

PILOT PLANT INVESTIGATION OF OZONE DISINFECTION OF PHYSICO-CHEMICALLY TREATED MUNICIPAL WASTEWATER

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Abstract. An ozonation pilot plant was installed at the Montréal Urban Community Wastewater Treatment Plant (MUCWTP) to assess the feasibility of employing a full scale ozone disinfection system. Wastewater characteristics such as turbidity, COD, TOC, BOD, pH, ORP and suspended solids were monitored to assess their effect on ozone disinfection. Fecal coliforms (FC) were used as indicators to measure disinfection performance. Ozone disinfection was capable of reducing the fecal coliform counts from typical 0.4 - 4 million CFU/100 ml to thousands, hundreds or tens per 100 ml depending on the dose applied. None of the parameters monitored could be correlated with the ozone dose required to achieve particular disinfection efficiency. Pilot tests showed that an ozone dose of 17 mg/l reduced the percentage of cases (observed in this study) for which the concentration of FC in the effluent was higher than 5000 CFU/100 ml (as required by the Quebec Ministry of the Environment) to 10%. A dose of 20 mg/l reduced the number of occurrences to 2%. An integrated CT value (ozone residual x detention time) of 0.15 mg-min/l was needed to achieve a FC survival ratio of 3.1×10^{-3} (i.e. to reach the target FC value). Results of a comparison study showed that when alum was substituted for FeCl_3 as a coagulant in the treatment process at the MUCWTP, ozone disinfection efficiency was enhanced. No additional toxicity in the wastewater could be attributed to ozonation. An increase in the biodegradability of the wastewater following ozonation was observed.

Introduction

The Montréal Urban Community Wastewater Treatment Plant (MUCWTP) is a physicochemical plant presently treating an average flow of $15 \text{ m}^3/\text{s}$ (maximum $45 \text{ m}^3/\text{s}$), mainly from the North interceptor of the Island of Montréal. The South interceptor is still under construction and functions intermittently (hence it is responsible for occasional significant H_2S concentrations in the wastewater). The processes at the MUCWTP include screening, grit removal, and sedimentation following chemical addition (FeCl_3 @ 6 - 20 mg Fe^{3+}/l and anionic polyelectrolyte [Percol 902, Allied Colloids] @ 0.2 - 0.3 mg/l). Discharge is into the St Lawrence River, and a tentative limit has been set for fecal coliform (FC) discharge of 5000 CFU/100 ml during the summer months. This is based on the Québec Ministry of the Environment requirement of 200 CFU/100 ml for swimming at a location 4 km downstream, taking into account dilution by the river.

In an assessment of the St-Lawrence river as a drinking water source (for example, by communities downstream of Montréal), trihalomethanes and chloro-organic levels were noted to be of concern (Levallois, 1990). The MUCWTP is actually equipped with a chlorination system but it is not operational due to these environmental concerns. Besides, a dechlorination system at the MUCWTP has the disadvantage of requiring large dechlorination tanks due to the large flow rates involved. Thus ozone disinfection would appear to be an appropriate disinfection alternative. Furthermore, ozone could be

injected directly into the 5 km long, below-grade outfall tunnel (3 hours retention time at average flow), thus reducing the cost of the contacting infrastructure.

Therefore, the objective of this study was to investigate the feasibility of using ozone disinfection for this type of relatively low quality wastewater discharge.

Materials and Methods

The pilot plant, engineered in association with Ozonia North America Ltd., consisted of two stainless-steel columns (Figure 1), each 5.8 m high and 0.15 m diameter. Only the first column was used for ozone diffusion in the present study. Ceramic diffusers supplied ozone generated from a liquid oxygen source, at a gas flow rate of 0.35 m³/h and O₃ concentrations of 0.5 to 2.3% by weight, depending on the electrical current setting of the ozone generator (Ozonia, LN 103). The countercurrent liquid flow rate was 0.5 m³/h. In the later part of this study, two internally mixed and interconnected equalisation tanks of 4 m³ total capacity were used upstream of the pilot plant to smooth out COD and other variations in the quality of the MUCWTP effluent and to assist with the interpretation of ozonation performance.

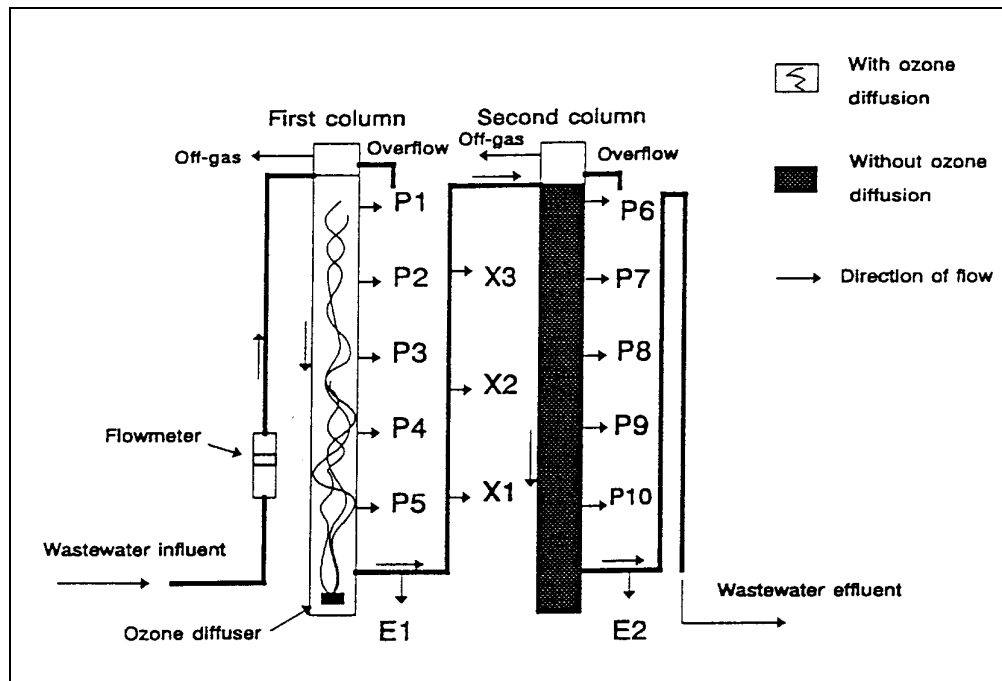


Figure 1: Schematic of the pilot plant

The ozone concentrations in the influent gas and off-gas were measured by UV absorbance monitors (Griffin, EG-2001-HC) and residual O₃ was measured at various points in the columns by the indigo trisulfonate method (Gordon et al, 1987). When testing conditions were varied in a single set of tests, a time interval of at least twice the detention time (approximately 12 minutes @ 500 l/h) was allowed to reach steady state. Before each set of tests and at the end of each day of sampling, the pilot plant was flushed with water to prevent buildup of biological films.

Fecal conforms (FC) were used as indicators to measure disinfection performance. The following parameters were measured according to Standard Methods (APHA et al, 1992) to assist and predict ozone disinfection performance: COD, BOD₅, SS, TOC, ORP, DO, temperature, pH, and turbidity. Other parameters were measured occasionally, such as H₂S, NH₃, NO₂-NO₃, and colour.

Results and Discussion

The range of values for COD, BOD₅, TOC, turbidity and FC of the undisinfected MUCWTP effluent, between July and October 1992, are summarised in Table 1.

Table 1: Characteristics of the NWCWTP effluent.

	Range	Median
COD (mg/l)	40 - 170	99
TOC (mg/l)	10 - 40	25
BOD ₅ (mg/l)	26 - 48	33
Turbidity (NTU)	6 - 15	10
Fecal conforms (CFU/100 ml)	0.4 - 4 million	1.6 million

Step input tracer studies indicated an average detention time of 12.3 min in the first column, with a relatively high dispersion number (D/ul) of 0.124. The residence time distribution curve (E(t)) is shown in Figure 2. It has an asymmetrical Gaussian distribution shape, the tail being caused by liquid carried upwards by the ozone bubbles. An examination of ozone profiles in the pilot plant column showed that the reactor exhibits plug flow over its intermediate 4 m length; however at the top and bottom, the introduction and evacuation of liquid leads to a relatively large degree of mixing.

Experiments were conducted with FeCl₃ treated wastewater from the beginning of July until mid-October 1992. The average temperature of the wastewater was approximately 21°C. Most tests were performed between 14h00 and 22h00. Effluent FC concentrations measured at point E1 after ozonation are shown in Figure 3 for all tests. It is clear that there is a lack of correlation between ozone dose and FC survival; this is due to the variability of the characteristics of the wastewater. A probability plot for tests with effluent FC higher than the target 5000 CFU/100 ml (60 out of 178 tests) is shown in Figure 4. This figure shows that an ozone dose of 17 mg/l reduced the number of cases for which the concentration of fecal conforms at the effluent was higher than the target level to 10%. A dose of 20 mg/l reduced this number to 2%. It should be noted that these are the applied dosages; ozone transfer efficiency (OTE) based on off-gas measurements varied between 90 and 99% depending on the COD and the ozone dose. OTE increased with higher COD. Samples taken from the second column generally yielded higher FC concentrations. This is presumably due to sloughed biofilms, favourable growth conditions resulting from supersaturated dissolved oxygen levels (35-40 mg/l) and the low velocity and Reynolds number (0.46 m/min and 1160 respectively), and from the fact that the pilot plant was not operated continuously.

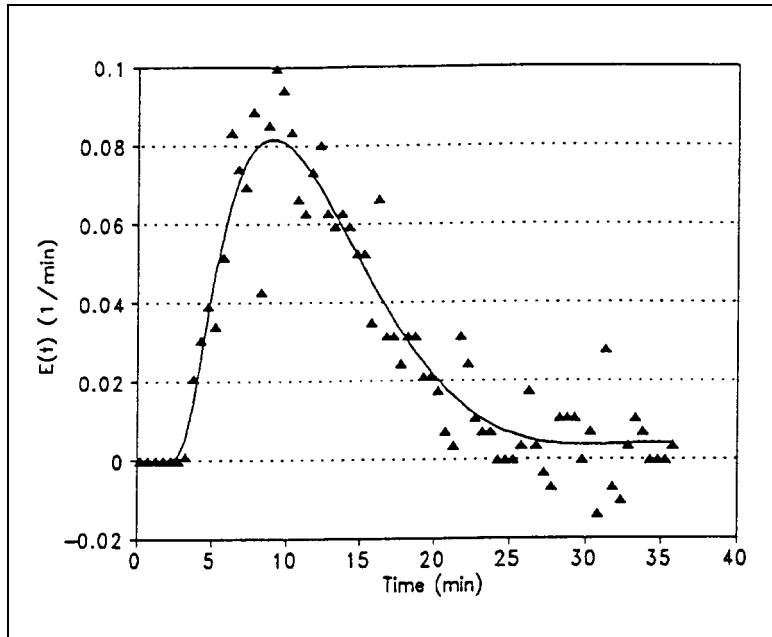


Figure 2: Residence time distribution for the first column with a liquid flow of $0.5 \text{ m}^3/\text{h}$.

When all tests were considered, an ozone dose of 15 mg/l was sufficient in 90% of the cases to reduce the FC concentrations at the effluent to a value lower than 5000 CFU/100 ml. An ozone dose of 19 mg/l was sufficient in 99% of the cases.

Ozone residuals at different points in the pilot plant were measured in order to calculate an integrated CT value (where C and T were residual concentrations and detention times at points P1, P2... E1 in the first column, respectively) and to ascertain the persistence of ozone in the wastewater. The integrated CT value measures the exposure of the wastewater to the ozone from the inlet at the top of column 1 to the sampling point at E1.

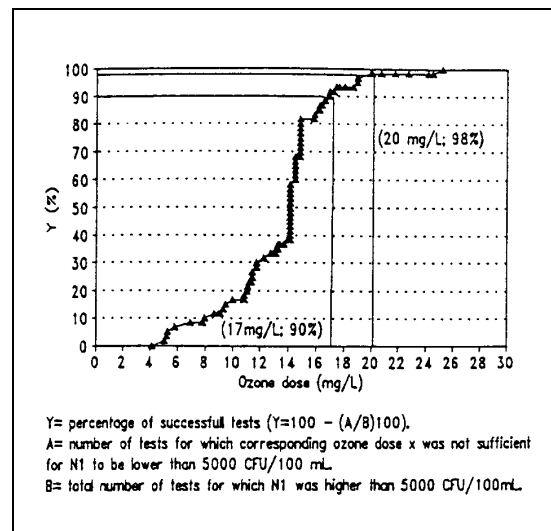
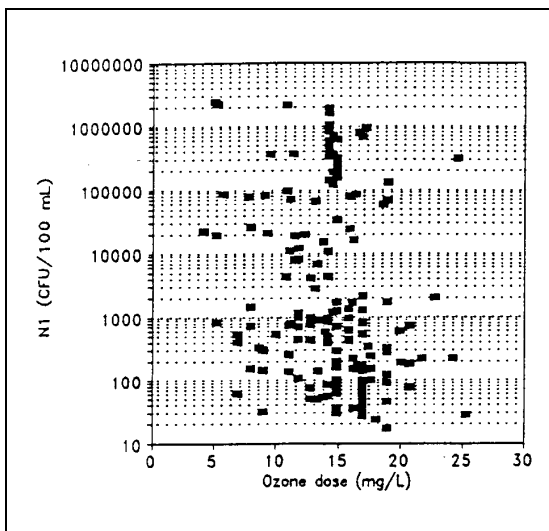


Figure 3: Fecal coliform concentrations after ozonation versus ozone dose

Figure 4: Probability plot for fecal conforms below target levels.

Results are shown in Figure 5 and demonstrate that for a FC survival ratio N_1/N_0 of 3.1×10^{-3} (required to reach the target FC level) a CT value of 0.15 mg-min/l is needed. For a N_1/N_0 reduction of 4 log units or greater, CT values of 2.3 and 2.9 mg-min/l were required for 90% and 98% of the cases tested, respectively.

Ozone profiles in the pilot plant were measured from points Pl..P10, Xl..X3, E1 and E2 (refer to Figure 1). Figure 6 shows results corresponding to different ranges of COD. The ozone injection point corresponds to an abscissa value of 12 minutes in Figure 6. Wastewater with a low COD will result in a higher ozone residual and lower ozone consumption rates. With a range of ozone doses of 14 - 16.5 mg/l and a COD of 50 - 80 mg/l the life of ozone is approximately 10 minutes (average pH 6.9). It should be noted that these ozone dosages are not necessarily optimal for disinfection. They were chosen to yield correspondingly high ozone residual levels for accurate measurements of persistence.

Efforts were made to correlate typical chemical wastewater parameters such as COD and TOC to the ozone dose required for disinfection. Unfortunately all these failed; this may be explained as being due to:

- 1) a "wide variety" of influent characteristics.
- 2) the inability of COD measurements to reflect the oxygen equivalent of the inorganic matter content of the wastewater that is susceptible to oxidation by ozone.
- 3) differences in reaction rates of ozone with the chemicals present in the wastewater to be treated which could not be duplicated in the COD test.
- 4) the fact that TOC is independent of the oxidation state of the organic matter, and as in the case of COD does not measure inorganics that are susceptible to oxidation.

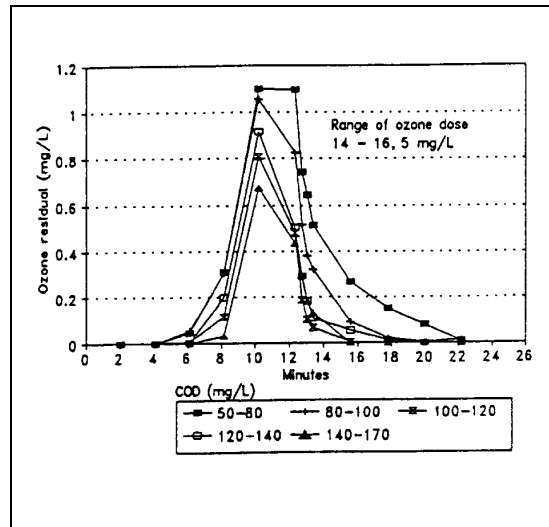
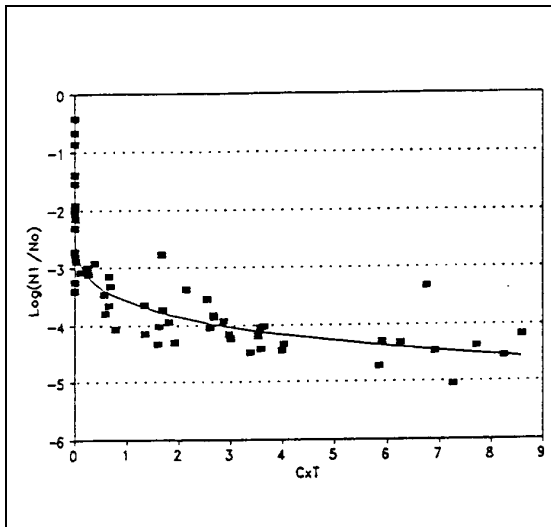


Figure 5: Log(N_1/N_0) versus CT.

Figure 6: Ozone profile in the pilot plant for a flow of 0.5 m³/h.

However, after equalisation tanks were employed to yield constant COD levels, reasonable dose-response curves were obtained. Figure 7 shows 5 sets of results from these tests. Figure 8 shows the only successful linear correlation, which was for ozone doses of 8 - 10 mg/l and all CODs (including those from unequalised flows).

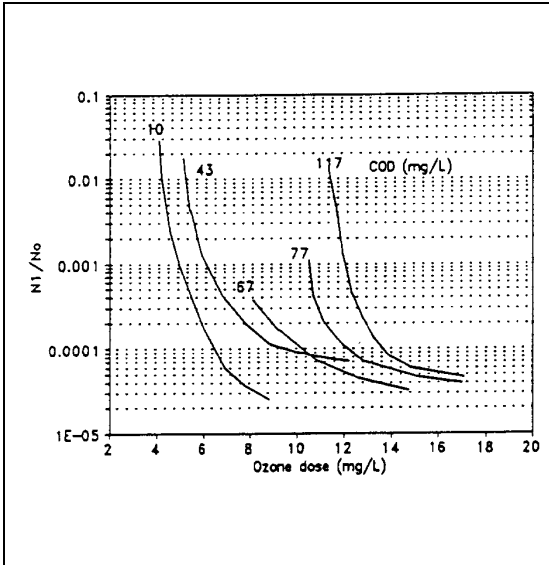


Figure 7: N_1/N_0 versus ozone dose for some equalised tests.

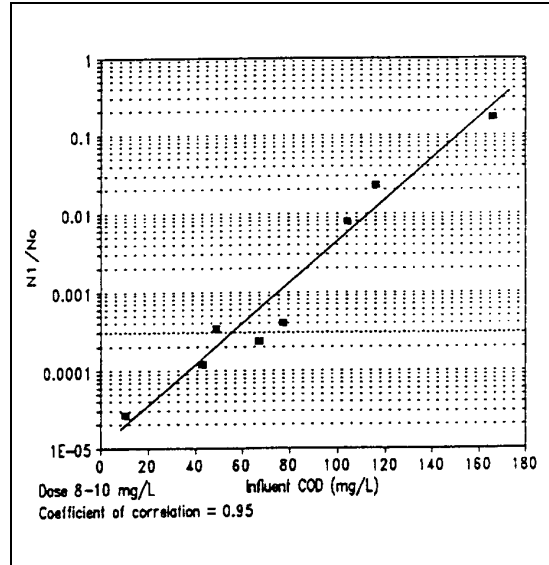


Figure 8: N_1/N_0 versus COD for an ozone dose range of 8-10 mg/l.

The effect of ozonation on COD and TOC was measured; as a typical result, an average ozone dose of 14 mg/l reduced both COD (median 98 mg/l) and TOC (median 25 mg/l) by approximately 5%. Sixteen BOD measurements were made over the course of the study; these covered a range of 25 - 45 mg/l. Ozonation at an average dose of 18 mg/l increased BOD₅ by an average of 14%. A similar result has been obtained by several other researchers who attributed it to increased biodegradability as a result of reduced molecular mass due to ozonation (EPA, 1986).

Turbidity, pH, SS and ORP were also monitored in an attempt to correlate the characteristics of the wastewater with ozone dose requirements for disinfection, but unfortunately no significant correlations could be obtained. Furthermore, ORP measurements were rather unstable in the wastewater. The NH₃-N concentration varied between 9 and 14 mg/l; ozonation had no effect on these concentrations. It is thought that the presence of organic materials may have protected NH₃ from oxidation. Fe^{2+/3+} concentrations in the coagulated and settled wastewater varied between 1.6 and 4.5 mg/l; ozonation (dose 14 - 19 mg/l) appeared to decrease these by 0 to 1.5 mg/l, probably by oxidation and precipitation of the Fe²⁺ form. Nitrates and nitrites concentrations were less than 0.05 mg/l in almost all cases. On the other hand, concentrations of H₂S in the effluent, which varied between non-detectable and 0.8 mg/l were consistently reduced to zero by the ozone.

Toxicity tests were performed in the laboratories of the Québec Ministry of the Environment using daphnia, or with Microtox and Ames procedures. Ozone disinfection was not found to cause any toxicity in the wastewater.

Results with Alum Treated Wastewater

Results of a comparison study between an FeCl₃ treated wastewater and an alum treated wastewater (March 1993, wastewater temperature 9°C) indicated that ozone disinfection efficiency was increased when alum was used, as shown in Figure 9. It is seen that for the target level of 5000 CFU/100 ml in the effluent, a 40% reduction in the ozone dose required was observed. Furthermore, the COD reduction percentage was higher with FeCl₃ treated wastewater (Table 2), implying that more ozone is chemically consumed and as a result is not available for disinfection. Wastewater characteristics in the influent of the MUCWTP are assumed to be the same in the two series of tests, as confirmed by the composite COD measurements which were around 130 mg/l. FC concentrations in the effluent (before disinfection) were lower with alum (see Table 3) as discovered also in previous studies conducted at the MUCWTP (Gehr et al, 1993). Table 3 summarises the characteristics of the wastewater in the two test series and shows that COD levels were higher and turbidity lower with alum treated wastewater.

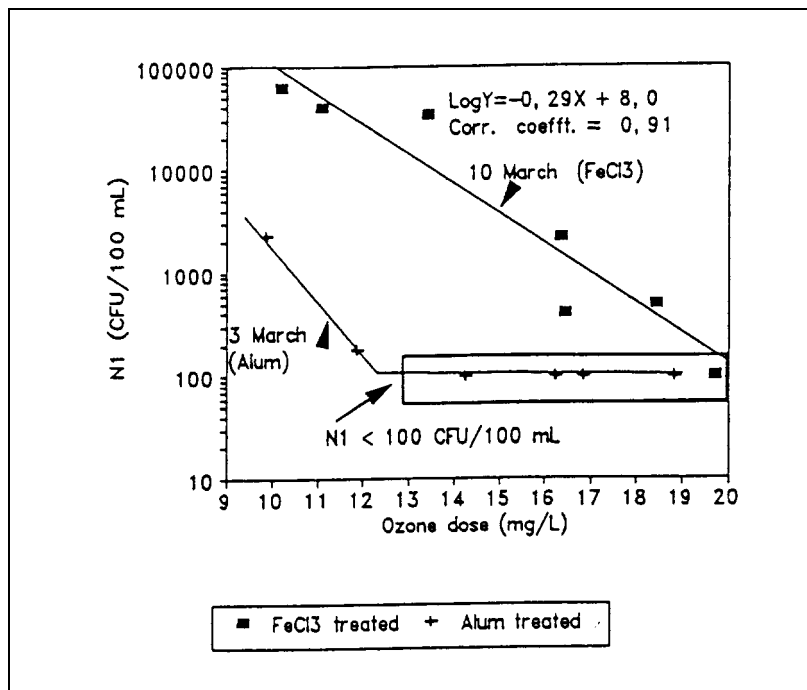


Figure 9: N₁ vs ozone dose for comparison tests with alum and FeCl₃.

Table 2 : Effects of ozonation on COD reduction.

	COD reduction (%)	Average ozone dose (mg/l)
Alum tests	5.4	14.6

FeCl ₃ tests	13.5	15.4
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Table 3: Characteristics of the MUCWTP effluent.

	Fecal conforms (N ₀) (CFU/100 ml)	COD (mg/l)	Turbidity (NTU)
3 March (Alum)	270 000	126	9.6
4 March (Alum)	260 000	129	9.4
9 March (FeCl ₃)	560 000	90	13
10 March (FeCl ₃)	317 000	76	13

Conclusions

Results of tests using an ozonation pilot plant installed at the Montréal Urban Community Wastewater Treatment plant have indicated that ozone was capable of reducing the fecal coliform -counts from typical 0.4 - 4 million CFU/100 ml to below 1,000 per 100 ml depending on the ozone dose applied. However, it was impossible to predict ozone disinfection performance based on monitored parameters such as COD, TOC, BOD, pH, ORP and SS. An ozone dose of 17 mg/l reduced the percentage of cases for which the concentration of fecal conforms in the effluent was higher than 5000 CFU/100 ml (required by the Québec Ministry of the Environment) to 10%. A dose of 20 mg/l reduced this number to 2%. For a FC survival ratio (N_1/N_0) of 3.1×10^{-3} (required to reach the target FC level), a CT value of 0.15 mg-min/l was needed. For a N_1/N_0 reduction of 4 log units or greater, CT values of 2.3 and 2.9 mg-min/l were required for 90% and 98% of the cases tested, respectively. The effect of ozonation at 14 mg/l on COD and TOC was a reduction of approximately 5% for both parameters. Furthermore, ozonation at an average dose of 18 mg/l increased BOD₅ by an average of 14%. Ozone did not react with NH₃-N (9 - 14 mg/l) under the treatment conditions at the MUCWTP. However, concentrations of up to 0.8 mg/l of H₂S were consistently reduced to zero by the ozone. Results of a comparison study showed that if alum were substituted for FeCl₃ in the treatment process at the MUCWTP, ozone disinfection efficiency would be enhanced. Ozone disinfection itself was did not cause any increased toxicity in the wastewater.

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Keywords: ozone, disinfection, physicochemical wastewater treatment, pilot plant.

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