

Using ozone to reduce recalcitrant compounds and to enhance biodegradability of pulp and paper effluents

L. Bijan and M. Mohseni

Department of Chemical and Biological Engineering, University of British Columbia, 2216 Main Mall, Vancouver, B.C., V6T 1Z4, Canada (E-mail: mmohseni@chml.ubc.ca)

Abstract The effect of ozone based oxidation on removing recalcitrant organic matter (ROM) and enhancing the biodegradability of alkaline bleach plant effluent was investigated. A bubble column ozonation tower was used in the study. The experiments were carried out at different temperatures (20°C and 60°C) and pH (9 and 11), with a number of biological and chemical parameters being monitored including BOD₅, COD, TC, pH, color, and molecular weight distribution of organics (nominal cut off of 1,000 Da). Biodegradability of the effluent was determined based on BOD₅/COD of the wastewater throughout the process. For all the experiments, ozonation enhanced the biodegradability of the effluent by 30–40%, which was associated with noticeable removal of ROM including high molecular weight (HMW) and color-causing organics by about 30% and 60%, respectively. While the biodegradability of HMW fraction increased by about 50%, there was no biodegradability improvement for low molecular weight (LMW) portion, which was originally readily biodegradable (with BOD₅/COD of about 0.5). Statistical analysis of variance (ANOVA) revealed neither pH nor temperature played significant role on the ozonation process at 95% confidence level.

Keywords Advanced oxidation; alkaline bleach plant effluent; biodegradability; molecular weight distribution; ozonation; recalcitrant compounds

Introduction

Effective removal of harmful organic compounds from effluents is the ultimate objective of the pulp and paper industry as it pursues the long-term goal of eliminating its impacts on the environment. Biological oxidation processes including activated sludge and aerated lagoon are conventionally used in the industry to mineralize the organic contaminants. Although significant portion of the biodegradable components is removed using these systems, pulp mill effluents contain noticeable amount of compounds that are recalcitrant to the biological treatment. The recalcitrant portion is generally recognized as residual chemical oxygen demand (COD) or adsorbable organic halogen (AOX) in the treated pulp mill wastewater. Welander *et al.* (1997) reported that only 30–40% COD removal is obtained in the pulp mills applying aerated lagoon and higher removals of up to 60–70% can be achieved using biomass support materials. Ataberk and Gökçay (1997) studied the treatment of chlorinated organics in bleached kraft mill effluents and observed that 30–40% of AOX is removed using activated sludge process.

Earlier study (Boman and Frostell, 1988) suggests HMW compounds as the predominant portion of the ROM of the bleach plant effluent since these compounds are not metabolized biologically due to their size and complex structure. Eriksson and Kolar (1985) used ¹⁴C-labeled chlorolignins, as representatives of HMW compounds present in the pulp mill effluents, and observed merely 4% degradation by microorganisms obtained from aerated lagoons. In addition, Jokela *et al.* (1993) reported that low molecular weight (LMW) compounds contribute to ROM. The authors studied the biological removal of the bleach plant chlorinated organics, measured as AOX, and concluded that the molecular weight distribution changed towards the larger molecules after conducting biological treatment. Chemical

composition and the amount of chlorinated organics with different molecular weight for different process streams have been studied in detail (Sågfors and Starck, 1988; Dahlman *et al.*, 1994, 1995; McKague and Carlberg, 1996). Sågfors and Starck (1988) conducted gel permeation chromatography (GPC) and found 65–75% and 20% of UV absorbing components of the alkaline and the acidic effluents in the HMW region, respectively. McKague and Carlberg (1996) reported that alkaline effluent from bleach plant generally contains more chlorinated HMW compounds (95%) than chlorination stage wastewater (70%). Dahlman *et al.* (1995) analyzed chemical composition of different process streams and concluded that the biorefractory portion of the pulp mill effluent as well as bleach plant wastewater mainly comprises oxidized lignin compounds, which are produced through the reaction of lignin with chlorine dioxide in the process. The non-biodegradable nature of ROM along with their major contribution (more than 40%) to the total organics in final pulp mill effluents (Dahlman *et al.*, 1995) creates major challenge for biological treatment. Given the fact that conventional biological processes are not effective enough to degrade biorefractory compounds, there is an increasing interest for a process capable of removing recalcitrant compounds from pulp mill effluents.

Advanced oxidation processes (AOPs) are among promising technologies for complete abatement of a broad range of pollutants and have found extensive application for the treatment of industrial wastewater. Biodegradability enhancement, color removal, and toxicity abatement associated with AOPs are a few benefits that are normally achieved by such wide-ranging industries as dye manufacturing, textile producing, tannery manufacturing, and agricultural processing wastewater plants (Beltrán *et al.*, 1997, 1999; Lin and Lai, 2000; Di Iaconi *et al.*, 2002; Zenaitis *et al.*, 2002; Wang *et al.*, 2003; Yang *et al.*, 2003). AOPs rely on a series of radical-based reactions that hydroxyl radical ($\cdot\text{OH}$) is the major contributor. This radical is a short-lived, extremely potent oxidizing agent that participates in a variety of chemical reactions, among them dehalogenation and cleavage of chemical bonds, which both could be advantageous for the removal of chlorinated and HMW organics. The common processes for the production of hydroxyl radicals are O_3/OH^- , O_3 or $\text{H}_2\text{O}_2/\text{UV}$, $\text{O}_3/\text{H}_2\text{O}_2$, $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$, and photocatalysis. These processes involve applying strong oxidants (ozone or hydrogen peroxide), which are promoted by other factors including ultraviolet (UV) radiation, hydroxide ion and photocatalysts.

There have been some attempts to reduce the amount of chemical oxidants required for AOPs by applying these processes to individual effluent streams (Hostachy *et al.*, 1997; Mansilla *et al.*, 1997; Nakamura *et al.*, 1997; Oeller *et al.*, 1997; Helble *et al.*, 1999; Bijan and Mohseni, 2003). Oeller *et al.* (1997) applied O_3/UV process to the biologically treated paper mill effluent and observed significant biodegradability improvement of the wastewater. Effluent biodegradability was determined based on the biodegradability ratio (measured as BOD_5/COD), which increased from 0.05 to 0.37. The authors also reported that temperature increase from 25 to 40°C did not improve COD removal of the effluent. The effect of temperature was also studied by Hostachy *et al.* (1997) who applied ozone on acidic bleach plant effluent. While the biotreatability of the effluent increased during the ozonation process, temperature did not show significant effect on the biodegradability improvement of the acidic bleach plant effluent. In a different study, Helble *et al.* (1999) reported significant improvement of up to 0.3 in BOD_5/COD for the biologically treated paper mill wastewater using ozonation alone followed by fixed bed biofilm reactors. Nakamura *et al.* (1997) treated kraft pulp mill wastewater using the combination of ozone and activated sludge and reported some improvements in the biodegradability of the effluent. In particular, the authors studied the effect of pH on the degradation of lignin and organic acids such as muconic acid in the ozonation process. Nakamura *et al.* (1997) suggested that the strong alkaline condition resulted in selective degradation of lignin and

observed that this resulted in the enhanced production of oxalic acid that was consequently removed using activated sludge.

Overall, all these research activities presented promising results on the potential effectiveness of AOPs towards enhancing the biodegradability of the pulp and paper mill effluents. However, the application of this technology to the whole mill effluent may not be economically feasible because of the large flow rate and relatively high concentration of biodegradable organics. It would be more desired to apply AOPs to smaller individual process wastewater streams that possess high levels of ROM. The selective degradation of HMW recalcitrant compounds would make them more biodegradable and, in turn, could help their subsequent removal using biological techniques. This research has focused on ozone based oxidation of alkaline bleach plant effluent because of its significant contribution to the amount of ROM particularly HMW organics in the ultimate pulp mill effluent (Dahlman *et al.*, 1995). The effect of temperature and pH of the effluent on the overall efficacy of the ozonation treatment, with respect to the biotreatability enhancement, has been studied. This provides valuable insight with respect to the kinetics of oxidation reactions and the mass transfer of ozone as a function of temperature and pH. This research is also beneficial in providing an in-depth understanding to the whole oxidation process by monitoring numerous environmental parameters.

Materials and methods

Wastewater

Wastewater for the ozonation experiment was obtained from Norske Skog pulp mill in Elk Falls, BC, Canada. The mill processes approximately 1,800 tonnes/day of wood, primarily hemlock, Douglas fir, cypress, and SPF (spruce, fir, pine) and produces both semi-bleached and fully bleached pulp using elemental chlorine free (ECF) process. Wastewater was collected from the alkaline step (E-stage) of the fully bleached line while processing sawdust pulp. As received, the wastewater was fully characterized for BOD₅, COD, TC, pH, and color. Table 1 shows the summary of the results.

Ozonation set-up

Ozone based oxidation experiments were conducted in a bench-scale bubble column reactor (plexi-glass, diameter = 0.1 m, height = 2 m) (Figure 1). The purity of oxygen in the air was increased using pressure swing adsorption (PSA) and the oxygen-rich gas was passed through an ozone generator capable of producing ozone using a silent electric discharge mechanism. The ozone was dispersed at the bottom of the reactor that was previously charged with 7 litres of alkaline bleach plant effluent. The flow rate of the inlet gas was set to 185 mL/min and the ozone concentration was 0.11 mg/mL in the gas phase. The exhaust gas stream from the column passed through two wash bottles, in series, containing potassium iodide (KI) solution (2%) to trap disposed ozone. The first wash bottle had a spare port allowing for sampling from the KI solution in the course of the experiments. The second trap was used as a control to make sure all the escaped ozone was trapped. The wastewater in the reactor was constantly recirculated using a peristaltic pump (1,000 mL/min) to ensure complete mixing. For the experiments conducted at high temperature, a water bath

Table 1 Initial characteristics of the alkaline bleach plant effluent

BOD ₅ (mg/L)	282.2 ± 2.2
COD (mg/L)	1,586.3 ± 48
TC (mg/L)	676.6 ± 3.5
pH	11.03
Color (C.U.)	1,542.27

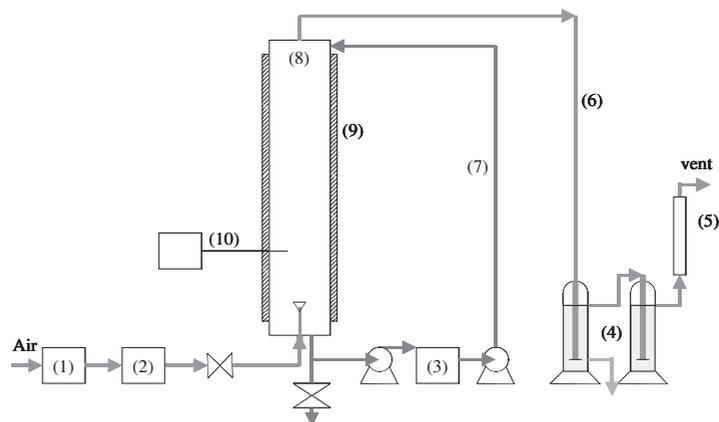


Figure 1 Schematic diagram of the advanced oxidation (ozonation) set-up; 1) Oxygen separator, 2) Ozone generator, 3) Water bath, 4) Wash bottles, 5) Gas flow meter, 6) Exhaust gas line, 7) Liquid recycle line, 8) Bubble column reactor, 9) Heating coils and insulator, 10) Thermocouple and temperature controller

was added to the liquid recycle line for heating purposes and controlling the temperature. Also, the reactor, wrapped with heating coils around the wall, was insulated to prevent heat loss from the reactor. A thermocouple connected to a temperature controller unit (Digitrol II, Glas-Col) was installed in the reactor to measure and control the temperature.

Experimental procedure

Ozonation experimental work focused on the removal of recalcitrant organics and the effects of temperature and pH on ozonation efficiency. The effects of temperature and pH were studied because of their effects on ozone solubility and kinetics of the oxidation reaction. Factorial experimental design (2^2 design) allowed for studying the impact of each parameter. The two levels for temperature were set to 20°C and 60°C and those for pH to 9 and 11. These levels, chosen based on the industrial resources and information obtained from the literature, covered a range in which alkaline effluent would be available for the treatment. Hydrochloric acid was used to decrease the initial pH of the alkaline effluent for experiments conducted at low pH. All the ozonation experiments were conducted for 120 minutes and samples were taken at different time intervals (0, 10, 20, 30, 45, 60, 90, and 120 minutes) to monitor various chemical (ozone concentration in the gas and liquid phases) and environmental parameters including BOD₅, COD, TC, pH, color, and molecular weight distribution. The ratio of BOD₅/COD was regarded as a parameter representing the biodegradability of the original wastewater as well as its fractions (HMW and LMW). Ozone dosage was obtained based on the consumption of ozone per volume of the wastewater.

Molecular weight separation of organics was carried out using cross flow membrane ultrafiltration. For these experiments, a cylindrical ceramic membrane (Membralox ceramic membrane, Pall Corporation) with nominal cut off of 1,000 Da was installed in a membrane housing and wastewater samples (before and after ozonation) were pumped axially through the membrane tube. Filtrate was collected from the outside of the membrane. The initial volume of the wastewater used for filtration in the reservoir was set to 300 mL. After recovering more than 55% (165 mL) of the initial sample as filtrate, the retentate was diluted with 400 mL distilled water and filtration was continued. This allowed for better separation of HMW (MW > 1,000 Da) and LMW (MW < 1,000 Da) components of the wastewater. The total recovery was adjusted to 80% (560 mL) for all samples. At the end of each filtration stage, the membrane was washed with sodium hydroxide (4%) and distilled water and its permeability was checked.

Sample analysis

Samples taken at different time intervals were measured for BOD₅, COD, TC, pH, color, and soluble ozone. Also, ozone concentration in the gas phase (trapped in the wash bottles) was monitored over the course of the experiment.

BOD₅ and COD measurements were performed according to Standard Methods 5210B and 5220D, respectively (APHA, 1995). Sludge obtained from the secondary treatment of a local pulp mill was used to seed the BOD test. All the experiments were run in triplicate. Total Carbon (TC) of the samples was measured using a TOC analyzer (TOC-5050 Shimadzu). TC of all samples was measured at least four times. Color was measured based on the proposed standard method (H.5) reported by the Canadian Pulp and Paper Association (1993). pH was measured by a pH meter (PerpHecT meter, Model 330, Thermo Orion).

Ozone concentration in the liquid phase (soluble ozone) was determined according to Standard Method 4500-O₃B (APHA, 1995). However, the method was modified based on the properties of the wastewater with respect to the color and colloids. In these measurements, samples taken from the column were divided into two portions. The first portion was regarded as the main sample containing ozone while the second portion was used as the blank with its dissolved ozone removed by sparging nitrogen through the sample. Then, both samples were added to the reagent (indigo solution) immediately as described in the standard method and were kept in the dark until their absorbance was measured. This was necessary due to the sensitivity of the reagent to light. Both blank and main samples were filtered using a filter paper (1 μm) to remove colloids and the absorbance was measured at 600 nm. Ozone concentration in the gas phase was determined based on the Ozone Demand-Semi Batch method (2350E, APHA, 1995).

Results and discussion

Overall biodegradability enhancement

The quotient of BOD₅/COD, which compares the amount of oxygen consumed biologically in 5 days with the total oxygen required for chemical oxidation of the compounds in the sample, was regarded as the biotreatability ratio to determine the portion of biodegradable organics in the wastewater. The alkaline bleach plant effluent, as received, showed low initial biodegradability ratio of 0.18 ± 0.01 , indicating non-biodegradable characteristics of the effluent. As a reference, BOD₅/COD for municipal wastewater is almost 0.4–0.6.

The results of normalized biodegradability ratios (Figure 2) imply that ozonation improved the biodegradability of the alkaline bleach plant effluent successfully for the experiments conducted under different pH and temperature. Such increases in BOD₅/COD ratio are due to the production of more biodegradable compounds (observed as biological oxygen uptake enhancement) and improvement in the oxidation state of organics (monitored as reduction in the oxygen consumed chemically per unit of carbon). This study reveals that BOD increase provides the dominant contribution to the biodegradability enhancement since improvement in the oxidation state (measured by reduction in COD/TC) was very limited (less than 17%) as observed in Figure 3. Overall, ozonation produced more biodegradable components while the total amount of organic compounds remained constant (Figure 4) and their oxidation state changed slightly (Figure 3).

Further analysis of the ozonated wastewater shows changes in the molecular weight distribution with the HMW compounds being removed significantly (Figure 4). A comparison between the reduction in HMW fraction and the biodegradability enhancement indicates their direct correlation. As seen, Figure 4 shows HMW compounds were roughly removed by 30–40% and Figure 2 implies the biodegradability of the wastewater increased by the same amount accordingly. This also supports the hypothesis that HMW compounds

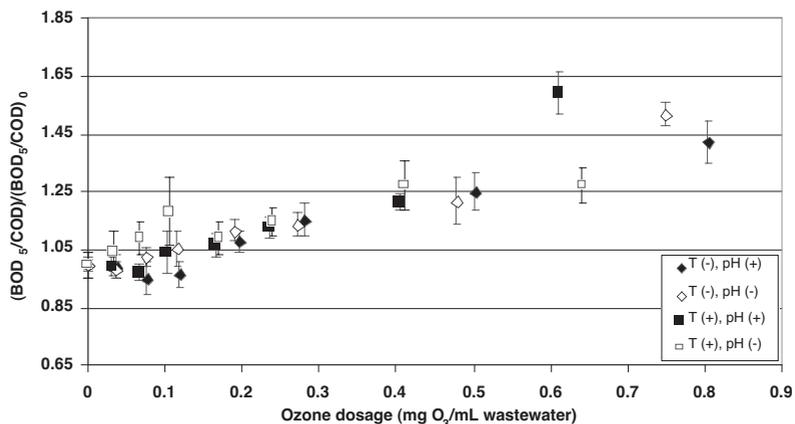


Figure 2 Biodegradability improvement by normalized biodegradability ratio for alkaline bleach plant effluent during ozonation experiment (inlet gas flow rate = 185 mL/min, O_3 concentration in the input gas = 0.11 mg/mL, T (-) = 20°C, T (+) = 60°C, pH (-) = 9, pH (+) = 11)

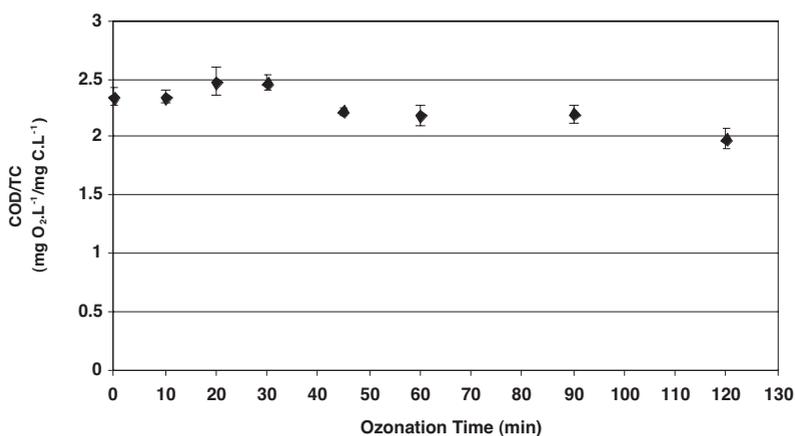


Figure 3 Oxidation state of the compounds in the alkaline bleach plant effluent during ozonation experiment (T = 20°C, pH = 11, inlet gas flow rate = 185 mL/min, O_3 concentration in the input gas = 0.11 mg/mL)

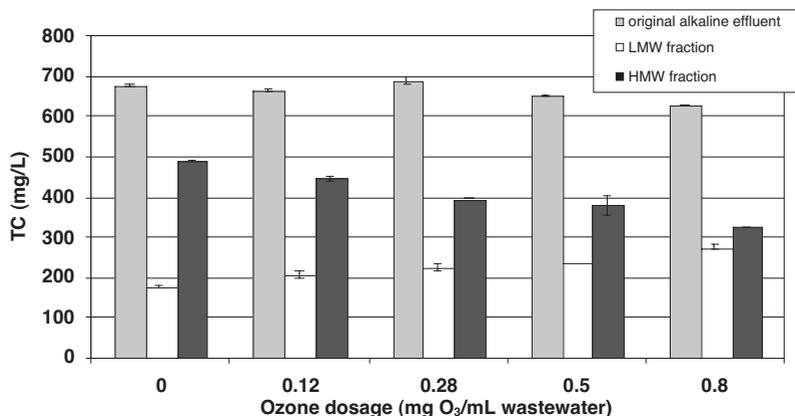


Figure 4 TC variations of the organics with different molecular weight distribution for alkaline bleach plant effluent during ozonation experiment (nominal cut off = 1,000 Da, T = 20°C, pH = 11, inlet gas flow rate = 185 mL/min, O_3 concentration in the input gas = 0.11 mg/mL)

contribute to the recalcitrant fraction of the alkaline bleach plant effluent. Hence, removing HMW compounds from the effluent could play a significant role in enhancing the biodegradability of the wastewater. In addition, considerable color removal of the wastewater in the ozonation treatment (Figure 5) indicates effective reaction of ozone and radicals with HMW compounds that also constitute significant portion of the color causing components of the wastewater.

Biodegradability of HMW and LMW fractions

The effect of ozone on the biotreatability improvement of HMW and LMW portions of the alkaline bleach plant effluent is shown in Figures 6 and 7. BOD_5/COD of the HMW fraction of the wastewater increased by about 50% during the experiment (Figure 6). However, the BOD_5/COD of the LMW fraction did not increase and remained constant at about 0.5 over the entire course of the experiment (Figure 7). These results indicate that ozone was more effective on the HMW compounds than LMW components under all experimental conditions. This was predictable since ozone more likely reacts with HMW organics that constitute dominant portion (more than 70%) of the wastewater (Figure 4) and have double bonds in their chemical structure (Dahlman *et al.*, 1995). Selective reaction of ozone towards HMW color causing compounds is the main reason for breaking the bonds and converting the complex structure of HMW organics into smaller and more biodegradable molecules.

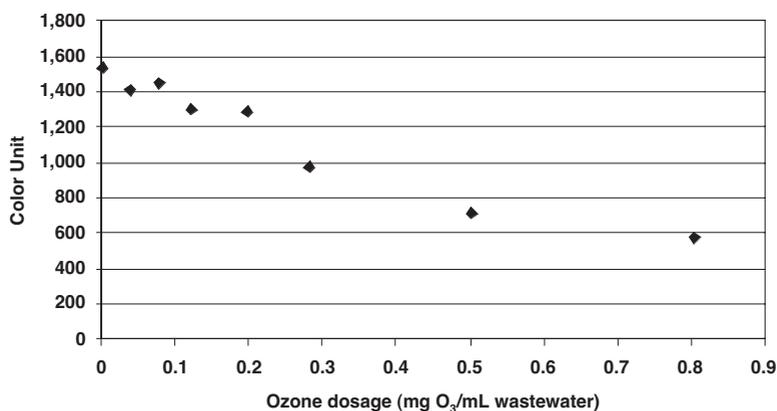


Figure 5 Color removal of alkaline bleach plant effluent during ozonation ($T = 20^{\circ}\text{C}$, $\text{pH} = 11$, inlet gas flow rate = 185 mL/min , O_3 concentration in the input gas = 0.11 mg/mL)

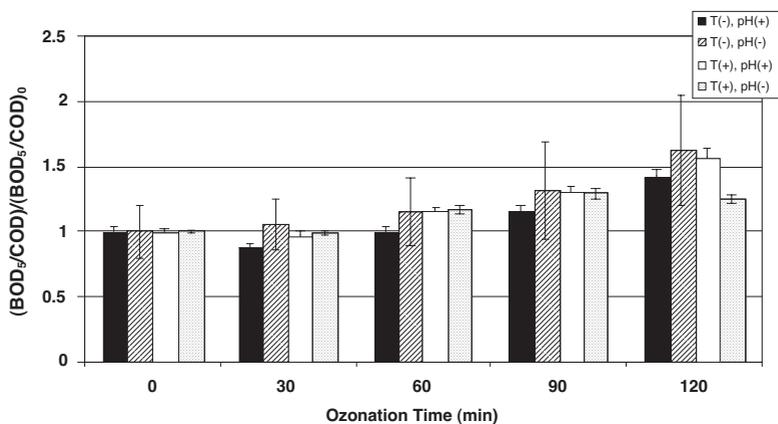


Figure 6 Variations of normalized biodegradability ratio of HMW compounds for alkaline bleach plant effluent during ozonation experiment (inlet gas flow rate = 185 mL/min , O_3 concentration in the input gas = 0.11 mg/mL , $T(-) = 20^{\circ}\text{C}$, $T(+)$ = 60°C , $\text{pH}(-)$ = 9 , $\text{pH}(+)$ = 11)

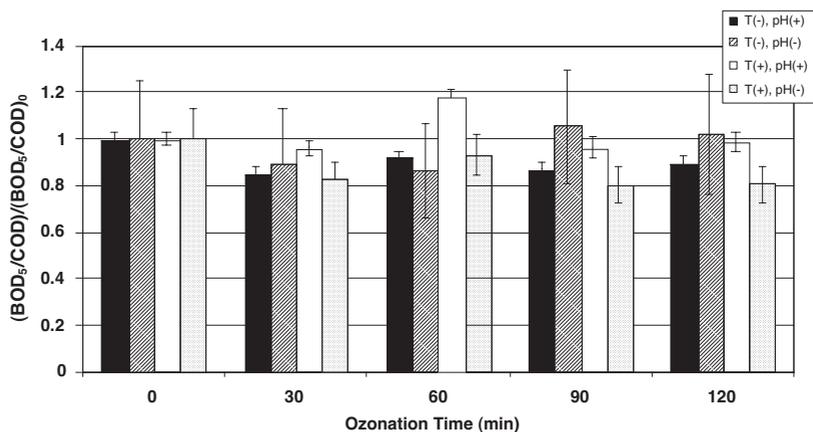


Figure 7 Variations of normalized biodegradability ratio of LMW compounds for alkaline bleach plant effluent during ozonation experiment (inlet gas flow rate = 185 mL/min, O_3 concentration in the input gas = 0.11 mg/mL, T (-) = 20°C, T (+) = 60°C, pH (-) = 9, pH (+) = 11)

As for LMW fraction, it seemed that these compounds were likely at their ultimate biodegradability state and ozonation could not enhance their biotreatability further. Also, it is postulated that the LMW components generated as a result of cleavage of HMW compounds (see Figure 4) have the same biodegradability characteristics as the initial LMW compounds. Further research is being conducted to examine these hypotheses and better understand the properties of HMW and LMW fractions before and after ozonation.

Effects of temperature and pH

Analysis of variance (ANOVA) was conducted to determine the significance of experimental conditions with respect to pH and temperature. The results (Figures 2, 6, and 7) indicate that within the ranges investigated in this work, neither temperature nor pH played a significant role on the ozonation process at 95% confidence level. As it can be seen from Figures 2, 6, and 7 the error bars representing standard deviation for 3 to 5 samples overlap with each other meaning they are not statistically different.

For the temperature not having any impact on the ozonation process is likely the result of changes in the solubility of ozone and the kinetics of the oxidation reactions. The solubility of ozone in water decreases by 2.5 times as temperature increases from 20 to 60°C (Kosac-Channing and Helz, 1983; Eul *et al.*, 2001). Kinetics of the oxidation reaction and its dependency with temperature is quite abstruse and involves many different radical-based reactions. Therefore, quantitative analysis of the impact of temperature on the ozonation reaction kinetics was not investigated. Nonetheless, some qualitative assessment can be made based on the Arrhenius' law:

$$K(T) = A \exp(-E_a/RT)$$

where $K(T)$ is the kinetic rate constant as a function of temperature (T), A is Arrhenius' constant, E_a is activation energy, and R is universal gas constant. Overall, it is concluded that oxidation rate changes obtained by increasing temperature are countered by the lower concentration of ozone in the solution, which is a result of significantly lower mass transfer of ozone to the aqueous phase. Hence, as observed in this work, the impact of temperature on the overall ozonation process would become negligible. These results also agree with those reported in the literature (Hostachy *et al.*, 1997; Oeller *et al.*, 1997) where temperature did not affect the removal of COD and/or the increase in BOD_5/COD .

The impact of pH on the ozonation process is driven by the selectivity of ozone towards specific compounds in the effluent and the kinetics of the reaction between hydroxide ions and ozone. The latter is one of the most important reactions that initiates radical based oxidation reactions involving hydroxyl radicals:



As seen, higher pH will result in enhanced ozone consumption and, consequently, hydroxyl radical generation rates. The initiation reaction between ozone and hydroxide ion (with rate constant of $70 \text{ M}^{-1}\text{s}^{-1}$) (Pedit *et al.*, 1997) could reduce the concentration of ozone available for selective and direct oxidation of HMW and color causing compounds. This could result in some reduced efficiency with respect to color removal and/or HMW compounds degradation. On the other hand, the formation of more $\cdot\text{OH}$ with increases in pH might be beneficial to the process. Hydroxyl radical is a very strong oxidant and reacts with many organic compounds with rate constants in the order of 10^6 – $10^9 \text{ M}^{-1}\text{s}^{-1}$ (Pedit *et al.*, 1997). At the same time, hydroxyl radical is non-selective and reacts indiscriminately with all the compounds among them scavengers including carbonate and bicarbonate that are present in the effluent. Hence, the total reaction kinetics could be affected significantly. It can be concluded that the complex nature of the process will bring different forces that play significant roles, when pH of the solution changes, and eventually offset each other.

Overall, ozone treatment has shown to improve the biodegradability of the alkaline bleach plant effluent. It was evident that ozone is more effective towards color causing and HMW fraction of the effluent. Given the fact that HMW compounds make significant portion of the recalcitrant components of the alkaline bleach plant effluent, it would be beneficial to specifically target these compounds through effective consumption of ozone and hydroxyl radicals. Therefore, it is recommended that the initial removal of LMW fraction of the wastewater be considered as a means of enhancing the removal of recalcitrant HMW compounds and improving the overall effectiveness of the ozonation treatment.

Conclusion

Overall, ozonation of the alkaline bleach plant effluent demonstrated potentials for enhancing the quality of the wastewater. In particular, this research showed the following.

- Ozonation is capable of improving the biodegradability of the alkaline effluent by 30–40% at ozone dosages of 0.6–0.8 mg O_3/mL .
- Ozonation process resulted in the removal of more than 30% of HMW constituents of the effluent, resulting in reducing the level of recalcitrant and non-biodegradable compounds in the alkaline effluent.
- Biodegradability of the HMW portion of the alkaline effluent improved noticeably (>50%) during ozonation process. However, no biodegradability improvement was observed for LMW fraction of the effluent.
- Temperature (ranging between 20°C and 60°C) and pH (between 9 and 11) did not play a significant role on the ozonation of the alkaline bleach plant effluent at 95% confidence level.
- Noticeable color removal (>70%) of the wastewater was observed indicating selective reaction of ozone with organics particularly HMW compounds that also contribute significantly to the color of the alkaline effluent.

Acknowledgement

The authors acknowledge the Natural Sciences and Engineering Research Council of Canada (NSERC), University Graduate Fellowship (UGF), Hydroxyl Systems Inc., and

Norske Skog Pulp Mill in Elk Falls (Campbell River, BC) for financial and technical assistance and providing pulp mill wastewater. Also, the authors would like to appreciate Dr. S. Duff and Dr. E. Hall for their advice.

References

- American Public Health Association (APHA), Eaton, A.D., Clesceri, L.S., Greenberg, A.E. (ed.) (1995). *Standard Methods for the Examination of Water and Wastewater*. APHA, Washington DC.
- Ataberk, S. and Gökçay, C.F. (1997). Treatment of chlorinated organics in bleached kraft mill effluents by activated sludge process. *Wat. Sci. Tech.*, **36**(2–3), 147–150.
- Beltrán, F.J., García-Araya, J.F., Frades, J., Álvarez, P. and Gimeno, O. (1999). Effects of single and combined ozonation with hydrogen peroxide or UV radiation on the chemical degradation and biodegradability of debittering table olive industrial wastewaters. *Wat. Res.*, **33**(3), 723–732.
- Beltrán, F.J., González, M. and González, J.F. (1997). Industrial wastewater advanced oxidation. Part I. UV radiation in the presence and absence of hydrogen peroxide. *Wat. Res.*, **31**(10), 2405–2414.
- Bijan, L. and Mohseni, M. (2003). Ozone based treatment and its impact on the biodegradability of biorefractory compounds in pulp mill wastewater. *Proc. 16th World Congress of the International Ozone Association*, Las Vegas, Nevada, USA.
- Boman, B. and Frostell, B. (1988). Some aspects of biological treatment of bleached pulp effluents. *Nordic Pulp Paper Res. J.*, **3**, 13–18.
- Canadian Pulp and Paper Association (1993). *Technical Section Standard Test Methods*, CPPA (Montréal).
- Dahlman, O.B., Reimann, A.K., Strömberg, L.M. and Mörck, R.E. (1995). High molecular weight effluent materials from modern ECF and TCF bleaching. *TAPPI Journal*, **78**(12), 99–109.
- Dahlman, O., Reimann, A., Strömberg, L.M. and Mörck, R.E. (1994). On the nature of high molecular weight effluent materials from modern ECF- and TCF- Bleaching. *Proc. International Pulp Bleaching Conference Preprints*. Tech. Section, CPPA, Montreal, p. 123.
- Di Iaconi, C., Lopez, A., Ramadori, R., Di Pinto, A.C. and Passino, R. (2002). Combined chemical and biological degradation of tannery wastewater by a periodic submerged filter (SBBR). *Wat. Res.*, **36**, 2205–2214.
- Eriksson, K. and Kolar, M. (1985). Microbial degradation of chlorolignins. *Environ. Sci. Tech.*, **19**, 1086–1089.
- Eul, W., Degussa, A.G., Moeller, A. and Steiner, N. (ed.) (2001). *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley and Sons, Inc.
- Helble, A., Schlayer, W., Liechti, P.A., Jenny, R. and Möbius, C.H. (1999). Advanced effluent treatment in the pulp and paper industry with a combined process of ozonation and fixed bed biofilm reactors. *Wat. Sci. Tech.*, **40**(11–12), 343–350.
- Hostachy, J.C., Lenon, G., Piscicchio, J.L., Coste, C. and Legay, C. (1997). Reduction of pulp and paper mill pollution by ozone treatment. *Wat. Sci. Tech.*, **35**(2–3), 261–268.
- Jokela, J.K., Laine, M., Ek, M. and Salklnja-Salonen, M. (1993). Effect of biological treatment on halogenated organics in bleached kraft pulp mill effluents studied by molecular weight distribution analysis. *Environ. Sci. Technol.*, **27**(3), 547–557.
- Kosac-Channing, L.F. and Helz, G.R. (1983). Solubility of ozone in aqueous solutions of 0–0.6M ionic strength at 5–30°C. *Environ. Sci. Technol.*, **17**(3), 145–149.
- Lin, S.H. and Lai, C.L. (2000). Kinetic characteristics of textile wastewater ozonation in fluidized and fixed activated carbon beds. *Wat. Res.*, **34**(3), 763–772.
- Mansilla, H.D., Yeber, M.C., Freer, J., Rodriguez, J. and Baeza, J. (1997). Homogeneous and heterogeneous advanced oxidation of a bleaching effluent from the pulp and paper industry. *Wat. Sci. Tech.*, **35**(4), 273–278.
- McKague, A.B. and Carlberg, G. (1996). Pulp Bleaching and The Environment. In: *Pulp Bleaching: Principles and Practice*. Dence, C.W., Reeve, D.W. (ed.), Tappi Press: 749–765.
- Nakamura, Y., Sawada, T., Kobayashi, F. and Godliving, M. (1997). Microbial treatment of kraft pulp wastewater pretreated with ozone. *Wat. Sci. Tech.*, **35**(2–3), 277–282.
- Oeller, H.J., Demel, I. and Weinberger, G. (1997). Reduction in residual COD in biologically treated paper mill effluents by means of combined ozone and ozone/UV reactor stages. *Wat. Sci. Tech.*, **35**(2–3), 269–276.
- Pedit, J.A., Iwamasa, R.J., Miller, C.T. and Glaze, W.H. (1997). Development and application of a gas-liquid contactor model for simulating advanced oxidation processes. *Environ. Sci. Technol.*, **31**, 2791–2796.
- Sågfors, P.E. and Starck, B. (1988). High molar mass lignin in bleached kraft pulp mill effluents. *Wat. Sci. Tech.*, **20**(2), 49–58.
- Wang, F., Smith, D.W. and Gamal El-Din, M. (2003). Oxidation of aged raw landfill leachate with O₃ only and O₃/H₂O₂ and molecular size distribution. *Proc. 16th World Congress of the International Ozone Association*, Las Vegas, Nevada, USA.
- Welander, T., Löfqvist, A. and Selmer, A. (1997). Upgrading aerated lagoons at pulp and paper mills. *Wat. Sci. Tech.*, **35**(2–3), 117–122.
- Yang, Y., Shang, N., Yu, Y. and Ma, H. (2003). Ozonation of dyes and textile wastewater in a rotating packed-bed reactor. *Proc. 16th World Congress of the International Ozone Association*, Las Vegas, Nevada, USA.
- Zenaitis, M.G., Sandhu, H. and Duff, S.J. (2002). Combined biological and ozone treatment of log yard run off. *Wat. Res.*, **36**, 2053–2061.