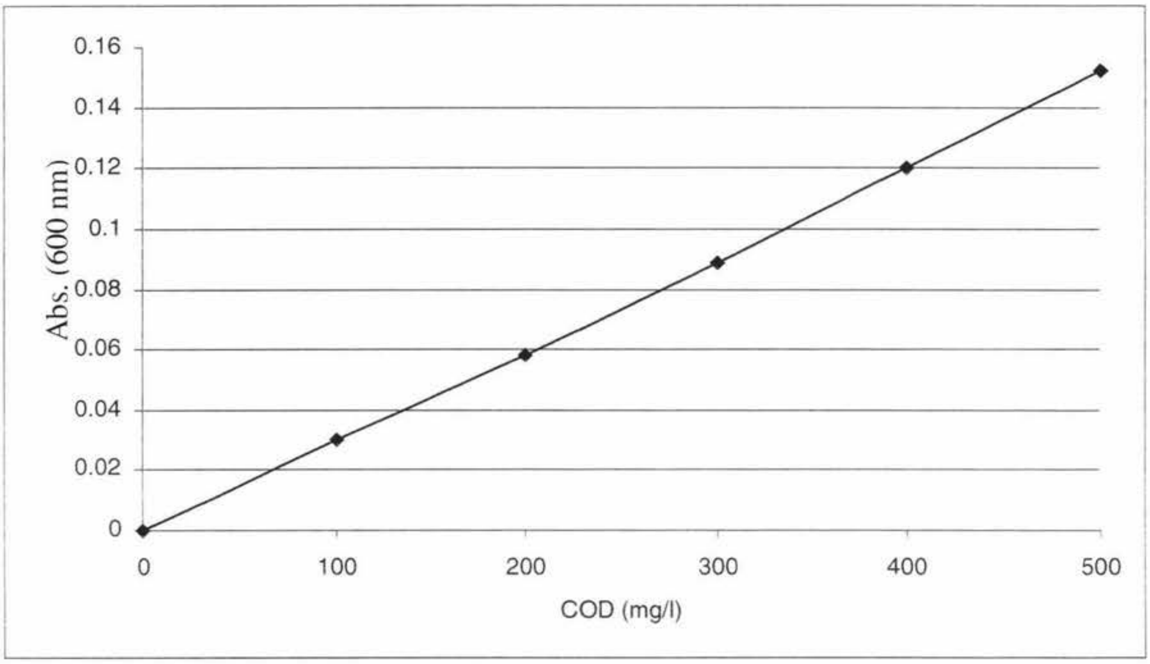

Fig.A1.3 Potassium hydrogen phthalate standard curve for COD measurements

1.3.3 BOD_5 Measurements

The BOD_5 value was tested with BOD Trak^{TM} instrument system (HACH Company, U.S.A) and the method was described in BOD Trak^{TM} Instrument Manual (Hach, 1997). Because the bleaching effluent was assumed to contain toxic organic compounds, a special consideration during a sample preparation was given to this possibility. The BOD_5 samples tested were prepared by diluting the grab samples to 1/2 strength using distilled water to reduce the possible influence produced by the toxic organic compounds and the BOD_5 results were multiplied by 2 to obtain the actual value for BOD_5 tested.

Seed inocula (BOD)

Effluents from the aerobic lagoon (zone) at 20 °C were used as seeds for BOD_5 tests. The seed volume was 30% of overall test sample volume.

Sample preparation

The grab sample was diluted to 1/2 strength using distilled water (the ratio of sample to distilled water by v/v was 1:1) and to this was transferred 30% seeds to make up the BOD_5 test sample (the ratio of diluted sample to seeds by v/v was approximately 2:1).

BOD test procedure

1) The sample of 95 ml or 160 ml (depending on effluent characteristics) was transferred the BOD_5 testing bottle. A 3.8 cm magnetic stir bar and BOD Nutrient Buffer Pillow (see TABLE A1.1) were added. A cap containing lithium hydroxide powder (see TABLE 1.1) was placed in the neck of the bottle and was sealed using Stopcock Grease. Then, the bottle was put on the chassis of the BOD Trak instrument and properly connected to the tubes. After setting the test duration to 5 days and choosing a corresponding BOD testing range, the BOD Trak instrument was settled in the incubator (CONTHERM Digital Series Cooled Incubator, New Zealand) with a temperature of 20 ± 1°C. At the end of the 5th day test, the data for BOD_5 measurement were transferred from the BOD Trak instrument to a computer and downloaded.

Calculation of BOD value

The sample BOD value was calculated from following formula:

BOD value = (BOD observed)-(Decimal fraction of seed used *BOD seed)/Decimal fraction of sample used

Where the seed BOD value was obtained from testing a pure seed sample at the same time as the sample test.

In this study, the decimal fraction of seed used was 0.3 (30% seed) and the decimal fraction of sample used is 0.7 (70% sample). Therefore, the BOD_5 value was calculated as follows:

BOD_5 value = (BOD_5 observed)-(0.3*BOD_5 seed)/0.7

The grab sample BOD_5 value was determined by multiplying the BOD_5 values obtained from above by a factor of 2 to compensate the initial dilution.

A2. Data & Information Associated with Results

A2.1 Color Removal Formula Development

The chemical treatment of bleaching effluent shows that ozone reacted with colorant compounds contained in the effluent and effectively changed most of them to non-colored oxidation products. To do this, the bleaching effluent was processed in a batch mode with a constant ozone flowrate so that the % color removal achieved (or the % color remaining in the treated bleaching effluent) was determined only by the ozonation reaction time for the specific bleaching effluent that was subjected to the experimental conditions. This assumption leads to the mathematical formula:

$$dC_t'/dt = -k*C_t'$$

Where C_t' is the percentage color remaining in the bleaching effluent at reaction time t, k is the color removal rate constant and the negative "-" means that the color remaining in the bleaching effluent diminishes with the increase in the ozonation time. The equation can be further developed as:

$$dC_t'/C_t' = -k*dt$$

$$\int(1/C_t')dC_t' = -k*\int dt$$

$$\ln C_t'|_0^t = -k*t$$

$$\ln C_t' - \ln C_0' = -k*t$$

$$\ln(C_t'/C_0') = -k*t$$

$$C_t'/C_0' = e^{-k*t}$$

$$C_t' = C_0 e^{-k*t}$$

Where C_0 is the initial % color of the bleaching effluent at time t = 0. C_0 can also be considered as the total removable color that is equal to the ultimate color removal C_u.

Thus, color removal (C_t) is:

$$\begin{aligned} C_t &= C_u - C_t' \\ &= C_u - C_u*e^{-k*t} \\ &= C_u(1-e^{-k*t}) \end{aligned}$$

As the color removal obtained for the Eo and mixed effluents was high (85% to 89%) during ozone treatment, the ultimate color removal for these effluent treatments can be assumed 100.

A2.2 Data Concerning Color removal during Ozone Treatment

TABLE A2.1

Color removal results and formula development for the first batch of Eo effluent

Time (min)	Experiment		$k' = -[\ln(1 - C_t'/100)]/t$	$C_t = 100[1 - EXP(-0.0112*t)]$
t	Color units	Color removal % C_t'	k'	Model color removal % C_t
0	633	0	~	0
20	529	16.43	0.0090	20.07
40	456	27.96	0.0082	36.11
60	333	47.39	0.0107	48.93
80	233	63.19	0.0125	59.18
100	174	72.51	0.0129	67.37
120	148	76.62	0.0121	73.92
140	104	83.57	0.0129	79.15
160	100	84.20	0.0115	83.34
180	93	85.31	0.0107	86.68
STDVE(SD)	~	~	0.0017	~
AVERAGE(k)	~	~	0.0112	~

where $EXP(-0.0112*t) = e^{-0.0112*t}$

STDVE (SD) - Standard deviation

AVERAGE (k) - Average k value (average rate of color removal)

Confidence limit calculation for "k":

The k value for the first batch of Eo effluent was calculated according to data in the above table (using a 95% confidence limit).

$n = 9 \quad t_s = 2.3 \quad SD = 0.0017 \quad k = 0.0112$

$\text{Limit} = k \pm SD*t_s/\sqrt{n} = 0.0112 \pm (0.0017*2.3/\sqrt{9}) = 0.0112 \pm 0.00130$

Where n is the experimental sample number, t_s is the factor determined from Fig.A1.1).

TABLE A2.2.

Color removal results and formula development for the second batch of Eo effluent

Time (min)	Experiment		$k'=-[\ln(1-C_t'/100)]/t$	$C_t = 100[1-\mathrm{EXP}(-0.00586*t)]$
t	Color units	Color removal % C_t'	k'	Model color removal % C_t
0	4142	0	~	0
20	3821	7.75	0.00403	11.06
40	3522	14.97	0.00405	20.90
60	3201	22.72	0.00430	29.64
80	2847	31.27	0.00469	37.42
100	2511	39.38	0.00500	44.35
120	2168	47.66	0.00539	50.50
140	2052	50.46	0.00502	55.97
160	1567	62.17	0.00608	60.84
180	1302	68.57	0.00643	65.17
200	1071	74.14	0.00676	69.03
220	873	78.92	0.00708	72.45
240	731	82.35	0.00723	75.50
260	604	85.42	0.00741	78.21
280	537	87.04	0.00730	80.62
300	478	88.46	0.00720	82.76
STDVE(SD)	~	~	0.00128	~
AVERAGE(k)	~	~	0.00586	~

Where EXP(-0.00586*t) = $e^{-0.00586*t}$

STDVE (SD) - Standard deviation

AVERAGE (k) - Average k value (average rate of color removal)

Confidence limit calculation for "k":

The k value for the second batch of Eo effluent was calculated according to data in the above table (using a 95% confidence limit).

$n = 15 \quad t_s = 2.2 \quad SD = 0.00128 \quad k = 0.00586$

$\mathrm{Limit} = k \pm SD*t_s/\sqrt{n} = 0.00586 \pm (0.00128*2.2/\sqrt{15}) = 0.00586 \pm 0.000726$

Where n is the experimental sample number, t_s is the factor determined from Fig.A1.1.

TABLE A2.3

Color removal results and formula development for the first batch of mixed effluent

Time (min)	Experiment		$k'=-[\ln(1-Ct'/100)]/t$	Ct = 100[1-EXP(-0.01326*t)]
t	Color units	Color removal % Ct'	k'	Model color removal % Ct
0	756	0	~	0
20	626	17.20	0.00943	23.29
40	463	38.76	0.01226	41.16
60	300	60.32	0.01540	54.87
80	215	71.56	0.01572	65.38
100	167	77.91	0.01510	73.45
120	144	80.95	0.01382	79.63
140	111	85.32	0.01370	84.38
160	104	86.24	0.01240	88.02
180	96	87.30	0.01146	90.81
STDVE(SD)	~	~	0.00207	~
AVERAGE(k)	~	~	0.01326	~

Where EXP(-0.01326*t) = $e^{-0.01326*t}$

STDVE (SD) - Standard deviation

AVERAGE (k) - Average k value (average rate of color removal)

Confidence limit calculation for "k":

The k value for the first batch of mixed effluent was calculated according to data in the above table (using a 95% confidence limit).

$n = 9 \quad t_s = 2.3 \quad SD = 0.00207 \quad k = 0.01326$

$\text{Limit} = k \pm SD^*t_s/\sqrt{n} = 0.01326 \pm (0.00207^*\ 2.3\ /\sqrt{9}\ ) = 0.01326 \pm 0.00158$

Where n is the experimental sample number, t_s is the factor determined from Fig.A1.1.

TABLE A2.4

Color removal results and formula development for the second batch of mixed effluent

Time (min)	Experiment		$k'=-[\ln(1-Ct'/100)]/t$	$Ct = 100[1-EXP(-0.0074*t)]$
t	Color units	Color removal % Ct'	k'	Model color removal % Ct
0	3310	0	~	0
20	2940	11.18	0.0059	13.76
40	2615	21.00	0.0059	25.62
60	2246	32.15	0.0065	35.85
80	1896	42.72	0.0070	44.68
100	1556	52.99	0.0075	52.29
120	1317	60.21	0.0077	58.85
140	1082	67.31	0.0080	64.51
160	910	72.51	0.0081	69.39
180	739	77.67	0.0083	73.61
200	631	80.94	0.0083	77.24
220	593	82.08	0.0078	80.37
240	500	84.89	0.0079	83.07
260	463	86.01	0.0076	85.40
280	418	87.37	0.0074	87.41
300	392	88.16	0.0071	89.14
STDVE(SD)	~	~	0.0008	~
AVERAGE(k)	~	~	0.0074	~

Where $EXP(-0.0074*t) = e^{-0.0074*t}$

STDVE (SD) - Standard deviation

AVERAGE (k) - Average k value (average rate of color removal)

Confidence limit calculation for "k":

The k value for the second batch Mix effluent was calculated according to data in the above table (using a 95% confidence limit).

$n = 15 \quad t_s = 2.2 \quad SD = 0.0008 \quad k = 0.0074$

$\text{Limit} = k \pm SD*t_s/\sqrt{n} = 0.0074 \pm (0.0008*2.2/\sqrt{15}) = 0.0074 \pm 0.00046$

Where n is the experimental sample number, t_s is the factor determined from Fig.A1.1.

A2.3 Data Concerning COD Removal during Ozone Treatment

TABLE A2.5

% COD Changes with time in the first batch of Eo & mixed effluent treated with ozone

Eo effluent (E_{o1})		
Time(min)	COD (mg/l)	COD removal (%)
0	1250	0
20	1183	5.36
40	1150	8
60	1150	8
80	1150	8
100	1150	8
120	1133	9.36
140	1117	10.64
160	1100	12
180	1100	12
Mixed effluent (Mix_1)		
0	1185	0
20	1167	1.52
40	1150	2.95
60	1100	7.17
80	1083	8.61
100	1067	9.96
120	1017	14.18
140	983	17.05
160	983	17.05
180	965	18.57

TABLE A2.6

% COD changes in the second batch of Eo & mixed effluents treated with ozone after 300 minutes.

Eo effluent (Eo_2)		
Time(mine)	COD (mg/l)	COD removal (%)
0	3000	0
300	2500	17
Mixed effluent (Mix_2)		
0	2415	0
300	2110	13

A2.4 Data Concerning BOD_5 Changes during Ozone Treatment

TABLE A2.7

% BOD_5 changes in bleaching effluents treated with ozone before and after treatment

Eo effluent	BOD5(mg/l)	
Time(min)	The first batch	The second batch
0	294	166
180	391	~
300	~	218
BOD_5 Increase (%)	33	31
Mixed effluent		
0	289	186
180	367	~
300	~	259
BOD5 Increase (%)	27	39

A2.5 Data Concerning Biological Treatment

TABLE A2.8

Results for bleaching effluents treated in an anaerobic-aerated lagoon system

Batch No.	Effluent	Treatment	Item	Color CP.U	COD mg/l	BOD_5 mg/l
1	Eo[1]		Influent	470	1250	294
		Anaerobic zone	Effluent	474	1050	125
		Aerobic zone	Effluent	597	817	44
	OEo[2]		Influent	157	1100	391
		Anaerobic zone	Effluent	373	883	120
		Aerobic zone	Effluent	310	617	35
	Mix[3]		Influent	563	1185	289
		Anaerobic zone	Effluent	608	1067	138
		Aerobic zone	Effluent	735	767	22
	OMix[4]		Influent	179	965	367
		Anaerobic zone	Effluent	429	820	141
		Aerobic zone	Effluent	321	617	20

[1] Initial Eo stage effluent.
[2] Ozonated Eo effluent.
[3] Initial mixed effluent.
[4] Ozonated mixed effluent.

TABLE A2.9

Results for bleaching effluents treated with an aerated lagoon system

Batch No.	Effluent Type	Category Item	Color	COD	BOD_5
			CP.U	mg/l	mg/l
2	Eo	Influent	2903	3000	166
		Effluent	2537	2110	59
	OEo	Influent	769	2500	218
		Effluent	933	1650	39
	Mix	Influent	2194	2415	186
		Effluent	1828	1650	47
	OMix	Influent	619	2110	259
		Effluent	716	1310	28

TABLE A2.10

COD loading in influent to biological treatment.

Batch 1	Ozonated		Non-ozonated	
Category Item	COD mg/l	COD loading kg/m^3d	COD mg/l	COD loading Kg/m^3d
Eo_1	1100	0.112	1250	0.127
Mix_1	965	0.098	1185	0.121
Eo_2	2500	0.13	3000	0.150
Mix_2	2110	0.11	2415	0.121

TABLE A2.11

Error range in color and BOD_5 changes

Category Item	Combined process	Separate process		
		Ozonation alone	Biological system alone	Sum
% BOD_5 removal	88 ± 3.3	-33 ± 3.3	85 ± 3.3	52 ± 3.3
% Color removal	34 ± 0.1	67 ± 0.1	-27 ± 0.1	40 ± 0.1

Comments on color and BOD_5 changes:

TABLE A2.11 suggests that data for % BOD_5 removal observed during the combined process (88 ± 3.3) is greater than that obtained from the sum of the separate process (52 ± 3.3). The difference is beyond the error range of ± 3.3.

Results of % color removal is 34 ± 0.1 for the combined process and 40 ± 0.1 for the sum of the separate process. The difference is in excess of the error range of ± 0.1.

The explanation for these differences is possibly due to the changes in chemical structure for some of the organic materials during ozone pretreatment and the loading of the influent to biological treatment for ozonated effluent and non-ozonated effluent was slightly different.

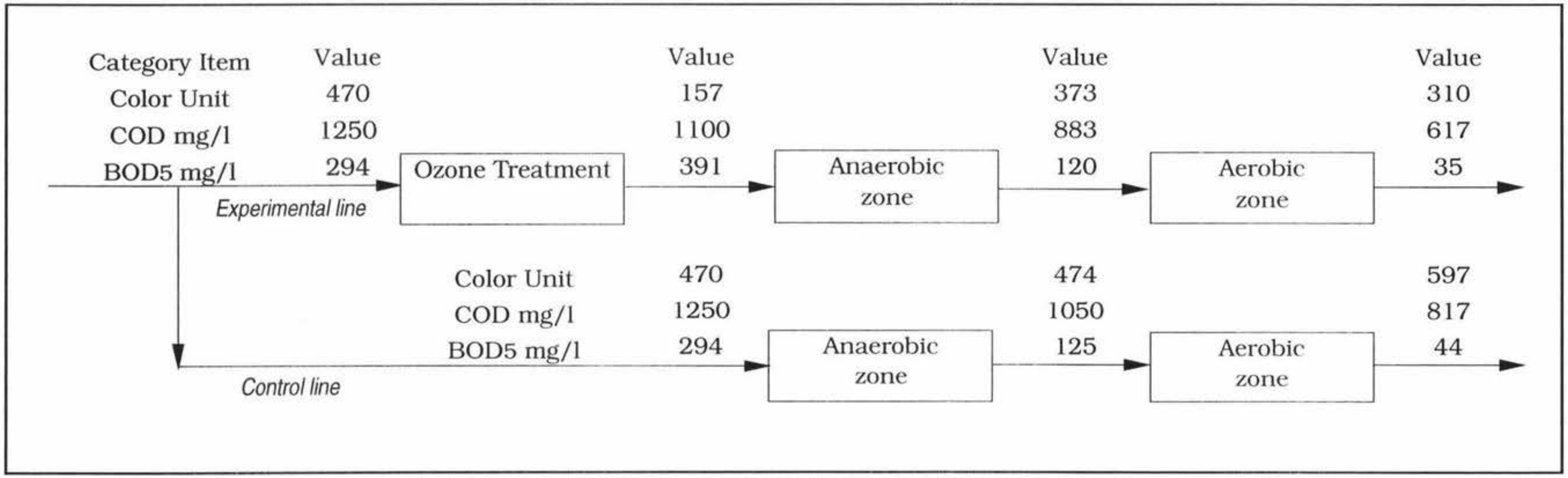

Fig. A2.1 Process diagram with numerical data for Eo$_1$ effluent treated with firstly ozonation process and then an anaerobic-aerobic lagoon.

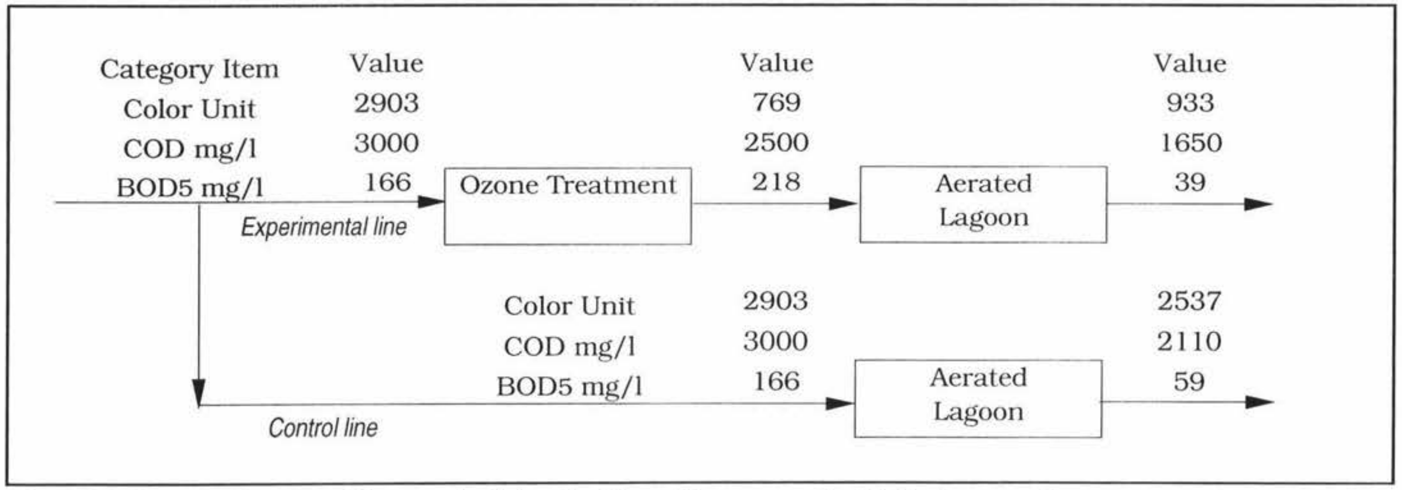

Fig. A2.2 Process diagram with numerical data for Eo$_2$ effluent treated with firstly ozonation process and then an aerated lagoon.

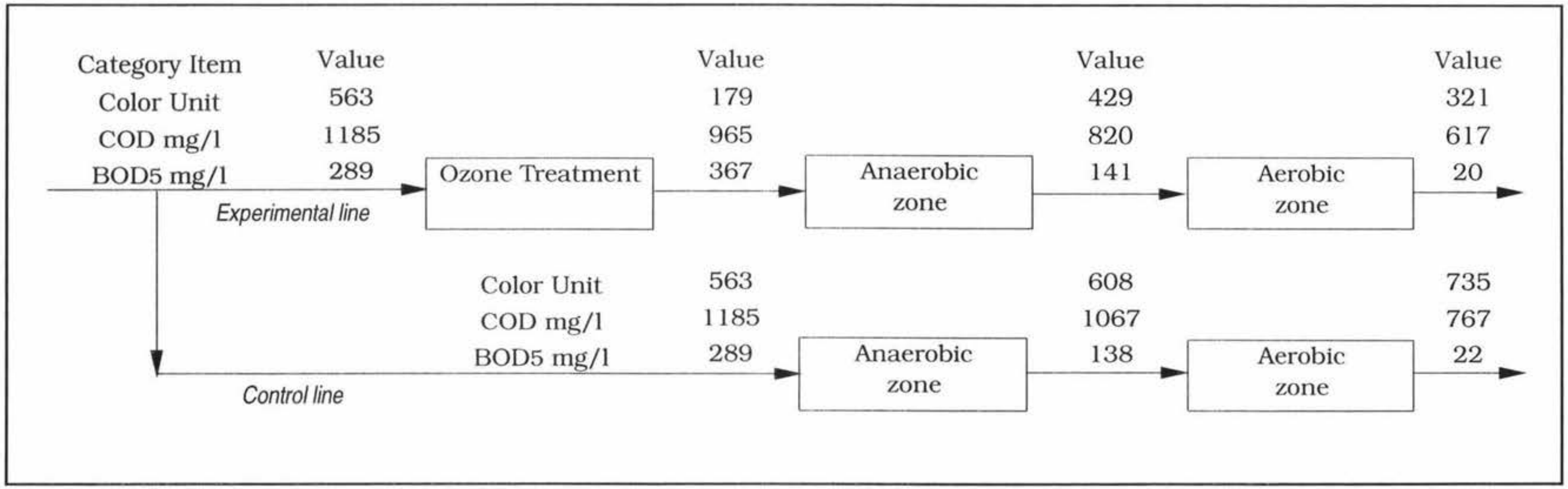

Fig.A2.3 Process diagram with numerical data for Mix$_1$ effluent treated with firstly ozonation process and then an anaerobic-aerobic lagoon.

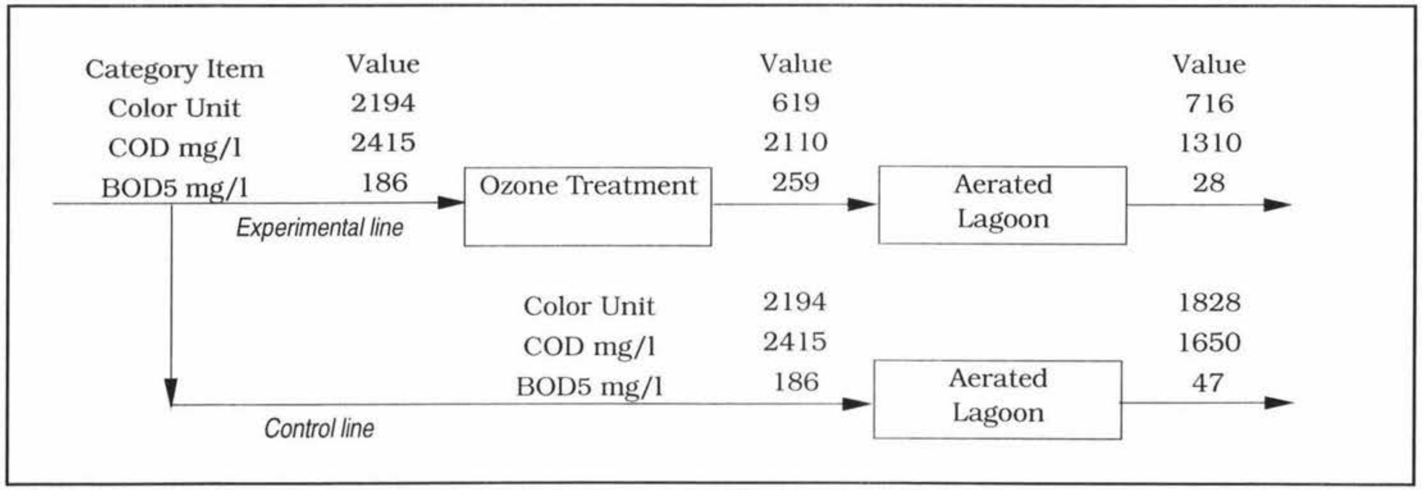

Fig.A2.4 process diagram with numerical data for the Mix$_2$ effluent treated with firstly ozonation process and then an aerated lagoon.