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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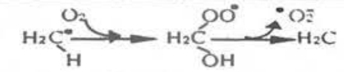
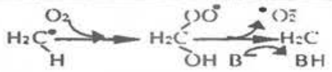
ERRATA SHEET

PART 1. 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	Stachelin 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:

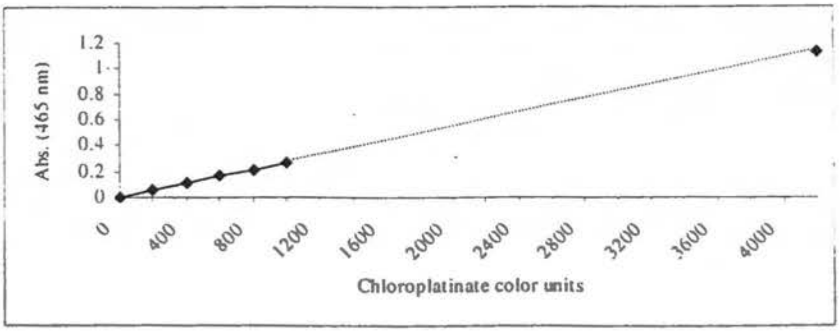


Fig.A1.2 Chloroplatinate color units standard curve for determination of effluent color.

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.

Dr. Volker Schwarz for his useful advice and assistance during the course of the study.

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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.