5.1 Characterization of Mill Effluents

For the first set of BOD tests unacclimatized seeds, which were collected during the plant visit, were used. The second set of samples were analysed using acclimatized seed.

As expected, the BOD results showed inhibitory effects for first set of samples, and the rate constant, Ke for secondary effluent was 0.05 / day compared to 0.1 to 0.12 / day obtained using acclimatized seed. Toxic and inhibitory effects were more obvious for bleach effluent which exerted a BOD of 34 mg/L for undiluted sample in respirometer, and dilution improved the BOD to about 200 mg/L (Appendix I).

During the characterization stage major emphasis was placed on optimizing the dilution for BOD test such that the improvement in biotreatability could be measured and comparisons be made between ozonated and unozonated samples. BOD bottles were set up for five different dilutions and BOD_5 vs Dilution was plotted for the effluent samples (Figures 5, 6 and 7). The detailed results are given in Appendix I. 1:100, 1:75 and 1:40 dilutions were selected for bleach, primary and secondary effluents, respectively. The same dilutions were used for setting up the BOD bottles for both ozonated and unozonated samples and thus eliminating the effects of unexpected factors on BOD values.

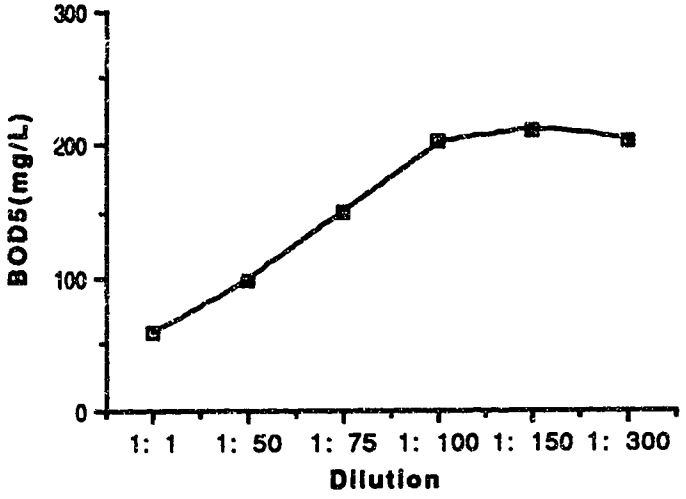

Figure 5. Dilution Optimization for Bleach Effluent

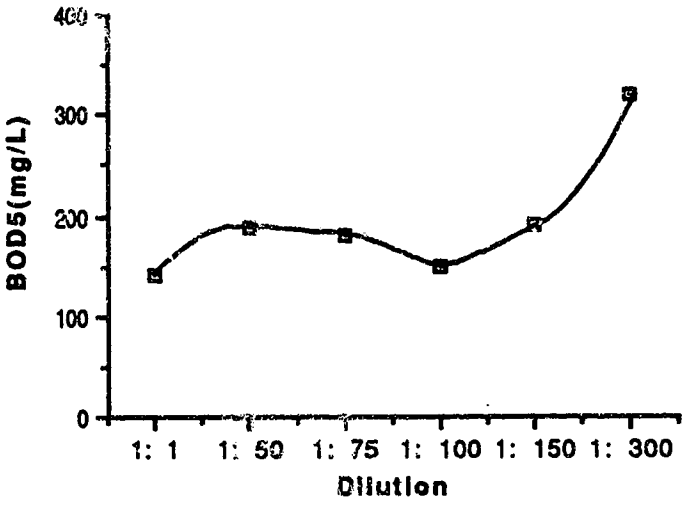

Figure 6. Dilution Optimization for Primary Effluent

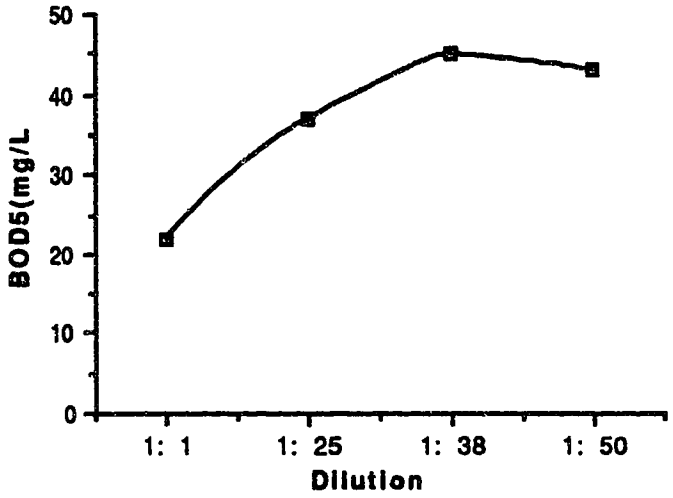

Figure 7. Dilution Optimization for Secondary Effluent

The effluent samples were analyzed for suspended solids, COD, TOC, (filtered and unfiltered), TOX, total phosphate and TKN.

COD/TOC ratio for the effluents was between 2.92 and 3.56, which is characteristic for industrial waste (Eckenfelder, 1966) (Appendix I).

Total suspended solids in the primary effluent were of the order of 100 mg/L which indicate an effective primary treatment at the mill. TSS for secondary effluent were about 90 mg/L but most of them were as volatile suspended solids, and therefore indicate the necessity of secondary clarification in the treatment system (Table 4).

For bleach effluent colour varied between 2,430 and 16,000 units. The large variation in colour was due to grab samples which were collected during different process conditions. Colour for primary and secondary effluent was 1850 and 1770 units, respectively. This supports

the findings that colour is hardly affected during conventional treatment processes.

Table 4. Characteristics of the Pulp Mill Effluent (Actual Range Measured)

PARAMETERS	Bleach Effluent	Primary Effluent	Secondary Effluent
SUS. SOLIDS (mg/L)			
Total	80 to 220	85 to 120	83 to 108
Volatile	60 to 185	50 to 90	66 to 88
BOD5 (mg/L)	200 to 220	180 to 205	26 to 41
BOD20 (mg/L)	360 to 460	270 to 300	56 to 108
T.O.C.(mg/L)			
Filtered	430 to 860	150 to 220	118 to 160
Unfiltered	440 to 860	170 to 240	150 to 200
C.O.D. (mg/L)			
Filtered	990 to 2760	480 to 650	360 to 480
Unfiltered	1170 to 2800	610 to 695	450 to 570
COD/TOC (Unifltered)	2.7 to 3.3	3.6 to 2.9	3.0 to 2.9
COD/TOC (Filtered)	2.3 to 3.2	3.2 to 3.0	3.1 to 3.0
COLOUR (mg Pt/L)	2430 to 16000	1850	1525 to 1770
T.O.X. (mg/L)	175	60	41
Total Phosphate (mg/L)	0.48	0.62	0.62
Chloride (mg/L)	1138	514	484
Kjeldahl Nitrogen (mg N/l)	40	2.64	2.84

The concentrations of total organic halides were 175 mg/L for bleach effluent, 60 mg/L for primary and 41 mg/L for secondary effluent and, the percentage removal of TOX in aerated lagoon was about 30%.

Samples were also analyzed for total coliform using m-T7 agar to obtain a population. Total coliform in secondary effluent were in the order of 10^6 to 10^7 / 100 mL. The number of coliforms were equally high in primary effluent due to town sewage being combined with primary effluent after the clarifier. Bleach effluent, which was a direct process stream, had no bacterial population. Since the bacterial population in primary and secondary effluents was high, during the studies, the samples were stored at 4° C and the time delay between experimentation and analyses was minimized. Though the first stage was named as characterization, the overall characterization of the effluents was based on the average values of parameters for all the samples analysed during the entire study. The characteristics of the effluent samples are given in Table 4. The effluent, can be characterized as moderately strong.

5.2 Ozonation of Mill effluent

5.2.1 Bleach Effluent

5.2.1.1 Biochemical Oxygen Demand

Ozonation apparently had no effect on 5-day BOD, but the 20-day ozonated samples showed a decrease in BOD values (Table 5). Such results have frequently been reported in earlier studies. The apparently unchanged values of BOD were due to the fact that part of the ozone

reacted with simpler molecules and fulfilled the oxygen demand. At the same time it reacted with complex molecules and made them more biodegradable. As a net result there was no obvious change in BOD for ozonated and unozonated samples. However, ozonation decreased total biodegradable material in the sample.

K_e and L_o values were determined for ozonated and unozonated samples. A very narrow joint confidence region indicated best estimations of those constants (Table 6). K_e for 50 mg/L ozone sample was 0.23 compared to 0.20 for raw sample. However, for 100 mg/L ozone dose both K_e and L_o decreased. The effect of acclimatized and unacclimatized seed was also obvious (Table 6). The K_e values calculated for the BOD results with unacclimatized seed was much lower compared to acclimatized seed.

Table 5. Biochemical Oxygen Demand for Bleach Effluent

Sample	BOD5 (mg/L)	BOD20 (mg/L)
Raw sample	216	358
Oxygen	192	314
50 mg O3/L	199 to 247	313 to 344
100 mg O3/L	188 to 213	312 to 323

Table 6. K_e and L_o for Bleach Effluent

Sample	Ke (1/day)	Lo(mg/L)	Correlation Coefficient
Raw sample	0.08 (Un acclimatized seed)	593	-0.9643
"	0.2	364	-0.785
Oxygen	0.2	317	-0.7857
50 mg O3/L	0.23	315	-0.706
100 mg O3/L	0.21	320	-0.729

5.2.1.2 Chemical Oxygen Demand and Total Organic Carbon

The reduction in COD for bleach effluent was 79 mg/L at an ozone dose of 50 mg/L. For 100 mg/L ozone samples, the decrease in COD was 100 mg/L (Appendix II). The results were analyzed using ANOVA table, and the reduction in COD was found to be significant for ozonated samples. However, the results were not identical for primary and secondary effluents. Ozone effectiveness towards bleach effluent may be due to the fact that the effluent being highly coloured contains large number of molecules with unsaturated bonds. As a result ozone attacked those points readily. There was a good reproducibility of the COD results among the replicates (Appendix II).

For lower ozone doses, TOC remained unchanged as expected. 100 mg/L of ozone reduced the TOC slightly which may be due to the loss of volatile organics as well. TOC and COD samples for filtered

samples were more reliable, since they caused no analytical problems due to incomplete reaction of suspended solids.

5.2.1.3 Colour

Ozone reduced the colour significantly. Since most of the colour is associated with unsaturated bonds in a molecules, ozone has great affinity to attack those sites thus changing the basic characteristics of the molecule. During the ozonation studies, samples were left for few days but no obvious colour reversion was noticed as reported for the effluent treated with lime. For bleach effluent, reduction in colour followed a straightline relationship for the applied ozone doses (Figure 8 and Table 7). However, subsequent experiments with secondary effluent indicated that up to 85% of the colour present in the effluent was readily removed but for higher colour removal significantly high amount of ozone was required. Prat et al. (1988) and Melnyk and Netzer (1975) also reported that 85% of the colour which was readily removed, was due to simple compounds which reacted with ozone more effectively.

Table 7. Colour Removal for Bleach Effluent

Sample	True colour (Pt/Co units)	Colour removal (Pt/Co units)	% Removal
Raw sample	2430	-	
Oxygen	2430	-	
50 mg O3/L	1720	715	29.5
100 mg O3/L	1105	1330	54.5

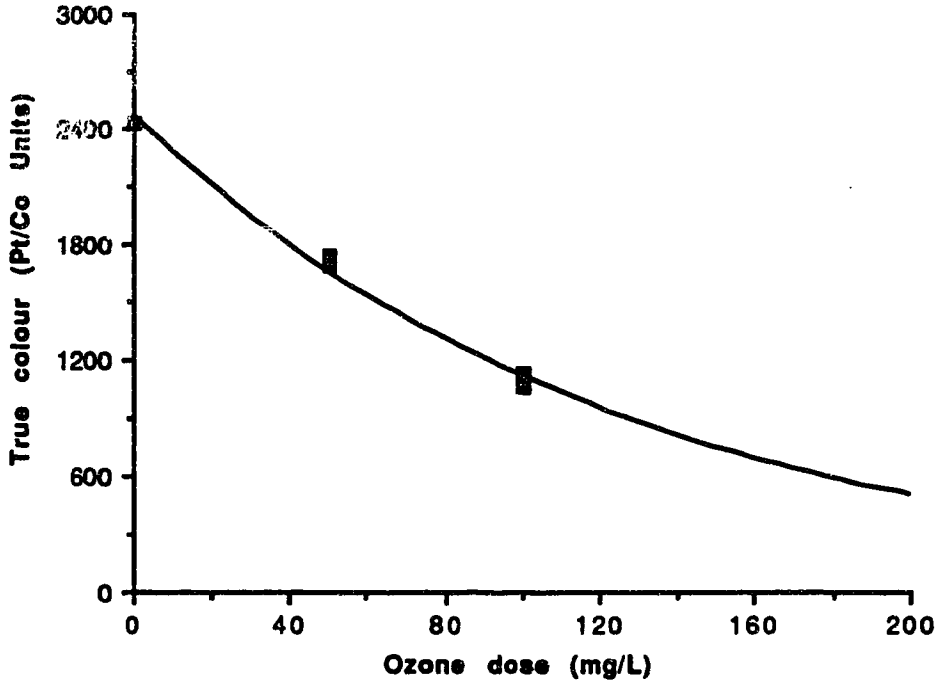

Figure 8. Colour Removal for Bleach Effluent

5.2.1.4 Suspended Solids

Ozone had no statistically significant effect on suspended solids of bleach effluent (Appendix II). The calculated value for 'F' was much

lower than the tabulated value at 95% confidence level and for (2,15) degrees of freedom.

5.2.2 Primary Effluent

A 24-h composite sample of primary effluent was treated with 50 and 100 mg/L of ozone similar to bleach effluent. Two genuine replicate experiments were conducted for each ozone dose and a control experiment was run with pure oxygen. The detailed results are given in Appendix III.

5.2.2.1 Biochemical Oxygen Demand

Similar to bleach effluent, primary effluent apparently showed no significant increase after ozonation (Table 8). The behaviour of the primary effluent sample can be explained on the same lines that for samples with high initial BOD. In those samples most of the ozone is wasted due to its reaction with simple and readily biodegradable compounds and therefore it is not effective at improving the BOD. This behaviour emphasizes the importance of selection of a suitable point of ozone application in the treatment process such that the applied ozone is more effectively used. This point is also important for the selection of ozone contacting / transfer system.

K_e and L_o values calculated for the ozonated samples showed an improvement in biotreatability compared to unozonated samples (Table 15). The joint confidence region plotted indicated a good estimate of parameters.

Table 8. Biochemical Oxygen Demand for Primary Effluent

Sample	BOD5 (mg/L)	BOD20 (mg/L)
Raw sample	205	279
C	174	308
50 mg O3/L	170 to 179	252 to 285
100 mg O3/L	178 to 182	267

Table 9. K_e and L_o for Primary Effluent

Sample	Ke (1/day)	Lo (mg/l)	Correlation Coefficient
Raw sample	0.19	292	-0.7937
"	0.25	264	-0.7776
Oxygen	0.16	298	-0.8918
50 mg O3/L	0.23	254	-0.8193
100 mg O3/L	0.23	260	-0.8162

5.2.2.2 Colour

Compared to bleach effluent , colour was more readily reduced for lower ozone dose. 50 mg/L of ozone reduced the colour of primary effluent by 850 units. Similar ozone dose for bleach effluent reduced the colour by 715 unit. However, for 100 mg/l ozone dose, the colour reduction was identical for both the effluents (Table 10 and Figure 9).

Table 10. Colour Removal for Primary Effluent

Sample	True Colour (Pt/Co units)	Colour Removal (Pt/Co units)	% Removal
Raw sample	1850	-	
Oxygen	1750	-	
50 mg O3/L	1000	850	46
100 mg O3/L	510	1345	73

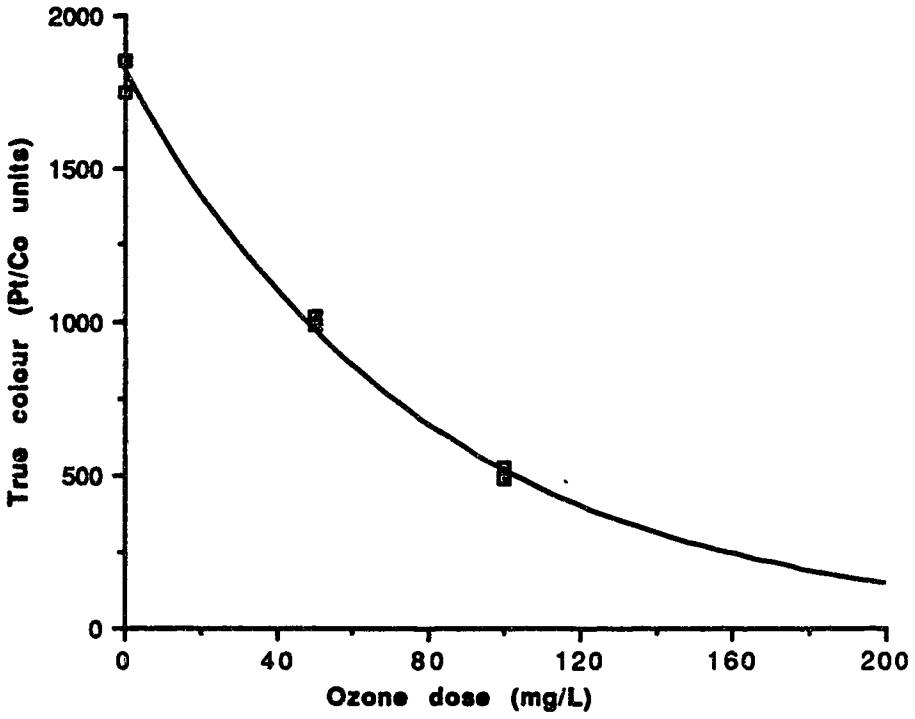

Figure 9. Colour Removal for Primary Effluent

5.2.2.3 Chemical Oxygen Demand and Total Organic Carbon

COD for ozonated samples was lower than unozonated samples. The decrease in COD was significant at 95% confidence level. The calculted value for F was 6.63 compared to tabulated value of $F_{95}(2,15)$ of 3.68.

The decrease for primary effluent was not as much as bleach effluent. Bleach effluent being a highly coloured effluent had more unsaturated bonds and provided more sites where ozone could react. With primary effluent which has a large variety of compounds, part of the applied ozone might have had additional reaction and reacted in different ways. This might be the reason, a clear relationship could not be established between applied ozone doses and its effect on COD (Appendix III).

5.2.2.4 Suspended Solids

Lower ozone dose did not reduce the suspended solids significantly, but for 100 mg./L ozone dose, reduction in suspended solids was noticeable (Appendix III).

5.2.3 Secondary Effluent

Similar to bleach and primary effluent, secondary effluent for the first set of experiment was treated with 50 and 100 mg/L of ozone. BOD results showed significant improvement for the ozonated samples (Table 11). To confirm the results, four more replicate experiments were conducted. All the four experiments showed a similar increase in the BOD values for the ozonated samples. Two more samples of secondary effluent were treated with 150 mg/L of

ozone dose and one experiment was conducted for 200 mg/L of ozone dose to establish the pattern of improvement for higher ozone doses. All the samples were analyzed for COD, TOC, suspended solids and colour. The detailed results are given in Appendices IV, V, VI and VII).

Table 11. Biochemical Oxygen Demand for Secondary Effluent

Sample	BOD5 (mg/L)	BOD20 (mg/L)
Raw sample	26 to 41	56 to 108
Oxygen	34 to 39	62 to 116
50 mg O3/L	45 to 59	78 to 120
100 mg O3/L	50 to 71	102 to 148
150 mg O3/lL	73 to 81	123 to 140
200 mg O3/L	90	138

5.2.3.1 Biochemical Oxygen Demand

Samples of ozonated and unozonated effluent were set up for BOD test in identical manner and titrated to estimate BOD for 1,2,3,4,5,7,10 and 20 days. K_e and L_o values were calculated and joint confidence region was plotted to check the accuracy of parameter estimation.

Six replicate experiments were conducted for 50 and 100 mg/L ozone doses for the purposes of statistical calculations. The statistical calculations are given in Appendix IX. The calculated values for "t"

were higher than table values, therefore the H_0(null hypothesis) is incorrect and there was a significant improvement in BOD_5 of the secondary effluent with ozonation (Appendix IX). The results were also analyzed using ANOVA table which confirmed the significant improvement in BOD_5 for ozonated samples.

Table 12. K_o and L_o for Secondary Effluent

Sample	Ke (1/day)	Lo (mg/L)	Correlation Coefficient
Raw sample	0.05	209	-0.9918
	(Unacclimated seed)		
	0.15	63	-0.8633
	0.1	70	-0.9184
	0.11	66	-0.8987
	0.13	70	-0.9041
Oxygen	0.13	70	-0.8831
	0.11	74	-0.9333
50 mg O3/L	0.2	82	-0.8382
	0.24	86	-0.7012
	0.16	87	-0.8079
	0.19	83	-0.8059
	0.19	82	-0.6905
	0.19	77	-0.7006
	0.15	88	-0.8368
	0.17	83	-0.7383
100 mg O3/L	0.24	99	-0.8065
	0.19	111	-0.7322
	0.15	116	-0.8277
	0.16	115	-0.8402
	0.16	113	-0.8696
	0.19	104	-0.845
	0.15	114	-0.7751
	0.17	107	-0.8159
	0.19	114	-0.7115
	0.21	104	-0.6835
150 mg O3/L	0.15	126	-0.7929

5.2.3.2 Colour

Colour was more effectively removed from secondary effluent. For 50 mg/L ozone dose the reduction was about 1000 units compared to 715 and 850 unit for the bleach and primary effluent respectively. However, for higher ozone doses the reduction tapered off (Tables 13 and Figure 10).

Table 13. Colour Removal for Secondary Effluent

Sample	True Colour (Pt/Co Units)	Colour Removal (Pt/Co Units)	% Removal
Raw Sample	1525 to 1770		
Oxygen	1550 to 1820		
50 mg O3/L	500 to 700	950 to 1060	58 to 67
100 mg O3/L	250 to 370	1205 to 1470	77 to 85
150 mg O3/L	170 to 215	1360 to 1600	86 to 90
200 mg O3/L	185	1585	90

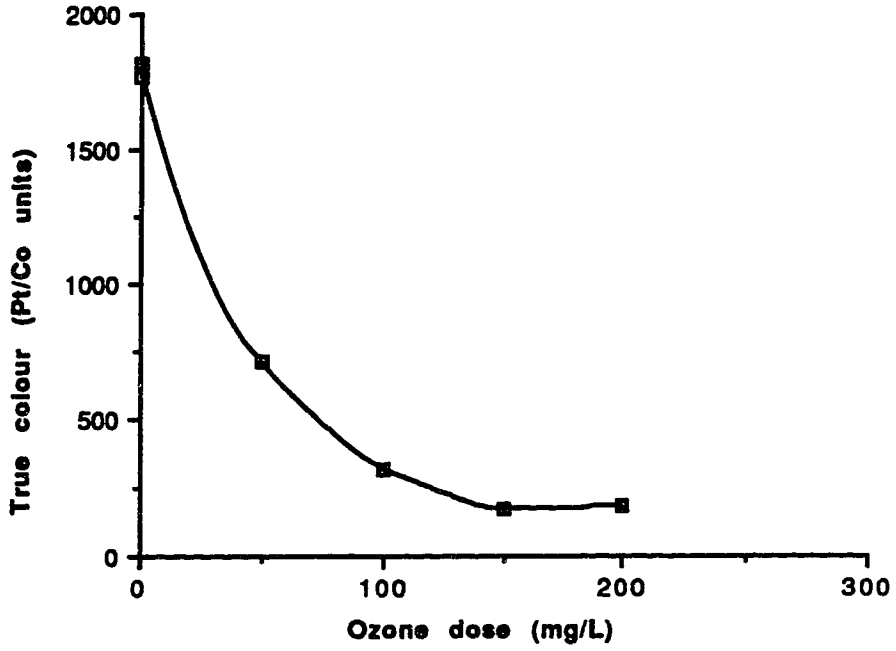

Figure 10. Colour Removal for Secondary Effluent

5.2.3.3 Suspended Solids

Reduction in suspended solids was less in comparison to the improvement in BOD or colour reduction (Appendices IV,V,VI and VII). 50 mg/L of ozone had no significant effect on TSS and VSS, but the reduction in suspended solids for 100 mg/L ozone dose was found to be significant by 't' test. The statistical calculations are given in Appendix IX. Analysis of variance, performed for no ozone dose, 50 mg/L and 100 mg/L ozone doses indicated a small but significant reduction in total suspended solids of secondary effluent. The calculated value of 'F' was 5.76 compared to tabulated value of $F_{95}(2,15)$ as 3.68.

5.2.3.4 Chemical Oxygen Demand

Reduction in COD showed no pattern which could be related with applied ozone doses (Appendices IV,V,VI and VII). Statistically there was no significant effect of ozonation on COD of secondary effluent. The mechanism of ozone effect on COD, as discussed before, seemed to be complex and is not a simple addition reaction. The effluent also had large amounts of complex organics, which might not be completely oxidized during COD test.

6.0 DISCUSSION

The three basic objectives of ozonation study were: to investigate the improvements in biotreatability, over all treatability of mill effluents and identify the suitable location of ozone application.

As described in introduction (Section 1.0) and literature review (Section 2.0), the conventional methods of effluent treatment were not sufficient to achieve the high standards of treatment. Ozone is an attractive alternative to treat the effluent more effectively.

The available literature on this subject supports ozone to be effective for the removal of colour, odour, surface active and foaming compounds; reduction in COD, improvement in biotreatability of the effluent, and degradation of organochlorines and dioxins. A couple of studies also indicated that the ozonation process might be economical for the removal of colour from the effluent. The points missing in the available literature are:

1. most of the studies have been conducted with single effluent stream (i.e. primary effluent, secondary effluent or bleach effluent);
2. it is difficult to correlate the results from different studies, since the effluents are not from the same source and their characteristics vary considerably;
3. ozone doses vary from 10 mg/L to 550 mg/L;
4. reactors, which have pronounced effect on the overall efficiency of ozonation process, were different for all the studies, therefore

the efficiency obtained for one reactor need not be same for another system.

The studies were designed to investigate the effect of ozone on the characteristics of pulp mill effluent by controlling the ozone dose. The available literature also indicated the significance of proper location of ozone application. The first objective was achieved by designing a batch reactor in which a better control on ozone dose was achieved. For the second objective, samples were collected from three different locations at the mill.

The reactor was found to be effective with respect to ozone doses (Figure 3). A maximum variation of 5 mg ozone was achieved among the replicate experiments for all ozone doses. The accuracy of the ozone doses was evident with the potassium iodide titration method and from the colour reduction for replicate samples for all the effluents, which was found to be consistent.

During the ozone determination the level of potassium iodide solution in the 6 mm connecting glass joint was noticed to be critical with respect to ozone diffusion into the potassium iodide solution (i.e. the cylindrical section of the reactor). When the potassium solution was filled well up in the connecting glass tube, the small surface area was excellent at reducing the ozone diffusion into the potassium iodide solution as the ozone / oxygen mixture was filling the reactor. Under the above conditions the amount of ozone transferred into the potassium iodide solution was as low as 0.5 mg. The amount of ozone

diffused into the effluent, therefore, was insignificant compared to the applied ozone doses ranging between 50 and 200 mg/L.

A well acclimatized seed are important to have a better estimate of BOD for industrial waste. Most often for industrial waste it is necessary to add a population of microorganisms capable of oxidizing the biodegradable organic matter in the sample. The use of non-acclimated biological seed in the BOD test is probably the factor most commonly responsible for erroneous BOD results (Eckenfelder, 1966). This is particularly true when considering complex industrial wastes. The initial seed can be obtained from the waste treatment facility treating similar wastewater, if possible, otherwise surface water (preferably 3 to 8 km below the discharge) receiving wastewater discharges contain satisfactory microbial population. It is best to acclimatize the biological culture in a continuous reactor although fill and draw batch units are frequently used (Eckenfelder, 1966). The diluted wastewater is fed to the initial microbial seed, increasing the wastewater strength over a period of time. Once the continuous or batch system has been subjected to the undiluted waste, the mixed contents should be aerated until the organic removal by the seed organism reaches a maximum level. Once this has occurred the system can be considered acclimated. For domestic-industrial waste the time required may be about a week. However, for industrial waste containing high concentrations of complex organic compounds, it may take several weeks (Eckenfelder, 1966).

The presence of toxic materials in the wastewater sample may have a bio-toxic or bio-static effect on the seed organisms (Eckenfelder, 1966). This effect is evidenced by the BOD values which increase with sample dilutions. It is therefore necessary to predetermine the dilution value above which the biochemical oxygen demand is consistent. If toxicity is due to heavy metals, their effect can be eliminated by chelation (Eckenfelder, 1966).

In the initial stage of study, seed were collected from the pulp mill laboratory and set up for acclimatization purpose. The first set of samples were analyzed using unacclimatized seed and rest of the BOD test during the entire study were conducted using well acclimatized seed. The BOD values obtained for these two set of tests pointed out toxic and inhibitory effects of the mill effluents. The toxic effects were more significant for bleach stream which exerted a BOD of 34 mg/L with unacclimatized seed compared to 200 with acclimatized microorganisms. K_e value for for secondary effluent was 0.05/day with unacclimatized seeds compared to 0.1 to 0.12 with acclimatized seed. Inhibitory effect were reduced by selecting a suitable dilution for BOD tests for each effluent.

During the appropriate dilutions determinations for the three samples, it was noted that for 20-days BOD the microorganisms were very well acclimated, and the BOD for different dilutions was identical.

Oxidation of nitrogenous materials adds to the BOD values which are generally considered as a measure of carbonaceous fraction of the sample.

The measurement of carbonaceous oxygen demand can be done in two ways: by retarding nitrification in the BOD test by adding inhibitors, or by allowing nitrification to take place and subtracting its demand from the overall results (Eckenfelder, 1966). It should be recognized that nitrification occurs in most of the effluents which have undergone a biological treatment, and exerts an oxygen demand on the receiving waters. Therefore, nitrogenous oxygen demand should be considered as part of the total oxygen demand on the receiving environment. For the BOD test, Allythiourea at a concentration of 10 mg/L, as recommended by Young (1981) was added to the dilutioin water. The BOD values, therefore, represent Carbonaceous Biochemical Oxygen Demand (CBOD).

The concentrations of total organic halides were 175 mg/L for bleach effluent, 60 mg/L for primary and 41 mg/L for secondary effluent and, the percentage removal of TOX in aerated lagoon was about 30% (Table 4). The measured removal of TOX was close to the value reported by Bryant et al. (1987). It was planned to study the effect of ozonation on the TOX of the mill effluents, but the inconsistent results of TOX obtained in the subsequent samples due to operational problems with the Organic Halides Analyzer, resulted in the effort being abondoned. The analysis of the samples for TOX was limited to one sample for the purpose of characterization. It would be interesting if the effects of ozonation on organic halides had been determined in conjunction with the ultrafiltration. The results could have given the insight on the ozonation effects which were expected to degrade the

larger molecules into simpler forms. These simpler molecules formed are reduced during subsequent biological treatment. The fate of the organohalides have always been questionable in the receiving waters. It has been identified that it is the lower molecular compounds which are more toxic to the aquatic organisms than the larger molecules (Bonsor et al. 1988). However, it is also reported that the larger molecules, once discharged into the receiving waters start slowly degrading and form lower molecular weight compounds, which would have more damaging effects on the receiving water. In a situation where ozone could be used as an intermediate stage of treatment during the biological treatment process, it would react with complex compounds forming other molecules that might be relatively toxic but more biodegradable. The removal of these compounds would be quite possible with a better acclimated bacterial population in the biological treatment system.

Experiments were run in duplicate for bleach and primary effluent. The improvement in biotreatability and BOD was insignificant for these samples. Secondary effluent showed an improvement in biotreatability as well as an increase in the total quantity of biodegradable organics. For secondary effluent six replicate experiments were conducted to check the statistical significance of the results. Two more experiments were conducted for 150 mg/L and one experiment was run for 200 mg/L ozone dose to investigate the effects of higher ozone doses on the effluent characteristics.

6.1 Biochemical Oxygen Demand

Ozonation of bleach effluent (BOD_5=216 mg/L) resulted in improvement in biotreatability i.e. higher K_e values (Table 14, Figure 11), but the total quantity of biodegradable material decreased with ozonation both for 50 and 100 mg O_3/L doses. The increase in K_e value for 50 mg/L was higher and the decrease in L_o was lower compare to 100 mg O_3/L dose.

Table 14. Ke and Lo values for Bleach, Primary and Secondary Effluents

SAMPLE	Ke(1/day)	Lo(mg/L)
BLEACH EFFLUENT		
Raw sample	0.20	364
Oxygenated sample	0.20	317
50 mg O3/L dose	0.23	315
100 mg O3/L dose	0.21	320
PRIMARY EFFLUENT		
Raw sample	0.19 to 0.25	264 to 292
Oxygenated sample	0.16	298
50 mg O3/L dose	0.23	254
100 mg O3/L dose	0.23	260
SECONDARY EFFLUENT		
Raw sample	0.1 to 0.15	60 to 80
Oxygenated sample	0.1 to 0.13	65 to 80
50 mg O3/L dose	0.15 to 0.24	80 to 90
100 mg O3/L dose	0.15 to 0.24	100 to 120
150 mg O3/L dose	0.15	126

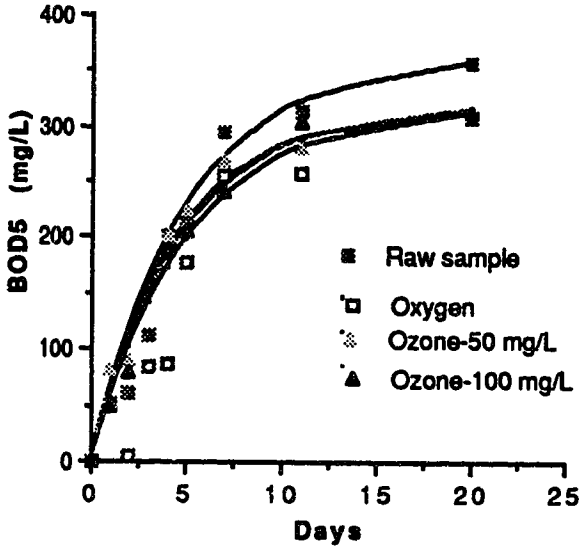

Figure 11. Biochemical Oxygen Demand for Bleach Effluent

Similarly for primary effluent (BOD_5=205 mg/L) the K_e values decreased slightly with ozonation, whereas the L_o remained same (Table 14 and Figure 12).

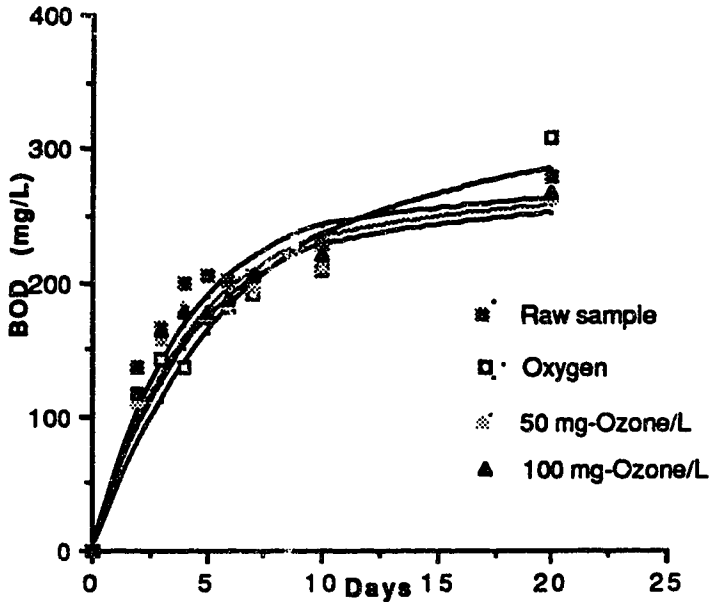

Figure 12. Biochemical Oxygen Demand for Primary Effluent

The apparent ineffectiveness of ozone for the effluents having high initial BOD had most frequently been reported for pulp mill effluents. This tendency can be explained when we look at the TOC values. It was observed that for all the ozone doses there was a small decrease in the TOC values i.e. some of the simple compounds were completely oxidized and removed from the effluent. More complex compounds reacted with ozone and the resulted simple compounds were available for biodegradation, as a result the overall effect of ozonation was completely masked. Similar results have been reported by Smith and Furgason (1974) (Figure 13).

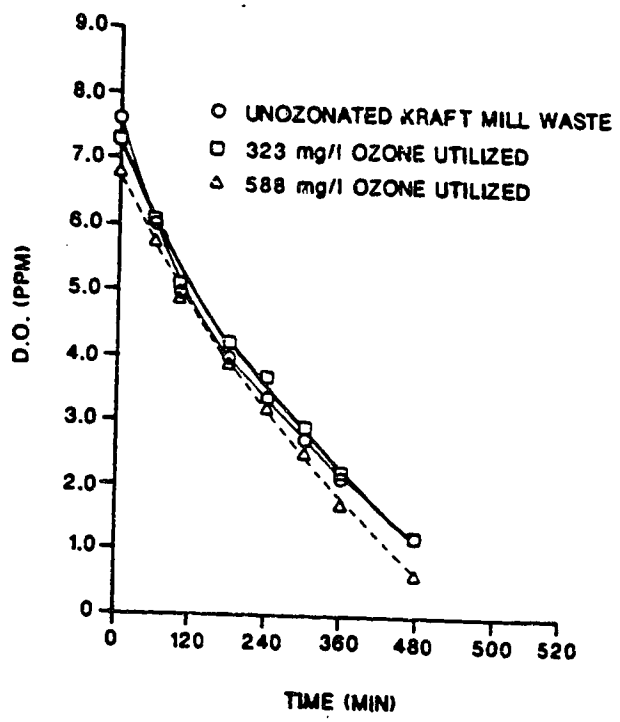

Figure . Oxygen Uptake Study (Adapted from Smith and Furgason 1976)

In comparison to bleach and primary effluent, secondary effluent (BOD_5=26 to 41 mg/L) showed a significant improvement in K_e and L_o values (Table 14, Figures 14).

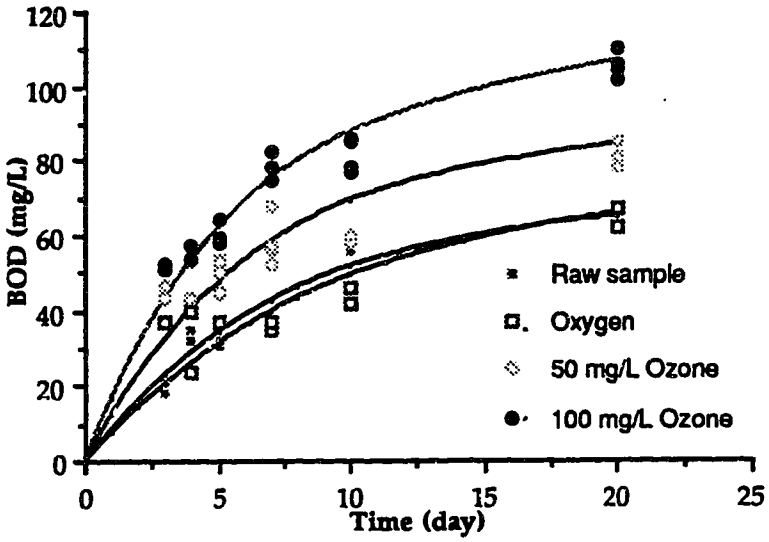

Figure 14. Biochemical Oxygen Demand for Secondary Effluent

Between 65% to 100% improvement in BOD was noted for 50 and 100 mg/L of ozone doses. Both 5-day and 20-day BOD increased with ozonation. The increase in BOD for secondary effluent with ozonation supports the theory that for effluents with high initial BOD part of the ozone reacted with simple compounds and fulfilled their oxygen demand. The other part of ozone reacted with complex molecules, which were not readily biodegradable, and changed them into a simpler form. However, with secondary effluent which had already 80 to 90% of simple compounds removed during biological treatment, and had greater proportion of complex molecules, ozone was more effective towards them. Sozanska and Sozanski (1989) reported a threshold limit of 23 mg/L of initial BOD for an increase or

decrease in the BOD for ozonated samples. However, that limit is dependent on the proportion of complex molecules present in the sample, and also the ozone contacting device. If the ozone molecules are brought in contact more rapidly with the effluent molecules there is a possibility of ozone reacting with a larger number of molecules than reacting with a single molecules to greater extent.

The rate of BOD removal (or effect on BOD) is a function of ozone concentration in the effluent. Reaction of ozone for the effect on BOD can be written as:

$$-dr / dt = k\, C_{BOD}\, C_{O3} \qquad (20)$$

As ozone concentration reduced to zero in the effluent, the rection ceases. Ozonation of primary and bleach effluent resulted in no significant increase in BOD, whereas for secondary effluent, ozonation improved BOD. This phenomenon indicated that there were competing reactions occuring with ozone. As a result ozone was much quickly consumed in primary and bleach effluents, before it could react with complex molecules and improve the BOD.

Secondary effluent, which already had undergone biological treatment, had complex compounds with low BOD_5; ozone attacked these compounds effectively and converted them into simpler forms which were subsequently biodegraded at a faster rate.

Secondary samples with an initial BOD_5 between 26 to 41 mg/L showed an average increase in BOD_5 of 65% and 100% for 50 and 100 mg O_3/L doses respectively. The relatively improvement in BOD_5 for an increase in ozone dose from 100 to 150 mg O_3/L was smaller than

the increase from 50 to 100 mg O_3/L dose. Similarly the increase in BOD_5 for an ozone dose increased from 150 to 200 mg O_3/L was smaller than that for 100 to 150 mg O_3/L. It was believed that up to 100 mg O_3/L dose ozone had more opportunity to react with rather complex compounds, while a further increase in dose resulted in ozone reacting with some of the already degraded compounds along with complex molecules. As a result the effectiveness of ozone was less (Table 15).

K_e and L_o values which represent the biotreatability and total amount of biodegradable material in an effluent, increased with ozonation. The newly formed molecules in the effluent after reacting with ozone, were consumed by microorganisms at about twice the rate of raw sample.

Table 15. Improvement in BOD for Various Ozone Doses

SAMPLE	Bleach Effluent		Primary Effluent		Secondary Effluent	
	BOD5 (mg/L)	BOD20 (mg/L)	BOD5 (mg/L)	BOD20 (mg/L)	BOD5 (mg/L)	BOD20 (mg/L)
Raw Sample	216	358	205	279	26-41	56-108
Oxygen-dose	192	314	174	308	34 to 39	62-116
50 mg O3/L	199-247	313-344	170-179	252-285	46-59	78-120
100 mg O3/L	188-213	312-323	178-182	267	50-71	102-148
150 mg O3/L	-	-	-	-	73-81	123-140
200 mg O3/L	-	-	-	-	90	138

A slight bump in the BOD curves was noticed for secondary effluent even though the total kjeldahl nitrogen was between 3 to 5 mg-N/L. It was not believed that nitrification played any role in higher values of BOD for ozonated samples due to the fact that nitrogen inhibitor was added for BOD test, and unless NH_4 are broken off large molecules, it does not exert oxygen demand. Since the ozonated and unozonated samples were run in pairs, even if there could have been some nitrification the overall effect would be neutralized, as the difference in BOD values of ozonated and unozonated samples were taken under identical conditions.

The bumps in BOD curve can be expected for pulp mill effluents which have a range of simple alcohols and sugars to complex form of lignin compounds. Raabe(1968) identified three groups of compounds in pulp mill effluent with distinct differences in the rate of biodegradation (Figure 15).

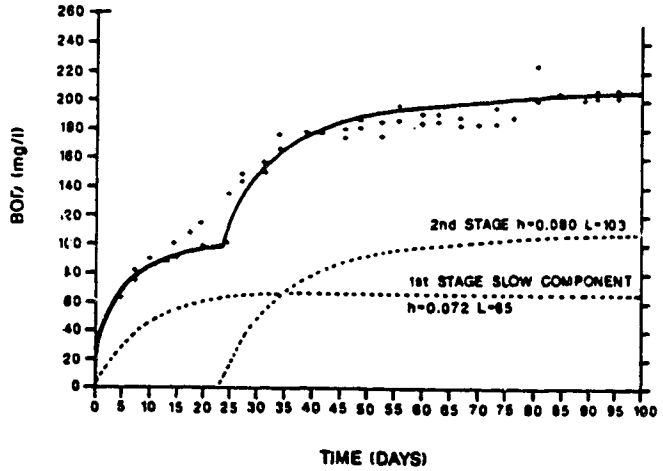

Figure 15. Long-term BOD Over 100 Day Period for Pulp Mill Effluent (Adapted from Raabe, 1968)

Initially it was planned to set-up the respirometer along with BOD bottles to study the oxygen uptake rate for undiluted samples. However, even with acclimatized seeds the oxygen uptake rate in respirometer were quite erratic and showed signs of inhibition effects. When the respirometer was checked for gas leaks, the increase in the micrometer readings after increasing the temperature by 0.3° C, was (±) 5 microlitre, which is within the limits of accuracy of the equipment (Appendix I). A significant difference was noted between the BOD values determined by bottle method and that of respirometer. Therefore, at a later stage it was decided to collect extensive data using 300 mL BOD bottle method. The results obtained subsequently had good reproducibility for replicates.

"t" statistics calculated for paired experiments indicated that pure oxygen had no significant effect on treatability. The results obtained for the oxygenated samples were similar to the raw samples (Appendix IX).

On the other hand there was a significant improvement in BOD_5 for 50 and 100 mg O_3/L doses. The tabulated values of 't' at 95% and 99.9% were 2.015 and 5.893; whereas the calculated values were 5.331 and 8.265 for 50 and 100 mg O_3/L doses respectively. Analysis of variance also indicated a highly significant improvement in BOD after ozonation. Residuals were plotted to confirm the assumptions of constant variance and normal distribution for the data.

The BOD equation was solved for K_e and L_o using a computer program for the solution of non-linear equations. The joint confidence

region was plotted to check the reliability of these parameters. The smaller a joint confidence the better the estimates for the parameters; while a large and irregular joint confidence would mean the calculated values of the parameters are not reliable (Berthouex et al., 1971).

The BOD rate constant K_e for raw sample was between 0.1 to 0.15; and the improved values for 50 and 100 mg O_3/L doses were between 0.15 to 0.24 and 0.15 to 0.24/d respectively (Table 14). The best estimates of K_e were 0.17/d for 50 mg O_3/L, 0.21 for 100 mg O_3/L (Table 16). Melnyk and Netzer (1977) reported that after ozonation there was an overall increase in biotreatable organics, but the resulting molecules degraded at a slower rate. In the present studies this trend was observed at higher ozone doses, but all the ozone doses improved the biotreatability in comparison to unozonated sample.

The Ke and Lo value for raw sample were plotted on the grids that of 50 mg/L and 100 mg/L ozone doses (Figures 16 and 17). Since the calculated value of raw sample did not fall within the JCR of ozonated samples, it indicated that there is a significant difference in the biotreatability of ozonated and unozonated samples.

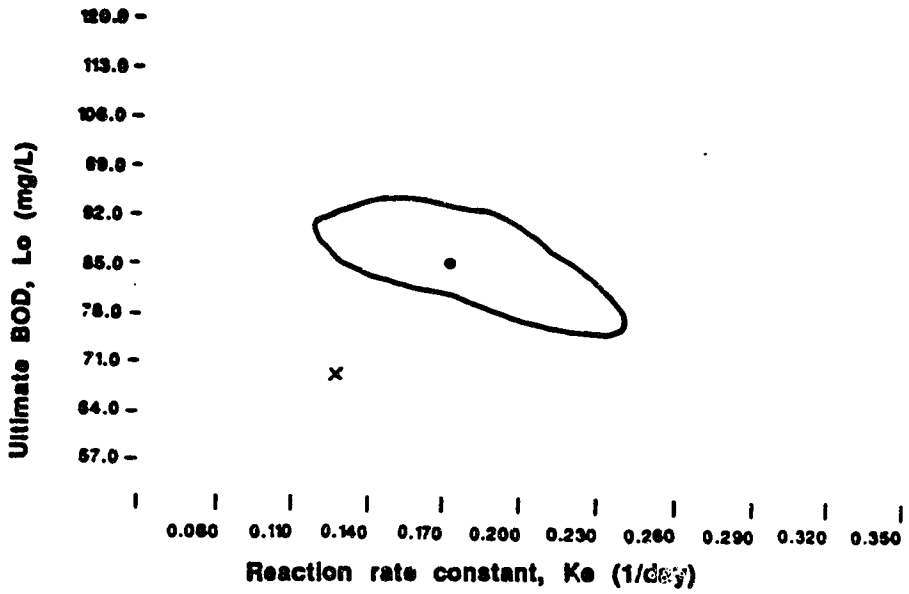

Figure 16. Appriximate 95% Joint Confidence Region for 50 mg O3/L Dose for Secondary Effluent

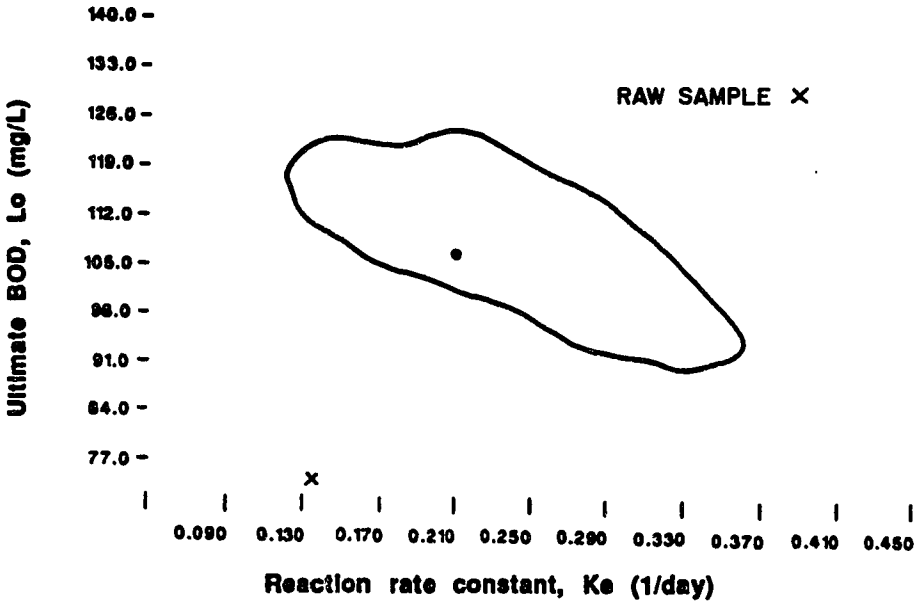

Figure 17. Approximate 95% Joint Confidence Region for 100 mg O3/L Dose for Secondary Effluent

Table 16. K_e and L_o of the Plotted JCR for Secondary Effluent

Sample	Ke (1/day)	Lo (mg/L)	Correlation Coefficient
Raw Sample	0.13	70	-0.9041
50 mg O3/L	0.17	83	-0.7383
100 mg O3/L	0.21	104	-0.6835

6.2 Colour Removal

Ozone was extremely effective for the reduction of colour from pulp mill effluents. Irrespective of the effluent streams, colour removal was evident for all ozone doses. Ozone reduced the colour by altering the molecular structure of the compounds; with no by products generated requiring separate handling.

The effectiveness of ozone increased from bleach<primary effluent<secondary effluent. It seemed that the colour causing molecules in bleach stream were relatively complex in nature and as a result the colour removal was noted to be smaller compare to primary and secondary effluents. It was also noted that biological treatment had a significant effect on the colour causing molecules and made them more reactive with ozone. It is also possible that, biological treatment reduced the competing colour causing molecules in the secondary

effluent. As a results, ozone was more effective with secondary effluent.

Reaction of ozone for colour removal can be given as:

$$-dr / dt = k\, C_{colour}\, C_{O3} \qquad (21)$$

For low ozone dose and high initial colour concentration, the rate of colour removal will become a pseudo-first order reaction and depends on the concentration of ozone in the effluent. As ozone is consumed in the effluent, decolourization reaction ceases. Thus colour removal is a function of ozone stability in the effluent as well the competative reactions which occur along with decolourization. Ozone being selective, reacts with more reactive species in the effluent. These species may be organic or inorganic in nature. The competing reactions were evident during the colour removal for bleach, primary and secondary effluents. It looked like bleach effluent had more reactive species, as a result part of the ozone was consumed by those molecules. The colour causing molecules had to compete with them to react with ozone. The colour removal for bleach effluent was 750 units for an applied ozone dose of 50 mg/L. Primary effluent which had relatively less non colour species, was decolourized to higher extent. The colour removal was 840 APHA units. Secondary effluent which already had undergone biological treatment, the more reactive species had been removed during the biological treatment and therefore, had smaller number of species which were competing with colour causing

molecules for reacting with ozone. This resulted in higher colour reduction for secondary effluent.

At higher ozone doses, the decolourization reaction might become a second order reaction. There was enough ozone present in the effluent to satisfy the demand of more reactive species and react with colour causing molecules. As a result, ozone was equally effective for bleach, primary and secondary effluents at 100 mg/L ozone dose.

The colour reduction for all three wastewater streams was between 680 to 1095 unit for the 50 mg/L ozone dose, whereas for the 100 mg/L ozone dose the corresponding reduction was between 1300 to 1470 units (Table 17).

Table 17. Colour Reduction (Platinum Cobalt Units) for Mill Effluents

Ozone dose (mg/L)	Bleach Effluent			Pond Influent			Secondary Effluent		
	X	Range	% reduction	X	Range	% reduction	X	Range	% reduction
50	715	680 to 745	28 to 31	850	840 to 860	45 to 47	1025	950 to 1060	58 to 67
100	1330	1330 to 1360	53 to 56	1345	1325 to 1360	80 to 84	1350	1205 to 1470	77 to 85
150	-	-	-	-	-	-	1480	1360 to 1600	86 to 90
200	-	-	-	-	-	-	1585	1585	90

The wide spread in colour reduction for lower ozone dose and smaller spread at higher dose might be interpreted that, for higher ozone doses the ozone is equally reactive with all the effluents (Figure 18).

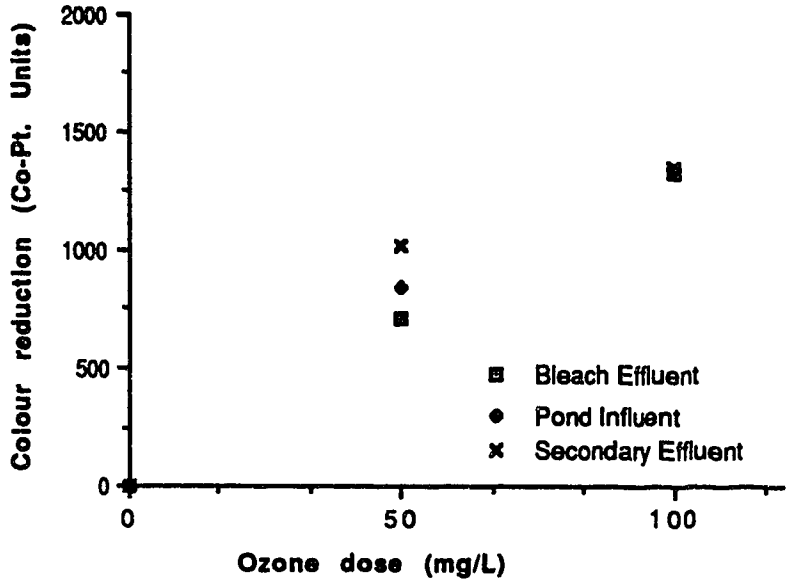

Figure 18. Colour Reduction Spread for Mill Effluents

Secondary effluent which was examined in detail had an initial colour between 1525 to 1770 units. The reduction in colour for 50 mg O_3/L was 58 to 67%; for 100 mg O_3/L the corresponding reduction was 77 to 85%. But further increase in ozone doses resulted a small reduction in the total colour units (Table 17). This exponential behaviour supported the assumption that there were at least two groups of compounds responsible for total colour in the mill effluents with different reactivity towards ozone (Figure 19). The first group of compounds, which was dominant and constituted up to 85% of the

total colour in secondary effluent, reacted readily. The second group of compounds which were more resistant reacted relatively slowly with ozone.

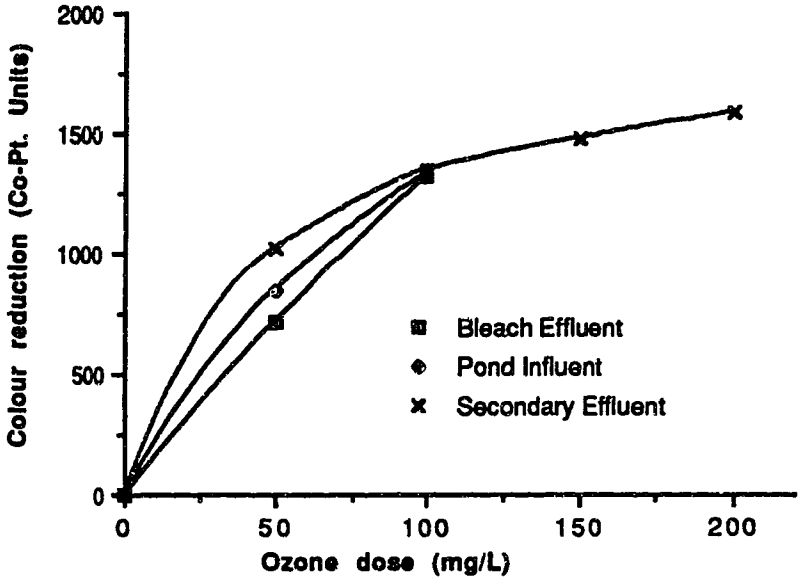

Figure 19. Colour Removal for Mill Effluents

Ng et al. (1978) suggested a relationship between applied ozone dose and colour reduction for kraft mill effluent which is given as Equation (2).

The measured colour removal for bleach effluent was 715 and 1330 units for an applied ozone dose of 50 and 100 mg/L respectively. The calculated reduction from the above relationship was 730 and 1200 units.

6.3 Chemical Oxygen Demand and Total Organic Carbon

The chemical oxygen demand is a measure of the organic matter in the sample which can be oxidized by strong oxidizing agents such as permanganate and dichromate in acid solution. Theoretically it would be expected that BOD of a wastewater to be equal to the COD, but it is not true for various reasons (Eckenfelder, 1966).

1. Many organic compounds which are dichromate oxidizable are not biochemically oxidizable. This aspect is very common for industrial wastewaters.
2. The BOD results may be affected by lack of seed acclimation and toxic effects, giving low readings. The COD results are independent of these variables.
3. Chlorides are oxidized by dichromate, provision should be made to eliminate this interference (Eckenfelder, 1966). High COD values will occur by the oxidation of chlorides by dichromate.

This interference is eliminated by adding $HgSO_4$ (10:1 ratio of $HgSO_4$:Cl) to the reaction mixture.

It was suspected earlier that the concentration of chloride might be high in the samples due to chlorine bleaching operation, however, the chloride contents were measured between 300 to 600 mg chloride/ L of the samples. At these chloride concentrations 0.4 g $HgSO_4$ was enough to reduce the interference of chloride on COD test. Three blank test, under identical conditions, were conducted for each set of COD determinations.

Unlike BOD and colour reduction, the trend in COD and TOC was not clear, and it was hard to draw any conclusions from the results. Theoretically for 100 mg O_3/L dose the drop in COD value should have been 100 mg, if all the ozone reacted. The reaction did not seem to be only addition reaction. On the other hand ozone reacted with some of the molecules and oxidized them completely, resulting in a loss of carbon as well as oxygen. These factors might have affected the reduction in COD which was not reproducible for replicate experimental runs.

To establish the analytical technique, standard COD analysis were done adding 500 mg Cl/L which corresponded to the level of chlorides present in primary effluent and secondary effluent. The results had a standard deviation of 20 mg/L and 36 mg/L respectively at 250 mg/L and 500 mg/L COD levels. The corresponding coefficient of variance were 7% for both the analyses. The above variations were within the levels given by Standard Methods(APHA, AWWA, WPCF, 1985) (Appendix I).

TOC reduction ranged between 10 to 20 mg/L for 50 to 200 mg/L ozone doses (Appendix X). Similar to COD there was no clear correlation for TOC reduction at various ozone doses. Even though the reduction in TOC was small and statistically insignificant, the decrease was very consistent for all the ozone doses, and could not be ignored.

The relationship between COD and TOC values might not be clear for the following reasons:

1. some of the fibrous material present in the effluents might not be oxidized during COD and TOC determination of unozonated samples, but might be more reactive after ozonation, as a result the expected drop in COD was not noticed,
2. simultaneous decrease in TOC for ozonated samples; and
3. unexplainable interference in COD analyses.

On a broad basis, it could be concluded that ozone application decreased the chemical oxygen demand and total organic carbon of pulp mill effluents.

COD/TOC ratio for the effluent samples was about 3 which is characteristic for industrial waste (Appendix X). The ratio did not change significantly for ozonated and unozonated samples. This might be due to the fact that for ozonated samples, there was a decrease in TOC along with COD.

6.4 Suspended Solids

Effect of ozone on suspended solids of the mill effluents was unclear similar to COD and TOC (Appendix X). There was no significant decrease in total suspended for 50 mg O_3/L. The decrease in TSS was significant at 100 mg/L ozone dose. The decrease was 12% for secondary effluent, 6% for bleach effluent and 24% for primary effluent. For bleach and primary effluent samples, the experiments for ozone doses were conducted in duplicate, and for secondary effluent sample, six replicate experiments were carried out.

7.0 CONCLUSIONS

1. Ozonation of bleach effluent (BOD_5=216 mg/L) resulted in slight improvement in biotreatability (i.e. K_e factor) but the total quantity of biodegradable organics decreased as well. No statistically significant improvement in BOD_5 was noted.
2. Primary effluent (BOD_5=205 mg/L) sample showed a slight decrease in both K_e factor and total amount of biodegradable material. However, no significant effect on BOD_5.
3. Secondary samples with initial BOD_5 in the range of 26 to 41 mg/L showed a significant improvements both in biotreatability as well as the total quantity amount of biodegradable organics. The average improvement in BOD_5 for secondary effluent was 65% and 100% for an ozone doses of 50 and 100 mg/L respectively.
4. The most significant improvement with ozonation was colour removal. The effectiveness of ozone for removing colour was highest when the effluent had undergone biological treatment. For secondary effluent the average reduction in colour was 62% for 50 mg O_3/L dose and 82% for 100 mg O_3/L.

5. Unlike BOD and colour, a clear relationship could not be established for the reduction in suspended solids, COD and TOC for various ozone doses.

8.0 RECOMMENDATIONS

The results indicated that ozonation was an effective treatment for the overall improvement in treatability of pulp mill effluent. Since ozone was found to be more effective for the improvement of BOD by breaking complex compounds, and colour removal of secondary effluent, it would likely be most useful if applied at an intermediate stage, after a partial biological treatment of mill effluent for the removal of simple organics. An ozone dose of 100 mg/L seemed to be most optimum for this particular case.

Having an understanding of ozonation for the removal of basic contaminants in pulp mill effluents, further research should be directed towards more specific problems such as the effects on organic halides and other complex compounds. Ultrafiltration technique would be helpful for finding the extent of degradation of the compounds in the pulp mill effluents.

9.0 REFERENCES

APHA, AWWA and WPCF. 1985. Standard Methods for the Examination of Water and Wastewater, 16th edition, Denver, Colo.

Arhippainen, B and Malinen, R. 1987. Cost compentativeness of oxygen bleaching. Proc. TAPPI, International Oxygen Delignification Conference, 23-27.

Bauman, H.D. and Richmond Lutz. 1974. Ozonation of a kraft mill effluent. TAPPI, 57, 5, 116-119.

Berthouex, P.M. and Hunter, W.G. 1971. Journ., Sanitary Eng. Div., ASCE, 97, SA4:393-407.

Berthouex, P.M., and Hunter, W. G. 1971. Problems associated with planning BOD experiments. Journ., Sanitary Eng. Div., ASCE, 6, 333-344.

Bonsor, N., Mc Cubbin, N., and Sprague, J.B. 1988. MISA: Kraft Mill Effluents in Ontario. Ontario Ministry of Environment, Toronto, Ontario: 260 pp.

Box, G.P., Hunter, W.G. and Hunter, J.S. 1978. Statistics For Experimenters. John Wiley & Sons, New York, 93-106.

Bryant, C.W., Amy, G.L. and Allman, B.C. 1987. Organic halides and organic carbon distribution and removal in a pulp and paper wastewater lagoon. Journ. Water Poll. Control Fed. 59, 10, 890-896.

Buley, V.F. 1973. Potential oxygen application in the pulp and paper industry. TAPPI. 56, 7, 101-104.

Chen, T., Fredrickson, E.E., Cormack, J.F. and Young, S.R. 1974. Four biological systems for treating integrated paper mill effluent. TAPPI. 57, 5, 111-115.

Cook, T.E., Farmer, F.A., Reid, J. and Rowbottom, R. 1973. The Effect of Pulp and Paper Mill Effluents on the Taste and Odour of the Receiving Water and the Fish Therein. Pulp and Paper Magszine of Canada, 74, 97-106.

Dorica, J., and Wong, A. 1979. Detoxification of linerboard effluents using physical-chemical techniques. Pulp and Paper Canada. 80, 3, 65-68.

Eckenfelder,W.W. 1966. Industrial Water Pollution Control. McGraw Hill, New York, 1-43.

Edde, H. 1984. Environmental Control for Pulp and Paper Mills. Park Ridge, New Jersey: Noyes Publications, 179 pp.

Edmonton Journal, July 8, 1989.

Edward, A.L. 1981. Aquatic Pollution. John Wiley and Sons Inc., 183-197.

EPS. 1975. Toxicity of wastewater discharges and their effects on receiving water at Northwest Pulp and Paper Company. Hinton, Alberta. Surveillance report EPS, 5-NW-75-1, Edmonton, Alberta. 40 p.

EPS. 1983. The Basic Treatment Technology of The Pulp and Paper Industry and Its Environmental Protection Practices. Training

Manual EPS-6-EP-83-1. Environmental Protection Programs Directorate, Ottowa, Ontario.

EPS. 1984. State-of-the Art of The Pulp and Paper Industry and Its Environmental Protection Practices Economic and Technology Review Report. EPS-3-EP-84-2. Environmental Protection Programs Directorate, Ottawa, Ontario.

Fell, W. F. and Reid, M.T. 1987. Effluent Treatment Associated with a Modernization Program at Ontario Paper Company. Pulp and Paper Canada. 88, 5, 40-45.

Furgason, R.R., Harding, H.L., Langeland, A.W. and Smith, M.A. 1974. Ozone treatment of kraft mill effluents: Part 1. General Characterstics. Am. Inst. of Chemi. Eng. Symp. Series. "Processing and utilization of forest products". 70, 139, 32-38.

Germgard, U., Karlsson, R.M., Kringstad, K., De Sousa, F. and Stromberg, L. 1985. Oxygen bleaching and its impact on some environmental parameters. Svensk Papperstidning, 88,12 R113-117.

Halliburton, D. and Ruthman, E.T. 1989. The Development of Federal Programmes to Address Pollution from The Pulp and Paper Industry. Proc. Conference on Environmental Aspects of Pulping Operations and Their Wastewater Implications. Edmonton, Alberta. July, 27-28.

Idner, K. 1987. Oxygen bleaching of kraft pulp- high consistancy vs medium consistancy. Proc. TAPPI 1987 International Oxygen Delignification Conference, pp. 195-200.

Katuscak, S., Hrvik, A. and Mahdalik, M. 1971. Ozonation of lignin. Part 1. Activation of lignin with ozone. Paper Och Tra, 9, 519-524.

Kovacs, T.G., and Voss, R.H. 1986. Factors Influencing the Effect of Bleached Kraft Mill Effluents on Drinking Water Quality. Water Research, 20,1185-1191.

Leach, J.M., Thakore, A.N. 1975. Isolational Identification of Constituents Toxic to Juvenile Rainbow Trout (Salmo gairdneri) in Caustic Extraction Effluents from kraft pulp mill bleach plants. Journ. Fisheries Res. Board of Can., 32,1249-1257.

Lee, J.W., Peterson, D.L. and Slickney, R. 1989. Anaerobic Treatment of Pulp and Paper Mill Wastewaters. Proc. Conference on Environmental Aspects of Pulping Operations and Their Wastewater Implications. Edmonton, Alberta. July, 27-28.

Mark, V.D., Rony, A.J. and Rump, H.H. 1987. Dioxin: Treatment with ozone. 42nd Prudue University Industrial Waste Conference Proceedings. Section Fifteenth, 499-507.

McCubbin, N. 1983. Alternative to Fossil Fuel for the Lime Kiln. Proc.,CPPA Energy Conference, Ottawa.

McKagua, A.B. 1988. Characterization and Identification of Organic Chlorine Compounds in Bleach Plant Effluents. Colloquium on Measurement of Organochlorines, University of Toronto. Feb. 16-17, 1988.

Melnyk, P.B., and Netzer, A. 1976. Reaction of ozone with chromogenic lignin in pulp and paper mill wastewater. Second Int. Symp. on Ozone Technology Proc. 321-335.

Melnyk, P.B., Jedkins, D. and Netzer, A. 1977. An ozone reactor for colour removal from pulp bleachery wastes. TAPPI, 60, 3, 97-100.

Metcalf and Eddy. 1979. Wastewater Engineering Treatment Disposal Reuse. Second Edition, McGraw Hill, pp 92-93.

National Council of the Paper Industry for Air and Stream Improvement (NCASI). 1971. An Investigation of Improved Procedures for Measurement of Effluent and Receiving Water Colour. Technical Bulletin No.253, December 1971.

Nebel, C., Gottschling, R.D. and O'Neill, H.J. 1974. Ozone: A new method to remove colour in secondary effluents. Pulp and Paper, 48,10, 142-145.

Ng, K.S., Mueller, J.C. and Walden, C.C. 1978. Ozone treatment of kraft mill wastes. Journ. Water Poll. Control Fed., 50, 7, 1742-1749.

Norstrom, H.A. 1987. Reducing the discharges to Water - Technical Objectives. Proc. Second IAWPRC Symposium on Forest Industry Wastewaters, June 9-12, Tampere, Finland.

Oikari, A. and Holmbom, B. 1986. Assessment of Water Contamination by Chlorophenolics and Resin Acids with the Aid of Fish Bile Metabolites. Aquatic toxicology and environmental fate: ninth volume. Philadelphia: American Society of Testing and Materials, ASTM STP 921, 252-267.

Oikari, A.O.J. 1986. Metabolites of Xenobiotics in the Bile of Fish in Waterways Polluted by Pulp Mill Effluents. Bulletin of Environmental Contamination and Toxicology, 36, 429-436.

Passino, D.R.M. and Smith, S.B. 1987. Acute Bioassay and Hazard Evaluation of Representative Contaminants Detected in Great Lakes Fish. Environmental Toxicology and Chemistry, 6, 901-907.

Prat, C., Vicente, M. and Esplugas, S. 1989. Ozanation of Bleaching waters of the Paper Industry. Water Researc[illegible], 23, 1, 51-55.

Raabe, E.W. 1968. Biochemical oxygen demand and degradation of lignin in natural waters. Journ. Water Poll. Control Fed., 40, 5, Part 2, 145-150.

Rice, R.G. and Browning, M.E. 1981. Ozone Treatment of Industrial Wastewater. Pollution Technology Review Series. Noyes Data Corporation, Park Ridge, New Jersey, 230-261.

Smith, L.L. Jr., Kramer, R.H. and MacLeod, J.C. 1965. Effects of Pulpwood Fibers on Fathead Minnows and Walleye Fingerlings. Journ. Water Poll. Contorl Fed.,. 37, 1, 130-140.

Smith, M.A., and Furgason, R.R. 1976. Use of ozone in the treatment of kraft pulp mill liquid wastes. Part 2. Biodegradation. Second Int. Symp. on Ozone Technology, Proc., 309-320.

Sozanska, Z. , and M.M. Sozanski. 1989. Efficiency of ozonation as a unit process in the treatment of secondary effluents from pulp and paper industry. IOA, Ninth Ozone World Congress Proceedings. June 3-9, 1989. New York, 2, 203-220.

Tench, L. and Harper, S. 1987. Oxygen Bleaching Practices and Benefits: An Overview. TAPPI, 11, 55-61.

Tschirley, F.H. 1986. Dioxin. Scientific American, 254, 2, 29-35.

Turner, E.W. 1989. Current Developments in Ontario Pulp and Paper Industry Regulations. Proc. Conference on Environmental Aspects of Pulping Operations and their Wastewater Implications. Edmonton, Alberta. July, 27-28.

WPCF 1980. Water Sampling for Process and Quality Control. Manual of Practice No. OM-1, Operation and Maintenance, pp103.

Young, J.C. 1973. Chemical methods for nitrification control. Journ. Water Poll. Control Fed., 45, 4, 637-646.

APPENDIX I

CHARACTERIZATION OF MILL EFFLUENTS

Table I.1 Biochemical Oxygen Demand (sample-1)

Sample	Unfiltered		Filtered		Respirometer
	15 mL sample/L	30 mL sample/L	15 mL sample/L	30 mL sample/L	BOD
Bleach	195	98	114	38	34
Effluent	195	126	109	43	
Primary	147	58	Depletion of oxygen by seed		65
Effluent	143	59			
			was more than the sample		
Secondary	67	54			34
Effluent	69	49			
Acid	151	36	59	60	-
sewer	116	35	56	52	

Table I.2 Chemical Oxygen Demand (sample-1)

Sample	Unfiltered (mg/L)	Filtered (mg/L)
Acid Sewer	540	425
	564	646
Bleach Effluent	1553	1446
	1541	1494
	1569	32
		over titrated
Primary Effluent	608	443
	610	481
	622	501
Secondary Effluent	485	356
	505	358
	628	394

Table I.3 Total Organic Carbon (sample-1)

Sample	Unfiltered (mg/L)	Filtered (mg/L)
Acid Sewer	178	169
	180	171
	181	171
Bleach Effluent	852	745
	853	751
	855	772
Primary Effluent	169	153
	171	154
	172	154
Secondary Effluent	152	117
	167	118
	173	118

Table I.4 COD Test with Standard Solution of Potassium Hydrogen Phthalate

1. 500 mg Cl/L was added in the form of NaCl
2. $AgSO_4/H_2SO_4$ = 30 ml
3. $HgSO_4$ ~ 0.4 to 0.5 g

4. Amount of ferrous ammonium sulfate consumed for blank:
   1. 9.11 ml
   2. 9.14 "
   3. 9.45 "
   4. 9.48 "
   5. 9.52 "

Average= 9.34
Sandard deviation(Sd) = 0.2 ml

Actual COD (mg/L)	Estimated COD (mg/L)	Actual COD (mg/L)	Estimated COD (mg/L)
250	247	500	477
250	270	500	491
250	288	500	491
250	288	500	496
250	288	500	509
250	305	500	577

250 mg/L COD standard

Average = 281 mg/L
Standard deviation = 19.7 mg/L
Co-efficient of variation = Sd/Av. * 100 = 7 %

500 mg/L COD standard

Average = 507 mg/L
Standard deviation = 35.9 mg/L
Co-efficient of variation = Sd/Av. * 100 = 7%

Table I.5 T. tir . of Respirometer

1. Temperature was raised from 20 C to 20.3 C
2. Equalibrium time = 40 minutes

Flask No.	Micrometer reading (Initial)	Micrometer reading (Before correction) Test-1	Micrometer reading (After correction) Test-2
1	100	97.6	100.0
2	100	112.0	105.0
3	100	Check seal	100.0
4	100	101.0	100.0
5	100	98.6	100.0
6	100	96.6	100.0
7	100	98.8	98.4
8	100	97.8	100.0
9	100	98.0	100.0
10	100	99.0	100.0
11	100	98.2	96.6
12	100	99.0	100.0
13	100	99.0	100.0
14	100	145.4	100.0
15	100	99.0	96.0
16	100	Check seal	96.0
17	100	101.0	97.6
18	100	98.8	100.0
19	100	102.0	100.0
20	100	98.6	100.0

Table I.6 Optimization of Dilution for Bleach Effluent

Dilution	BOD5(mg/L)	BOD10 (mg/L)	BOD20(mg/L)
Respirometer	58	131	181
Bottle-method			
30 mL sample/1500	99	-	432
20 mL sample/1500	150	314	466
15 mL sample/1500	201	309	459
10 mL sample/1500	210	287	483
5 mL sample/1500	202	334	412

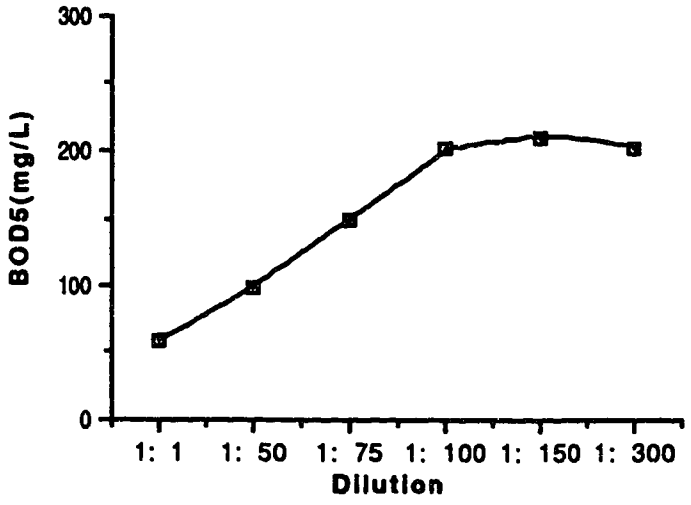

Figure I.1 Dilution Optimization for Bleach Effluent

Table I.7 Optimization of Dilution for Primary Effluent

Dilution	BOD5(mg/L)	BOD10 (mg/L)	BOD20(mg/L)
Respirometer (av)	140	193	240
Bottle-method			
30 mL sample/1500	189	-	278
20 mL sample/1500	181	182	286
15 mL sample/1500	150	221	269
10 mL sample/1500	190	239	319
5 mL sample/1500	316	412	424

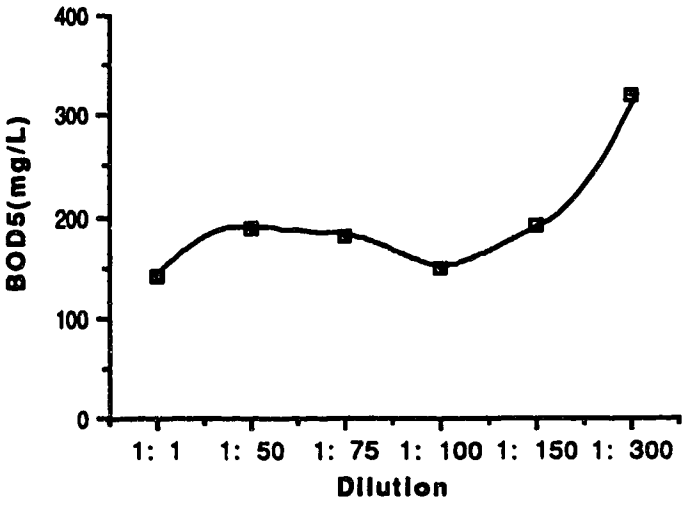

Figure I.2 Dilution Optimization for Primary Effluent

Table I.8 Optimization of Dilution for Secondary Effluent

Dilution	BOD5(mg/L)	BOD10 (mg/L)	BOD [illegible] mg/L)
Respirometer	22	65	98
Bottle-method			
60 mL sample/1500	37	-	99
40 mL sample/1500	45	79	121
30 mL sample/1500	43	84	118 135
20 mL sample/1500	-	-	191 148
10 mL sample/1500			148 257

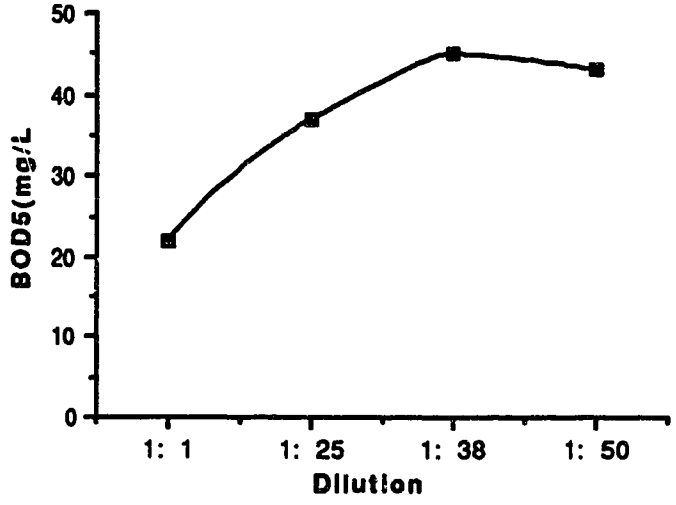

Figure I.3 Dilution Optimization for Secondary Effluent

Table I.9 Ke and Lo for Mill Effluents

Sample	K(e)/day	Lo (mg/L)
Bleach effluent		
Respirometer	0.06	302
range	0.04 to 0.08	227 to 378
Bottle-method	0.08	599
range	0.04 to 0.11	448 to 750
Primary effluent		
Respirometer	0.35	198
range	0.30 to 0.39	192 to 204
	0.19	267
	0.16 to 0.22	252 to 282
Bottle-method	0.18	293
range	0.10 to 0.27	246 to 339
Secondary effluent		
Respirometer	0.04	181
range	0.03 to 0.05	151 to 211
Bottle-method	0.05	200
range	0.03 to 0.07	150 to 250

Table I.10 Chemical Oxygen Demand and Total Organic Carbon

1. $HgSO_4$ ~ 1 g
2. $AgSO_4/H_2SO_4$ = 30 mL

Sample	COD (mg/L) Unfiltered	COD (mg/L) Filtered	TOC (mg/L) Unfiltered	TOC (mg/L) Filtered	COD/TOC
Bleach	2787	2627	860	863	Unfiltered
effluent	2793	2695	861	864	3.24
	2810	2764	862	865	Filtered
median	2793	2695	861	864	3.11
Primary	782	669	269	236	Unfiltered
effluent	786	712	269	237	3.00
	800	772	270	237	Filtered
median	786	712	269	237	2.92
Secondary	519	395	160	126	Unfiltered
effluent	569	398	160	127	3.56
	574	422	161	128	Filtered
median	569	398	160	127	2.92

For industrial wastes the COD/TOC ratio ~ 3 to 4

Table I.11 Suspended Solids for Mill Effluents

Sample	Total Suspended Solids (mg/L) 105 C	Volatile Suspended Solids (mg/L) 550 C
Bleach effluent	76	58
	80	61
	83	65
Primary effluent	102	79
	116	80
	122	86
Secondary effluent	90	70
	96	78
	102	88

APPENDIX II

OZONATION OF BLEACH EFFLUENT

Table II.1 Biochemical Oxygen Demand (mg/L) for Bleach Effluent

Days	Raw sample	Oxygen	50-Ozone Run#1	50-Ozone Run#2	100-Ozone Run#1	100-Ozone Run#2
1	52	-	14	82	21	49
2	50	5	19	89	53	80
3	112	84	92	158	125	159
4	201	86	147	200	154	189
5	211	173	189	240	188	207
5	216	178	199	247	188	213
5	221	192	207	256	203	214
7	278	251	240	279	239	280
7	295	256	248	292	241	280
7	300	269	256	294	242	-
11	271	255	264	349	246	310
11	313	258	277	349	267	312
11	324	279	284	349	283	317
20	324	256	311	284	248	303
20	341	302	312	301	296	314
20	350	308	316	303	305	316
20	356	311	343	306	308	320
20	358	314	344	313	312	323
20	359	-	366	315	316	347

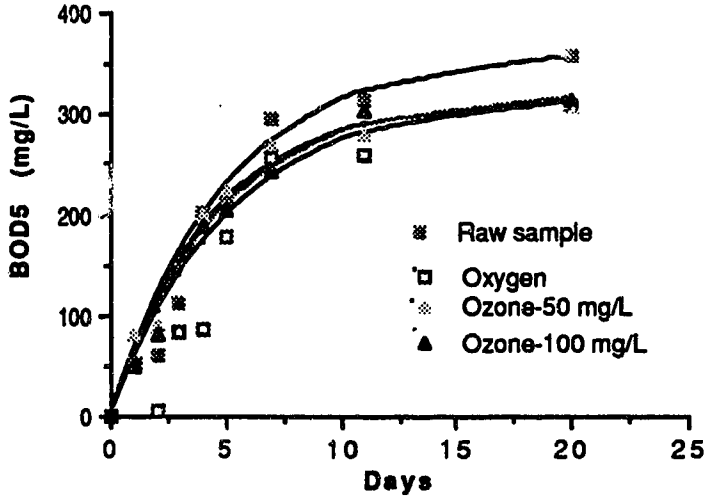

Figure II.1 Biochemical Oxygen Demand for Bleach Effluent

Table II.2 COD and TOC for Bleach Effluent

SAMPLE	COD (mg/L) (Unfiltered)	COD (mg/L) (Filtered)	TOC (mg/L) (Unfiltered)	TOC (mg/L) (Filtered)
Raw sample	1153	969	438	424
	1169	986	438	429
	1190	1017	438	429
Median	1169	986	438	429
Oxygen	1130	997	434	429
	1150	1003	436	431
	1170	1008	438	432
Median	1150	1003	436	431
50 mg O3/L	1073	965	424	430
Run#1	1093	997	427	431
	1117	1005	435	432
Median	1093	997	427	431
50 mg O3/L	1034	942	435	430
Run#2	1071	965	438	432
	1106	969	438	434
Median	1071	965	438	432
100 mg O3/L	1038	879	421	411
Run#1	1059	918	426	413
	1110	961	427	415
Median	1059	918	426	413
100 mg O3/L	1059	938	432	409
Run#2	1077	960	433	409
	1154	983	435	412
Median	1077	960	433	409

Table II.3 Suspended Solids for Bleach Effluent

SAMPLE	Total Suspended Solids (mg/L)	Volatile Suspended Solids (mg/L)
Raw sample	197	157
	200	180
	250	217
mean	217	185
Oxygen	183	150
	197	163
	207	170
mean	196	161
50 mg O3/L	157	127
Run#1	190	150
	200	163
mean	182	147
50 mg O3/L	237	193
Run#2	247	197
	250	200
mean	245	197
100 mg O3/L	200	147
Run#1	207	153
	207	160
mean	205	153
100 mg O3/L	190	157
Run#2	200	163
	223	180
mean	204	167

Table II.4 Colour Removal for Bleach Effluent

Sample	True colour (Pt/Co units)	Colour removal (Pt/Co units)	% Removal
Raw sample	2430	-	
Oxygen	2430	-	
50 mg O3/L (Run#1)	1750	680	28
50 mg O3/L (Run#2)	1685	745	31
100 mg O3/L (Run#1)	1135	1295	53
100 mg O3/ (Run#2)	1070	1360	56

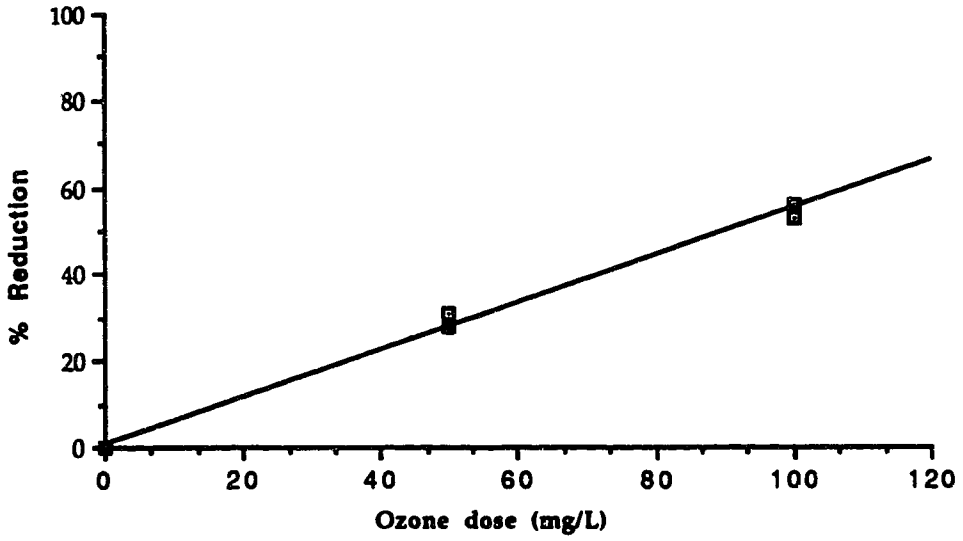

Figure II.5 % Colour Removal for Bleach Effluent

APPENDIX III

OZONATION OF PRIMARY EFFLUENT

Table III.1 Biochemical Oxygen Demand (mg/L) for Primary Effluent

Days	Raw sample	Oxygen	50-Ozone Run#1	50-Ozone Run#2	100-Ozone Run#1	100-Ozone Run#2
2	136	117	110	113	118	87
3	166	143	162	155	160	166
4	200	137	180	182	177	160
5	186	171	176	158	154	159
5	205	174	179	170	178	182
5	230	183	193	177	179	182
6	202	181	194	178	188	185
7	196	178	174	174	207	199
7	204	190	208	194	218	203
7	211	203	210	202	219	208
10	214	203	210	210	222	208
10	228	208	211	210	222	209
10	238	211	221	223	236	218
20	267	299	268	238	265	247
20	279	308	285	252	267	267
20	279	314	286	257	290	274

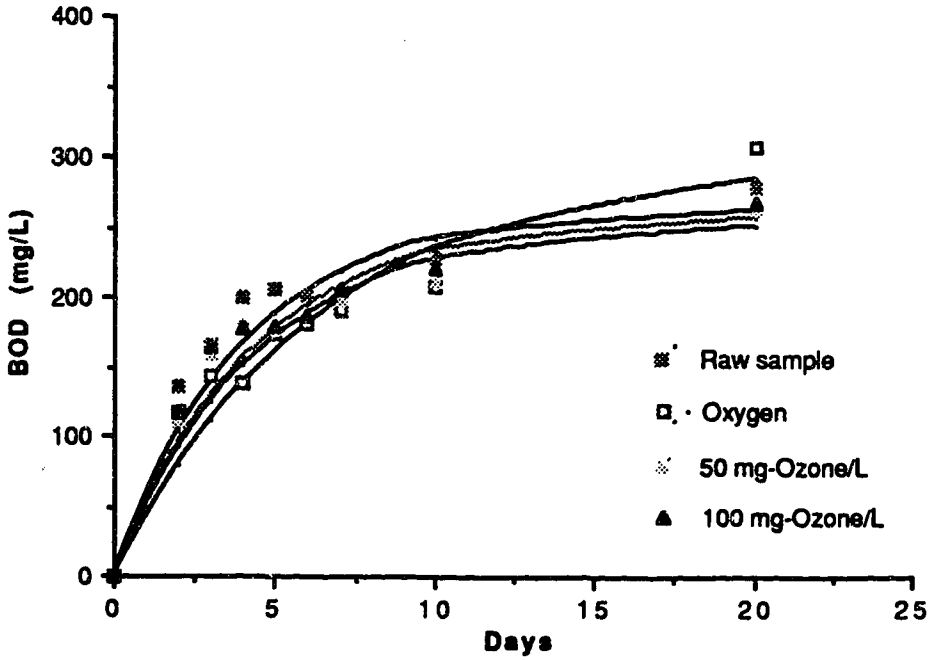

Figure III.1 Biochemical Oxygen Demand for Primary Effluent

Table III.2 COD and TOC for Primary Effluent

SAMPLE	COD (mg/L) (Unfiltered)	COD (mg/L) (Filtered)	TOC (mg/L) (Unfiltered)	TOC (mg/L) (Filtered)
Raw sample	688	633	243	218
	694	651	243	218
	696	788	244	219
Oxygen	690	521	234	205
	698	621	236	211
	706	625	236	212
50 mg O3/L	676	555	236	216
Run#1	678	588	237	218
	688	594	238	218
50 mg O3/L	651	566	236	220
Run#2	719	589	238	222
	725	611	240	222
100 mg O3/L	592	566	225	216
Run#1	621	574	226	217
	643	588	226	218
100 mg O3/L	657	523	230	216
Run#2	662	608	231	218
	694	613	232	219

Table III.3 Total and Volatile Suspended Solids for Primary Effluent

SAMPLE	TOTAL SUSPENDED SOLIDS (mg/L)	VOLATILE SUSPENDED SOLIDS (mg/L)
Raw sample	83	47
	83	50
	87	57
mean	84	51
Oxygen	63	37
	70	43
	77	67
mean	70	49
50 mg O3/L	70	50
Run#1	80	53
	63	50
mean	71	51
50 mg O3/L	63	37
Run#2	70	53
	80	40
mean	72	43
100 mg O3/L	63	50
Run#1	67	50
	60	43
mean	63	48
100 mg O3/L	73	50
Run#2	70	47
	40	23
mean	61	40

Table III.4 Colour Standard Data for Primary Effluent

Standard Colour (Pt/Co units)	Absorbance	Transmittance
0	0	100
25	0.003	99.0
50	0.015	96.4
100	0.029	93.3
150	0.046	90.1
200	0.061	86.9
250	0.073	84.2

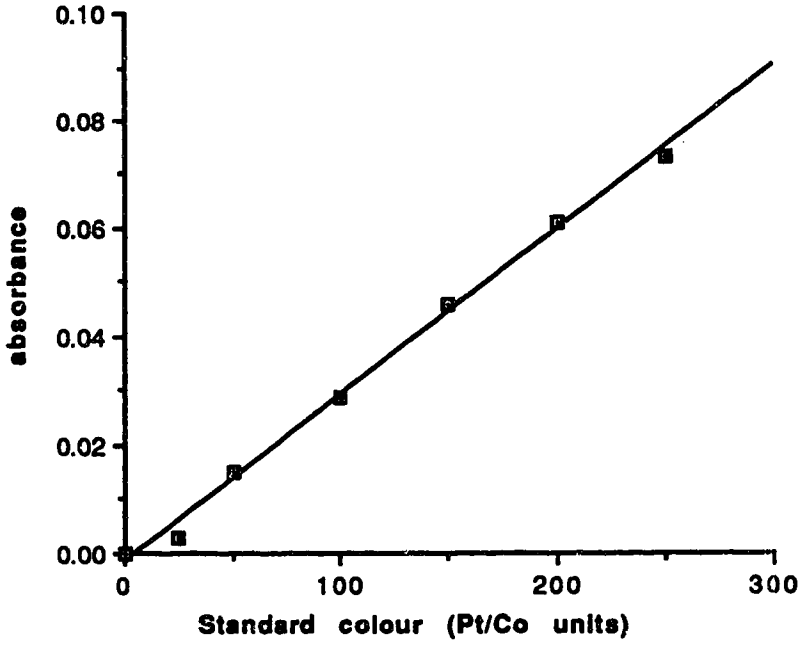

Figure III.4 Colour Standard Graph for Primary Effluent

Table III.5 Colour Removal for Primary Effluent

Sample	True Colour (Pt/Co units)	Colour Removal (Pt/Co units)	% Removal
Raw sample	1850	-	
Oxygen	1750	-	
50 mg O3/L (Run#1)	1010	840	45
50 gm O3/L (Run#2)	990	860	47
100 mg O3/L (Run#1)	525	1325	72
100 mg O3/L (Run#2)	490	1360	74

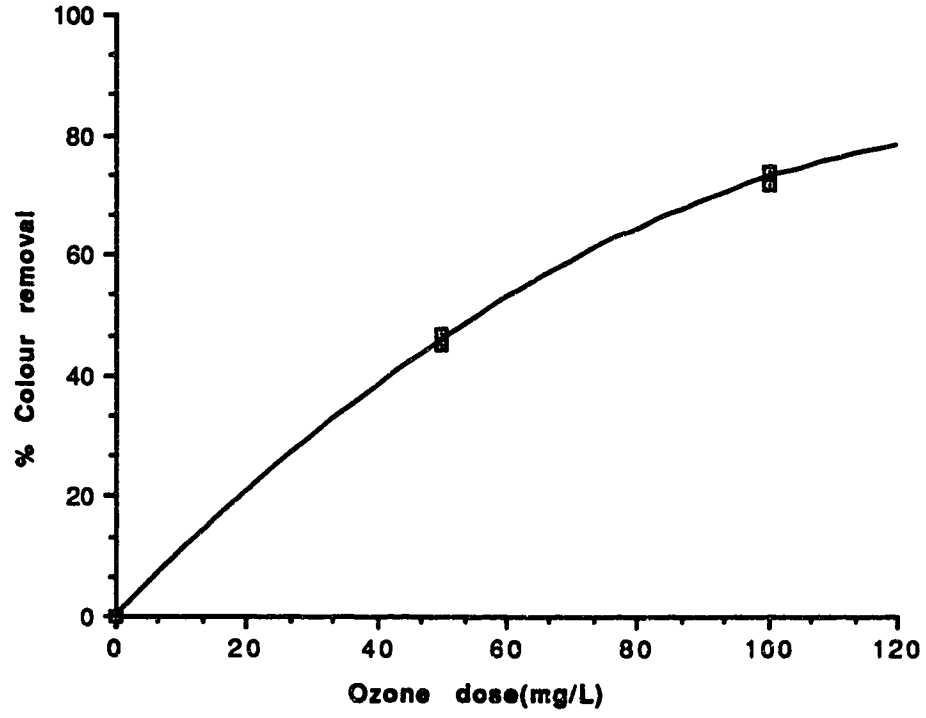

Figure III.6 % Colour Removal for Primary Effluent

APPENDIX IV

OZONATION OF SECONDARY EFFLUENT
(Run#1 and Run#2)

Table IV.1 Biochemical Oxygen Demand (mg/L) for Secondary Effluent

Days	Raw Sample	Oxgen	50-Ozone Run#1	50-Ozone Run#2	100-Ozone Run#1	100-Ozone Run#2
2	35	38	34	37	50	50
3	21	37	39	51	52	82
4	35	40	44	53	59	57
5	26	33	42	37	59	66
5	26	37	53	62	67	67
5	46	55	59	62	69	74
6	33	53	57	58	75	78
7	34	34	56	32	74	82
7	38	54	57	43	75	86
7	50	59	72	44	92	86
10	52	46	58	58	70	78
10	56	50	60	60	70	89
10	59	60	66	66	86	99
20	52	58	67	85	85	102
20	56	62	78	107	86	115
20	66	78	90	117	106	116

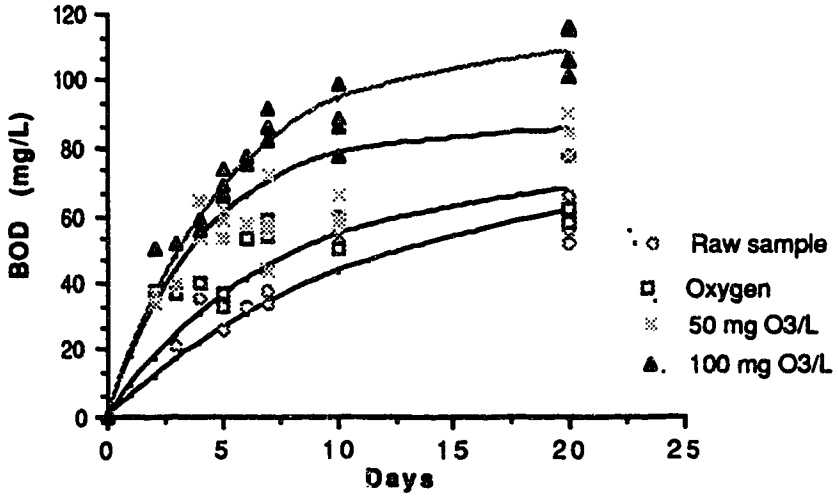

Figure IV.1 Biochemical Oxygen Demand for Secondary Effluent

Table IV.2 COD and TOC for Secondary Effluent

SAMPLE	C.O.D. (Unfiltered)	C.O.D. (Filtered)	T.O.C. (Unfiltered)	T.O.C. (Filtered)
Raw sample	402	336	149	136
	448	367	154	136
	653	379	154	138
Oxygen	441	336	148	130
	453	336	149	131
-	464	-	149	131
50mg/l Ozone	383	296	147	125
Run#1	454	301	147	125
	456	311	147	127
50mg/l Ozone	384	282	147	126
Run#2	410	313	148	127
	415	343	149	127
100gm/lOzone	412	211	142	124
Run#1	415	340	142	125
-	-	-	143	126
100gm/lOzone	342	290	144	127
Run#2	363	292	145	128
	394	301	-	128

Table IV.3 Total and Volatile Suspended Solids for Secondary Effluent

SAMPLE	Total Suspended Solids (mg/L)	Volatile Suspended Solids (mg/L)
Raw sample	73	67
	83	63
	93	67
mean	83	66
Oxygen	77	63
	70	60
	63	53
mean	70	59
50-Ozone	77	63
Run#1	80	67
	83	67
mean	80	66
50-Ozone	77	63
Run#2	70	63
	73	63
mean	73	63
100-Ozone	63	60
Run#1	57	43
	70	60
mean	63	54
100-Ozone	73	60
Run#2	40	30
	60	57
mean	58	49

Table IV.4 Colour Standard for Secondary Effluent

Standard colour (Pt/Co units)	Absorbance	Transmittance
0	0.000	100
25	0.006	98.1
50	0.015	96.1
100	0.031	93.0
150	0.047	89.9
200	0.060	87.0
250	0.076	83.9
500	0.154	70.0

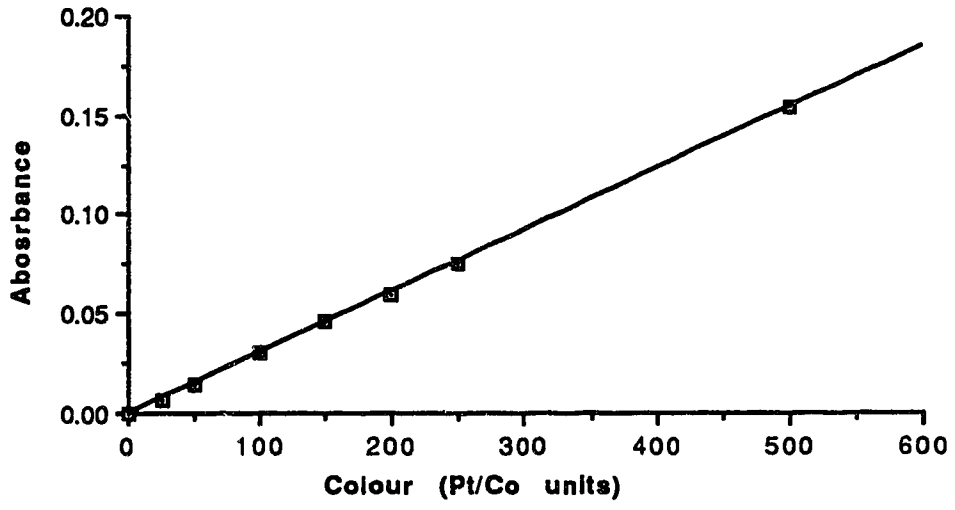

Figure IV.4 Colour Standard Graph for Secondary Effluent

Table IV.5 Colour Removal for Secondary Effluent

Sample	True colour (Pt/Co units)	Colour removal (Pt/Co units)	% Reduction
Raw sample	1525	-	0
Oxygen	1550	-	0
50 mg O3/L (Run#1)	575	950	62
50 mg O3/L (Run#2)	500	1025	67
100 mg O3/L (Run#1)	300	1225	80
100 mg O3/L (Run#2)	250	1275	84

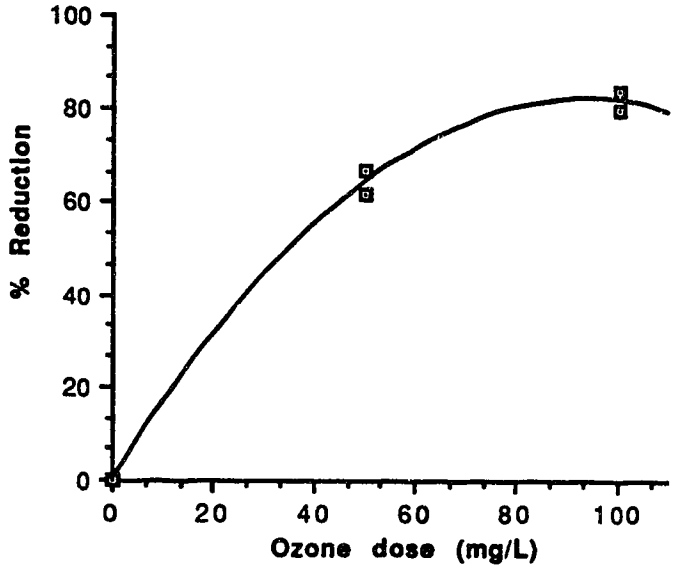

Figure IV.6 % Colour Reduction for Secondary Effluent

APPENDIX V

OZONATION OF SECONDARY EFFLUENT
(Run3# and Run#4)

Table V.1 Biochemical Oxygen Demand (mg/L) for Secondary Effluent

Days	Raw sample	Oxygen	50-Ozone Run#3	50-Ozone Run#4	100-Ozone Run#3	100-Ozone Run#4
3	18	31	47	43	50	51
4	32	24	35	43	49	54
5	31	31	40	43	40	42
5	32	37	50	45	48	58
5	57	39	54	69	50	64
6	32	18	23	46	65	68
7	37	31	46	58	58	74
7	38	35	52	59	75	82
7	43	37	68	66	78	87
10	45	42	55	54	85	71
10	59	42	63	56	87	72
10	59	42	71	58	91	77
17	54	55	81	86	110	109
20	62	61	71	78	86	110
20	71	67	75	85	96	112
20	79	72	81	85	105	115

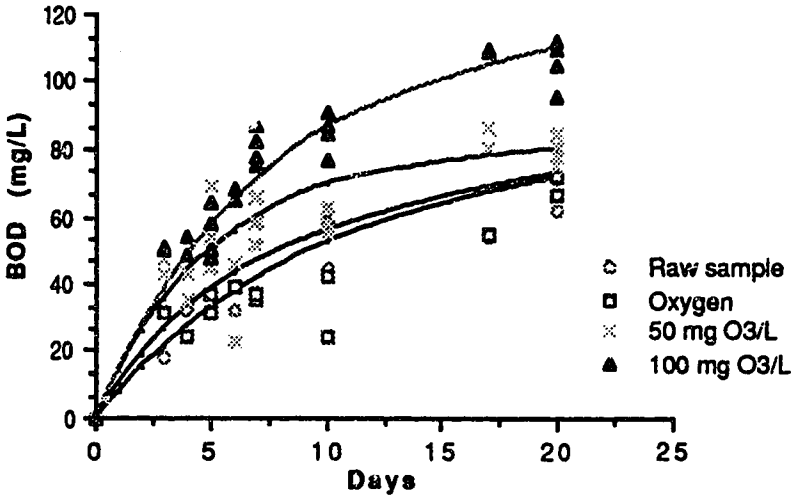

Figure V.1 Biochemical Oxygen Demand for Secondary Effluent

Table V.2 COD and TOC for Secondary Effluent

SAMPLE	COD (mg/L) (Unfiltered)	COD (mg/L) (Filtered)	TOC (mg/L) (Unfiltered)	TOC (mg/L) (Filtered)
Raw sample	512	478	197	148
	530	592	200	149
	566	636	204	149
Oxygen	-	-	195	144
	566	444	196	146
	570	602	216	148
50 mg O3/L	520	-	187	132
Run#1	520	434	190	133
	536	458	218	133
50 mg O3/L	-	-	183	134
Run#2	520	426	198	135
	588	488	211	136
100 mg O3/L	488	454	184	132
Run#1	498	490	185	135
	520	506	190	138
100 mg O3/L	520	-	183	133
Run#2	530	378	188	134
	536	424	190	136

Table V.3 Total and Volatile Suspended Solids for Secondary Effluent

SAMPLE	Total Suspended Solids (mg/L)	Volatile Suspended Solids (mg/L)
Raw sample	103	77
	110	80
	110	87
mean	108	81
Oxygen	97	73
	103	83
	110	87
mean	103	81
50 mg O3/L	97	77
Run#1	100	80
	100	83
mean	99	80
50 mg O3/L	93	70
Run#2	97	70
	100	77
mean	97	72
100 mg O3/L	83	60
Run#1	93	70
	93	77
mean	90	69
100 mg O3/L	103	67
Run#?	103	70
	110	80
mean	105	72

Table V.4 Colour Standard for Secondary Effluent

Standard colour (Pt/Co units)	Absorbance	Transmittance
0	0	100
25	0.010	97.2
50	0.018	95.8
100	0.035	92.0
150	0.052	89.0
200	0.064	86.5
250	[illegible]	83.0
500	0.162	69.0

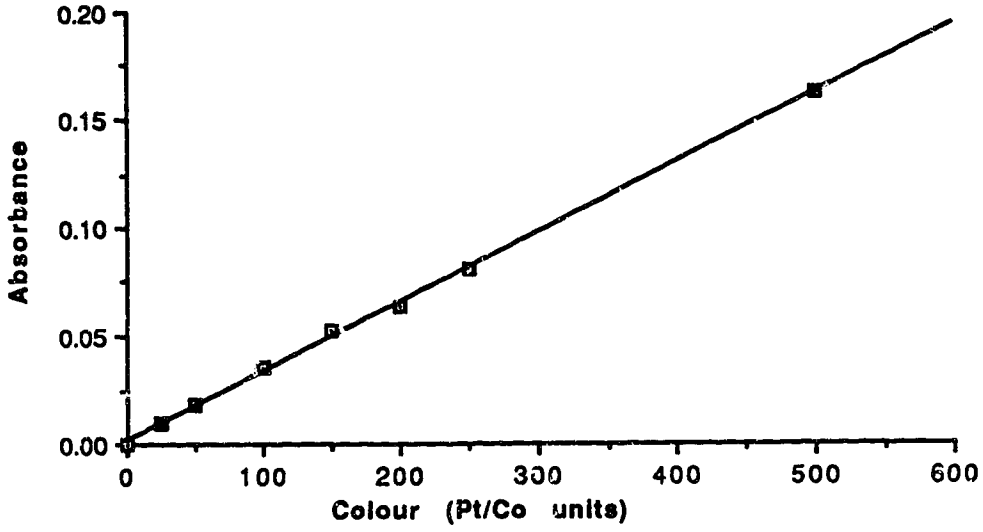

Figure V.4 Colour Standard Plot for Secondary Effluent

Table V.5 Colour Removal for Secondary Effluent

SAMPLE	True colour (Pt/Co units)	Colour reduction (Pt/Co units)	% Reduction
Raw sample	1720	-	-
Oxygen	1750	-	-
50 mg O3/L Run#1	625	1095	64
50 mg O3/L Run#2	625	1095	64
100 mg O3/L Run#1	250 270	1470 1450	86 84
100 mg O3/L Run#2	280 270	1440 1450	84 84

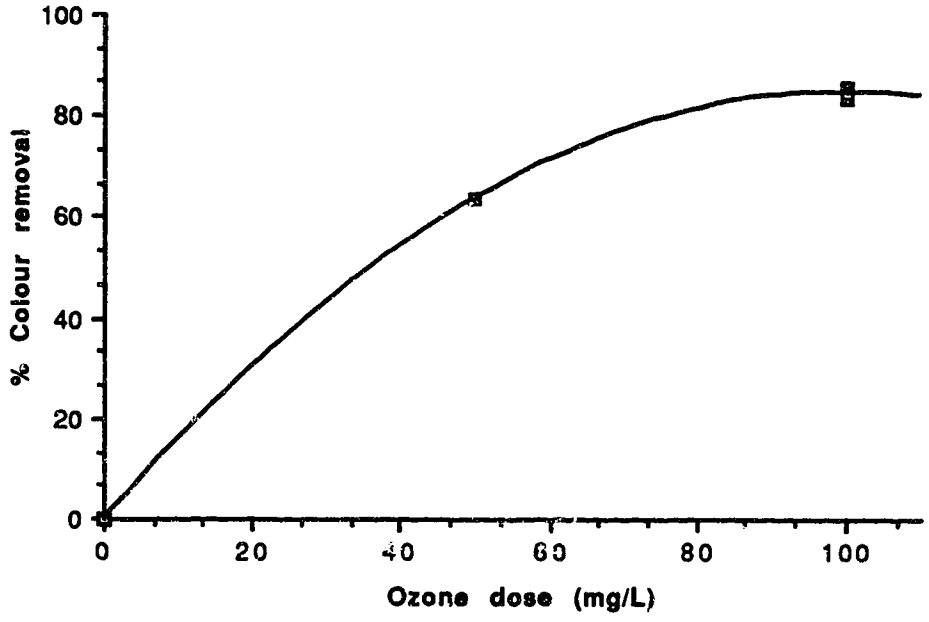

Figure V.6 % Colour Removal for Secondary Effluent

APPENDIX VI

OZONATION OF SECONDARY EFFLUENT
(Run #5)

Table VI.1 Biochemical Oxygen Demand (mg/L) for Secondary Effluent

Days	Raw sample	Oxygen	50 mg O3/L	100 mg O3/L	150 mg O3/L
5	33	31	40	51	61
5	36	34	46	63	63
5	55	43	48	69	73
10	63	65	60	92	97
10	65	67	67	103	98
10	70	67	72	105	108
20	90	89	88	112	110
20	92	91	89	115	123
20	102	91	100	127	126

Table VI.2 COD and TOC for Secondary Effluent

SAMPLE	COD (mg/L) (Unfiltered)	COD (mg/L) (Filtered)	TOC (mg/L) Unfiltered)	TOC (mg/L) (Filtered)
Raw sample	462	381	205	160
	524	406	207	161
	599	408	209	162
Oxygen	461	265	209	150
	492	373	209	152
	502	402	213	152
50 mg O3/L	439	325	197	139
	446	363	199	140
	473	390	201	140
100 mg O3/L	439	307	195	144
	451	360	199	145
	483	361	201	146
150 mg O3/L	99	286	190	139
	385	296	191	139
	420	361	192	140

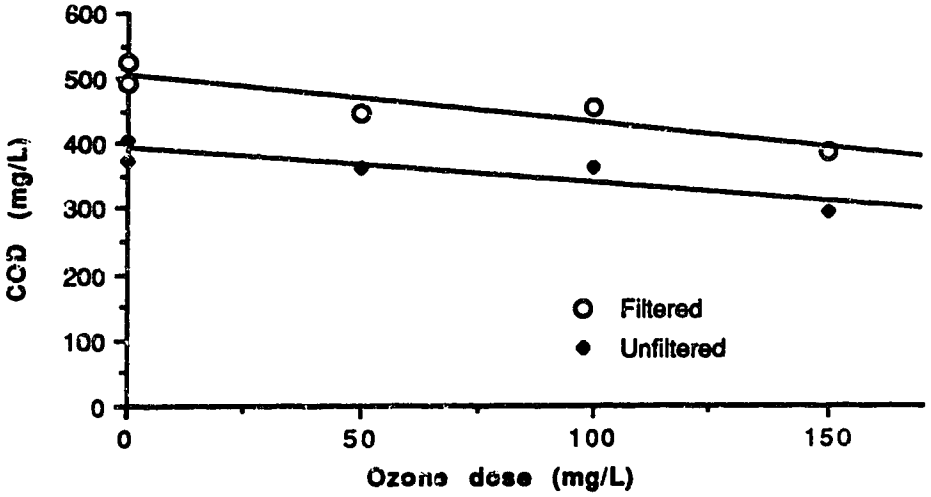

Figure VI.1 Chemical Oxygen Demand for Secondary Effluent

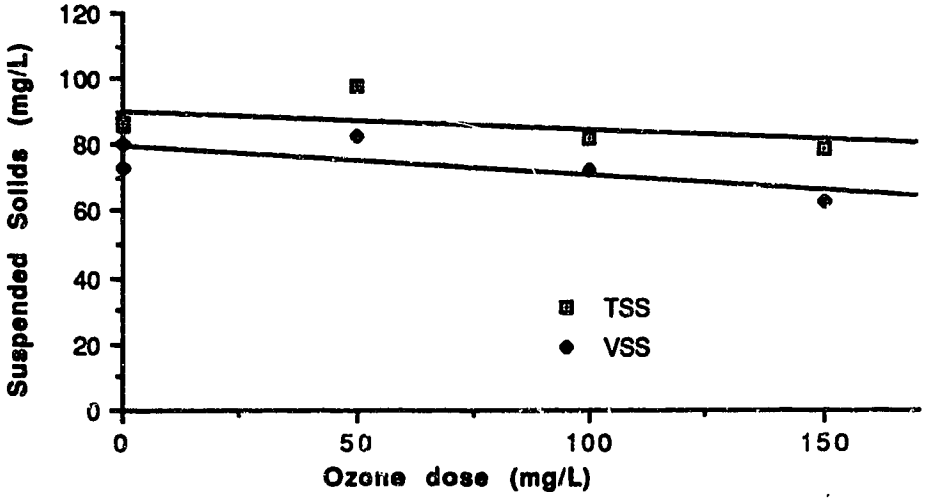

Table VI.2 Total and Volatile Suspended Solids for Secondary Effluent

Table VI.3 Total and Volatile Suspended Solids for Secondary Effluent

Sample	Total Suspended Solids (mg/L)	Volatile Suspended Solids (mg/L)
Raw sample	83	70
	85	70
	90	80
mean	86	73
Oxygen	87	77
	87	80
	88	83
mean	87	80
50 mg O3/L	93	83
	98	83
	103	83
mean	98	83
100 mg O3/L	80	60
	83	77
	83	83
mean	82	72
150 mg O3/L	77	60
	77	63
	83	67
mean	79	63

Table VI.4 Colour Standard for Secondary Effluent

Standard Colour (Pt/Co units)	Absorbance	Transmittance
0	0	100
50	0.020	95.5
100	0.035	92
150	0.045	90
200	0.066	85.8
250	0.078	83
250	0.080	83
500	0.165	68.5

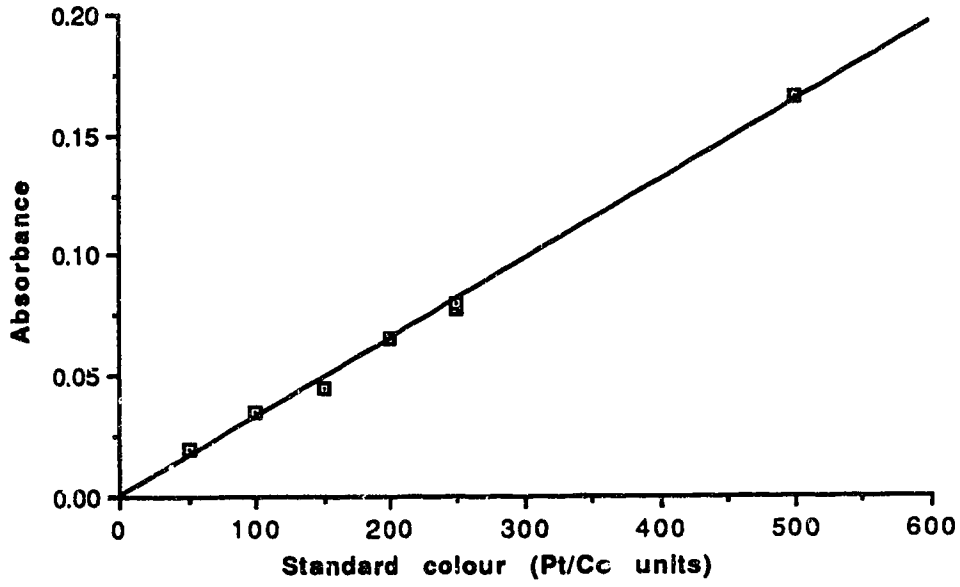

Figure VI.3 Colour Standard Plot for Secondary Effluent

Table VI.5 Colour Reduction for Secondary Effluent

Sample	True colour (Pt/Co units)	Colour reduction (Pt/Co units)	% Reduction
Raw sample	1575	-	-
Oxygen	1575	-	-
50 mg O3/L	660	915	58
100 mg O3/L	370	1205	77
150 mg O3/L	215	1360	86

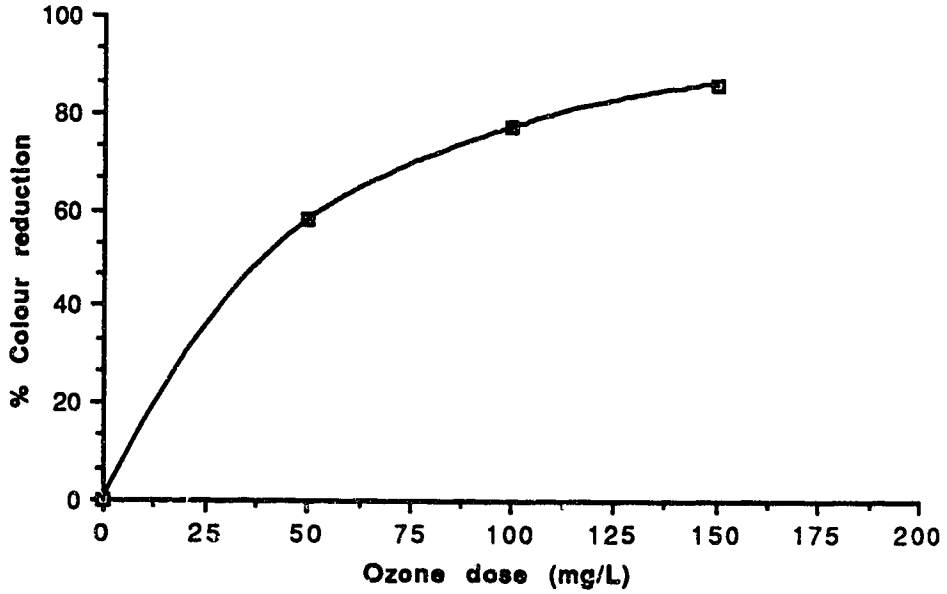

Figure VI.5 % Colour Reduction for Secondary Effluent

APPENDIX VII

OZONATION OF SECONDARY EFFLUENT (Run #6)

Table VII.1 Biochemical Oxygen Demand (mg/L) for Secondary Effluent

Days	Raw sample	Oxygen	50-Ozone	100-Ozone	150-Ozone	200-Ozone
5	41	39	55	58	63	58
5	38	43	56	71	63	90
5	52	46	58	72	81	98
10	66	70	90	95	95	109
10	66	74	90	99	95	118
10	70	75	92	101	100	121
20	100	103	124	157	150	141
20	108	116	130	158	150	144
20	123	124	132	159	151	155

Table VII.2 COD and TOC for Secondary Effluent

SAMPLE	COD (mg/L) (Unfiltered)	COD (mg/L) (Filtered)	TOC (mg/L) (Unfiltered)	TOC (mg/L) (Filtered)
Raw sample	398	359	197	144
	451	367	199	145
	473	676	201	145
Oxygen	391	352	198	142
	441	372	198	143
	703	392	199	143
50 mg O3/L	430	342	187	135
	441	347	187	136
	465	352	189	136
100 mg O3/L	398	309	178	130
	437	338	178	131
	445	373	184	131
150 mg O3/L	383	297	167	128
	391	309	168	128
	391	338	171	129
200 mg O3/L	348	305	163	126
	387	309	163	127
	447	312	167	127

Table VII.3 Total and Volatile Suspended Solids for Secondary Effluent

SAMPLE	Total Suspended Solids (mg/L)	Volatile Suspended Solids (mg/L)
Raw sample	90	70
	93	70
	97	73
mean	93	71
Oxygen	87	70
	90	73
	97	77
mean	91	73
50 mg O3/L	90	67
	93	77
	97	77
mean	93	73
100 mg O3/L	87	67
	90	73
	90	77
mean	89	72
150 mg O3/L	77	63
	80	63
	80	67
mean	79	64
200 mg O3/L	77	63
	80	63
	87	63
mean	81	63

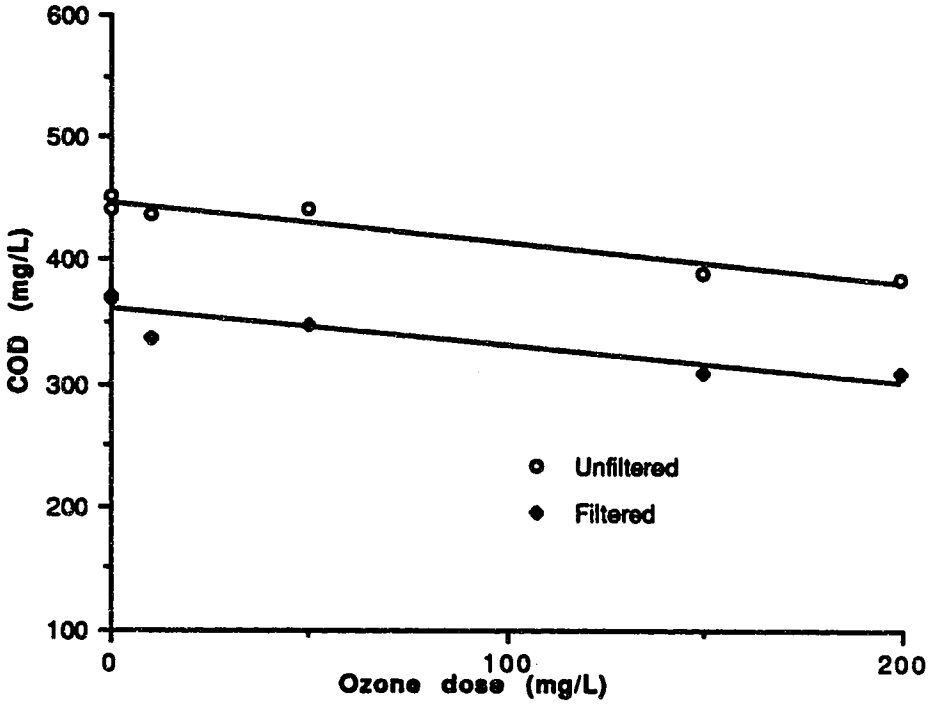

Figure VII.1 Chemical Oxygen Demand for Secondary Effluent

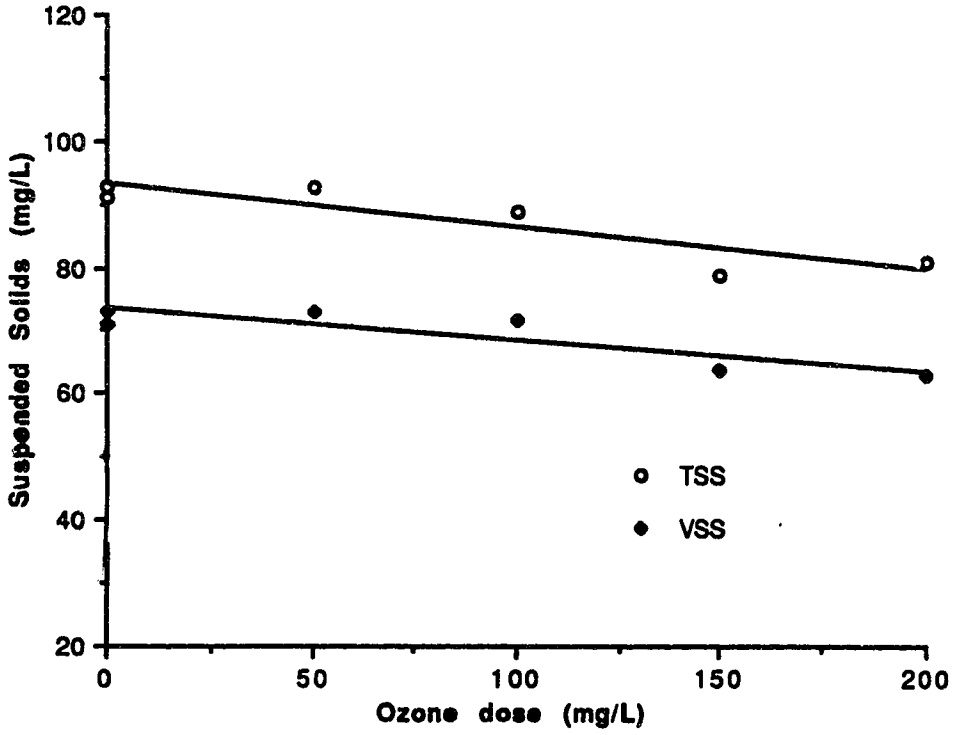

Figure VII.2 Total and Volatile Suspended Solids for Secondary Effluent

Table VII.4 Colour Standard Data for Secondary Effluent

Standard Colour (Pt/Co units)	Absorbance Run#1	Transmittance Run#1	Absorbance Run#2	Transmittance Run#2
0	0	100	0	100
25	0.015	96.0	0.015	96.0
50	0.021	94.0	0.022	95.0
100	0.036	92.0	0.035	92.0
150	0.052	89.0	0.052	92.0
200	0.069	85.5	0.068	85.5
250	0.081	83.0	0.085	82.0
500	0.162	69.0	0.170	69.0
500	0.162	69.0	0.168	68.0

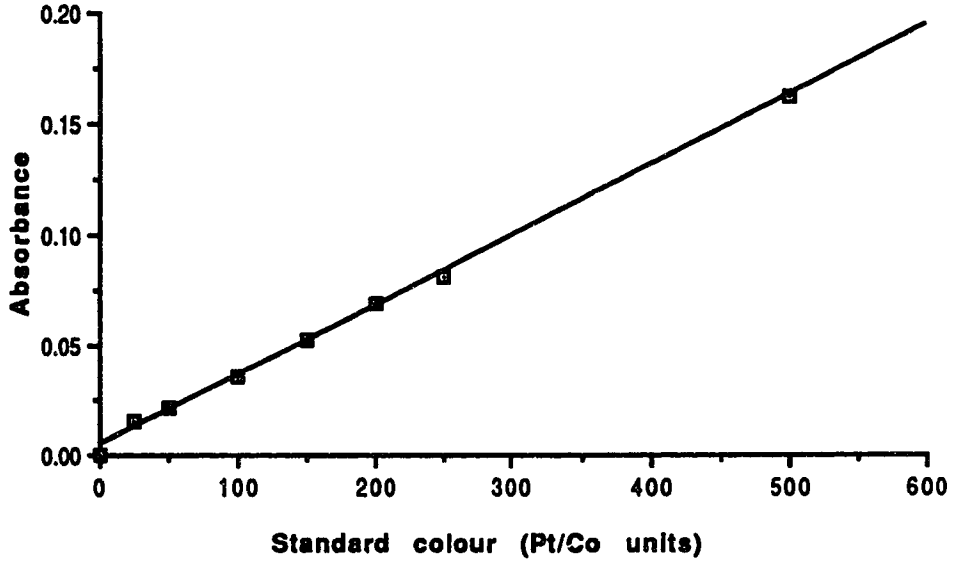

Figure VII.3 Colour Standard Plot for Secondary Effluent

Table VII.5 Colour Reduction for Secondary Effluent

Sample	True colour (Pt/Co units)	Colour reduction (Pt/Co units)	% Reduction
Raw sample	1770		
Oxygen	1820		
50 mg O3/L	710	1060	60
100 mg O3/L	320	1470	82.5
150 mg O3/L	170	1600	89.8
200 mg O3/L	185	1585	89.4

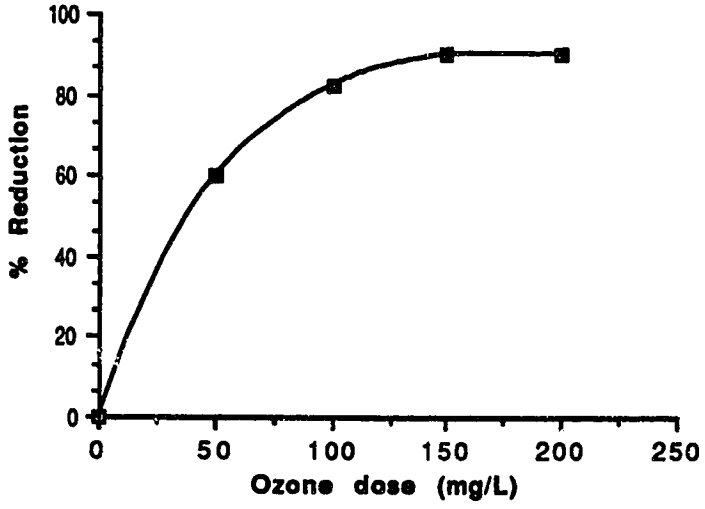

Figure VII.5 Colour Reduction for Secondary Effluent

APPENDIX VIII

CALIBRATION OF OZONE SYSTEM

VIII.1 Calibration of Ozone Generation System

VIII.1.1 Oxygen Flow Rate Measurement Using Wet Test Meter

With top of the rotameter float touching "10" mark
flow rate = 3L in 77 seconds
= 2.338 L/min
Corrected Gas Flow Rate = $(P_m)(T_s) / (P_s)(T_m) * V_m$
Room temperature = 20° C
Barometric pressure = 700 mm Hg
P_m = (Barometric pressure + Gauge pressure - P_w)
= (700 - 17.535)
= 682 mm Hg
V_s = 682 * 273 * 2.338/ 760 * 293
= 1.96 L/min

VIII.1.2 Measurement of Reactor Volume

1. Volume of the reactor measured by adding water
V = (475 + 5 +2.5)
= 482.5 mL

2. Volume of the reactor measured by weight/density method:
Temperature of the water = 19° C
Density of water at 19° C = 0.99843 g/mL
Weight of the beaker + water = 788.90 g
Weight of the beaker = 312.86 g
Weight of the water = 476.04 g
Volume of the water=weight (g)/ density(g/mL)
=476.04 / 0.99843
= 476.8 mL
Error = (482.5 - 476.8) *100 / 476.8 = 1.19%

VIII.1.3 Volume of the Spherical Section of the Reactor

1. Measured by adding water = (500 + 500 + 150 +33)=1083 mL

2. Measured by weight / density method:
   Weight of the beaker + water = 1379.7 g
   Weight of the beaker = 309.7 g
   Weight of the water = 1070 g
   Volume of the water = 1070 / 0.99843 = 1071.7 mL
   Error = (1083 - 1071.7) * 100 / 1071.7 = 1.05%

VIII.1.4 Amount of Ozone Diffused into Cylindrical Part of the Reactor

VIII.1.4.1 minutes ozone and 10 minutes nitrogen @ 3 L/min

Molarity of thiosulfate = 0.005 M
1 mL of 0.005 M thiosulfate = 120 μg O_3 (Standard Methods, APHA, AWWA, WPCF, 1985)
Volume of thiosulfate consumed for titration = 9.06 ml
Amount of ozone diffused into the reactor =9.06 * 0.12
= 1.1 mg O_3

VIII.1.4.2 10 minutes ozone and 20 minutes nitrogen @ 3 L/min

Volume of thiosulfate consumed = 4.2 mL
Amount of ozone diffused = 4.2 * 0.12 = 0.5 mg O_3

VIII.1.5 % Concentration of Ozone/Oxygen Mixture Required for Ozone Doses

Volume of the sample in the reactor = 477 mL

For 50 mg O_3/L dose, amount of ozone required = 50 * 477 / 1000
= 23.8 mg O_3

For 100 mg O_3/L dose, amount of ozone required = 47.7 mg O_3

For 150 " " " " " " " " " " " " = 71.5 mg O_3

For 200 " " " " " " = 95.3 mg O_3

Volume of the spherical section of the reactor = 1083 ml

Density of the Ozone / Oxygen mixture = $1.3285 * 10^{-3}$ g / mL

Mass of the gas mixture = 1083 mL* $1.3285 *10^{-3}$ mg /mL
= 1438.8 mg

% Ozone Concentration
= mass of ozone required * 100/ mass of gas

For 50 mg O_3 /L dose = 23.8 * 100 /1438.8
= 1.654 % (wt / wt)

For 100 mg O_3 /L dose = 47.7 * 100 / 1438.8
= 3.314 % (wt / wt)

For 150 mg O_3 /L dose = 71.5 * 100 / 1438.8
= 4.969 % (wt / wt)

For 200 mg O_3 /L dose = 95.3 * 100 / 1438.8
= 6.623 % (wt / wt)

APPENDIX IX

STATISTICAL CALCULATIONS

IX.1 Statistical test for 5-day BOD Improvements

Raw	Oxygen	50 mgO_3/L	100 mgO_3/L
	37	53	67
		59	67
32	37	50	50
		45	58
36	34	46	63
41	39	56	71
X" = 33.75	36.75	51.50	62.70
n = 4	4	6	6
S_2 = 40.25	4.25	30.70	57.90
F(test) S_2 / S_1			
	0.105	0.763	1.438
F(3,3)0.05 = 9.28		F(5,3)0.05 = 9.01	

Since the tabulated value is greater than calculated, the data can be pooled together.

Oxygen	50 mgO_3/L	100 mgO_3/L
(d)	(d)	(d)
11	27	41
	33	41
5	18	8
	13	26
0	10	27
2	15	30
$d'' = 4.5$	19.3	30.5
$n = 4$	6	6
$S_2 = 16.25$	78.7	81.9
$S = 4.03$	8.87	9.04
$S_d = 2.015$	3.621	3.690
t (calculated) = 2.233	5.331	8.265
t (3, 0.025) = 3.182	t (5,0.025) = 2.571	
(table values)	t (5,0.001) = 5.893	

Since the calculated values for "t" are higher than table values, therefore the Ho(null hypothesis) is incorrect and there is a significant improvement in BOD_5 of the secondary effluent with ozonation.

IX.2 't' test for Total Suspended Solids (mg/L)

Raw sample	Oxygen	50 mg O3/L	100 mg O3/L
83	70	80	63
108	103	73	58
86	87	99	90
93	91	97	105
		98	82
		93	89
X" = 92.50	87.75	98.00	81.17
n = 4	4	6	6
$S_1^2 = 124.3$	$S^2_2 = 186.3$	$S^2_3 = 197.3$	$S^2_4 = 524.9$
F(test)	S12 / S22		
	1.498	1.587	4.220

F(3,3) 95% = 9.280

Since the tabulated value is greater than calculated value, it means the variance is same, the data can be pooled together and treated as on paired basis.

$S_2 = \Sigma (d - d")2 / np - 1$

$S_d = S / \sqrt{np}$

$t = d" / S_d$

d = (Raw sample - Oxygen or 50 mgO_3/L or 100 mgO_3/L)

Oxygen (d)	50 mg O_3/L (d)	100 mg O_3/L (d)
13	3	20
5	10	25
0	9	18
2	11	3
	0	4
	0	4
d" = 5.0	5.5	12.3
n = 4	6	6

For Oxygenated sample

$S_2 = 32.66$

$S = 5.714$

$S_2 = 5.714 / \sqrt{4} = 2.857$

t (calculated) = 5.0 / 2.857 = 1.750

t (3,0.025) = 3.182

Since the calculated value of "t" is less than tabulated, there is no significant change in suspended solids due to oxygenation.

For 50 mg O_3/L ozone dose

$S_2 = 25.91$

$S = 5.089$

$S_d = 2.073$

t (calculated) = 5.5 / 2.073 = 2.653

t (3,0.025) = 3.183

No significant change in TSS due to 50 mgO_3/L dose.

For 100 O_3/L ozone dose

$S_2 = 52.23$

$S = 7.227$

$S_d = 2.940$

t (calculated) = 12.3 / 2.940 = 4.184

t (5,0.025) = 2.571

There is a significant reduction in TSS with 100 mg O_3/L dose.

APPENDIX X

SUMMERY OF COD, TOC AND SS FOR MILL EFFLUENTS

Table X.1 Chemical Oxygen Demand (mg/L) for Mill Effluents (Unfiltered)

Sample	Bleach effluent	Primary effluent	Secondary effluent			
			(Run 1&2)	(Run 3&4)	(Run 5)	(Run 6)
Raw sample	1169	694	448	566	524	451
Oxygen	1150	698	453	566	492	441
50 mg O3/L (Run1)	1093	678	454	520	446	441
50 mg O3/L (Run2)	1071	719	410	520	-	-
100 mg O3/L(Run1)	1059	621	415	498	451	437
100 mg O3/L(Run2)	1077	662	363	530	-	-
150 mg O3/L	-	-	-	-	385	391
200 mg O3/L	-	-	-	-	-	387

Table X.2 Chemical Oxygen Demand (mg/L) for Mill Effluents (Filtered)

Sample	Bleach Effluent	Primary Effluent	Secondary Effluent			
			(Run 1&2)	(Run 3&4)	(Run 5)	(Run 6)
Raw sample	986	651	367	478	406	367
Oxygen	1003	621	336	444	373	372
50 mg O3/L(Run1)	997	588	301	434	363	347
50 mg O3/L(Run2)	965	611	313	426	-	-
100 mg O3/L(Run1)	918	574	276	490	360	338
100 mg O3/L(Run2)	960	608	292	378	-	-
150 mg O3/l	-	-	-	-	296	309
200 mg O3/l	-	-	-	-	-	309

Table X.3 Total Organic Carbon (mg/L) for Mill Effluents (Unfiltered)

Sample	Bleach Effluent	Primary Effluent	Secondary Effluent			
			(Run 1&2)	(Run 3&4)	(Run 5)	(Run 6)
Raw sample	438	243	154	200	207	199
Oxygen	436	236	149	196	209	198
50 mg O3/L(Run1)	427	237	147	190	199	187
50 mg O3/L(Run2)	438	238	148	198	-	-
100 mg O3/L(Run1)	426	226	142	185	199	178
100 mg O3/L(Run2)	433	231	144	188	-	-
150 mg O3/L	-	-	-	-	191	168
200 mg O3/L	-	-	-	-	-	163

Table X.4 Dissolved Organic Carbon (mg/L) for Mill Effluents

Sample	Bleach Effluent	Primary Effluent	Secondary Effluent			
			(Run 1&2)	(Run 3&4)	(Run 5)	(Run 6)
Raw sample	429	218	136	149	161	145
Oxygen	431	211	131	146	152	143
50 mg O3/L(Run1)	431	218	125	133	140	136
50 mg O3/L(Run2)	432	222	127	135	-	-
100 mg O3/L(Run1)	413	217	125	135	145	131
100 mg O3/L(Run2)	409	218	128	134	-	-
150 mg O3/L	-	-	-	-	139	128
200 mg O3/L	-	-	-	-	-	127

Table X.5 COD/TOC for Mill Effluents (Unfiltered)

Sample	Bleach Effluent	Primary Effluent	Secondary Effluent			
			(Run 1&2)	(Run 3&4)	(Run 5)	(Run 6)
Raw sample	2.67	2.86	2.91	2.83	2.53	2.27
Oxygen	2.64	2.96	3.04	2.89	2.35	2.23
50 mg O3/L(Run1)	2.56	2.86	3.09	2.74	2.24	2.36
50 mg O3/L(Run2)	2.46	3.02	2.77	2.63	-	-
100 mg O3/L(Run1)	2.49	2.75	1.91	2.69	2.27	2.46
100 mg O3/L(Run2)	2.49	2.87	2.52	2.82	-	-
150 mg O3/L	-	-	-	-	2.02	2.33
200 mg O3/L	-	-	-	-		2.37

Table X.6 COD/TOC for Mill Effluents (Filtered)

Sample	Bleach effluent	Primary effluent	Secondary effluent			
			(Run 1&2)	(Run 3&4)	(Run 5)	(Run 6)
Raw sample	2.3	2.99	2.7	3.2	2.52	2.53
Oxygen	2.33	2.94	2.56	3.04	2.45	2.6
50 mg O3/L(Run1)	2.31	2.7	2.41	3.26	2.59	2.55
50 mg O3/L(Run2)	2.23	2.75	2.46	3.16	-	-
100 mg O3/L(Run1)	2.22	2.65	2.21	3.63	2.48	2.58
100 mg O3/L(Run2)	2.35	2.79	3.06	2.82	-	-
150 mg O3/L	-	-	-	-	2.13	2.41
200 mg O3/L	-	-	-	-	2.37	2.43

Table X.7 Total Suspended Solids (mg/L) for Mill Effluents

Sample	Bleach Effluent	Primary Effluent	Secondary Effluent			
			1 & 2	3 & 4	5	6
Raw sample	217	84	83	108	86	93
Oxygen	196	70	70	103	87	91
50 mg O3/L (Run#1)	182	71	80	99	98	93
50 mg O3/L (Run#2)	245	72	73	97	-	-
100 mg O3/L (Run#1)	205	63	63	90	82	89
100 mg O3/L (Run#2)	204	61	58	105	-	-
150 mg O3/L	-	-			79	79
200 mg O3/L	-	-			-	81

Table X.8 Volatile Suspended Solids (mg/L) for Mill Effluents

Sample	Bleach Effluent	Primary Effluent	Secondary Effluent			
			1 & 2	3 & 4	5	6
Raw sample	185	51	66	81	73	71
Oxygen	161	49	59	81	80	73
50 mg O3/L (Run#1)	147	51	66	80	83	74
50 mg O3/L (Run#2)	197	43	63	72	-	-
100 mg O3/L (Run#1)	153	48	54	69	73	72
100 mg O3/L (Run#2)	163	40	49	72	-	-
150 mg O3/L	-	-			63	64
200 mg O3/L	-	-			-	63