This is to certify that the
dissertation entitled

Ozonation, Ultrafiltration, and Biofiltration for the Control of
NOM and DBP in Drinking Water

presented by

Kuan-chung Chen

has been accepted towards fulfillment
of the requirements for the

Ph.D. degree in Environmental Engineering

Susan J. Masten
Major Professor's Signature

April 30, 2003
Date

MSU is an Affirmative Action/Equal Opportunity Institution

OZONATION, ULTRAFILTRATION, AND BIOFILTRATION FOR THE CONTROL OF NOM AND DBP IN DRINKING WATER

By

Kuan-chung Chen

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Civil and Environmental Engineering

2003

ABSTRACT

OZONATION, ULTRAFILTRATION, AND BIOFILTRATION FOR THE CONTROL OF NOM AND DBP IN DRINKING WATER

By

Kuan-chung Chen

Ozone is an effective disinfectant that can inactivate microorganisms and reduce the formation of disinfection by-products (DBPs). Ultrafiltration and nanofiltration membranes are also capable of removing DBP precursors and pathogens. However, natural organic matter (NOM), which is ubiquitous in surface water, can result in membrane fouling. A novelly designed ozonation/membrane system followed by biofiltration, which is expected to enhance ozone mass transfer and reduce membrane fouling, was used in this study. The effect of this system on the rate of ozone mass transfer, the transformation of the NOM in terms of the variation of UV-254, humic substances and non-humic substances, assimilable organic carbon (AOC), and biodegradable organic carbon (BDOC) was assessed. The effect of operational parameters on the control of DBPs and ozonation by-products was also investigated. Tubular ceramic membranes with a molecular weight cut-off of 15 kD were used in the system.

A mathematical model was developed and used to calculate the volumetric mass transfer coefficient of ozone for the bench-scale system. This model was successfully predicted the dissolved ozone concentration in the water tank. The effects of two different mixers, simple Y mixer (SYM) and high efficiency mixer (HEM), on the rate of ozone mass transfer were investigated. With HEM, greater values of ozone volumetric mass transfer coefficient were obtained at lower ozone doses.

Lake Lansing water was used to study the transformation of NOM. Water temperature, ozone gas flow rate, and ozone dose were controlled. The ozonation/membrane system removed 15-30% of the dissolved organic carbon (DOC). The removal efficiency increased to 69-88%, when followed by biofiltration. Concentrations of AOC and BDOC significantly increased after treatment using the ozonation/membrane system but were effectively removed by subsequent biofiltration. The UV-254 absorbance decreased by up to 85% and humic substances were converted to non-humic substances after treated by the ozonation/membrane system.

The formation of trihalomethanes (THMs) and haloacetic acids (HAAs) was effectively decreased by the system and by its subsequent biofiltration. Although the concentrations of aldehydes and ketoacids increased significantly after ozonation, these compounds were removed effectively by the subsequent biofiltration. The decrease of chlorine demand was limited when treatment consisted of only ozonation/membrane. With biofiltration, the chlorine demand of water decreased by 60-90%.

Correlations between AOC and ozonation by-products were also investigated. The sum of ozonation by-products (aldehydes + 2-butanone + ketoacids), the concentration of aldehydes, and the concentration of methyl glyoxal were well correlated with AOC and could be good surrogate parameters for the AOC measurement.

To my parents and my wife for their love and support.

ACKNOWLEDGEMENTS

I would like to express my deepest gratitude to my advisor, Dr. Susan J. Masten, for the opportunity to start and complete this research. She freely shared her wealth of knowledge on ozonation with me and offered valuable suggestions that helped me overcome obstacles that I encountered in this research. This research would not have been completed without her support. I would also like to thank my committee members Dr. Mackenzie L. Davis, Dr. Syed A. Hashsham, and Dr. Simon H. R Davies for seeing me through this long journey and for offering good advice at critical points along the way.

I would like to thank Dr. Xianda Zhao who gave me valuable suggestions and comments on this work with his expertise. I also acknowledge Mr. Yan-lyang Pan for his technical support in the laboratory. I would also like to thank Mr. Hung-hsu Yen for the time he spent discussing data analysis with me. Thanks also to all of my friends who have listened to me moan, rejoice, complain, laugh, and ponder my way through these past years.

Finally, I would like to thank my family. I wish to thank my wife, Ya-yun, who not only gave me moral support but also helped me organize tons of data during this research. She has accompanied me through the ups and downs in these years and no one could ask for a better friend in life than she has been to me. With her love and support, life is much more pleasant and colorful. I also thank my parents, my sisters, and my in-laws, for their love, encouragement and support. Thank you all for giving me this opportunity to do what I love.

TABLE OF CONTENTS

CHAPTER 1

INTRODUCTION

CHAPTER 2

BACKGROUND

CHAPTER 3

MASS TRANSFER OF OZONE IN THE OZONATION/MEMBRANE PROCESS

CHAPTER 4

THE EFFECT OF OZONATION/MEMBRANE PROCESS ON THE CHARACTERISTICS OF NATURAL ORGANIC MATTER

CHAPTER 5

THE USE OF OZONATION/MEMBRANE PROCESS FOR THE CONTROL OF DISINFECTION BY-PRODUCTS

CHAPTER 6

CORRELATION BETWEEN THE FORMATION OF ASSIMILABLE ORGANIC CARBON AND OZONATION BY-PRODUCTS

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

LIST OF TABLES

LIST OF FIGURES

ABBREVIATIONS

DBPs	Disinfection by-products
NOM	Natural organic matter
UV-254	Ultraviolet absorbance measured at 254 nm
AOC	Assimilable organic carbon
BDOC	Biodegradable organic carbon
DOC	Dissolved organic carbon
THMs	Trihalomethanes
HAAs	Haloacetic acids
D/DBPR	Disinfectants/Disinfection By-Products Rule
TOC	Total organic carbon
HS	Humic substances
NHS	Non-humic substances
UF	Ultrafiltration
MWCO	Molecular weight cutoff
SDS THMs	Simulated distribution system THMs
SDS HAAs	Simulated distribution system HAAs
SYM	Simple Y inline mixer
HEM	High efficiency inline mixer

CHAPTER 1

INTRODUCTION

1.1 SIGNIFICANCE

The production of disinfection by-products (DBPs) during the disinfection process in drinking water treatment has become a very important issue since some DBPs, such as trihalomethanes (THMs), have been found to have carcinogenic properties (Kool et al. 1985; Morris et al. 1992; Mughal 1992). Because of their perceived health risk, the United State Environmental Protection Agency (USEPA) promulgated the Stage 1 of the Disinfectants/Disinfection By-Products Rule (D/DBPR) in December of 1998 and issued the final rule on January 16, 2001. The maximum contaminant level (MCL) for total THM (TTHM) was lowered from 100 μg/L to 80 μg/L as a running annual average (RAA-MCLs) for the sum of five haloacetic acids (HAA5) and for the bromate were set at 60 μg/L and 10 μg/L, respectively (Pontius 2000; Pontius 2001; Pontius 2002; USEPA 1998). The draft version of the Stage 2 DBPR, which was proposed on October 17, 2001, further requests that the locational RAA (LRAA), which means the annual average at each monitoring site, of TTHM/HAA5 should be below 120/100 μg/L in Phase 1 (three years for all systems after rule promulgation) and below 80/60 μg/L in Phase 2 (six years for large and medium systems, eight and a half years for small systems required to do *Cryptosporidium* monitoring, and seven and a half years for all other small systems after rule promulgation) (Pontius 2001; Pontius 2002; Pontius 2003). Therefore, the development of novel methods to effectively remove DBP precursors in order to meet the more stringent regulations concerning DBPs is a major need of the water treatment industry.

In response to the new D/DBP rule, the number of ozonation installations continues to grow each year in the United States. In 1997, there were about 200 drinking water treatment plants using ozone (Naude 1997). In 2001, the number increases to about 350 (Ozone News 2001). Ozone was first applied in the drinking water treatment process as a disinfectant in 1893 at Oudshoorn, Netherlands. It is an effective alternative disinfectant and a more powerful oxidant than chlorine, which is now widely used as a disinfectant in the United States. Ozone is capable of decreasing the numbers of microorganisms (Lee and Deininger 2000) and the concentration of DBP precursors (Cipparone et al. 1997; Yavich 1998). It also reacts with organic substances and increases their biodegradability (Takeuchi et al. 1997). Ozonation has also been found to reduce the concentrations of DBPs in finished water. Further reductions in DBPs concentrations could be achieved if ozonation is followed by biological treatment because of the conversion of total organic carbon (TOC) to more easily biodegradable organic carbon (BDOC) during ozonation (Shukairy and Summers 1992). However, this conversion is limited because of the low solubility of ozone in water and the slow reactivity of TOC with ozone, requiring long contact time.

Another effective approach to remove DBP precursors and pathogens is the application of membrane process. It is considered as one of the best available technologies (BAT) for meeting the Stage 2 D/DBP requirements (Arora et al. 1997). During the last decade, better membranes have been developed and the characterization of membrane surfaces and causes of membrane fouling are better understood (Carroll et al. 2000; Clark et al. 1998; Lin et al. 2001). Some membrane processes, such as nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF), use pressure as the driving force to maintain constant flux across the membrane and produce reliable finished water. These membrane filtrations provide physical barriers to turbidity, pathogens, and natural organic matter (NOM), which are rejected by membranes and become the residuals. This technology is suitable for water treatment plants that need to be upgraded to comply with the stringent drinking water standards or for those to serve small communities (Cleveland 1999; Taylor and Wiesner 1999).

The objective of this research project was to study the feasibility of combined ozonation and membrane technology for controlling DBP precursors in drinking water and improving the quality of the treated water. Biofiltration following the ozonation/membrane system was used to investigate the biodegradability of water treated by the proposed system and evaluate the removal efficiency of DBP precursors and biodegradable organic matter (BOM) by biotreatment. Several potential advantages of ozonation/membrane/biofiltration treatment are:

1. The mixing of gas phase ozone and the water stream within the membrane is expected to increase the ozone solubility and concentration in water, enhance the ozone mass transfer, minimize the required ozone dosage, enhance organic matter broken down by ozonation, and maintain stable permeate flux of membrane.
2. The ozonation/membrane process is expected to decrease the formation of chlorinated DBPs in the finished water, inactivate the pathogens in the permeate of membrane and residual stream, reduce membrane fouling, increase the efficiency of NOM destruction by ozone, and enhance the formation of BOM which can be readily removed by the subsequent biotreatment of the proposed system.
3. The longer contact time between ozone and water in the proposed system than that in conventional ozonation is expected to convert the NOM to a greater

percentage of ozonation by-products, which are more hydrophilic, polar, and readily biodegraded. These ozonation by-products are good substrates for microorganisms and can be removed by the following biofiltration process. Therefore, the concentration of dissolved organic carbon (DOC) can be reduced, which lessens the chlorine demand and the DBP level in the treated water.

If the proposed ozonation/membrane system is successfully developed, it will help drinking water treatment plants upgrade or retrofit their conventional systems to comply with the D/DBPR.

1.2 OBJECTIVES

Five particular objectives that were investigated are,

1) To assess the effect of ozonation on the properties (e.g. humic substances, non-humic substances, biodegradable dissolved organic carbon, assimilable organic carbon) of NOM in the proposed ozonation/membrane process.
2) To investigative the effect of ozonation/membrane system and biotreatment on the formation of regulated DBPs and ozonation by-products at various operational conditions.
3) To investigate the effect of control parameters (e.g. flow rate, ozone dose, temperature) on the rate of ozone mass transfer in the proposed system.
4) To develop a mathematical model for ozone mass transfer that can be used to characterize the rate of ozone mass transfer in the proposed system as a function of operating conditions.
5) To establish the relationships between the properties of NOM and DBPs, and between assimilable organic carbon (AOC) and ozonation by-products.

1.3 HYPOTHESES

The following hypotheses were tested in this study:

1) The mass transfer of ozone from the gaseous phase into the liquid phase can be enhanced by combining two treatment processes, ozonation and membrane filtration, into one single unit. The high ozone mass transfer rate achieved by using the proposed system will minimize the applied ozone dosage required to treat drinking water to an acceptable quality.
2) The coefficient of ozone mass transfer will increase as the water flowrate, gas flowrate, ozone dose, or water temperature increases.
3) The injection of ozone and water mixture into the membrane module will increase the permeate flux of membrane and maintain a stable permeate flux during operation. The membrane-fouling problem will be reduced as ozone bubbles scrub the surface of membrane.
4) The long hydraulic retention time of the proposed system is expected to transform humic substances (HS) into non-humic substances (NHS), reduce levels of TOC and ultraviolet absorption measured at 254 nm (UV-254), and increase the biodegradability of treated water.
5) The ozonation/membrane system will effectively decrease the formation of DBPs compared to that obtained with conventional ozonation.
6) Biotreatment following the proposed system will result in the improved removal of DBP precursors and the reduction of ozonation by-products, TOC, and AOC.
7) Ozonation by-products can be decomposed by ozonation and also degraded by microorganisms.
8) The ultrafiltration membrane used in this study can not effectively retain AOC.

9) There exist correlations between HS and UV-254, TOC and DBPs, and ozonation by-products and AOC.

1.4 REFERENCES

Arora, H., LeChevallier, M. W., and Dixon, K. L. (1997). "DBP occurrence survey." *Journal American Water Works Association*, 89(6), 60-68.

Carroll, T., King, S., Gray, S. R., Bolto, B. A., and Booker, N. A. (2000). "The fouling of microfiltration membranes by NOM after coagulation treatment." *Water Research*, 34(11), 2861-2868.

Cipparone, L. A., Diehl, A. C., and Speitel, G. E. (1997). "Ozonation and BDOC removal: Effect on water quality." *Journal American Water Works Association*, 89(2), 84-97.

Clark, M. M., Allgeier, S., Amy, G., Chellam, S., DiGiano, F., Elimelech, M., Freeman, S., Jacangelo, J., Jones, K., Laine, J. M., Lozier, J., Marinas, B., Riley, R., Taylor, J., Thompson, M., Vickers, J., Wiesner, M., and Zander, A. (1998). "Committee report: Membrane processes." *Journal American Water Works Association*, 90(6), 91-105.

Cleveland, C. T. (1999). "Big advantages in membrane filtration." *Journal American Water Works Association*, 91(6), 10-10.

Kool, H. J., van Kreijl, C. F., and Hrubec, J. (1985). "Mutagenic and Carcinogenic Properties of Drinking Water." Water Chlorination: Chemistry, Environmental Impacts, and Health Effects, R. L. Jolley, W. A. Brungs, and R. B. Cumming, eds., Lewis Publ., Chelsea, Mich.

Lee, J., and Deininger, R. A. (2000). "Survival of bacteria after ozonation." *Ozone-Science & Engineering*, 22(1), 65-75.

Lin, C. F., Liu, S. H., and Hao, O. J. (2001). "Effect of functional groups of humic substances on UF performance." *Water Research*, 35(10), 2395-2402.

Morris, R. D., Audet, A. M., Angelillo, I. F., Chalmers, T. C., and Mosteller, F. (1992). "Chlorination, Chlorination by-Products, and Cancer - a Metaanalysis." *American Journal of Public Health*, 82(7), 955-963.

Mughal, F. H. (1992). "Chlorination of Drinking Water and Cancer: A Review." *Jour. Envir. Pathol., Toxicol. & Oncol.*, 11(5,6), 287-292.

Naude, A. (1997). "Finding Choices in Disinfection." *Chemical Market Reporter*, 252(15), FR5-FR6.

Ozone News. (2001). "Regulations/Cryptosporidium." B. L. Loeb, ed., International Ozone Association, Cincinnati, Ohio, 6.

Pontius, F. W. (2000). "Regulations in 2000 and beyond." *Journal American Water Works Association*, 92(3), 40-+.

Pontius, F. W. (2001). "Regulatory update for 2001 and beyond." *Journal American Water Works Association*, 93(2), 66-80.

Pontius, F. W. (2002). "Regulatory compliance planning to ensure water supply safety." *Journal American Water Works Association*, 94(3), 52-+.

Pontius, F. W. (2003). "USEPA's drinking water regulations." *Journal American Water Works Association*, 95(3), 57-+.

Shukairy, H. M., and Summers, R. S. (1992). "The Impact of Preozonation and Biodegradation on Disinfection by-Product Formation." *Water Research*, 26(9), 1217-1227.

Takeuchi, Y., Mochidzuki, K., Matsunobu, N., Kojima, R., Motohashi, H., and Yoshimoto, S. (1997). "Removal of organic substances from water by ozone treatment followed by biological activated carbon treatment." *Water Science and Technology*, 35(7), 171-178.

Taylor, J. S., and Wiesner, M. (1999). "Membranes." Water Quality and Treatment, American Water Works Association, Ch.11.

USEPA. (1998). "Disinfectants and Disinfection By-products, Final Rule." Fed. Reg., 69394.

Yavich, A. A. (1998). "The Use of Ozonation and Biological Fluidized Bed Treatment for the Control of NOM in Drinking Water," Ph.D. Dissertation, Michigan State University, East Lansing, MI.

CHAPTER 2

BACKGROUND

In this chapter, background literature relevant to this research is provided. The important characteristics of NOM and the formation and influence of biodegradability of organic matter in treated water are described in Section 2.1. The formation of major DBPs is discussed in Section 2.2. The health risks caused by pathogens are discussed in Section 2.3. Finally, four treatment technologies, ozonation, membrane filtration, ozonation/biotreatment, and ozonation/membrane, are reviewed and discussed in Section 2.4.

2.1 ORGANIC MATTER IN DRINKING WATER

Organic matter, which occurs in the environment either as the result of natural processes or human activities, is ubiquitous in aquatic systems. Typical concentrations of NOM in aquatic systems are reported to range from 0.5 to 100 mg/L as organic carbon (Frimmel 1998).

The constituents of aquatic organic matter include humic materials from plants and algae, microorganisms and their metabolites, and aliphatic and aromatic hydrocarbons. Some of this material can cause adverse health effects if they are not removed during water treatment. Humic materials are recognized as the precursors of DBPs; pathogenic microorganisms can, potentially, spread diseases; and other organic substances present in treated water can consume disinfectant, thereby requiring higher disinfectant dosages to achieve regulatory criteria, and possibly increasing the pathogenic bacteria regrowth potential in the distribution system.

2.1.1 Natural Organic Matter

NOM is made up of a heterogeneous mixture of organic compounds. Diverse types of NOM, which originate from various environmental systems, such as forests, marshes, and swamps, are presence in surface waters (Krasner et al. 1996a). NOM that originates from surface waters contains low fractions of phenolic and aromatic compounds and mainly comes from algal and bacterial biomass, which is mostly aliphatic and totally devoid of lignins (Goel et al. 1995). The low molecular weight, relatively soluble fulvic acids make up the significant fraction of this material. In contrast, NOM originating from soils is derived from terrestrial vegetation, which has high aromatic constituents (Goel et al. 1995).

NOM in drinking water supplies poses significant concerns to the water utility and may significantly influence many aspects of water treatment. Conventional water treatment processes cannot effectively remove NOM. The presence of NOM can decrease the effectiveness of oxidants or disinfectants, and may cause the formation of DBPs due to its reactivity with disinfectants (e.g., see Glaze et al. 1993; Krasner et al. 1996b; Owen et al. 1995; Rencken 1994). It also causes bacterial regrowth in the distribution system, fouling of filtration membranes, and reduces granular activated carbon (GAC) adsorber bed life (Bouwer and Crowe 1988; Krasner et al. 1996a). Only a small portion of the constituents of NOM are biodegradable since, by definition, NOM is the recalcitrant fraction of organic material remaining after natural decomposition (Goel et al. 1995).

Several analytical techniques, such as ^{13}C magnetic nuclear resonance (Preston 1987; Wilson 1987), transmission electron microscopy (Leppard 1992), and NOM fractionation on XAD resins (Leenheer 1981; Martin-Mousset et al. 1997), have been applied to characterize aquatic NOM. NOM is also typically quantified in terms of

TOC. Although NOM is heterogeneous in nature, an easily measured parameter, specific ultraviolet absorbance (SUVA) at 254nm, was found to be a powerful indicator for its reactivity toward oxidants (Westerhoff et al. 1999). A paucity of information, however, exists describing the detailed characterization of NOM, which includes determining its chemical composition and reactivity in a broad range of waters (Owen et al. 1995).

2.1.2 Humic Substances

Dissolved organic carbon (DOC), the organic matter in water that passes through a 0.45 µm membrane filter, can be divided into humic and nonhumic fractions. These two fractions, also called humic substances and nonhumic substances, are commonly classified on the basis of their water solubility at acidic or basic pH values (Malcolm 1985).

Humic substances, which represent a complex mixture of molecules of various sizes and shapes, are more hydrophobic in character and comprise humin and humic and fulvic acids. Due to their heterogeneous nature and composition, no single structural formula can be given to them.

Humic substances are the primary precursors of chlorination byproducts, such as THMs (Collins et al. 1986; Ichihashi et al. 1999; Manahan 1993; Reckhow et al. 1990). Organic and inorganic pollutants, many of which are insoluble in water, can sorb to humic substances and therefore, be transported in the water with the humic substances (Collins et al. 1986; Stevenson 1985; Thurman 1985). They are resistant to both microbiological and chemical breakdown. Malcolm (1985) found that humic substances comprise approximately 50% of the DOC in uncolored streams in the United States. In his study, fulvic acid accounted for approximately 90% of the humic substances and only 10% or less was humic acid.

The composition of humic substances in surface water is different from that in groundwater. Humic substances from surface water usually contain an average of 52% carbon and 42% oxygen, whereas, humic substances from groundwater contain greater than 60% carbon and less than 30% oxygen (Thurman and Malcolm 1981). The color per unit of carbon of humic substances from groundwater is also considerably less than that from surface water (Thurman 1985).

Aquatic humic substances contain aromatic structures with large numbers of carboxyl groups, some phenolic groups, alcohol OH groups, methoxyl groups, ketones, and aldehydes (Liao et al. 1982; Reckhow et al. 1990). The average molecular weight of aquatic humic acids usually ranges from 2000 to 3000 daltons, and that of aquatic fulvic acids is from 800 to 1000 daltons (MacCarthy and Suffet 1989; Wershaw and Aiken 1985a). Thurman et al. (1982) pointed out that the average molecular weight for humic substances from surface water is 100 to 2000 daltons. In contrast, the molecular weight of humic acids from soil is as large as several hundred thousand daltons.

The characteristics of the functional groups on humic and fulvic acids, which influence the solubility of humic substances (Perdue 1985), provide insight into the applicability of various water treatment processes for the removal of NOM. Humic substances with the highest carboxylic acidity and thus highest charge density are generally more difficult to remove by conventional treatment, direct filtration, or softening processes (Collins et al. 1986). For example, fulvic acids have higher carboxylic and phenolic acidity, therefore, have a higher charge density than humic acids, and are more difficult to coagulate by charge neutralization. However, the humic fraction of DOC is more easily removed by adsorption or coagulation. Granular activated carbon (GAC) removes humic and higher apparent molecular weight (AMW) NOM. It also provides some reduction in the levels of nonhumic and lower AWM DOC. Coagulation reduces SUVA and shows the preferential removal of the humic fraction of NOM and higher-molecular-weight NOM (Owen et al. 1995).

The nonhumic substances comparing with the humic substances are more hydrophilic in character and are comprised of hydrophilic acids, proteins, amino acids, and carbohydrates (Owen et al. 1995). The nonhumic fraction is of concern in water treatment because it forms a significant percentage of the regulated or potentially regulated DBPs. In addition, the nonhumic fraction of DOC may contribute to a higher fraction of the BDOC, which may cause of bacteria regrowth in the distribution systems (Mogren et al. 1990). Therefore, decreasing the nonhumic fraction concentrations in drinking water to levels that are as low as technically and economically feasible is also an important issue (Leenheer 1985).

2.1.3 Molecular Weight Distribution

Molecular weight is a valuable tool to characterize complex organic compounds, such as humic substances (Wershaw and Aiken 1985b). Some researchers have shown that molecular weight characterization of the DOC provides a means for identifying potential treatment strategies (Amy et al. 1988; Chadik and Amy 1987).

Low molecular weight and nonhumic material are difficult to remove by either coagulation or adsorption (Owen et al. 1995). Collins and colleagues (1986) found that conventional treatment processes were rather ineffective in removing DOC having a molecular weight of less than 500 daltons. In contrast, higher molecular weight material proved to be more amenable to removal than lower molecular weight material. Owen et al. (1995) and Amy et al. (1992) found that chemical coagulation could effectively remove higher molecular weight material. Water sources with material of medium molecular weight (e.g., 1000 to 5000 daltons) can also be effectively adsorbed by activated carbon (Amy et al. 1992).

Molecular weight distributions may shift during the treatment processes. Yavich (1998), Owen et al. (1995), and Amy et al. (1988) observed that ozonation did not result in NOM destruction, but converted material with higher molecular weight to lower molecular weight. This shift of molecular weight distribution not only changes the properties of NOM (Owen et al. 1995) but also reduces the trihalomethane formation potential (THMFP) (Amy et al. 1988; Amy et al. 1992).

Two main methods, gel permeation Chromatography (GPC) and ultrafiltration (UF), are used to estimate the molecular weight. These two techniques separate the humic substances based on molecular size rather than molecular weight. Thus, the results are usually expressed as apparent molecular weight (AMW) distribution. Kim and colleagues (1989) compared the AMW values for several aquatic samples all measured by the GPC and UF methods and found that the values assigned by UF were higher than those assigned by GPC. Similar observations were reported by Thurman et al. (1982).

2.1.4 Biodegradable Dissolved Organic Carbon

Biodegradable dissolved organic carbon (BDOC) is a fraction of DOC that can be mineralized by heterotrophic microorganisms. Some researchers (Bablon et al. 1991a; Van der kooij et al. 1989; Volk et al. 1993) found that the use of ozonation as the disinfectant increases the regrowth potential of bacteria of a water by converting part of the refractory carbon into BDOC. These unwanted bacteria have the potential to spread disease, to cause unpleasant tastes, order, and color in the distribution system, and to increase pipe corrosion problems (Korshin et al. 1996; Levy et al. 1986). Removing BDOC from the finished water has several advantages. It reduces the extent of bacteria regrowth in the distribution system. It reduces the fraction of the NOM having a high disinfectant reactivity, hence reducing the chlorine demand of treated water and increasing the likelihood that a sufficiently high chlorine residual can be maintained in the distribution system. Removing BDOC also results in the elimination of some precursors of DBPs, thereby lowering the concentration of DBPs in the treated water (Bablon et al. 1991a; Cipparone et al. 1997; Shukairy and Summers 1992).

Servais and colleagues (1993) investigated the threshold value of BDOC for which there is no BDOC consumption within the distribution system. They concluded that if the BDOC value is less than 0.15 mg C/L, water can be considered as biologically stable in the absence of free chlorine, which means the bacterial growth in the distribution system is very limited. However, Rittmann (1995) indicated that BDOC could cause problems during distribution even its concentration is as low as 0.02 mg C/L.

Siddiqui and colleagues (1997) found that the conversion of DOC to BDOC reaches a maximum at an applied O_3/DOC ratio of 1:1 (mg/mg) for Silver Lake water containing DOC levels ranging from 3 to 6 mg/L. This result is consistent with other researchers' results (Cipparone et al. 1997; Volk et al. 1993). Moreover, the DOC concentrations were not significantly reduced when the applied ozone dose was increased beyond 1.0 mg O_3/mg DOC ratio (Paode et al. 1997; Siddiqui et al. 1997; Volk et al. 1993).

The measurement of BDOC has been used mainly to indicate the quality of raw and finished waters and evaluate the performance of biotreatment processes (e.g., biological filtration) in water treatment plants. BDOC measurement assesses the organic carbon that can be potentially biologically oxidized during the biotreatment processes (Huck 1990). The concentrations of BDOC cannot be measured by simple chemical methods, because a great variety of compounds comprise BDOC and many of them are difficult to quantify and cumbersome to isolate (Siddiqui et al. 1997). As such, several methods for measuring biodegradable organic matter in water have been introduced (Huck 1990). There are two main and conceptually different approaches to measuring it. One approach assesses easily assimilable organic carbon (AOC), which represents the regrowth potential of heterotrophic bacteria in water and was developed by van der Kooij, Visser, and Hijnen (1982). The method is based on measuring the maximum growth level (colony forming units, CFU) of a selected pure culture or cultures of bacteria, inoculated into autoclaved samples of drinking water (Van der Kooij 1995; Van der kooij et al. 1982). For the AOC determination, two selected microorganisms, *Pesudomonas fluorescens* strain P17 and *Spirillum* strain NOX, are both able to reproduce at low substrate concentrations and utilize different groups of compounds (Van der Kooij 1995). The *Pesudomonas fluorescens* strain P17 mainly utilizes amino acids, carbohydrates, and aromatic acids. The *Spirillum* strain NOX mainly utilizes carboxylic acids.

The other approach was developed by Servais, Billen, and Hascoët (1987). This method is based either on the reduction of DOC during incubation or on an estimate of the flux of organic matter utilized by bacteria. The inoculum bacteria used in this method is obtained from the natural environment from which the water sample originated. Incubation occurs in the dark at room temperature for a period of

10 to 30 days. Joret and colleagues (1988; 1991) using an aerated biofilm on sand particles to measure BDOC, reduced the incubation time to 3 to 5 days. The principal BDOC method that is currently widely used is the recirculating acclimated-sand column technique (Mogren et al. 1990). A glass column partially filled with biologically active sand serves as the main body of the reactor. The sample is recirculated through the column, and DOC is measured daily until the concentration of DOC no longer changes with time.

Some researchers (Siddiqui et al. 1997) found that a positive correlation was obtained between BDOC and AOC; both parameters had a tendency to plateau at an applied O_3/DOC dosage of 2 mg O_3/mg DOC. However, Charnock and KjØnnØ (2000) found that the correlations between AOC and BDOC for both raw and drinking water were not significant. The authors suggest that the results may indicate that the AOC and BDOC analyses target different fractions of BOM.

2.2 DISINFECTION BY-PRODUCTS

In 1974, Rook first reported that THMs were formed when chlorine reacted with naturally occurring humic substances in water treatment plants and water distribution systems. Subsequently, several researchers also reported the production of THMs and other halogenated organics such as HAAs, haloacetronitriles, haloalcohols, and haloketones during the chlorination process (e.g., see Christman et al. 1983; Ichihashi et al. 1999; Richardson et al. 1999; Singer 1994; Stevenson 1994). Generally, the DBPs can be divided into two groups: organic DBPs and inorganic DBPs. Organic DBPs include aldehydes, ketones, ketoaldehydes, carboxylic acids, aldo acids, keto acids, hydroxyl acids, alcohols, esters, and alkanes (Anderson et al.

1985; Haag and Hoigné 1983). Reported inorganic DBPs include bromate, hypobromite, and hydrogen peroxide (Haag and Hoigné 1983).

A. Chlorinated DBPs

THMs and HAAs are considered to be the major chlorination byproducts in water treatment (Oxenford 1996). Four chemicals, chloroform, dichlorobromomethane, dibromochloromethane, and bromoform, are well known as the predominant THMs formed during chlorination (McGuire and Meadow 1988). A number of factors that affect the formation of THMs are the nature of aquatic humic substances, chlorine dose, reaction time, bromide ion concentration, preozonation, temperature, and pH (Trussell and Umphres 1978).

Five major HAAs includ monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), and dibromoacetic acid (DBAA). Their formation can be appreciable if drinking water is chlorinated under slightly acidic pH values, distributed under neutral distribution system pH values, and containing low bromide concentrations (Singer et al. 1995).

The other DBPs that have been observed during the chlorination process of drinking waters are organic halides, haloacetonitriles, haloketones, chloropicrin, cyanogens chloride, chlorite, and chlorate (Andrews and Ferguson 1996).

B. Ozonation DBPs

Some researchers found that both THMs and HAAs are also formed when chlorine or chloramines were applied following the ozonation of waters containing NOM (Reckhow and Singer 1990; Richardson et al. 1999; Uden and Miller 1983). Richardson and colleagues (1999) found that the majority of the identified ozone

DBPs contained oxygen in their structures. No halogenated DBPs were observed unless high natural levels of bromide (Br^-) existed in the raw water and chlorine or chloramines were used as a secondary disinfectant.

Other reported ozonation byproducts are aldehydes (formaldehyde, acetaldehyde, glyoxal, and methylglyoxal), ketones, glyoxylic, and pyruvic acids (Paode et al. 1997; Weinberg and Glaze 1996).

C. Bromate

Bromate (BrO_3^-) is a DBP that results when bromide containing waters are ozonated. Reactions of ozone with bromide in aqueous media are shown in Figure 3.1 (Haag and Hoigné 1983). Hypobromous acid (BrOH) is formed when ozone, chlorine, or chloramine oxidizes bromide ion during the water treatment. Then the BrOH in turn reacts with DOC to form brominated DBPs (Haag and Hoigné 1983; Rook 1974; Rook et al. 1978; Song et al. 1997). NOM, ozone dose, bromide concentration, pH, and temperature are factors that influence bromate formation.

The concentration of bromide in water is important because it not only reacts with ozone and forms bromate, but also affects the formation of other DBPs. In some instances, bromide is passed conservatively through the treatment processes (e.g., coagulation, GAC, ion exchange) resulting in higher Br^--to-NOM ratios than are present in bulk waters prior to treatment (Owen et al. 1995). The Br^--to-NOM ratios affect the DBP speciation (Krasner et al. 1996b).

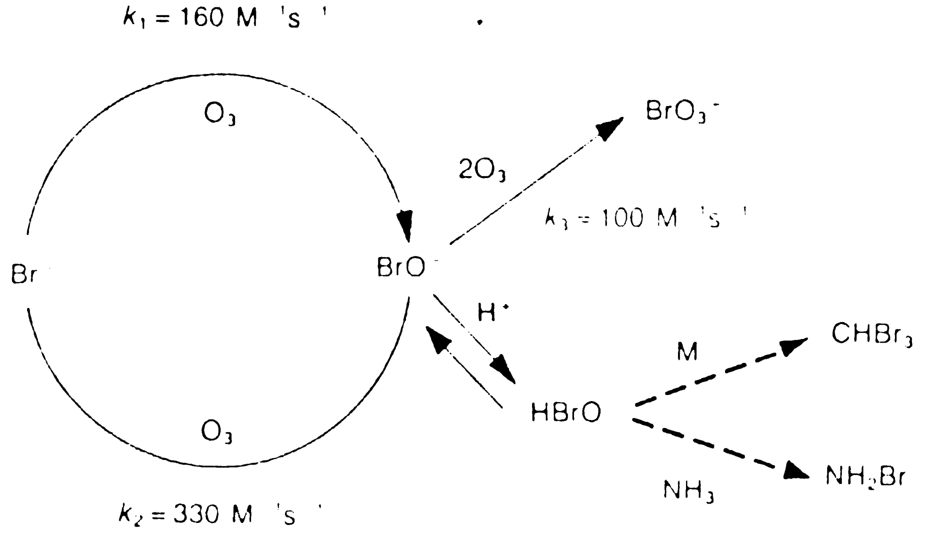

Figure 2.1 Reactions of ozone with bromide in aqueous media, M represents organic matter. (Haag and Hoigné 1983)

D. Treatment

Chemical coagulation, a process that is already operational at many treatment plants, is capable of removing both turbidity and THM precursors when the process is optimized. Reckhow and Singer (1990) reported that alum coagulation effectively removes significant fractions of the DBP precursors. However, some researchers pointed out that either bromide or brominated haloforms cannot be removed effectively through the coagulation process (Chadik and Amy 1983; Owen et al. 1995).

Ozonation followed by biotreatment is able to remove ozonation DBPs efficiently because of the high biodegradable characteristics of those DBPs. However, Siddiqui and co-workers (1997) reported that a drawback of the ozonation of high bromide containing waters is once the bromate formed ozonation-biofiltration treatment scheme cannot effectively remove it during biofiltration. The combination of ozonation/biotreatment process will be discussed in Section 3.4.3.

The other promising technique for removing DBPs precursors is the membrane process. Membranes are good barriers of turbidity causing material, pathogens, and DBP precursors. DBP precursors removal of up to 99% can be achieved depending on the characteristics of the applied membrane. A more detailed investigation will be discussed in Section 2.4.2.

2.3 PATHOGENS

Pathogens commonly exist in many types of water sources. They can enter surface water sources through surface runoff from numerous sources including, livestock grazing areas and feedlots, from sewage effluent, or untreated or poorly treated wastewater. Pathogens are also found in ground water sources, which are naturally filtered by the geological material. Septic tank effluent, runoff from agricultural areas, and wastewater are often the sources of contamination.

The Microbiological Contaminants Research Committee of the AWWA Research Division determined that four bacterial, three viral, and three protozoan microorganisms, and one set of bacterial toxins that are of greatest concern to the water industry (LeChevallier et al. 1999a; LeChevallier et al. 1999b). These microorganisms and toxins can cause disease, infecting the human lungs, stomach, upper gastrointestinal tract, liver, kidney, and central nervous system. Typical symptoms of infection are cough, fatigue, dehydration, weight loss, fever, diarrhea, abdominal cramps, nausea, permanent nerve damage, headache, and muscle pain. Whether an individual becomes illness depends on the number of organisms ingested, the health status of the individual, and the resistance of the person to the organism or toxin. Generally, children, the elderly, and other immuno-compromised or immuno-deficient individuals are at particular risk.

Drinking water treatment plants provide barriers between people and pathogens to protect public health. Pathogens are removed or inactivated in different treatment units. Nieminski and Ongerth (1995) compared the effectiveness of removing *Giardia* and *Cryptosporidium* by conventional treatment and direct filtration. They found that both properly operated conventional treatment and direct filtration can achieve 3-log removal of *Giardia* cysts, but only about 2.5-log removal of *Cryptosporidium* oocysts. If the performance of treatment changed and raw water turbidity fluctuated, a high variability in cyst concentration was observed in effluent.

In the past decade, several waterborne outbreaks have drawn the attention of water suppliers, public health professionals, and researchers. Solo-Gabriele and Neumeister (1996) reviewed numerous outbreaks of *Cryptosporidiosis.* They found those outbreaks had occurred in drinking water treatment plants that were meeting existing regulatory requirements. Thus, they suggest that filtration system of conventional treatment process should be operated at optimum level exceeding existing regulatory requirements, because chlorination process alone is incapable of providing adequate protection of public health from *Cryptosporidium* outbreaks. Also, Fox and Lytel (1996) reported that *Cryptosporidium* oocysts were able to pass through one of two treatment plants in Milwaukee, Wisconsin, with other particles during a high turbidity period in March and April 1993. This waterborne outbreak caused illness in more than 400,000 people.

Coliform bacteria have been used as the indicator to access the microbiological quality of drinking water for many decades. Craun and colleagues found that coliform bacteria are adequate indicators for the potential existence of bacteria and viruses in drinking water, but they are inadequate as an indicator for waterborne protozoa. That is because oocysts are more resistant to water disinfectants than coliform bacteria.

Several researchers (Frost et al. 1996; Kramer et al. 1996; Moore et al. 1994) discussed waterborne disease surveillance systems and point out that outbreaks are probably underreported because of current reporting systems. Most current surveillance programs are based on disease reporting by health care providers and clinical laboratories. Because of the same symptoms of enteric infections, the unawareness of infection, and insufficiently specific symptoms to identify pathogens, outbreaks are probably inadequately investigated or unrecognized.

2.4 TREATMENT

2.4.1 Ozonation

Ozone has been used widely as an alternative disinfectant to chlorine, chloramines, and chlorine dioxide. It is a powerful oxidant and preferentially oxidizes electron-rich moieties, which contain carbon-carbon double bonds, and aromatic alcohols (Bablon et al. 1991b). Ozone also acts as an electrophil reacting with molecular sites with a strong electronic density, and as a nucleophil reacting with molecular sites with electronic deficiencies (Bablon et al. 1991b). Due to the reactivity of the most commonly occurring contaminants and the relatively short contact time in ozonation contactors, complete oxidation of these chemicals rarely happen. Therefore, partially oxidized organic compounds, such as aldehydes, ketones, organic acids, and alcohols, are produced during the ozonation of drinking waters.

Ozone is partially soluble in water. Its solubility decreases with an increase in water temperature and increases with an increase in partial pressure of ozone (or, correspondingly, in the ozone concentration in the gas stream) according to Henry's Law. The higher the concentration or partial pressure of ozone in the gas stream, the higher the ozone solubility in the water and the higher mass transfer efficiencies of ozone. One other factor that affects ozone mass transfer is the existence of reactive material such as NOM in the water. If the concentrations of reactive species are high, then the mass transfer efficiencies are increased and the demand for ozone will be greater.

Ozonation reactions in aqueous solution involve either direct reactions with molecular ozone or indirect ones with the hydroxyl radical (Bablon et al. 1991b; Hoigné and Bader 1975; Peleg 1976). During the ozonation of water, a portion of the ozone reacts directly with DOC and the remaining amount of ozone decomposes to form the hydroxyl (HO·) radical. The decomposition reaction is catalyzed by hydroxide ions and other dissolved compounds such as NOM. OH radicals can react with DOC and accelerate the decomposition of ozone (Bablon et al. 1991b; Hoigné and Bader 1975; Staehelin and Hoigné 1985).

Factors that favor the molecular ozone reaction pathway are pH values below 6, the absence of redox metal ions, such as Fe(II) and Fe(III), and the presence of compounds having unsaturated carbon-carbon bonds. Studies show that reactions with molecular ozone are comparatively slow and highly selective compared with reactions involving the hydroxyl radical, which are faster and relatively nonselective (Haag and Yao 1992; Hoigné and Bader 1983). The net result of the molecular ozone reactions is usually the formation of aldehydes, ketones, and carboxylic acids (Glaze et al. 1988; Maggiolo 1978; Miltner et al. 1992; Schechter and Singer 1995).

In contrast, ozone rapidly decomposes into hydroxyl radicals at pH values above 8. When targeting compounds such as NOM, which react slowly with molecular ozone, the hydroxyl radical is the preferred oxidant. The reaction of organic compounds with hydroxyl radicals will produce organic free radicals that ultimately result in the formation of aldehydes, ketones, alcohols, and carboxylic acids. Some of the aldehydes including formaldehyde, acetaldehyde, glyoxal, and methylglyoxal are of particular concern due to their mutagenicity and carcinogenicity (Bull and McCabe 1984).

Molecular ozone and OH radical reactions, both of which occur during ozonation, can result in the cleavage of larger molecules. This results in lower molecular weight material and the formation of more polar compounds, which are more hydrophilic (e.g., see Amy et al. 1988; Amy et al. 1992; Flogstad and Odegaard 1985; Kaastrup and Halmo 1989; Koechling et al. 1996; Owen et al. 1995). A decrease in the concentration of UV absorbing compounds of NOM was also observed during ozonation (Amy et al. 1988; Kaastrup and Halmo 1989; Koechling et al. 1996; Shukairy et al. 1994; Yavich 1998). Some researchers found that DOC concentration was not affected at ozone-to –DOC ratios ranging between 0 and 2.5 mg O_3/mg C (Owen et al. 1995; Shukairy et al. 1994). However, Cipparone et al. (1997) observed increasing TOC removal with increasing ozone dosage concentration. Takeuchi et al (1997) observed that only partial breakage of C-C chains occurred during ozonation but that DOC did not significantly decrease. Some researchers observed that the biodegradability of ozonated water increased with increasing the ozone dose (Siddiqui et al. 1997; Somiya et al. 1986). Takahashi et al (1995) found the ratio of BOD_5/COD increased from 0.02~0.03 to 0.25 as the ratio of O_3/TOC increased from 0 to 3.5.

Replacing chlorination with ozonation as the primary disinfectant can significantly reduce the formation of THMs and HAAs. This was observed when using the chlorine or chloramine as a secondary disinfectant (Richardson et al. 1999). In the presence of NOM, ozonation results in the formation of partial oxidation compounds, which are less reactive with chlorine in forming THMs (Amy et al. 1988). The required ozone dosage and the formation of aldehydes and ketoacids increased with increasing the NOM concentration (Najm and Krasner 1995). As the ozone dosage increased, THMs and HAAs formation decreased (Cipparone et al. 1997). The ozonation of water containing humic substances results in the formation of hydroxyl, carbonyl, and carboxyl groups, and aliphatic and alicyclic ketones (Anderson et al. 1985; Glaze et al. 1989). Gracia and colleagues (1996) obatined similar results as they identified 110 different organic compounds resulting from ozonation of humic substances.

One drawback of ozonation is the formation of bromate (BrO_3^-) ion in waters containing bromide (Br^-) ion (Siddiqui and Amy 1993). Either a molecular ozone or a hydroxyl radical pathway can form bromate ion, which is mainly dependent on ozone dosage, alkalinity, and pH of the water (Najm and Krasner 1995; Siddiqui et al. 1995). Ozone can oxidize the bromide ion to form hypobromous acid (HOBr), which in turn reacts with NOM to form brominated DBPs (Richardson et al. 1999).

Factors that influence the bromate formation are initial bromide concentration, the concentration of NOM, the presence of ammonia, the pH of water, the addition of hydrogen peroxide, ozone dosage, temperature, and alkalinity (e.g., see Croue et al. 1996; Minear and Amy 1996; Siddiqui and Amy 1993; Song et al. 1997; Von Gunten and Hoigné 1996). Increasing the initial bromide concentration and ozone dosage increases the bromate concentration in treated water (Croue et al. 1996; Minear and Amy 1996; Najm and Krasner 1995). Higher dosages of ozone cause significant production of bromate ion and shifts in the speciation from brominated THMs toward chlorinated THMs (Miltner et al. 1992; Speitel et al. 1993). The formation of bromate ion also increased as the concentration of bicarbonate ion increased because of the increase of ozone stability (Croue et al. 1996). Other factors that favor bromate ion formation are low OH radical scavengers, high temperature, high alkalinity and high pH value (Siddiqui and Amy 1993; Song et al. 1997; Symons et al. 1994). Increasing the pH value results in increasing the $OBr^-/HOBr$ ratio and promoting bromate formation. Song et al. (1997) reported that pH value is a more important factor than ozone dosage that affects bromate formation.

There have been some conflicting reports relating to the effect of DOC concentration on bromate ion formation. Najm and Krasner (1995) reported that the formation of bromate ion increased with the DOC concentration. However, Siddiqui and colleagues (1995) found that DOC has been shown to decrease bromate ion formation. Similar results were obtained by Song et al (1997).

2.4.2 Membrane

The membrane process has been considered to be an effective means of removing turbidity, organics, microorganisms, and DBP precursors and to comply with the more stringent regulatory controls. It offers several advantages, compared to conventional treatment, such as i) providing high quality water, ii) minimizing disinfectant demand, iii) being more compact, iv) easier control of operation and maintenance, and v) less production of sludge (Nakatsuka et al. 1996).

A. Microfiltration

Microfiltration (MF) is a filtration process that use porous membranes to separate particles in water with pore diameters between 0.1 and 10 μm. Ultrafiltration

(UF) uses finer porous membranes, having average pore diameters between 10 and 1000 Å, to separate microsolutes and water. While MF and UF membranes can achieve effective removal of particles and microorganisms, they are not as effective in removing color and dissolved constituents.

Wiesner et al. (1991) used ceramic MF membranes with and without coagulation as a pretreatment step for waters with moderate to high turbidities and concentrations of TOC and THMFP. They reported that the removal of turbidity, UV254, TOC and THMFP were 99%, 60-87%, 48-59% and 40-65%, respectively. Significant removal of TOC could be achieved by MF alone. Scanlan et al. (1997) studied the effectiveness of MF and UF of a low turbidity, moderate color and TOC water source. They found that UF was more effective at particle removal than MF, with or without chemical addition; however, the operation times of MF were much longer than those of UF. The concentrations of THMs and HAAs in treated water did not consistently meet the Stage 2 D/DBP requirements.

B. Ultrafiltration

Two studies (Fu et al. 1994; Taylor et al. 1987) showed that NOM can be effectively rejected during filtration by low and medium pressure membranes, such as UF and NF. As NOM was removed by UF and NF, the chlorine demand of the permeate was decreased (Escobar and Randall 1999; Jacangelo et al. 1995).

Chadik et al. (1991) used several UF membranes with different nominal pore size to separate the NOM into several AMW fractions. The "reactivity", defined as the ratio of the THMFP to the nonpurgeable organic carbon (NPOC), was used to estimate the THMFP of the NOM in each AMW fraction. They found that there was no trend as to one fraction being more reactive than another and the THMFP was found to be principally associated with the concentrations of NPOC. A substantial portion of THMFP (up to 45%) was associated with the AMW fraction of less than 5000 daltons.

Jacangelo et al. (1995) evaluated the efficacy of combined powdered activated carbon (PAC) and UF for removing DBP precursors. They found that UF alone could not remove DBP precursors effectively because of its high molecular weight cutoff (MWCO). Less than 15% of the TOC and less than 10% of the THM and HAA precursors were removed in their study. However, DBP precursor removal increased with increasing PAC dosages in the combined PAC-UF treatment. Since bromide was not removed by the combined treatment, increasing of the bromide-to-TOC ratio was observed as TOC was removed by the PAC. They also reported that membrane fouling was retarded at a 30 mg/L PAC dose, but further study of the effect of PAC on membrane fouling is needed.

C. Nanofiltration

Nanofiltration (NF) is a low-pressure-driven membrane process. Compared with reverse osmosis (RO), NF yields very good rejection rates of large molecules and is much more energy efficient than RO. Several studies have demonstrated large removals of DBP precursors from ground and surface water using NF. Laîné et al. (1993) reported that NF membranes were effective for DBP precursor removal but ineffective for removing bromide, thereby resulting in increases in the bromide to TOC ratio and the proportion of brominated to chlorinated THMs.

Siddiqui and colleagues (2000) evaluated NF, UF, and MF to determine the rejection of DBP precursors from low turbidity surface waters in Colorado. They found that the average rejections of DOC, THMFP, HAAFP, and CHFP (chloral hydrate formation potential) of NF were all over 85%. MF was only moderately effective in particle removals, with virtually no DBP precursors removal provided. UF alone removed less than 30% of DOC. NF membranes with MWCO less than 300 daltons removed an average of 90% DOC. Only 40% reduction of DOC was observed on permeates of NF with 500 daltons of MWCO. Bromide rejections were among 40 and 80% in the study. Similar observations were reported by Allgeier and Summers (1995).

Lozier and Carlson (1991) evaluated ultra-low pressure membrane processes, defined as typical transmembrane pressure requirements of 150 psi or less, to treat three surface waters in the eastern U.S. with TOC and THMFP concentrations ranging from 5 to over 50 mg/L and from 400 µg/L to greater than 2,000 µg/L, respectively. They found that the NF (MWCO < 300 daltons) and the UF (MWCO = 3,000 daltons) were capable of reducing THMFP to less than 60 µg/L and TOC levels by more than 90 percent.

NF needs pretreatment to reduce its cleaning frequency and lengthen its operation time. Therefore, some utilities are considering NF as an "add-on" option to their existing facilities for DBP precursor removal before final disinfection. Chellam et al. (1997a) treated water from the Occoquan Reservoir in Virginia with MF, UF, and conventional treatment as pretreatment followed by NF. MF removed 11% and 24% of the THM and HAA precursors, respectively. NF achieved greater than 90% rejection of TOC that resulted in greater than 95% rejection of THMs and HAAs precursors. These high removals of TOC and DBP precursors were observed to be independent of membrane operating conditions, suggesting that these compounds were predominantly rejected by mechanical sieving. There was no statistical difference between TOC concentrations in the MF and UF filtrates.

Mulford et al. (1999) used similar systems that incorporated MF or UF before NF to treat water containing 11mg/L TOC, 336 μg/L SDS THMFP, 227 μg/L SDS HAAFP, and 24mg/L chlorine demand. High removal efficiencies were achieved and the average concentrations of TOC, SDS THMFP, SDS HAAFP, and chlorine demand of finished water were 0.4 mg/L, 35 μg/L, 28 μg/L, and 6.5 mg/L, respectively. Chellam et al. (1997a) observed similar results and reported that surface water treated by a dual membrane system (e.g., MF followed by NF) can meet current and anticipated THMs and HAAs regulations. DiGiano and colleagues (1993) suggested that pretreatment of the raw water before NF would be necessary in order to remove THM precursors effectively if the concentrations of THMFP in the raw water is higher than 100 μg/L.

Taylor et al. (1987) tested NF and RO membranes ranging in MWCOs from 100 to 40,000 daltons with high-color groundwaters from Florida. They found that a RO membrane with MWCO of 100 daltons removed 98% of THMFP precursors. Its removal efficiency was just a little bit higher than that of a NF membrane with MWCO of 400 daltons, which removed 96% of THMFP precursors. But the RO membrane required 60% greater pressure and produced a 50% lower flux than NF. Amy et al. (1990) observed only a 65 to 70% reduction in THMFP by using NF membrane (MWCO < 500 daltons) for treating Colorado River water. The difference in the reductions of DBP in these studies may be caused by the different characteristics of NOM.

D. Membrane Fouling

One of the major problems in membrane processes is the decrease in permeate flux to far below its theoretical capacity, resulting from membrane fouling. Decreases in flux may occur as a result of concentration polarization, formation of gel layer on the membrane surface, or adsorption or plugging of organic and inorganic materials in the membrane pores. The fouling rates are influenced by the nature of the solutes, their concentrations, membrane type and pore size distribution, water quality, hydrodynamics and surface characteristics of the membrane (Field 1996). Membrane fouling lowers the economic efficiency of membrane treatment by reducing the quantity of treated water, produced shortening membrane life, and increasing the frequency of membrane cleaning.

Organic matter is often found to be a primary source of flux decline due to fouling of membrane systems (Nilson and DiGiano 1996; Ravindran et al. 1993). Fouling may be caused by the interaction of NOM with membrane surface or incorporation into its porous support. DiGiano et al. (1994) found the fouling of UF was attributed to TOC having a molecular weight greater than 30,000 daltons.

Bonner et al. (1991) found that a hydrophobic membrane will foul to a much greater extent relative to a hydrophilic one. Larger dissolved molecules caused more fouling on hydrophilic membrane than the smaller humic material, while on the hydrophobic membrane the fouling depended upon the solution conditions.

Pretreatment of raw water can reduce membrane fouling. Moulin et al. (1991) found that without pretreatment, the membrane fouling occurred within 15 min on MF but occurred on UF after 180 min of operation time. Some researchers suggest that combining MF or UF with NF could be a feasible way to reduce NF fouling (Chellam et al. 1997b). Carroll et al. (2000) demonstrated that coagulation pretreatment improves NOM removal and reduces fouling. Siddiqui et al. (2000) and Amy et al. (1993) showed that MF followed by NF could readily meet both turbidity and DBP regulations. Other researchers ((Laine et al. 1990) observed that combined PAC and membrane decreased irreversible membrane fouling, regardless of membrane hydrophobicity. However, Lin et al. (1999) found that the combined PAC-UF system significantly decreased the flux and increased the membrane fouling.

2.4.3 Ozonation/Biotreatment

Biological treatment is frequently employed downstream of ozonation since many of the ozonation by-products are biodegradable. Biodegradation of ozonated water was shown to be an effective treatment method for increasing water biostability, removing some DBP precursors, and increasing the chlorine residual (Cipparone et al. 1997). The goals of combined ozonation and biodegradation process are not only the direct destruction of DBP precursors through ozonation, but also the conversion of precursors to more biodegradable products and the transformation of higher molecular weight compounds to lower molecular weight compounds for subsequent removal during biological treatment (Leisinger and et al. 1981; Speitel et al. 1993).

Aldehydes, which are not easily removed during flocculation/coagulation by complexation with aluminum or iron salts, and other ozonation by-products, such as organic acids and ketoacids, are biodegradable and can serve as a carbon source for bacteria for growth and cell maintenance, which potentially cause regrowth problems in distribution system. The regrowth of bacteria in distribution systems can result in the formation of biofilms, unpleasant taste, odors, and color, and also result in biologically mediated corrosion and interference with microbiological monitoring (Lee et al. 1980; Miltner et al. 1992; Schechter and Singer 1995). In order to remove BDOC and prevent the occurrence of these problems, biotreatment methods such as biological activated carbon (BAC) and biofiltration following ozone treatment are employed in the water treatment process. Kasarabada (1997), Mellema (1998) and

Yavich (1998) used a combination of ozonation and biological fluidized bed treatment (FBT) system to investigate the removal efficiency of NOM. They found that the biodegradability of NOM increased after ozonation. They also reported that using the combined ozonation/FBT system for controlling the THM precursors in drinking water is technically and economically feasible.

Several researchers investigated the correlation between ozone dosage and biodegradability. An increase in biodegradability with increasing ozone dose was observed (Goel et al. 1995; Kasarabada 1997; Yavich 1998). Somyia and coworkers (1986) used the ratio of BOD/TOC versus the ratio of O_3/TOC to represent the change in biodegradability during ozonation. They ozonated humic acids samples and found that the amount of BOD degraded by microbes increased with an increase in ozonation dosage and gradually leveled off after an ozone dose of 2 mg O_3/mg TOC. Other researchers (Cipparone et al. 1997; Miltner et al. 1992; Shukairy et al. 1995; Siddiqui et al. 1997) observed the same trend but the extent of removal of DOC improved with increasing ozone dosage up to an O_3-to-DOC ratio of almost 1 mg O_3/mg TOC, after which the biodegradability was not significantly improved by ozonation. This may be caused by the different composition of NOM in different water sources.

As a result of the combined ozonation/biotreatment process, DBP formation potential is significantly reduced because the DOC concentration is reduced by biodegradation, and the reactivity of organic matter to subsequent chlorination can also be decreased (e.g., see Amy et al. 1988; Cipparone et al. 1997; Kasarabada 1997; Miltner et al. 1992; Shukairy et al. 1995; Yavich 1998). Yavich (1998) reported that the pilot scale ozonation/FBT system was able to remove up to 70% of THMFP at an EBCT of 180 minutes and ozone dose at 2 mg O_3/mg C. Siddiqui and colleagues

(1997) found the formation potentials of THMs, HAAs, and chloral hydrate were reduced by as much as 70 to 80% using ozonation-biofiltration treatment at an ozone dosage of 1.5 O_3 mg/mg DOC. They also observed a 40 to 50% decrease in DOC, and a 90 to 100% reduction in aldehydes after 5 days of biofiltration of ozonated water. Similar aldehydes removal efficiencies have been observed by several other researchers (Sketchell et al. 1995; Van Hoof and et al. 1986). Richardson and colleagues (1999) studied the effect of biofiltration on ozonation by-products. They found that 45 to 90% of carboxylic acids, approximately 50% of the AOC, 35 to 95% of aldehydes, ketones, and aldo and keto acids were removed by biofiltration. Combined ozonation and biodegradation process removed up to 50% of THM precursors and up to 70% of HAA precursors (Speitel et al. 1993).

The bromate ion, formed during ozonation, is a toxic inorganic compound. Miltner and colleagues (1992) found that biodegradation was less effective for controlling the formation of brominated compounds. However, Kirisits and Snoeyink (1999) showed that bromate removal efficiencies of up to 95% can be achieved if the influent dissolved oxygen (DO) concentration, nitrate concentration, and empty bed contact time (EBCT) are suitably controlled. In their study, bromate removal in the BAC column increased as the influent DO concentration was reduced from 8.0 to 4.5 mg/L or as the influent nitrate concentration was reduced. Higher bromate reduction was also observed at longer EBCTs. This may be caused by decreasing the hydraulic loading on the BAC column, then inducing an increase in the numbers of microorganisms.

2.4.4 Ozonation/Membrane

Few studies have been performed with the combination of ozonation and membrane processes since organic membranes, which have relatively large surface area per volume and are widely used in water and wastewater treatment, are prone to destruction by ozone. Several researchers (Castro and Zander 1995; Shanbhag et al. 1998; Shen et al. 1990) reported that membranes were damaged during ozone contacting and high replacement costs would be likely required. Thus, the use of ozonation processes in conjunction with membrane devices is an area that has yet to see much development. However, the ozonation/membrane process was found to be able to maintain high and stable permeate flux, reduce membrane fouling, and increasing ozone mass transfer efficiency.

In order to prevent the damage of membrane by ozone, a retention or aeration tank is often used between ozonation and the membrane module, allowing for stripping of residual ozone. Hyung and colleagues (2000) investigated the effect of ozonation on membrane flux and water quality in an ozonation/UF hybrid system. Water samples were collected from two unidentified locations in the Han River. Ozonated water was retained for one hour before being used as feed water to UF. They found that with the upstream water ozonation enhanced membrane flux regardless of ozone dose; whereas, for the downstream water, the membrane flux was increased or decreased depending on the ozone dose. About 22% of TOC, 64% of UV254, and 36-53% of TOC precursors were removed by this hybrid system and the ratio of THMFP/TOC was also decreased from 31.3 μg/mg of raw water to 19.7 μg/mg of permeate of the hybrid system at 9.4 mg/L ozone dose. O'Connell and Danos (1997) used a similar system to treat well water with elevated levels of iron and manganese. High removal rates, 97% of the iron and 91% of the manganese, were achieved and the quality of permeate remained consistent despite the fluctuation of feed quality.

Ozonation has proven to prevent foulants from adhering to the membrane surface, thereby decreasing membrane fouling. Hashino et al. (2000) reported that using a combined ozonation with an ozone resistant MF which is made of polyvinylidenefluoride (PVDF), high dissolved ozone concentrations on the membrane surface were necessary to obtain high permeate fluxes and to prevent membrane fouling. Kim and colleagues (1999) investigated the effect of ozone bubbling on flux recovery of ceramic membrane. The results showed that intermittent ozonation is effective for maintaining high permeation flux and to prevent membrane fouling caused by particle accumulation on the membrane surface.

Increasing the ozone mass transfer efficiency from gas to liquid phase is one of the benefits of the combined ozonation/membrane system. Usually, bubble columns, packed towers, staged towers, spray towers, and venturi scrubbers are conventionally used to achieve ozone mass transfer but their efficiencies are not very good. Shen and Semens (1990) investigated the ozone mass transfer coefficient (K_L) and specific interfacial area (a) of an ozonation/MF system. Comparing the volumetric mass transfer coefficient (K_La) values of bubble columns collected from the literature, they found that the hybrid system had the highest K_La value (by up to a factor of 110). This means that the hybrid system shows promise for efficiently transferring ozone.

In recent years, ceramic membranes have gained more attention because they can resist chemical corrosion and oxidation, extreme pH values, and have a high range of operating temperatures. Several researchers found that the combined ozonation and ceramic membrane process can achieve a high permeate flux (Kim et al.

1999; Moulin et al. 1991). No membrane damage was observed. Ozone transfer through various ceramic membranes was also investigated by Janknecht and colleagues (2000). They observed that the ceramic membrane with hydrophobic coating has much higher ozone mass transfer rates than that without hydrophobic coating. The mass transfer rates, surprisingly, were not adversely affected by the decay of ozone within the membrane. The energy demand of this system is in the same order of magnitude as the bubble column but the required contactor volume is smaller.

2.5 REFERENCES

Allgeier, S. C., and Summers, R. S. (1995). "Evaluating Nf for Dbp Control with the Rbsmt." *Journal American Water Works Association*, 87(3), 87-99.

Amy, G., Siddiqui, M., Ryan, J., Odem, W., Hendricks, D., and Champlin, T. (1993). "Membrane Separation of DBP Precursors from Low-Turbidity Surface Waters." Proc. 1993 Membrane Technology Conf., Baltimore, Md., 651-663.

Amy, G. L., Alleman, B. C., and Cluff, C. B. (1990). "Removal of Dissolved Organic-Matter by Nanofiltration." *Journal of Environmental Engineering-Asce*, 116(1), 200-205.

Amy, G. L., Kuo, C. J., and Sierka, R. A. (1988). "Ozonation of Humic Substances - Effects on Molecular-Weight Distributions of Organic-Carbon and Trihalomethane Formation Potential." *Ozone-Science & Engineering*, 10(1), 39-54.

Amy, G. L., Sierka, R. A., Bedessem, J., Price, D., and Tan, L. (1992). "Molecular-Size Distributions of Dissolved Organic-Matter." *Journal American Water Works Association*, 84(6), 67-75.

Anderson, L. J., Johnson, J. D., and Christman, R. F. (1985). "The Reaction of Ozone with Isolated Aquatic Fulvic-Acid." *Organic Geochemistry*, 8(1), 65-69.

Andrews, R. C., and Ferguson, M. J. (1996). "Minizing Disinfection By-Product Formation while Ensuring Giardia Control." Disinfection By-products in Water Treatment., R. A. Minear and G. L. Amy, eds., Lewis Publisher, Boca Raton, FL., 17-55.

Bablon, G., Bellamy, W. D., Bourbigot, M.-M., Daniel, F. B., Dore, M., Erb, F., Gordon, G., Langlais, B., Laplanche, A., Legube, B., Martin, G., Masschelein, W. J., Pacey, G., Reckhow, D. A., and Ventresque, C. (1991a). "Practical Application of Ozone: Principles and Case Studies." Ozone in Water Treatment: Application and Engineering, B. Langlais, D. A. Reckhow, and D. R. Brink, eds., Lewis Publisher, Chelsea, MI, 133-316.

Bablon, G., Bellamy, W. D., Bourbigot, M.-M., and et. al. (1991b). "Fundamental Aspects." Ozone in Water Treatment: Application and Engineering, B. Langlais, D. A. Reckhow, and D. R. Brink, eds., Lewis Publishers, Chelsea, MI, 11-132.

Bonner, F. A., II, and O'Melia, C. R. (1991). "Some Aspects of the Fouling of Ultrafiltration Membranes by Natural Organic Matter in Water Treatment." Proc. 1991 Membrane Technologies in the Water Industry, Orlando, Florida, 239-251.

Bouwer, E. J., and Crowe, P. B. (1988). "Biological Processes in Drinking-Water Treatment." *Journal American Water Works Association*, 80(9), 82-93.

Bull, R. J., and McCabe, L. J. (1984). "Risk Assessment Issues in Evaluating the Health Effects of Alternate Means of Drinking Water Disinfection." Water Chlorination: Chemistry, Environmental Impact, and Health Effects, R. L. Jolley and e. al., eds., Lewis Publishers, Chelsea, Mich.

Carroll, T., King, S., Gray, S. R., Bolto, B. A., and Booker, N. A. (2000). "The fouling of microfiltration membranes by NOM after coagulation treatment." *Water Research*, 34(11), 2861-2868.

Castro, K., and Zander, A. K. (1995). "Membrane Air-Stripping - Effects of Pretreatment." *Journal American Water Works Association*, 87(3), 50-61.

Chadik, P. A., and Amy, G. L. (1983). "Removing Trihalomethane Precursors from Various Natural-Waters by Metal Coagulants." *Journal American Water Works Association*, 75(10), 532-536.

Chadik, P. A., and Amy, G. L. (1987). "Coagulation and Adsorption of Aquatic Organic Matter and Humic Substances: An Analysis of Surrogate Parameters for Predicting Effects on Trihalomethane Formation Potential." Envir. Tech. Letters, 261.

Chadik, P. A., Pujals, V. J., and Fisher, J. H. (1991). "Removal of Natural Organic Matter and Reduction of THM Formation Potential in Florida Waters with Ultrafiltration." Proc. 1991 Membrane Technologies in the Water Industry, Orlando, Florida, 289-303.

Charnock, C., and Kjonno, O. (2000). "Assimilable organic carbon and biodegradable dissolved organic carbon in Norwegian raw and drinking waters." *Water Research*, 34(10), 2629-2642.

Chellam, S., Jacangelo, J. G., Bonacquisti, T. P., and Long, B. W. (1997a). "Effect Operating Conditions and Pretreatment for Nanofiltration of Surface Water." Proc. 1997 Membrane Technology Conf., New Orleans, LA, 215-231.

Chellam, S., Jacangelo, J. G., Bonacquisti, T. P., and Schauer, B. A. (1997b). "Effect of pretreatment on surface water nanofiltration." *Journal American Water Works Association*, 89(10), 77-89.

Christman, R. F., Norwood, D. L., Millington, D. S., Johnson, J. D., and Stevens, A. A. (1983). "Identity and Yields of Major Halogenated Products of Aquatic Fulvic-Acid Chlorination." *Environmental Science & Technology*, 17(10), 625-628.

Cipparone, L. A., Diehl, A. C., and Speitel, G. E. (1997). "Ozonation and BDOC removal: Effect on water quality." *Journal American Water Works Association*, 89(2), 84-97.

Collins, M. R., Amy, G. L., and Steelink, C. (1986). "Molecular-Weight Distribution, Carboxylic Acidity, and Humic Substances Content of Aquatic Organic-Matter - Implications for Removal During Water-Treatment." *Environmental Science & Technology*, 20(10), 1028-1032.

Croue, J. P., Koudjonou, B. K., and Legube, B. (1996). "Parameters affecting the formation of bromate ion during ozonation." *Ozone-Science & Engineering*, 18(1), 1-18.

DiGiano, F. A., Braghetta, A., Uten, B., and Nilson, J. (1993). "Nanofiltration Fouling by Natural Organic Matter and Role of Particles in Flux Enhancement." Proc. 1993 Membrane Technology Conf., Baltimore, Md, 273-291.

DiGiano, F. A., and et al. (1994). "Fouling of Nanofiltration Membranes by Natural Organic Matter." Proc. 1994 ASCE Natl. Conf. On Envir. Engrg., Boulder, Colo.

Escobar, I. C., and Randall, A. A. (1999). "Influence of NF on distribution system biostability." *Journal American Water Works Association*, 91(6), 76-89.

Field, R. W. (1996). "Mass Transport and the Design of Membrane Systems." Industrial Membrane Separation Technology, K. Scott and R. Hughes, eds., Blackie Academic & Professional, Glasgow, UK.

Flogstad, H., and Odegaard, H. (1985). "Treatment of Humic Waters by Ozone." *Ozone-Science & Engineering*, 7(2), 121-136.

Fox, K. R., and Lytle, D. A. (1996). "Milwaukee's crypto outbreak: Investigation and recommendations." *Journal American Water Works Association*, 88(9), 87-94.

Frimmel, F. H. (1998). "Characterization of natural organic matter as major constituents in aquatic systems." *Journal of Contaminant Hydrology*, 35(1-3), 201-216.

Frost, F. J., Craun, G. F., and Calderon, R. L. (1996). "Waterborne disease surveillance." *Journal American Water Works Association*, 88(9), 66-75.

Fu, P., Ruiz, H., Thompson, K., and Spangenberg, C. (1994). "Selecting Membranes for Removing Nom and Dbp Precursors." *Journal American Water Works Association*, 86(12), 55-72.

Glaze, W. H., Koga, M., Cancilla, D., Wang, K., McGuire, M. J., Sun, L. A., Davis, M. K., Tate, C. H., and Aieta, E. M. (1989). "Evaluation of Ozonation by-Products from 2 California Surface Waters." *Journal American Water Works Association*, 81(8), 66-73.

Glaze, W. H., Koga, M., Ruch, E. C., and Cancilla, D. (1988). "Application of Closed Loop Stripping and XAD Resin Adsorption for the Determination of Ozone By-products from Natural Water." Biohazards of Drinking Water Treatment, 201-210.

Glaze, W. H., Weinberg, H. S., and Cavanagh, J. E. (1993). "Evaluating the Formation of Brominated Dbps During Ozonation." *Journal American Water Works Association*, 85(1), 96-103.

Goel, S., Hozalski, R. M., and Bouwer, E. J. (1995). "Biodegradation of Nom - Effect of Nom Source and Ozone Dose." *Journal American Water Works Association*, 87(1), 90-105.

Gracia, R., Aragues, J. L., and Ovelleiro, J. L. (1996). "Study of the catalytic ozonation of humic substances in water and their ozonation byproducts." *Ozone-Science & Engineering*, 18(3), 195-208.

Haag, W. R., and Hoigné, J. (1983). "Ozonation of Bromide-Containing Waters - Kinetics of Formation of Hypobromous Acid and Bromate." *Environmental Science & Technology*, 17(5), 261-267.

Haag, W. R., and Yao, C. C. D. (1992). "Rate Constants for Reaction of Hydroxyl Radicals with Several Drinking-Water Contaminants." *Environmental Science & Technology*, 26(5), 1005-1013.

Hashino, M., Mori, Y., Fujii, Y., Motoyama, N., Kadokawa, N., Hoshikawa, H., Nishijima, W., and Okada, M. (2000). "Pilot plant evaluation of an ozone-microfiltration system for drinking water treatment." *Water Science and Technology*, 41(10-11), 17-23.

Hoigné, J., and Bader, H. (1975). "Ozonation of Water: Role of Hydroxyl Radicals as Oxidizing Agents." *Science*, 190, 782-784.

Hoigné, J., and Bader, H. (1983). "Rate Constants of Reactions of Ozone with Organic and Inorganic-Compounds in Water .1. Non-Dissociating Organic-Compounds." *Water Research*, 17(2), 173-183.

Huck, P. M. (1990). "Measurement of Biodegradable Organic-Matter and Bacterial-Growth Potential in Drinking-Water." *Journal American Water Works Association*, 82(7), 78-86.

Hyung, H., Lee, S., Yoon, J., and Lee, C. H. (2000). "Effect of preozonation on flux and water quality in ozonation- ultrafiltration hybrid system for water treatment." *Ozone-Science & Engineering*, 22(6), 637-652.

Ichihashi, K., Teranishi, K., and Ichimura, A. (1999). "Brominated trihalomethane formation in halogenation of humic acid in the coexistence of hypochlorite and hypobromite ions." *Water Research*, 33(2), 477-483.

Jacangelo, J. G., Laine, J. M., Cummings, E. W., and Adham, S. S. (1995). "Uf with Pretreatment for Removing Dbp Precursors." *Journal American Water Works Association*, 87(3), 100-112.

Janknecht, P., Wilderer, P. A., Picard, C., Larbot, A., and Sarrazin, J. (2000). "Investigations on ozone contacting by ceramic membranes." *Ozone-Science & Engineering*, 22(4), 379-392.

Joret, J. C., Levi, Y., Dupin, T., and Gilbert, M. (1988). "Rapid Method for Estimating Bioeliminable Organic Carbon in Water." Proc. 1988 AWWA Ann. Conf., Orlando, Florida, 1715-1725.

Joret, J. C., Levi, Y., and Volk, C. (1991). "Biodegradable Dissolved Organic-Carbon (Bdoc) Content of Drinking-Water and Potential Regrowth of Bacteria." *Water Science and Technology*, 24(2), 95-101.

Kaastrup, E., and Halmo, T. M. (1989). "Removal of Aquatic Humus by Ozonation and Activated Carbon Adsorption." Aquatic Humic Substances: Influence on Fate and Treatment of Pollutants, I. H. Suffet and P. MacCarthy, eds., American Chemical Society, Washington, DC., 697-726.

Kasarabada, A. N. (1997). "Use of THMFP, TOC and Chlorine Demand as Control Parameters for Monitoring the Performance of an Ozonation/FBT System," M.S. Thesis, Michigan State University.

Kim, J. O., Somiya, I., and Fujii, S. (1999). "Fouling Control of Ceramic Membrane in Organic Acid Fermenter by Intermittent Ozonation." Proceedings of the 14th Ozone World Congress, Dearborn, MI, 131-143.

Kim, J. S., Chian, E. S. K., Saunders, F. M., Michael Perdue, E., and Giabbai, M. F. (1989). "Characteristics of Humic Substances and Their Removal Behavior in Water Treatment." Aquatic Humic Substances: Influence on Fate and Treatment of Pollutants, I. H. Suffet and P. MacCarthy, eds., American Chemical Society, Washington, DC., 473-497.

Kirisits, M. J., and Snoeyink, V. L. (1999). "Reduction of bromate in a BAC filter." *Journal American Water Works Association*, 91(8), 74-84.

Koechling, M. T., Shukairy, H. M., and Summers, R. S. (1996). "Effect of Ozonation and Biotreatment on Molecular Size and Hydrophilic Fractions of Natural Organic Matter." Water Disinfection and Natural Organic Matter: Characterization and Control, R. A. Minear and G. L. Amy, eds., American Chemical Society, Washington, DC., 196-210.

Korshin, G. V., Perry, S. A. L., and Ferguson, J. F. (1996). "Influence of NOM on copper corrosion." *Journal American Water Works Association*, 88(7), 36-47.

Kramer, M. H., Herwaldt, B. L., Craun, G. F., Calderon, R. L., and Juranek, D. D. (1996). "Waterborne disease: 1993 and 1994." *Journal American Water Works Association*, 88(3), 66-80.

Krasner, S. W., Croue, J. P., Buffle, J., and Perdue, E. M. (1996a). "Three approaches for characterizing NOM." *Journal American Water Works Association*, 88(6), 66-79.

Krasner, S. W., Sclimenti, M. J., Chinn, R., Chowdhury, Z. K., and Owen, D. M. (1996b). "The Impact of TOC and Bromide on Chlorination By-Product Formation." Disinfection By-products in Water Treatment, R. A. Minear and G. L. Amy, eds., Lewis Publisher, Boca Raton, FL., 59-90.

Laine, J. M., Clark, M. M., and Mallevialle, J. (1990). "Ultrafiltration of Lake Water - Effect of Pretreatment on the Partitioning of Organics, Thmfp, and Flux." *Journal American Water Works Association*, 82(12), 82-87.

Laine, J. M., Jacangelo, J. G., Cummings, E. W., Carns, K. E., and Mallevialle, J. (1993). "Influence of Bromide on Low-Pressure Membrane Filtration for Controlling Dbps in Surface Waters." *Journal American Water Works Association*, 85(6), 87-99.

LeChevallier, M. W., Abbaszadegan, M., Camper, A. K., Hurst, C. J., Izaguirre, G., Marshall, M. M., Naumovitz, D., Payment, P., Rice, E. W., Rose, J., Schaub, S., Slifko, T. R., Smith, D. B., Smith, H. V., Sterling, C. R., and Stewart, M. (1999a). "Committee report: Emerging pathogens - bacteria." *Journal American Water Works Association*, 91(9), 101-109.

LeChevallier, M. W., Abbaszadegan, M., Camper, A. K., Hurst, C. J., Izaguirre, G., Marshall, M. M., Naumovitz, D., Payment, P., Rice, E. W., Rose, J., Schaub, S., Slifko, T. R., Smith, D. B., Smith, H. V., Sterling, C. R., and Stewart, M. (1999b). "Committee report: Emerging pathogens - viruses, protozoa, and algal toxins." *Journal American Water Works Association*, 91(9), 110-121.

Lee, S. H., Oconnor, J. T., and Banerji, S. K. (1980). "Biologically Mediated Corrosion and Its Effects on Water- Quality in Distribution-Systems." *Journal American Water Works Association*, 72(11), 636-645.

Leenheer, J. A. (1981). "Comprehensive Approach to Preparative Isolation and Fractionation of Dissolved Organic-Carbon from Natural-Waters and Wastewaters." *Environmental Science & Technology*, 15(5), 578-587.

Leenheer, J. A. (1985). "Fractionation Techniques for Aquatic Humic substances." Humic Substances in Soil, Sediment, and Water, G. Aiken and e. al., eds., Wiley-Interscience, New York, 409-429.

Leisinger, T., and et al. (1981). *Microbial Degradation of Xenobiotics and Recalcitrant Compounds*, Academic Press, London, England.

Leppard, G. G. (1992). "Evaluation of Electron Microscope Techniques for the Description of Aquatic Colloids." Environmental Particles, J. Buffle and H. P. van Leeuwen, eds., Lewis Publisher, Boca Raton, FL., 231-290.

Levy, R. V., Hart, F. L., and Cheetham, R. D. (1986). "Occurrence and Public-Health Significance of Invertebrates in Drinking-Water Systems." *Journal American Water Works Association*, 78(9), 105-110.

Liao, W., Christman, R. F., Johnson, J. D., Millington, D. S., and Hass, J. R. (1982). "Structural Characterization of Aquatic Humic Material." *Environmental Science & Technology*, 16(7), 403-410.

Lin, C. F., Huang, Y. J., and Hao, I. J. (1999). "Ultrafiltration processes for removing humic substances: Effect of molecular weight fractions and PAC treatment." *Water Research*, 33(5), 1252-1264.

Lozier, J. C., and Carlson, M. (1991). "Organics Removal from Eastern U.S. Surface Waters Using Ultra-Low Pressure Membranes." Proc. 1991 Membrane Technologies in the Water Industry, Orlando, Florida, 521-543.

MacCarthy, P., and Suffet, I. H. (1989). "Aquatic Humic Substances and Their Influence on the Fate and Treatment of Pollutants." Aquatic Humic Substances: Influence on Fate and Treatment of Pollutants, I. H. Suffet and P. MacCarthy, eds., American Chemical Society, Washington, DC., xvii-xxx.

Maggiolo, A. (1978). "Ozone's Radical and Ionic Mechanisms of Reaction with Organic Compounds in Water." Ozone/Chlorine Dioxide Oxidation Products of Organic Materials, R. G. Rice and J. A. Cotruvo, eds., Ozone Press Intl., Cleveland, Ohio.

Malcolm, R. L. (1985). "Geochemistry of Stream fulvic and Humic Substances." Humic Substances in Soil, Sediment, and Water, G. R. Aiken, D. M. McKnight, R. L. Wershaw, and P. MacCarthy, eds., John Wiley & Sons., New York, 181-209.

Manahan, S. E. (1993). "Environmental Chemistry of Water." Fundamentals of Environmental Chemistry, Lewis Publisher, Chelsea, MI., 388-390.

Martin-Mousset, B., Croue, J. P., Lefebvre, E., and Legube, B. (1997). "Distribution and characterization of dissolved organic matter of surface waters." *Water Research*, 31(3), 541-553.

McGuire, M. J., and Meadow, R. G. (1988). "Awwarf Trihalomethane Survey." *Journal American Water Works Association*, 80(1), 61-68.

Mellema, J. A. (1998). "The Use of Apparent Molecular Weight Distribution to Evaluate the Transformation of Natural Organic Matter During Ozonation and Biological Treatment," M.S. Thesis, Michigan State University, East Lansing, MI.

Miltner, R. J., Shukairy, H. M., and Summers, R. S. (1992). "Disinfection by-Product Formation and Control by Ozonation and Biotreatment." *Journal American Water Works Association*, 84(11), 53-62.

Minear, R. A., and Amy, G. L. (1996). "Water Disinfection and Natural Organic Matter: History and Overview." Water Disinfection and Natural Organic Matter: Characterization and Control, R. A. Minear and G. L. Amy, eds., American Chemical Society, Washington, DC., 1-9.

Mogren, E. M., Scarpino, P., and Summers, R. S. (1990). "Measurement of Biodegradable Dissolved Organic Carbon in Drinking Water." Proc. 1990 AWWA Ann. Conf., Cincinnati, Ohio, 573.

Moore, A. C., Herwaldt, B. L., Craun, G. F., Calderon, R. L., Highsmith, A. K., and Juranek, D. D. (1994). "Waterborne Disease in the United-States, 1991 and 1992." *Journal American Water Works Association*, 86(2), 87-99.

Moulin, C., Bourbigot, M. M., Tazi-Pain, A., and Faivre, M. (1991). "Potanilisation of Surface Waters by Crossflow Ultra- and Microfiltration on Mineral Membranes: Interest of Ozone." Proc. 1991 Membrane Technologies in the Water Industry, Orlando, Florida, 729-737.

Mulford, L. A., Taylor, J. S., Nickerson, D. M., and Chen, S. S. (1999). "NF performance at full and pilot scale." *Journal American Water Works Association*, 91(6), 64-75.

Najm, I. N., and Krasner, S. W. (1995). "Effects of Bromide and Nom on by-Product Formation." *Journal American Water Works Association*, 87(1), 106-115.

Nakatsuka, S., Nakate, I., and Miyano, T. (1996). "Drinking water treatment by using ultrafiltration hollow fiber membranes." *Desalination*, 106(1-3), 55-61.

Nieminski, E. C., and Ongerth, J. E. (1995). "Removing Giardia and Cryptosporidium by Conventional Treatment and Direct-Filtration." *Journal American Water Works Association*, 87(9), 96-106.

Nilson, J. A., and DiGiano, F. A. (1996). "Influence of NOM composition on nanofiltration." *Journal American Water Works Association*, 88(5), 53-66.

O'Connell, J., and Danos, S. (1997). "An Innovative Combination of Ozonation and Ultrafiltration." Proc. 1997 Membrane Technologies Conf., New Orleans, LA., 1127-1145.

Owen, D. M., Amy, G. L., Chowdhury, Z. K., Paode, R., McCoy, G., and Viscosil, K. (1995). "Nom - Characterization and Treatability." *Journal American Water Works Association*, 87(1), 46-63.

Oxenford, J. L. (1996). "Disinfection By-Products: Current Practices and Future Directions." Disinfection By-products in Water Treatment, R. A. Minear and G. L. Amy, eds., Lewis Publisher, Boca Raton, FL., 3-16.

Paode, R. D., Amy, G. L., Krasner, S. W., Summers, R. S., and Rice, E. W. (1997). "Predicting the formation of aldehydes and BOM." *Journal American Water Works Association*, 89(6), 79-93.

Peleg, M. (1976). "The Chemistry of Ozone in the Treatment of Water." Wat. Res., 361-365.

Pemberton, S. G., and Jones, B. (1999). "Ichnology of the pleistocene ironshore formation, Grand Cayman Island, British West-Indies." *Journal of Paleontology*, 62(4), 495.

Perdue, E. (1985). "Acidic Functional Groups of Humic Substances." Humic Substances in Soil, Sediment, and Water, G. Aiken and e. al., eds., Wiley-Interscience, New York.

Preston, C. M. (1987). NMR of Humic Substances and Coal. Techniques, Problems and Solutions, R. L. Wershaw and M. A. Mikita, eds., Lewis, Chelsea, 3-32.

Ravindran, V., Badriyha, B. N., and Pirbazari, M. (1993). "Crossflow Membrane Filtration for the Removal of Natural Organic Matter." Proc. 1993 Membrane Technology Conf., Baltimore, Md., 587-599.

Reckhow, D. A., and Singer, P. C. (1990). "Chlorination by-Products in Drinking Waters - from Formation Potentials to Finished Water Concentrations." *Journal American Water Works Association*, 82(4), 173-180.

Reckhow, D. A., Singer, P. C., and Malcolm, R. L. (1990). "Chlorination of Humic Materials - by-Product Formation and Chemical Interpretations." *Environmental Science & Technology*, 24(11), 1655-1664.

Rencken, G. E. (1994). "Ozonation at Wiggins-Water-Purification-Works, Durban, South- Africa." *Ozone-Science & Engineering*, 16(3), 247-260.

Richardson, S. D., Thruston, A. D., Caughran, T. V., Chen, P. H., Collette, T. W., Floyd, T. L., Schenck, K. M., Lykins, B. W., Sun, G. R., and Majetich, G. (1999). "Identification of new ozone disinfection byproducts in drinking water." *Environmental Science & Technology*, 33(19), 3368-3377.

Rittmann, B. E. (1995). "Fundamentals and Application of Biofilm Processes in Drinking Water Treatment." The Handbook of Environmental Chemistry, 61-87.

Rook, J. J. (1974). "Formation of Haloforms During Chlorination of Natural Waters." J. Water Treat. Exam., 234.

Rook, J. J., Gras, A. A., Vanderheijden, B. G., and Wee, J. D. (1978). "Bromide Oxidation and Organic Substitution in Water Treatment." *Journal of Environmental Science and Health Part a- Environmental Science and Engineering & Toxic and Hazardous Substance Control*, 13(2), 91-116.

Scanlan, P., Pohlman, B., Freeman, S., Spillman, B., and Mark, J. (1997). "Membrane Filtration for the Removal of Color and TOC from Surface Water." Proc. 1997 Membrane Technology Conf., New Orleans, LA., 127-141.

Schechter, D. S., and Singer, P. C. (1995). "Formation of Aldehydes During Ozonation." *Ozone-Science & Engineering*, 17(1), 53-69.

Servais, P., Billen, G., and Hascoet, M. C. (1987). "Determination of the Biodegradable Fraction of Dissolved Organic-Matter in Waters." *Water Research*, 21(4), 445-450.

Servais, P., Laurent, P., and Randon, G. (1993). "Impact of Biodegradable Dissolved Organic Carbon (BDOC) on Bacterial Dynamics in Distribution Systems." Proc. 1993 AWWA WQTC, Miami, Florida, 963-979.

Shanbhag, P. V., Guha, A. K., and Sirkar, K. K. (1998). "Membrane-based ozonation of organic compounds." *Industrial & Engineering Chemistry Research*, 37(11), 4388-4398.

Shen, Z. S., Semmens, M. J., and Collins, A. G. (1990). "A Novel-Approach to Ozone Water Mass-Transfer Using Hollow Fiber Reactors." *Environmental Technology*, 11(7), 597-608.

Shukairy, H. M., Miltner, R. J., and Summers, R. S. (1994). "Bromides Effect on Dbp Formation, Speciation, and Control .1. Ozonation." *Journal American Water Works Association*, 86(6), 72-87.

Shukairy, H. M., Miltner, R. J., and Summers, R. S. (1995). "Bromides Effect on Dbp Formation, Speciation and Control .2. Biotreatment." *Journal American Water Works Association*, 87(10), 71-82.

Shukairy, H. M., and Summers, R. S. (1992). "The Impact of Preozonation and Biodegradation on Disinfection by-Product Formation." *Water Research*, 26(9), 1217-1227.

Siddiqui, M., Amy, G., Ryan, J., and Odem, W. (2000). "Membranes for the control of natural organic matter from surface waters." *Water Research*, 34(13), 3355-3370.

Siddiqui, M. S., and Amy, G. L. (1993). "Factors Affecting Dbp Formation During Ozone Bromide Reactions." *Journal American Water Works Association*, 85(1), 63-72.

Siddiqui, M. S., Amy, G. L., and Murphy, B. D. (1997). "Ozone enhanced removal of natural organic matter from drinking water sources." *Water Research*, 31(12), 3098-3106.

Siddiqui, M. S., Amy, G. L., and Rice, R. G. (1995). "Bromate Ion Formation - a Critical-Review." *Journal American Water Works Association*, 87(10), 58-70.

Singer, P. C. (1994). "Control of Disinfection by-Products in Drinking-Water." *Journal of Environmental Engineering-Asce*, 120(4), 727-744.

Singer, P. C., Obolensky, A., and Greiner, A. (1995). "Dbps in Chlorinated North-Carolina Drinking Waters." *Journal American Water Works Association*, 87(10), 83-92.

Sketchell, J., Peterson, H. G., and Christofi, N. (1995). "Disinfection by-Product Formation after Biologically Assisted Gac Treatment of Water-Supplies with Different Bromide and Doc Content." *Water Research*, 29(12), 2635-2642.

Solo-Gabriele, H., and Neumeister, S. (1996). "US outbreaks of cryptosporidiosis." *Journal American Water Works Association*, 88(9), 76-86.

Somiya, I., Yamada, H., Nozawa, E., and Mohri, M. (1986). "Biodegradability and Gac Adsorbability of Micropollutants by Preozonation." *Ozone-Science & Engineering*, 8(1), 11-26.

Song, R., Westerhoff, P., Minear, R., and Amy, G. (1997). "Bromate minimization during ozonation." *Journal American Water Works Association*, 89(6), 69-78.

Speitel, G. E., Jr., Symons, J. M., Diehl, A. C., Sorensen, H. W., and Cipparone, L. A. (1993). "Effect of Ozone Dosage and Subsequent Biodegradation on Removal of Dbp Precursors." *Journal American Water Works Association*, 85(5), 86-95.

Staehelin, J., and Hoigné, J. (1985). "Decomposition of Ozone in Water in the Presence of Organic Solutes Acting as Promoters and Inhibitors of Radical Chain Reactions." *Environmental Science & Technology*, 19(12), 1206-1213.

Stevenson, F. J. (1985). "Geochemistry of Soil Humic Substances." Humic Substances in Soil, Sediment, and Water, G. R. Aiken, D. M. McKnight, R. L. Wershaw, and P. MacCarthy, eds., John Wiley & Sons., New York, 13-52.

Stevenson, F. J. (1994). "Humus Chemistry: Genesis, Composition, Reactions." John Wiley & sons. Inc., 48-53.

Symons, J. M., Speitel, G. E., Diehl, A. C., and Sorensen, H. W. (1994). "Precursor Control in Waters Containing Bromide." *Journal American Water Works Association*, 86(6), 48-60.

Takahashi, N., Nakai, T., Satoh, Y., and Katoh, Y. (1995). "Ozonolysis of Humic-Acid and Its Effect on Decoloration and Biodegradability." *Ozone-Science & Engineering*, 17(5), 511-525.

Takeuchi, Y., Mochidzuki, K., Matsunobu, N., Kojima, R., Motohashi, H., and Yoshimoto, S. (1997). "Removal of organic substances from water by ozone treatment followed by biological activated carbon treatment." *Water Science and Technology*, 35(7), 171-178.

Taylor, J. S., Thompson, D. M., and Carswell, J. K. (1987). "Applying Membrane Processes to Groundwater Sources for Trihalomethane Precursor Control." *Journal American Water Works Association*, 79(8), 72-82.

Texier, J. P., Huxtable, J., Rhodes, E., Miallier, D., and Ousmoi, M. (1998). "New data on the chronological situation of the aterian of Morocco and their implications." *Comptes Rendus De L Academie Des Sciences Serie Ii Mecanique Physique Chimie Sciences De L Univers Sciences De La Terre*, 88(8), 124-140.

Thurman, E. M. (1985). "Humic Substances in Groundwater." Humic Substances in Soil, Sediment, and Water, G. R. Aiken, D. M. McKnight, R. L. Wershaw, and P. MacCarthy, eds., John Wiley & Sons., New York, 87-103.

Thurman, E. M., and Malcolm, R. L. (1981). "Preparative Isolation of Aquatic Humic Substances." *Environmental Science & Technology*, 15(4), 463-466.

Thurman, E. M., Wershaw, R. L., Malcolm, R. L., and Pinckney, D. (1982). " Molecular Size of Aquatic Humic Substances." J. Org. Geochem., 27-35.

Trussell, R. R., and Umphres, M. D. (1978). "Formation of Trihalomethanes." *Journal American Water Works Association*, 70(11), 604-612.

Uden, P. C., and Miller, J. W. (1983). "Chlorinated Acids and Chloral in Drinking Warer." Jour. AWWA., 524-527.

Van der Kooij, D. (1995). "Significance and Assessment of the Biological Stability of Drinking Water." The Handbook of Environmental Chemistry, 89-102.

Van der kooij, D., Hijnen, W. A. M., and Kruithof, J. C. (1989). "The Effects of Ozonation, Biological Filtration and Distribution on the Concentration of Easily Assimilable Organic-Carbon (Aoc) in Drinking-Water." *Ozone-Science & Engineering*, 11(3), 297-311.

Van der kooij, D., Visser, A., and Hijnen, W. A. M. (1982). "Determining the Concentration of Easily Assimilable Organic- Carbon in Drinking-Water." *Journal American Water Works Association*, 74(10), 540-545.

Van Hoof, F., and et al. (1986). "Formation of Oxidation By-products in Surface Water Pre-ozonation and Their Behavior in Water Treatment." Wat. Supply, 93.

Volk, C., Renner, C., Roche, P., Paillard, H., and Joret, J. C. (1993). "Effects of Ozone on the Production of Biodegradable Dissolved Organic-Carbon (Bdoc) During Water-Treatment." *Ozone-Science & Engineering*, 15(5), 389-404.

Von Gunten, U., and Hoigné, J. (1996). "Ozonation of Bromide-Containing Waters: Bromate Formation through Ozone and Hydroxyl Radicals." Disinfection By-products in Water Treatment: The Chemistry of Their Formation and Control, R. A. Minear and G. L. Amy, eds., CRC Press, Inc., Boca Raton, FL., 187-206.

Weinberg, H. S., and Glaze, W. H. (1996). "An Overview of Ozonation Disinfection By-Products." Disinfection By-products in Water Treatment, R. A. Minear and G. L. Amy, eds., Lewis Publisher, Boca Raton, FL., 165-186.

Wershaw, R. L., and Aiken, G. R. (1985a). "Molecular Size and Weight Measurements of Humic Substances." Humic Substances in Soil, Sediment, and Water, G. R. Aiken, D. M. McKnight, R. L. Wershaw, and P. MacCarthy, eds., John Wiley & Sons., New York, 477-492.

Wershaw, R. L., and Aiken, G. R. (1985b). "Molecular Size and Weight Measurements of Humic Substances." Humic Substances in Soil, Sediment, and Water, G. R. Aiken, D. M. McKnight, R. L. Wershaw, and P. MacCarthy, eds., John Wiley & Sons., New York, 181-209.

Westerhoff, P., Aiken, G., Amy, G., and Debroux, J. (1999). "Relationships between the structure of natural organic matter and its reactivity towards molecular ozone and hydroxyl radicals." *Water Research*, 33(10), 2265-2276.

Wiesner, M. R., Schmelling, D. C., and Pickering, K. (1991). "Permeation Behavior and Filtrate Quality of Tubular Ceramic Membranes Used for Surface Water Treatment." Proc. 1991 Membrane Technologies in the Water Industry, Orlando, Florida, 371-383.

Wilson, M. A. (1987). NMR Techniques and Applications in Geochemistry and Soil Chemistry, M. A. Wilson, ed., Pergamon Press, Oxford, 182-216.

Yavich, A. A. (1998). "The Use of Ozonation and Biological Fluidized Bed Treatment for the Control of NOM in Drinking Water," Ph.D. Dissertation, Michigan State University, East Lansing, MI.

CHAPTER 3

MASS TRANSFER OF OZONE IN THE OZONATION/MEMBRANE PROCESS

3.1 INTRODUCTION

Since the discovery of potentially carcinogenic disinfection by-products in chlorinated water, the use of ozone as an alternative disinfectant has gradually increased in water treatment facilities. Although ozone effectively reduces the formation of THMs and HAAs (Amy et al. 1988; Cipparone et al. 1997; Richardson et al. 1999), its low aqueous solubility and the high production cost of ozone gas have limited ozone treatment applications. Thus, it is important to improve the rate of ozone mass transfer from gas phase to aqueous phase. Consequently, the development of an ozonation reactor with a high ozone mass transfer rate is needed.

Devices, such as stirred reactors, venturi scrubbers, bubble columns, and static mixers, which achieve efficient gas-liquid mass transfer in the ozonation of water and wastewater, are well documented in literature (e.g., see Barberis and Howarth 1991; Hsu et al. 2002; Ledakowicz et al. 2001; Richards et al. 1976; Roustan et al. 1987; Roustan et al. 1996; Sheffer and Esterson 1982; Wright et al. 1998). However, only three publications discuss the use of ozonation processes in conjunction with membrane filters (Janknecht et al. 2000; Shanbhag et al. 1998; Shen et al. 1990).

Membrane filters are effective for the removal of turbidity, organic matter, microorganisms, and some DBP precursors. Several researchers (Cui and Wright 1994; Klijn et al. 2000; Laborie et al. 1997; Laborie et al. 1998; Verberk et al. 2000) reported that injecting air directly into the feed water stream of membrane can enhance the permeate flux and control membrane fouling. Others observed similar results when ozonation preceded membrane filtration (Hashino et al. 2000; Kim et al. 1999).

We hypothesize that the combination of ozonation with membrane filtration will result in a reduction in the DBPs formation potential and the membrane fouling potential, maintain a stable permeate flux, and retain and inactive microorganisms as compared to either ozone or membrane filtration alone. As part of this work we investigated the effect of membrane filtration on the mass transfer of ozone.

In this study, a new ozone/membrane system was set up and the effects of various operational parameters on the ozone volumetric mass transfer coefficient were determined. The water flow rate, ozone gas flow rate, inlet ozone concentration, and temperature were varied. An ozone mass transfer model that predicts the ozone concentration profile during the period of mass transfer was developed. The ability of ozone gas injection to enhance the permeate flux of the membrane was studied. The ozone gas and water flow rates were varied during this portion of the study. Furthermore, due to the importance of volumetric mass transfer coefficient in the design and specification of ozonation equipment, the coefficient obtained from this study and from different ozonation contactors were compared. The efficiency of two ozone inline mixers, a simple Y inline mixer and a high efficiency inline mixer, were also investigated.

3.2 MATERIALS AND METHODS

3.2.1 Permeate Flux Enhancement Experiment

A specially designed ozonation/membrane system was used for investigating the enhancement of permeate flux by ozone injection. The schematic diagram of this system is shown in Figure 3.1. The membrane module and water tank served as ozone contactor. Deionized distilled water (DDI) was prepared and used in this study. Teflon tubing and stainless steel joints and valves were used throughout the system.

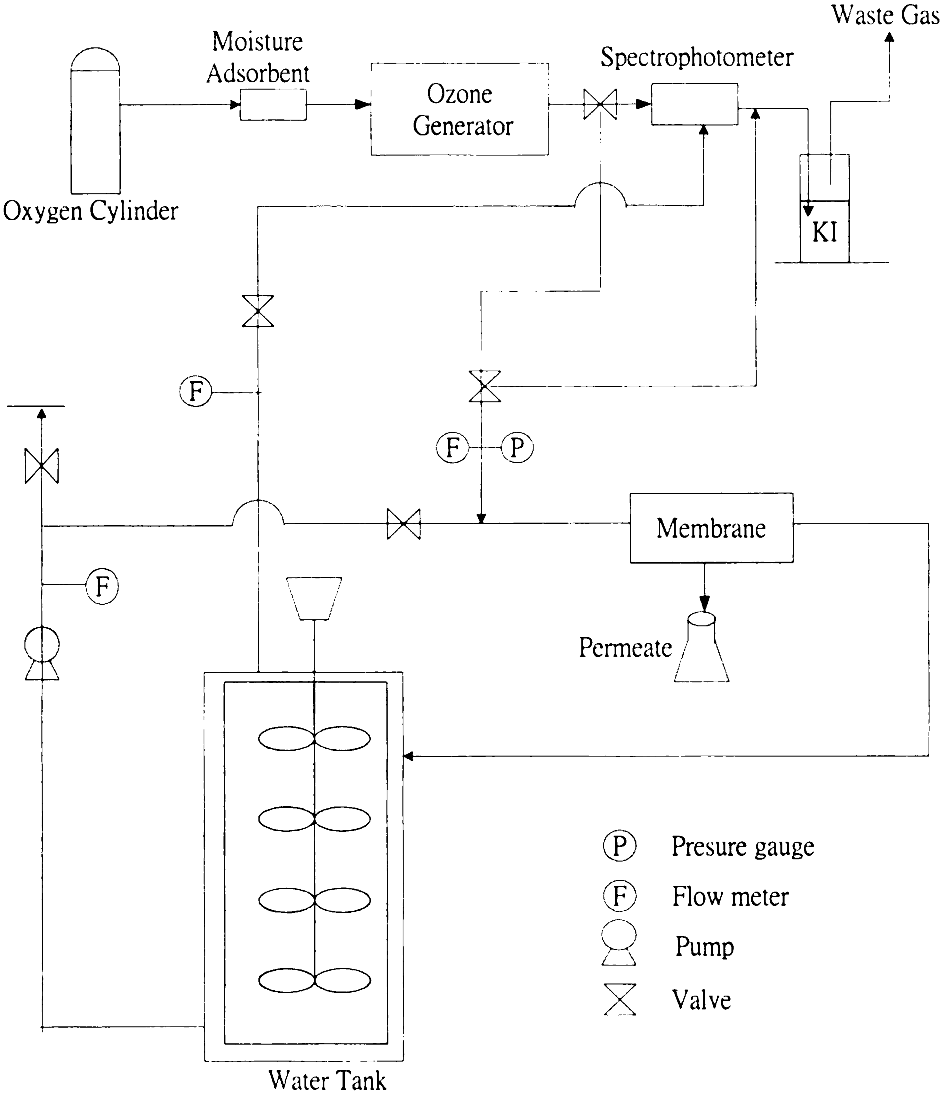

Figure 3.1 Experimental setup for measurement of permeate flux enhancement of ozone injection.

Tubular ceramic membranes (Clover, CéRAM Inside, Tami North America, St. Laurent, Québec, Canada) with a molecular weight cut-off of 15 kD were used in the system. The characteristics of the laboratory-scale ultrafiltration membrane are summarized in Table 3.1.

Table 3.1 Details of the ceramic membrane.

External diameter (mm)	Active length (cm)	Filtering area (cm^2)	Number of channels	Operating pH range	Cut-off range (kD)
10	25.0	95.2	3	0-14	15

Ozone was generated by feeding pure oxygen gas from a gas cylinder to the ozone generator (Model OZ2PCS, Ozotech Inc., Yreka, Calif.). The oxygen gas stream was dried using a molecular sieve trap prior to ozone generation. The ozone gas concentration was controlled using the electric current of the ozone generator. The wasted ozone gas was vented after passing the gas through a 2% potassium iodide (KI) solution to destroy any residual ozone gas.

Twenty-three liters of acidified DDI water were prepared in the water-jacked water tank, which was used to adjust the temperature of the DDI water. The temperature of the water was monitored by a thermometer. The water tank was equipped with a power mixer with four impellers to completely mix the water. The acidified DDI water was introduced with a centrifugal pump (Model 4RH12, Dayton Electric Mfg. Co., Niles, Illinois) through the housing of the membrane. Ozone gas was added into the water stream through a simple Y inline mixer (SYM) (see Figure

3.2) just before entering the membrane module. The DDI water circulated tangentially on the surface of the membrane. The permeate flowed out from the membrane housing through two permeate outlets and was collected to measure the flux. The rejected DDI water was continuously recirculated back to the water tank. The water flow rate and gas flow rate were varied by control valves from 2 to 5 L/min and 0 to 500 mL/min, respectively. The water temperature was controlled at 27 °C and the inlet ozone gas concentration was fixed at 2.5 g/m^3.

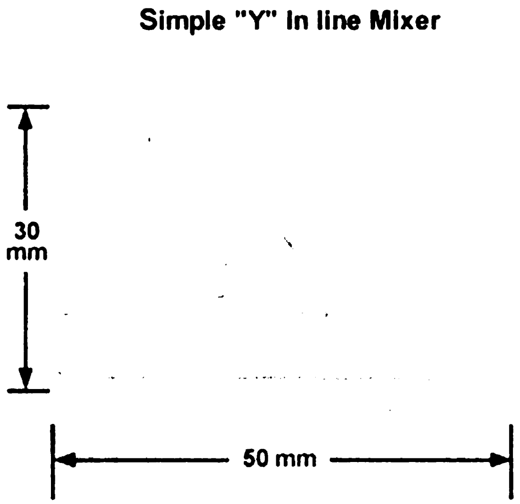

Figure 3.2 Simple Y inline mixer (SYM).

3.2.2 Mass Transfer Experiment

The experimental setup for the ozone mass transfer experiment was similar to that shown in Figure 3.1 but modified slightly. Since the retention time in the twenty-three-liter water tank was too long to avoid ozone decomposition and to reach steady state conditions, it was replaced by a 3.5-liter water-jacked glass reservoir made of Pyrex glass in this study. A schematic diagram of the experimental setup is shown in Figure 3.3. In order to prevent any interference from impurities and ozone self-decomposition, DDI water acidified to pH 2 using sulfuric acid was prepared and used in this study. Two ozone-water inline mixers, the simple Y inline mixer (SYM) and the high efficiency inline mixer (HEM) shown in Figures 3.2. and 3.4., respectively (Ozone Service, Burton, B.C., Canada), were used in the mass transfer study to compare their mass transfer efficiency.

The experimental procedure for mass transfer experiments was similar to that described in Section 3.2.1 with slight modification. A magnetic stirrer at the bottom of the water reservoir was used to completely mix the water. A peristaltic pump (Masterflex Model 7520-35, Cole-Parmer Co., Chicago, Illinois) was used to continuously pump the acidified DDI water that was prepared in a 1.5-liter water tank into the 3.5-liter water reservoir to compensate the water loss to permeate and due to sampling. Dissolved ozone concentrations in the permeate and in the water reservoir were monitored spectrophotometrically at 254 nm at appropriate time intervals. Ozone gas phase concentrations in the headspace of water reservoir were measured in the same manner. When the dissolved ozone concentration in water reservoir reached steady state conditions, the system operation was stopped.

Several operational factors, such as ozone concentration in the inlet gas phase, water flow rate, gas flow rate, and water temperature, which influence the ozone mass transfer and solubility were investigated. Table 3.2. summarizes the experimental conditions that were varied for the ozone mass transfer measurements.

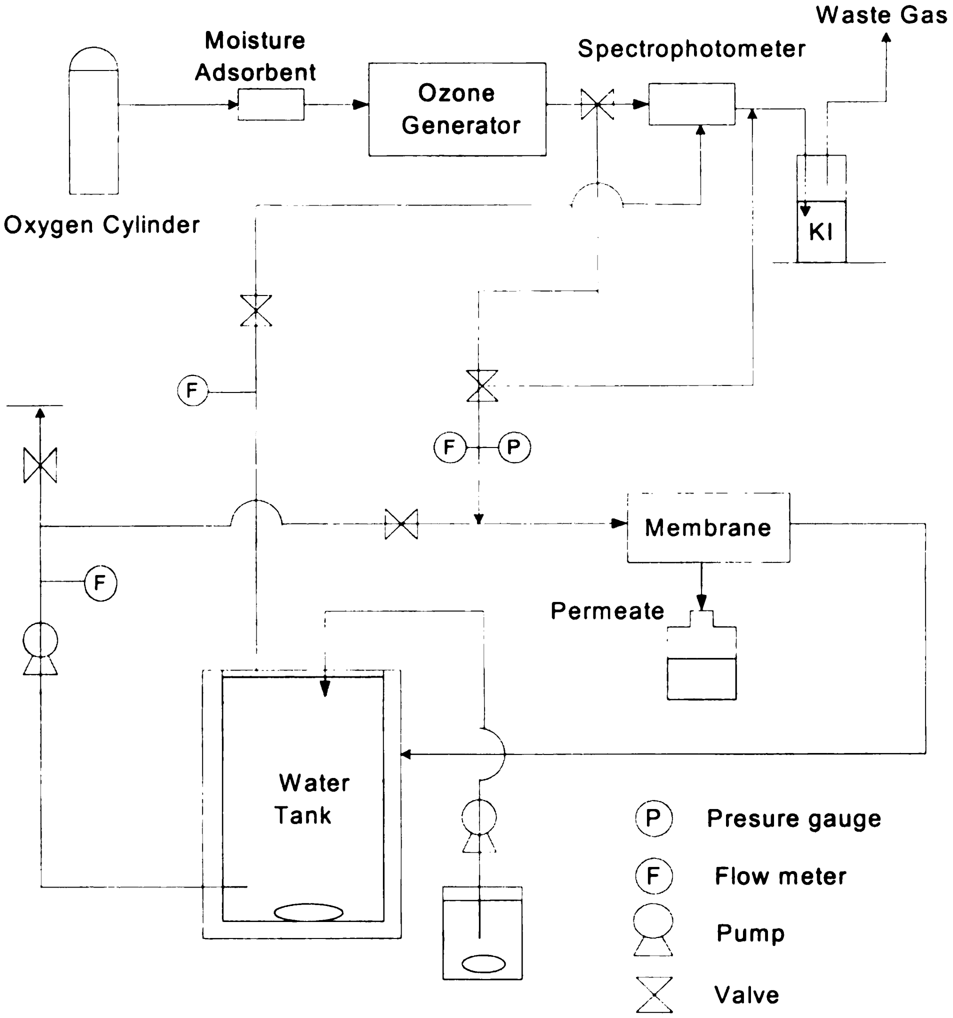

Figure 3.3 Experimental setup of the ozone mass transfer study.

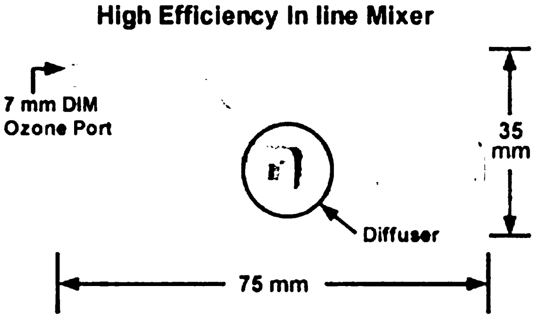

Figure 3.4 High efficiency inline mixer (HEM).

Table 3.2 Experimental conditions for the ozone mass transfer measurement.

Parameters	Values
Inlet ozone dose (g/m^3)	1.5, 2.5, 5.8, 12.5, 23.0, 36.0
Water flow rate (L/min)	2, 2.75, 3.5
Ozone gas flow rate (mL/min)	25, 50, 75, 100
Water temperature (°C)	10, 20, 30

3.2.3 Ozone Concentration Measurement

The concentration of ozone in the gas phase was measured at the wavelength 254 nm with an UV/VIS spectrophotometer (Milton Roy Genesis-5, Milton Roy, Inc., Rochester, NY) by passing ozone gas through a 2-mm quartz flow-through cell. An extinction coefficient of 3000 M^{-1}cm^{-1} at 254 nm (Hoigné 1988) was used for calculating ozone concentrations.

Dissolved ozone concentrations were also determined with an UV/VIS spectrophotometer (Milton Roy Genesis-5, Milton Roy, Inc., Rochester, NY). Samples were collected in a 1 cm quartz cell wrapped with parafilm to prevent ozone releasing to air. Then the quartz cell was placed immediately into the cell holder in the spectrophotometer to measure the absorbance of ozone at 258 nm. An extinction coefficient of 2950 $M^{-1}cm^{-1}$ at 258 nm (Bablon et al. 1991) was used for calculating aqueous ozone concentrations.

3.3 MATHEMATICAL MODEL OF OZONE MASS TRANSFER

In the bench-scale ozonation/membrane system, the transfer of ozone from the gas phase into the water can be described by the two-film theory as shown in Figure 3.5. If there is no gas accumulation in the gas-liquid interface, the mass flux from gas phase must equal that from liquid phase and can be described as follows (Canale and Weber 1972):

$$F = k_{gi}(p - p_i) = -k_{Li}(C - C_i) \qquad \text{Eq.3-1}$$

where F is the flux [M/L^2T]; k_{gi} is a convective ozone mass transfer coefficient in the gas phase [L/T]; p and p_i represents the ozone partial pressure in the gas phase and at the interface [M/L^3], respectively; k_{Li} is a convective ozone mass transfer coefficient in the liquid phase [L/T], and C and C_i are concentrations of dissolved ozone in the bulk liquid phase and at the interface [M/L^3], respectively. M, L, and T are the dimensions of mass, length, and time, respectively.

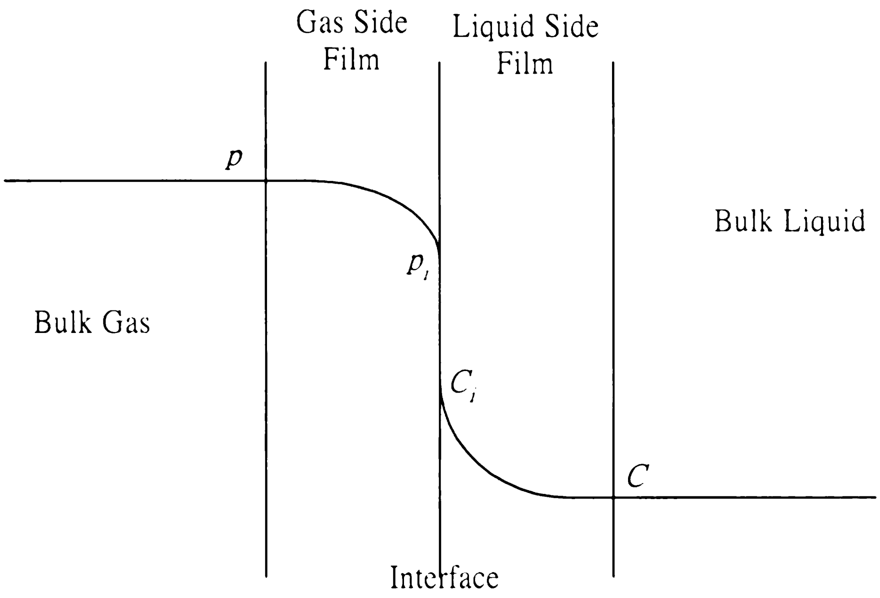

Figure 3.5 Two-film theory.

Since it is impossible to measure the partial pressure of ozone and the concentration of the dissolved ozone at the gas-liquid interface, the mass transfer coefficients are defined based on the ozone partial pressure in the bulk gas phase and dissolved ozone concentration in the bulk solution in equilibrium. Then, the flux can be expressed as:

$$F = k_g (p - p_e) = -k_L (C - C_S) \qquad \text{Eq.3-2}$$

where k_g and k_L are overall mass transfer coefficients based on the bulk gas and liquid phase concentrations, respectively; p_e is the partial pressure of ozone in equilibrium with C, and C_S is the concentration of dissolved ozone in equilibrium with p.

According to the Henry's law, the relationship between the molar concentration of ozone in water (C) and the ozone partial pressure (p), expressed as atm, in the gas phase can be written as (Weber Jr. and DiGiano 1996):

$$p = H \times C \qquad \text{Eq.3-3}$$

where H is the Henry's constant in units of atm-L/mole.

From Eq. 3-3, the following relationships can be deduced in solutions at equilibrium:

$$C_i = \frac{p_i}{H} \qquad \text{Eq.3-4}$$

$$C_S = \frac{p}{H} \qquad \text{Eq.3-5}$$

$$C = \frac{p_e}{H} \qquad \text{Eq.3-6}$$

Substituting Eq.3-4, Eq.3-5, and Eq.3-6 into Eq.3-1 and Eq. 3-2, and express k_L in terms of H, k_{gi} and k_{Li}, we can get the Eq.3-7:

$$\frac{1}{k_L} = \frac{1}{Hk_{gi}} + \frac{1}{k_{Li}} \qquad \text{Eq.3-7}$$

For sparingly soluble gases such as ozone, whose Henry's constant at 20 ^{o}C is 67.7 atm-L/mole (Weber Jr. and DiGiano 1996), H is sufficiently large that k_L can be approximated by k_{Li}. The mass transfer, therefore, is controlled by diffusion through the liquid film. Thus, the resistance of the gas film is very small and can be neglected, the liquid film resistance is considered to dominate ozone transport in the membrane contactor, and the Eq.3-7 can be rewritten as:

$$\frac{1}{k_L} \approx \frac{1}{k_{Li}} \qquad \text{Eq.3-8}$$

Thus, the overall mass transfer coefficient can be described by the liquid film mass transfer coefficient.

The confined volume of the ozonation/membrane system used to evaluate the ozone mass transfer mathematical model is depicted in Figure. 3.6.

The rate of mass transfer of ozone in the aqueous phase in the ozonation/membrane system can be described by the following equation.

$$V\frac{dC}{dt} = Q_{in}C_{in} - Q_{out}C_{out} - Q_S C + k_L A(C_S - C) - kVC$$

Eq.3-9

where C is the dissolved ozone concentration in the system [M/L^3]; C_S is the equilibrium dissolved ozone concentration in the system [M/L^3]; C_{in} and C_{out} are the dissolved ozone concentration in water entering and leaving the system [M/L^3], respectively; Q_{in}, Q_{out}, and Q_s are the volumetric flow rate of water entering, leaving the system and sampling form the system [L^3/T], respectively; A is the interfacial area through which mass transfer occurs [L^2]; V is the volume containing interfacial area [L^3]; k is the ozone decomposition rate in water [1/T].

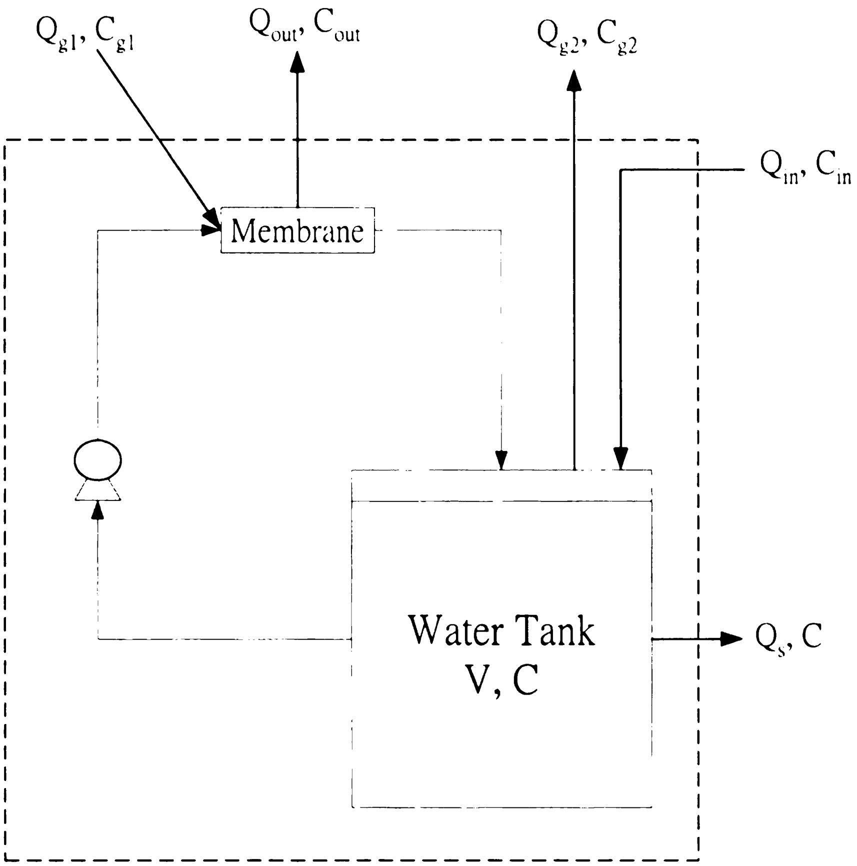

Figure 3.6 The ozonation/membrane system for ozone mass transfer modeling.

The dissolved ozone concentration in water entering the system was zero, thus $C_{in} = 0$. Therefore, the Eq.3-9 can be simplified and rearranged as:

$$\frac{dC}{dt} = k_L \frac{A}{V}(C_S - C) - \frac{1}{V}(Q_{out}C_{out} + Q_S C) - kC \qquad \text{Eq.3-10}$$

Let,

$$Z_{O3} = \frac{dC}{dt} + \frac{1}{V}(Q_{out}C_{out} + Q_S C) + kC \qquad \text{Eq.3-11}$$

Then Eq.3-10 can be rewritten as:

$$Z_{O3} = k_L \frac{A}{V}(C_S - C) \qquad \text{Eq.3-12}$$

Therefore, the ozone volumetric mass transfer coefficient can be obtained by plotting Z_{O3} against $(Cs\text{-}C)$.

Let $a = A/V$, then Eq.3-10 can be rewritten and rearranged as:

$$\frac{dC}{dt} = (-k_L a - \frac{Q_S}{V} - k)C + (k_L a C_S - \frac{1}{V} Q_{out} C_{out}) \qquad \text{Eq.3-13}$$

where a is the specific interfacial area [L^2/L^3].

Let,

$$A = -k_L a - \frac{Q_S}{V} - k \qquad \text{Eq.3-14}$$

and

$$B = k_L a C_S - \frac{1}{V} Q_{out} C_{out} \qquad \text{Eq.3-15}$$

Substituting Eq.3-14 and Eq.3-15 into Eq.3-13 yields:

$$\frac{dC}{dt} = A * C + B \qquad \text{Eq.3-16}$$

Let,

$$D = C + \frac{B}{A} \qquad \text{Eq.3-17}$$

Substituting Eq.3-17 into Eq.3-16, rearranging and integrating yields,

$$\int \frac{1}{D} dD = A \int dt \qquad \text{Eq.3-18}$$

where the boundary conditions are: $D_0 = C_0 + B/A$ at $t = 0$ and $D_t = C_t + B/A$ at any later time, t. Integrating Eq.3-18 with the boundary conditions given, yield:

$$C(t) = (C_0 + \frac{B}{A}) * e^{At} - \frac{B}{A} \qquad \text{Eq.3-19}$$

Substituting Eq.3-14 and Eq.3-15 into Eq.3-19 yields an equation for the dissolved ozone concentration at any time in the ozonation/membrane system,

$$C(t) = (C_0 + \frac{k_L aC_S - \frac{1}{V} Q_{out} C_{out}}{-k_L a - \frac{Q_S}{V} - k}) e^{(-k_L a - \frac{Q_S}{V} - k)t} - \frac{k_L aC_S - \frac{1}{V} Q_{out} C_{out}}{-k_L a - \frac{Q_S}{V} - k}$$

Eq.3-20

The ozone volumetric mass transfer coefficient ($k_L a$) was calculated and reported rather than the overall mass transfer coefficient (k_L) because of the difficulty in measuring the specific interfacial area (a) in the ozonation/membrane system.

3.4 RESULTS AND DISCUSSION

3.4.1 Permeate Flux Enhancement Experiment

The experimental results obtained from this study in which ozone was injected into the tubular ceramic membrane are summarized in Table 3.3. A plot of permeate flux vs. ozone gas flow rate for water flow rates varied from 2 to 5 L/min is shown in Figure 3.7.

Table 3.3 Effects of water flow rate and gas flow rate on permeate flux.

Water flow rate (LPM)	Ozone gas flow rate (mL/min)	Permeate flux (mL/hr)	Increased permeate flux (%)
2	0	49	0
	100	55	12.2
	200	60	22.4
	300	64	30.6
	400	76	55.1
	500	80	63.3
3	0	82	0
	100	90	9.8
	200	100	22.0
	300	106	29.3
	400	115	40.2
	500	123	50.0
4	0	140	0
	100	147	5.0
	200	156	11.4
	300	163	16.4
	400	172	22.9
	500	178	27.1
5	0	184	0
	100	199	8.2
	200	210	14.1
	300	218	18.5
	400	228	23.9
	500	235	27.7

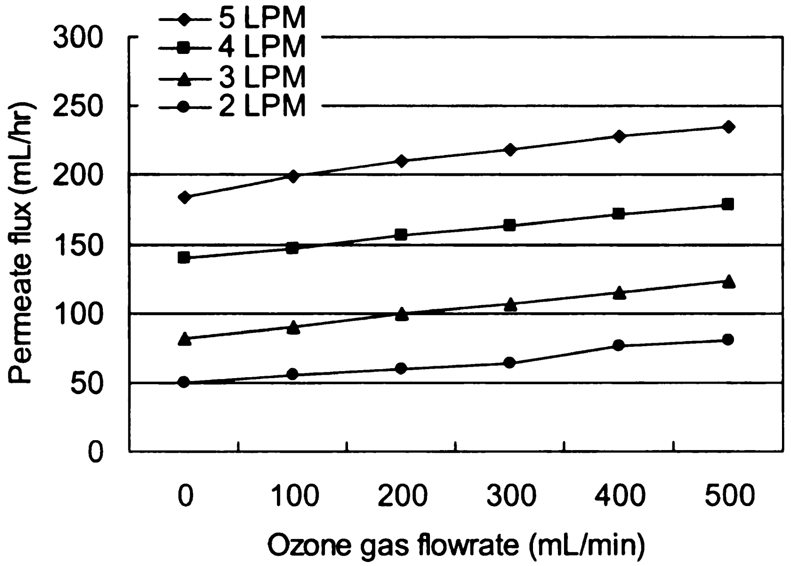

Figure 3.7 Effects of ozone gas flow rate on the permeate flux. Operating conditions: gaseous O_3 concentration, 2.5 g/m^3; water temperature, 27 °C; water flow rate varied from 2 LPM (L/min) to 5 LPM.

As shown above, increase in permeate flux can be achieved by either increasing water flow rate or increasing ozone gas flow rate. This result is consistent with the observation of other researchers (Cui and Wright 1994; Ducom et al. 2002; Laborie et al. 1997; Laborie et al. 1998; Mercier et al. 1995). The increase in water flow rate and ozone gas flow rate are thought to increase the transmembrane pressure, which results in the increase of permeate flux. Cheng and Wu (2003) reported that the permeate flux increases with the increase in water flow rate, gas flow rate, and the transmembrane pressure. Cui and Wright (1994) concluded that the injected air promotes turbulence near the membrane surface, increasing the superficial cross-flow velocity of the fluid, suppressing the polarisation layer and enhancing the ultrafiltration process. In this study, the rates of permeate flux increased by 5.0 and 63.3 %, depending on the system operating conditions. In addition, it is interesting to notice that at low water flow rates, the effect of ozone addition on permeate flux was more significant than that at higher water flow rates. Other researchers observed similar trend (Cui and Wright 1994; Laborie et al. 1998; Mercier et al. 1995).

3.4.2 Decomposition of Ozone in the Proposed System

Although the DDI water acidified to pH 2 with sulfuric acid was used in this study to minimize the effect of dissolved ozone decomposition on the mass transfer study, experiments of ozone decomposition in the novelly designed system were conducted to examine its effect on the rate constant of the decomposition of dissolved ozone. Decomposition rate constants of dissolved ozone at three different water temperatures are summarized in Table 3.4. Experimental results shown in Figures 3.8 to 3.10 indicate that the decomposition of dissolved ozone follows first-order kinetics and the decomposition rate can be expressed as:

$$-\frac{d[O_3]}{dt} = k_d [O_3] \qquad \text{Eq.3-21}$$

As seen in Table 3.4, the rate of ozone decomposition increased as the water temperature increased. The decomposition rate constant increased by ca. 180% and ca. 178% as the water temperature increased from 10 °C to 20 °C and from 20 °C to 30 °C, respectively. It appears that water temperature is an important factor in this proposed system and the decomposition rate constant can not be neglected even at low pH level when using the ozonation/membrane system. However, several researchers observed that the decomposition rate of dissolved ozone in acidic conditions is quite small under water temperature at 20 °C (Gurol and Singer 1982; Sotelo et al. 1987; Sugimitsu et al. 1989). Therefore, the increase of decomposition rate constant obtained in this study can not be explained only by the factor of increasing water temperature. Sotelo et al. (1987) observed that the decomposition rate of dissolved ozone increased when the agitation speed in the ozone contactor (a bubble column) increased. They explained that this was probably due to the occurrence of ozone desorption. In the proposed system used in this study, water was circulated by a centrifugal pump and the transportation of water through the chamber of pump head could offer a very violent agitation. Therefore, the desorption of dissolved ozone could contribute to the decomposition of dissolved ozone in this bench-scale system.

Table 3.4 Decomposition of dissolved ozone in DDI water acidified to pH 2 under different water temperatures in the proposed system.

Water temperature (°C)	Decomposition rate constant (k_d, min^{-1})	R^2
10	0.0132	0.9979
20	0.0240	0.9938
30	0.0427	0.9946

* water flow rate: 3.5 L/min.

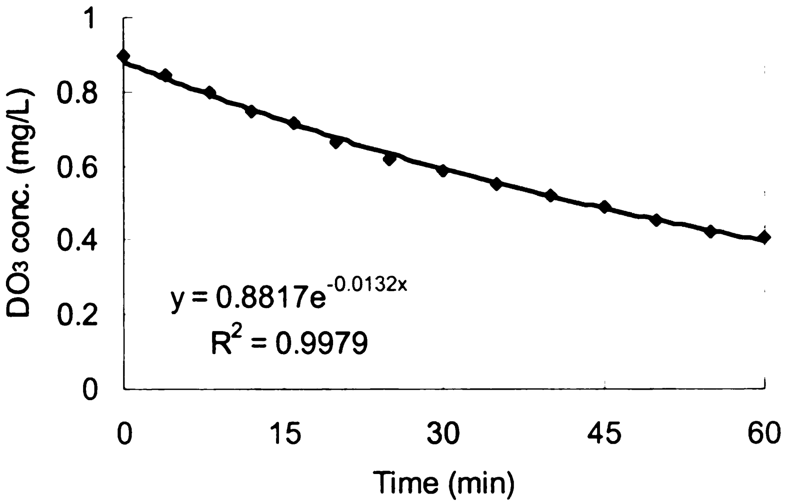

Figure 3.8 Ozone decomposition in DDI water for first-order kinetic at 10 °C. Operating conditions: pH 2; water flow rate, 3.5 LPM.

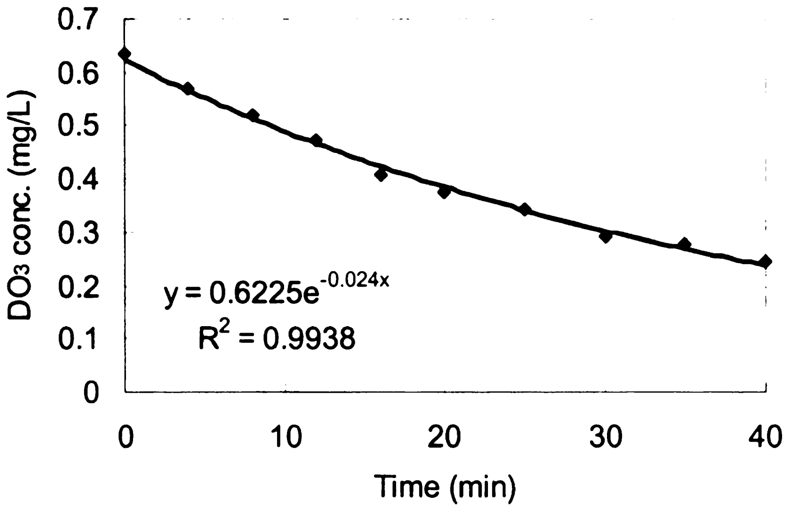

Figure 3.9 Ozone decomposition in DDI water for first-order kinetic at 20 °C. Operating conditions: pH 2; water flow rate, 3.5 LPM.

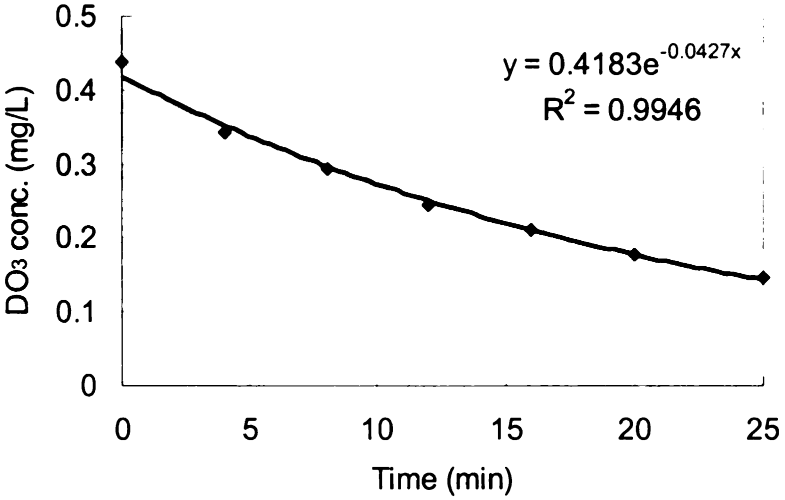

Figure 3.10 Ozone decomposition in DDI water for first-order kinetic at 30 °C. Operating conditions: pH 2; water flow rate, 3.5 LPM.

3.4.3 Ozone Mass Transfer Coefficient

The effects of variation in the ozone gas flow rate, water flow rate, inlet ozone concentration, and water temperature on the mass transfer of ozone in the ozonation/membrane system were determined. The SYM mixer shown in Figure 3.2 was used in this study. Dissolved ozone concentrations in the water tank and in the permeate and the permeate flux were determined experimentally. These data and Eq.3-12 were used to calculate the of volumetric mass transfer coefficient of ozone (Figure 3.11). It was assumed that the dissolved ozone was completely mixed in the water tank.

Table 3.5 lists the ozone volumetric mass transfer coefficients and dissolved ozone concentrations in the water tank and permeate for different inlet gas flow rates. From the experimental results, the volumetric mass transfer coefficient of ozone increased as the inlet gas flow rate increased. This is because the increase of gas flow rate further increases the turbulence on the gas-liquid interface, which increases the interfacial area and results in an increase of ozone absorption in water. Many researchers reported similar observations (Hsu et al. 2002; Roustan et al. 1987; Stankovic 1988; Wu and Masten 2001; Zhou and Smith 2000). Higher ozone concentrations in the water tank were also observed for higher inlet gas flow rates. Since the amount of ozone added into the system is larger at higher gas flow rates than at lower gas flow rates, the ozone concentrations in water tank follow similar trends as K_La.

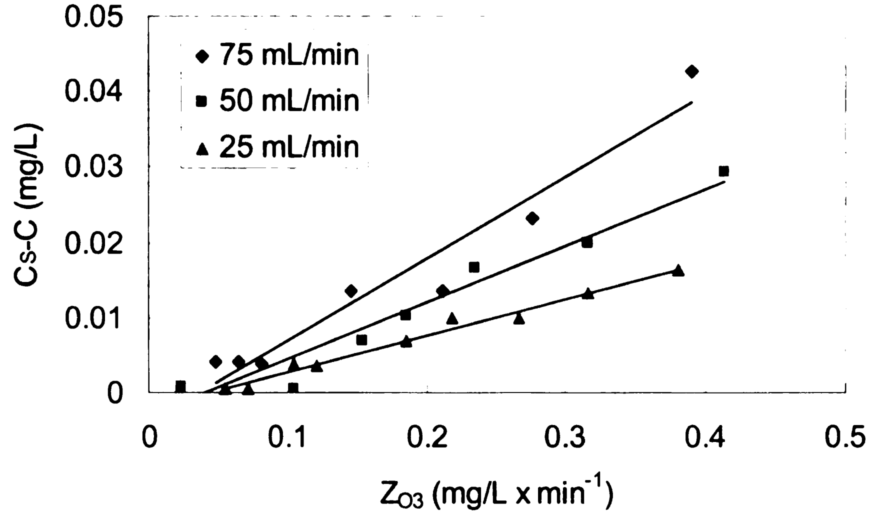

Figure 3.11 Method to fit the ozone volumetric mass transfer coefficients by linear regression at different ozone gas flow rates.

Table 3.5 Calculated values of ozone mass transfer coefficient (K_La) and experimentally determined ozone concentrations under different gas flow rates. (Operating conditions: water temperature 20 C, water flow rate 3.5 LPM, ozone dose 2.5 g O_3/m^3)

Inlet gas flow rate (mL/min)	K_La (min^{-1})	R^2	DO_3 in water tank (mg/L)*	DO_3 in permeate (mg/L)*
25	0.049	0.98	0.462	0.21
50	0.075	0.95	0.560	0.24
75	0.109	0.94	0.602	0.31
100	0.138	0.84	0.661	0.38

* Experimental data.

Table 3.6 Calculated values of the ozone volumetric mass transfer coefficient (K_La) and experimentally determined ozone concentrations under different water flow rates. (Operating conditions: water temperature, 20 C; gas flow rate, 100 mL/min; ozone dose, 2.5 g O_3/m^3)

Water flow rate (L/min)	K_La (min^{-1})	R^2	DO_3 in water tank (mg/L)*	DO_3 in permeate (mg/L)*
2.0	0.090	0.97	0.61	0.45
2.75	0.117	0.95	0.68	0.48
3.5	0.138	0.84	0.66	0.38

* Experimental data.

The calculated values of ozone volumetric mass transfer coefficient at different water flow rates and other parameters are given in Table 3.6. As shown in Table 3.6, the volumetric mass transfer coefficient increases as the water flow rate increases. In this ozonation/membrane system, the water was circulated between membrane unit and the water tank before it was filtered out of the system, which indicates that the water-gas contact time increases as the water flow rate increases and results in the increase of the ozone mass transfer rate. Several researchers reported that the injection of air into the liquid stream promotes turbulence in the membrane filtration unit (Mercier et al. 1997). Therefore, the increase of turbulence by increasing water flow rate also contributes to the increase of ozone volumetric mass transfer coefficient.

Table 3.7 presents the effect of ozone dose on the ozone volumetric mass transfer coefficient and dissolved ozone concentration. It shows a trend that the value of K_La first increases with increasing ozone doses and then decreases after it reaches a maximum value at ozone dose of 23 g/m^3. It is apparent that at high ozone doses, the diffusion of gaseous ozone becomes rate limiting, resulting in poor pass transfer efficiencies. Therefore, the value of K_La decreases for ozone doses exceeding 23 g/m^3. This also indicates that this bench-scale ozonation/membrane system has higher ozone mass transfer efficiency at low ozone doses than that at high ozone doses.

Table 3.7 Calculated values of ozone mass transfer coefficient (K_La) and experimentally determined ozone concentrations under different ozone doses. (Operating conditions: water temperature 20 C, water flow rate 3.5 LPM, gas flow rate 100 mL/min)

O_3 dose conc. (g/m^3)	K_La (min^{-1})	R^2	DO_3 in water tank (mg/L)*	DO_3 in permeate (mg/L)*
1.5	0.133	0.82	0.379	0.211
2.5	0.138	0.84	0.661	0.379
5.8	0.152	0.97	1.365	0.801
12.5	0.161	0.95	2.988	1.587
23.0	0.173	0.87	5.907	3.152
36.0	0.128	0.99	9.501	4.536

* Experimental data.

The ozone mass transfer coefficients and dissolved ozone concentrations in water at different water temperatures are listed in Table 3.8. It can be seen that the higher the water temperature, the higher value of K_La. Temperature affects the ozone mass transfer coefficient by: 1) changing the ozone solubility, 2) changing the rate of ozone molecular diffusion through the gas-liquid interface, and 3) changing the rate of ozone decomposition. An increase in temperature results in a decrease in the ozone solubility and an increase in the ozone molecular diffusion rate thus enhancing the ozone concentration gradient between gas phase and aqueous phase. Also the decomposition rate increases may increase ozone mass transfer. This promotes the ozone mass transfer rate and results in an increase in the value of K_La. However, the level of ozone mass transfer coefficient only slightly increased for the range of operating conditions studied. This is probably due to the low ozone dose (2.5 g/m^3) applied in this experiment or the configuration of this bench-scale system. The experimental results also indicate that the water temperature does not strongly affect the K_La value of ozone under the operating conditions used in this study.

Temperature also has strong influence on Henry's constant. An increase in temperature results in an increase in the Henry's constant (Faust and Aly 1999; Roth and Sullivan 1981). According to Equation 3-3, the ozone solubility decreases when the Henry's constant increases and the ozone partial pressure remains constant. Consequently, the dissolved ozone concentration in the water tank and in the permeate decreases.

Table 3.8 Calculated values of ozone mass transfer coefficient (K_La) and experimentally determined ozone concentrations under different water temperatures. (Operating conditions: water flow rate 3.5 LPM, gas flow rate 100 mL/min, ozone dose 2.5 g O_3/m^3)

Water temperature (°C)	K_La (min^{-1})	R^2	DO_3 in water tank (mg/L)*	DO_3 in permeate (mg/L)*
10	0.135	0.92	0.881	0.571
20	0.138	0.84	0.661	0.379
30	0.141	0.92	0.404	0.232

* Experimental data.

3.4.4 Simple Y Inline Mixer vs. High Efficiency Inline Mixer

The SYM is a Y shape Pyrex glass tube without diffuser. The HEM is similar to the SYM but with a build-in fused glass diffuser, which produces bubbles approximately 40 to 50 μm in diameter. Table 3.9 lists the ozone volumetric mass transfer coefficients and the dissolved ozone concentrations in the water tank under different operating conditions using the SYM and HEM. The effects of different mixers on the dissolved ozone concentration in the water tank under different operating conditions are shown in Figures 3.12 to 3.18.

As can be seen in the experimental results (Table 3.9), the values of K_La obtained using HEM are generally higher than those obtained using SYM except those of ozone doses between 5.8 and 36.0 g/m^3. The HEM allows for the injection of smaller-sized bubbles, which contain a higher interfacial area, into the feed water stream than does the SYM. However, K_La values obtained using HEM were observed only higher than those of SYM at lower ozone doses. It was also found that the dissolved ozone concentrations in the water tank when using the HEM were less than those with the SYM. In running the experiments, it was observed that with the HEM some bubbles generated from the diffuser accumulated on the top of it and did not mix with the feed water stream and move into the membrane module. This design problem may result in the low ozone mass transfer at higher ozone doses and reduced dissolved ozone concentrations in the water tank when using the HEM.

Table 3.9 Parameters comparison between Simple Y Mixer (SYM) and High Efficiency Mixer (HEM).

	Simple Y Mixer		High Efficiency Mixer	
Water flow rate (LPM)	K_La (min^{-1})	DO_3 in water tank (mg/L)	K_La (min^{-1})	DO_3 in water tank (mg/L)
3.5	0.138	0.661	0.162	0.560
	Simple Y mixer		High efficiency mixer	
Ozone dose (g/m^3)	K_La (min^{-1})	DO_3 in water tank (mg/L)	K_La (min^{-1})	DO_3 in water tank (mg/L)
2.5	0.138	0.661	0.162	0.560
5.8	0.152	1.365	0.161	1.217
12.5	0.161	2.988	0.159	2.843
23.0	0.173	5.907	0.136	5.223
36.0	0.128	9.501	0.134	8.898
	Simple Y mixer		High efficiency mixer	
Temperature (C)	K_La (min^{-1})	DO_3 in water tank (mg/L)	K_La (min^{-1})	DO_3 in water tank (mg/L)
10	0.135	0.881	0.148	0.780
20	0.138	0.661	0.162	0.560
30	0.141	0.404	0.179	0.342

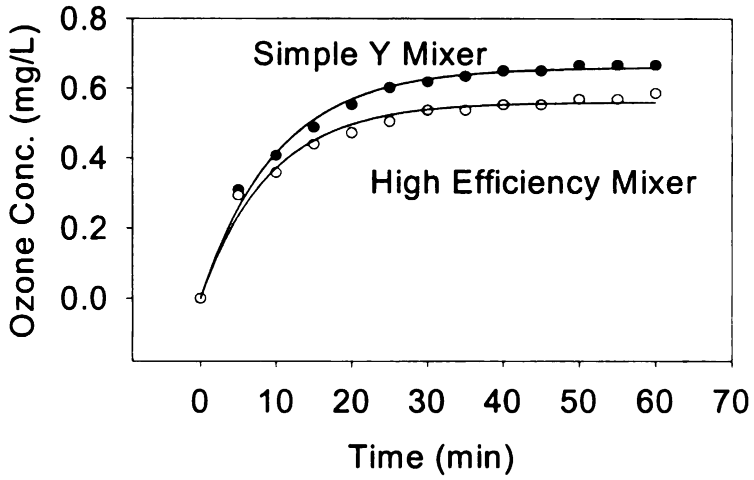

Figure 3.12 Comparison of dissolved ozone concentration using SYM and HEM mixers. (Operating conditions: water flow rate, 3.5 LPM; gas flow rate, 100 mL/min; water temperature, 20 °C; ozone dose, 2.5 g/m^3)

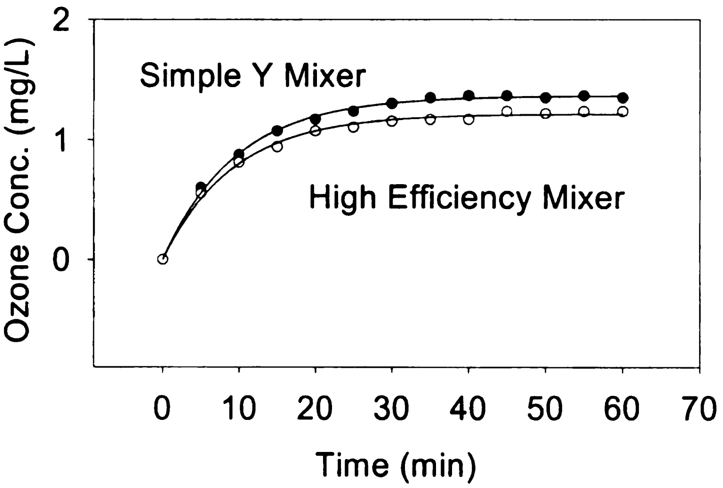

Figure 3.13 Comparison of dissolved ozone concentration using SYM and HEM mixers (Operating conditions: water flow rate, 3.5 LPM; gas flow rate, 100 mL/min; water temperature, 20 °C; ozone dose, 5.8 g/m^3)

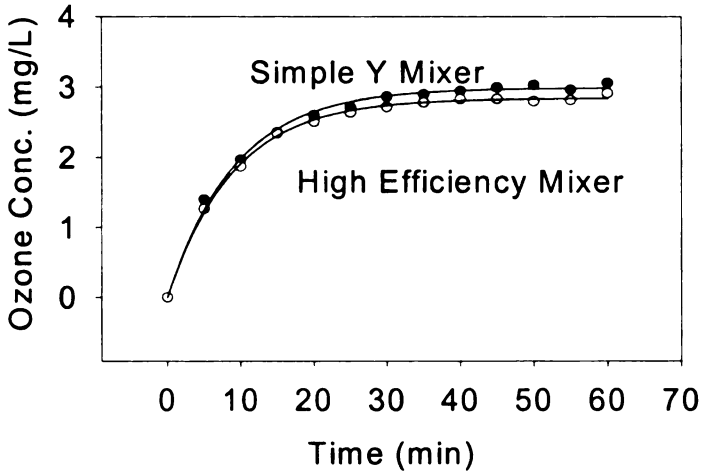

Figure 3.14 Comparison of dissolved ozone concentration using SYM and HEM mixers (Operating conditions: water flow rate, 3.5 LPM; gas flow rate, 100 mL/min; water temperature, 20 °C; ozone dose, 12.5 g/m^3)

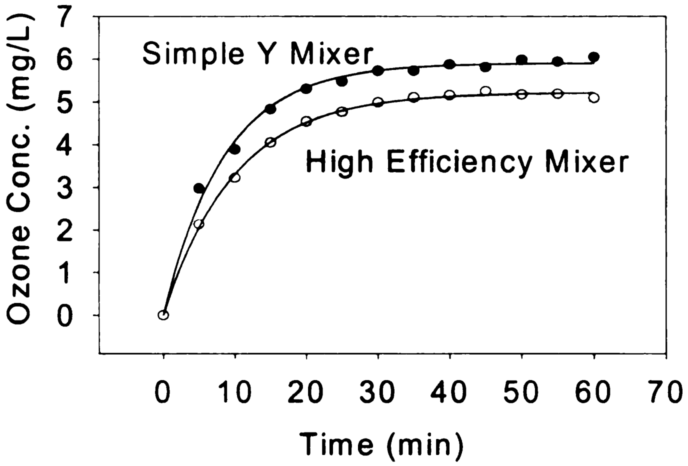

Figure 3.15 Comparison of dissolved ozone concentration using SYM and HEM mixers (Operating conditions: water flow rate, 3.5 LPM; gas flow rate, 100 mL/min; water temperature, 20 °C; ozone dose, 23.0 g/m^3)

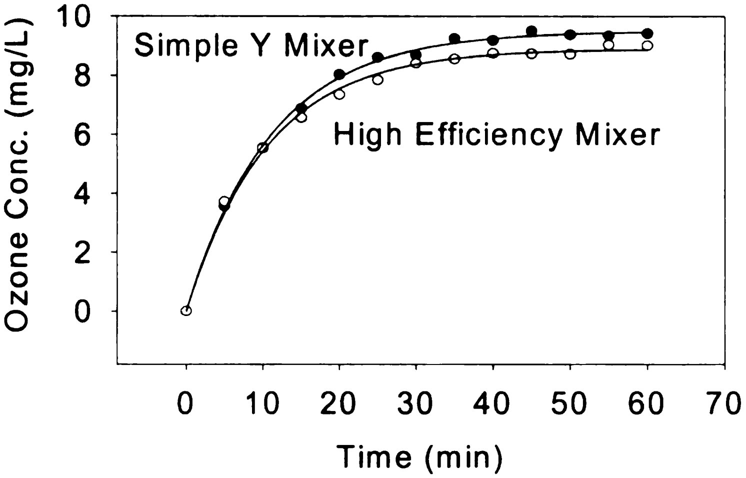

Figure 3.16 Comparison of dissolved ozone concentration using SYM and HEM mixers (Operating conditions: water flow rate, 3.5 LPM; gas flow rate, 100 mL/min; water temperature, 20 °C; ozone dose, 36.0 g/m^3)

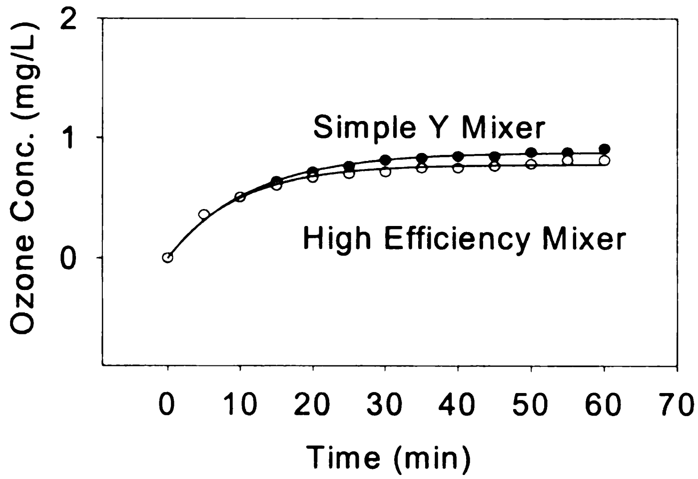

Figure 3.17 Comparison of dissolved ozone concentration using SYM and HEM mixers (Operating conditions: water flow rate, 3.5 LPM; gas flow rate, 100 mL/min; water temperature, 10 °C; ozone dose, 2.5 g/m^3)

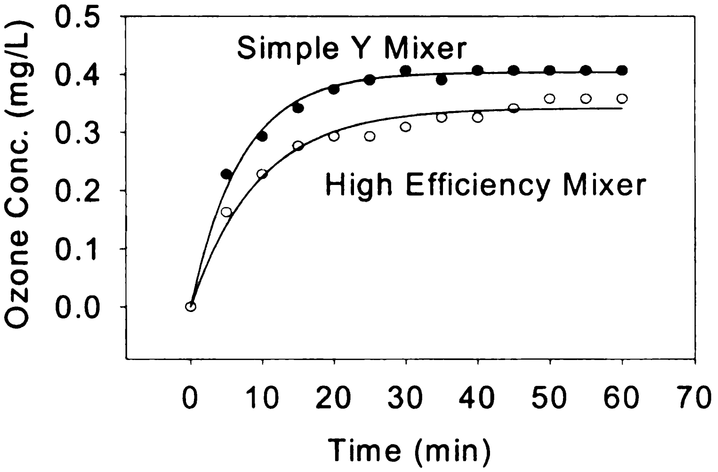

Figure 3.18 Comparison of dissolved ozone concentration using SYM and HEM mixers (Operating conditions: water flow rate, 3.5 LPM; gas flow rate, 100 mL/min; water temperature, 30 °C; ozone dose, 2.5 g/m^3)

3.4.5 Model Validation

The mathematical model developed in Section 3.3 was validated by comparing with the experimental data obtained in this study. Figures 3.19 to 3.23 present some of the comparison of simulations obtained using the mathematical model (Eq.3-20) and experimentally determined data for the dissolved ozone concentration in the water tank. Similar results are obtained for the other experimental conditions. The results indicate that the concentrations of dissolved ozone predicted by the model were slightly greater than the levels of experimental observation in the first 30 minutes of ozonation but were slightly lower after that. This may be due to the turbulent mixing of gas ozone and water in the early operating stage, which depresses the adsorption of ozone, and a gradually accumulation of dissolved ozone in the aqueous phase in the latter stage. Table 3.10 presents the steady-state concentrations of dissolved ozone obtained from experiments and model prediction under different operating conditions. The relative percentage differences between these two data are also provided. It shows good agreement between the experimental data and model predictions.

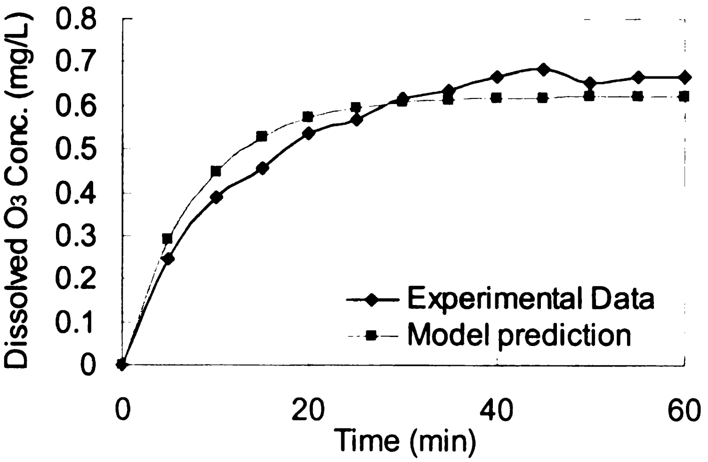

Figure 3.19 Comparison of experimental data and modeling data of dissolved ozone concentration in the water tank. Operating conditions: water flow rate, 2.75 LPM; gas flow rate, 100 mL/min; water temperature, 20 °C; ozone dose, 2.5 g/m^3.

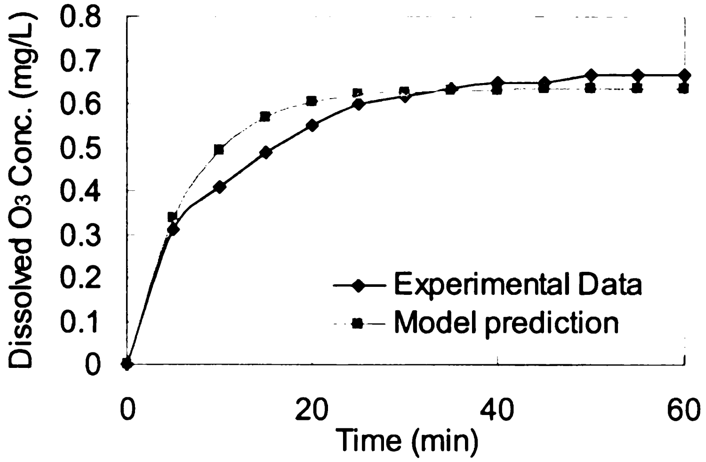

Figure 3.20 Comparison of experimental data and modeling data of dissolved ozone concentration in the water tank. Operating conditions: water flow rate, 3.5 LPM; gas flow rate, 100 mL/min; water temperature, 20 °C; ozone dose, 2.5 g/m^3.

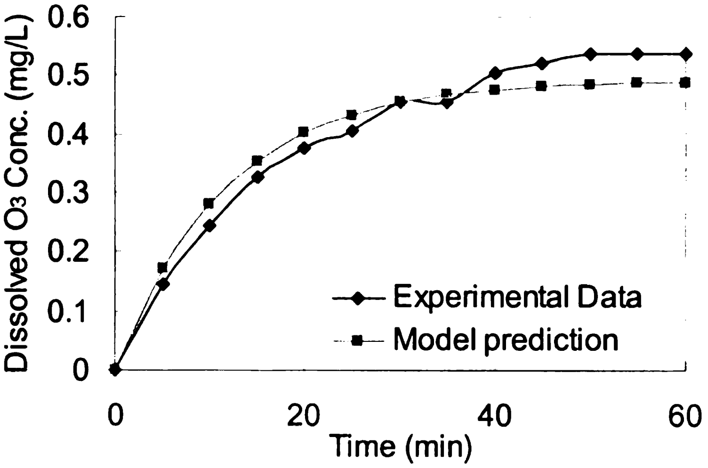

Figure 3.21 Comparison of experimental data and modeling data of dissolved ozone concentration in the water tank. Operating conditions: water flow rate, 3.5 LPM; gas flow rate, 50 mL/min; water temperature, 20 °C; ozone dose, 2.5 g/m^3.

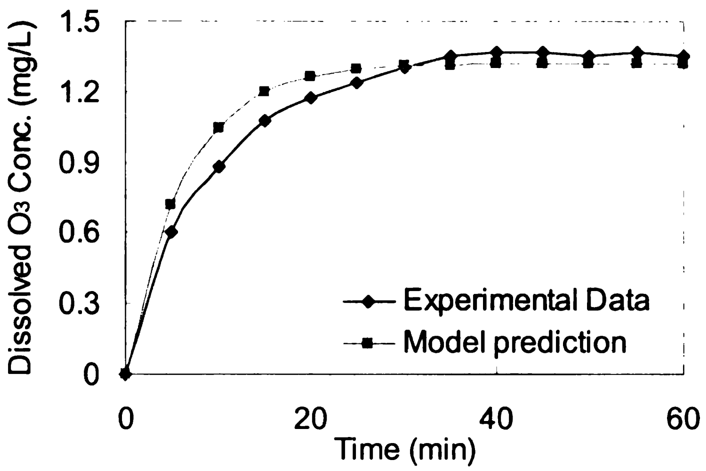

Figure 3.22 Comparison of experimental data and modeling data of dissolved ozone concentration in the water tank. Operating conditions: water flow rate, 3.5 LPM; gas flow rate, 100 mL/min; water temperature, 20 °C; ozone dose, 5.8 g/m^3.

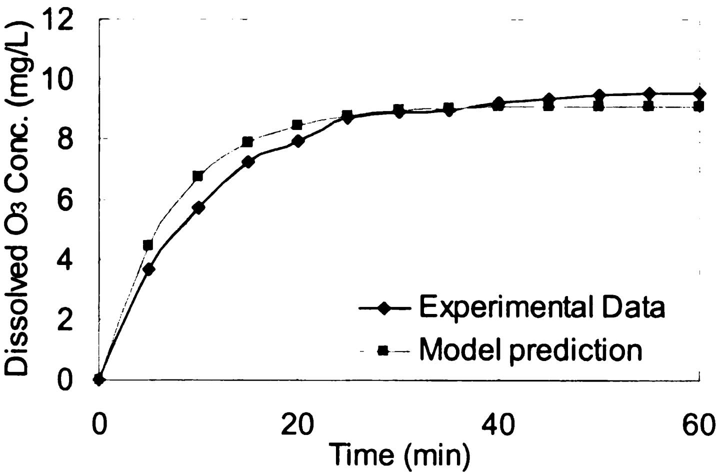

Figure 3.23 Comparison of experimental data and modeling data of dissolved ozone concentration in the water tank. Operating conditions: water flow rate, 3.5 LPM; gas flow rate, 100 mL/min; water temperature, 20 °C; ozone dose, 36.0 g/m^3.

Table 3.10 Comparison of model predictions and experimental data at steady-state of dissolved ozone concentration in the pH 2 DDI water under various operating conditions.

Water flow rate (L/min)[1]	Model DO_3 conc. (mg/L)	Exper. DO_3 conc. (mg/L)	Difference (%)
2	0.52	0.61	14.0
2.75	0.62	0.68	8.2
3.5	0.63	0.66	4.0
Gas flow rate (mL/min)[2]	Model DO_3 conc. (mg/L)	Exper. DO_3 conc. (mg/L)	Difference (%)
25	0.38	0.46	18.5
50	0.49	0.56	12.2
75	0.55	0.60	8.7
100	0.63	0.66	4.0
Ozone dose (g/m^3)[3]	Model DO_3 conc. (mg/L)	Exper. DO_3 conc. (mg/L)	Difference (%)
1.5	0.37	0.38	3.0
2.5	0.63	0.66	4.0
5.8	1.32	1.36	3.1
12.5	2.91	2.99	2.5
23.0	5.75	5.90	2.7
36.0	9.10	9.5	4.3
Water temperature (°C)[4]	Model DO_3 conc. (mg/L)	Exper. DO_3 conc. (mg/L)	Difference (%)
10	0.80	0.88	9.0
20	0.63	0.66	4.0
30	0.35	0.40	12.6

[1] Gas flow rate, 100 mL/min; ozone dose, 2.5 g/m^3; water temperature, 20 °C.

[2] Water flow rate, 3.5 LPM; ozone dose, 2.5 g/m^3; water temperature, 20 °C.

[3] Water flow rate, 3.5 LPM; gas flow rate, 100 mL/min; water temperature, 20 °C.

[4] Water flow rate, 3.5 LPM; gas flow rate, 100 mL/min; ozone dose, 2.5 g/m^3.

3.4.6 Comparison with Other Studies

Many factors, such as the configuration of the reactor, the interfacial area, the characteristics of water, the gas flow rate, the water flow rate, and temperature, can influence the volumetric mass transfer coefficient of ozone. Since the value of K_La is also related to the operating conditions, water source, and the design of the contactor, it is not possible to compare the mass transfer coefficient between research projects without considering these parameters. Therefore, the experimental results and operating conditions from this study have been compared to those in the literature (Table 3.11).

The value of K_La calculated from this study is the smallest among all values presented in Table 3.11. But as mentioned above, other parameters need to be taken into account. Many researchers reported that an increase of gas flow rate results in an increase of K_La value (Hsu et al. 2002; Roustan et al. 1987; Stankovic 1988; Zhou and Smith 2000). This is due to the greater turbulence achieved at higher flow rates, and a concomitant thinning of the gas-liquid film. As can be seen in Table 3.11, the gas flow rate used in this study is much smaller than the others. In addition, our system is the only one that does not have physical diffuser, which makes produce fine bubbles impossible. These two factors may result in lower values of K_La. However, the advantages of using low gas flow rate and no diffuser in the system are lowering operating cost and maintenance cost.

Wu and Masten (2001) investigated the K_La obtained in a semi-batch stirred reactor by using a smaller 1.5 liter water tank, higher gas flow rate, higher ozone dose, and fine bubble diffuser. The K_La values from their study are only slightly greater than those obtained in this study. Bin and colleagues (2001) used a bubble column (0.15 m ID, 5.5 m high) as an ozone contactor and applied high gas flow rate and finer bubbles. It is noticeable that they used pH 7 to 8 water and did not consider the effect of ozone auto-decomposition on the K_La. As such, the K_La values they obtained do not reflect the real values for their experimental system.

Zhou and Smith (2000) treated pulp mill wastewater using a bubble column. Since the chemical oxygen demand (COD) of the wastewater is 609 mg/L, it is reasonable to assume that K_La values they obtained were predominately due to the reaction of ozone with the COD. Roustan et al. (1996) applied the highest gas flow rate and water flow rate among all studies listed in Table 3.11 to treat tap water at pH 7.5 to 8.1. Although high K_La values were obtained from their study, their K_La values were not much higher than those obtained by Bin et al. (2001) who used lower water flow rate and applied finer gas bubbles. Sheffer and Esterson (1982) found that the mass transfer coefficient of ozone in tap water (pH 7.5 to 8.1) increased as the water flow rate increased. Thus, high gas flow rate, high water flow rate, and high pH of the water applied in other studies resulted in K_La values greater than what were obtained in this study.

Shen and Semmens (1990) used the membrane as an ozone contactor rather than as a physical barrier to investigate the ozone mass transfer. This was done because of the membrane's high interfacial area. Although, they reported the highest K_La value of ozone in Table 3.11, almost half (44%) of the ozone dosed in their experiments was estimated to be consumed by the experimental system. This is because of the membrane used in their experiment. The membrane was made of polypropylene, which was attacked by ozone and seriously damaged during the experiment.

Bollyky (1981) indicated that the general requirement for an ozone contactor include: 1) low cost, 2) minimal energy consumption, 3) minimal maintenance, 4) automated operation, 5) efficient mass transfer, 6) simple design, 7) preferably no moving parts, 8) nothing to clog, 9) flexibility to respond to the variations in operating parameters and water quality. The ozonation/membrane system studied can achieve reasonable ozone mass transfer, requires less gas flow rate and water flow rate (than comparable systems), and does not require diffuser, thereby reducing clogging. These may result in low energy consumption, low maintenance, and have economical advantage over other ozone contactors.

Table 3.11 K_La values and experimental conditions from this study and literature on ozone mass transfer

Reference	This study	Wu and Masten (2001)	Bin et al (2001)	Zhou and Smith (2000)	Roustan et al (1996)	Shen et al (1990)
K_La (min^{-1})	0.05 ~ 0.17	0.12 ~ 0.39	0.18 ~ 1.2	0.5 ~ 1.5	0.31 ~ 1.15	3.4 ~ 4.4
Temp (°C)	10, 20, 30	14, 22, 30	20 ~ 23	21 ± 2	12 ~ 19	25
Gas flowrate (L/min)	0.025 ~ 0.1	0.1 ~ 0.5	5 ~ 20	0.5 ~ 2.0	2 ~ 22	0.22
Water flowrate (L/min)	2.0 ~ 3.5	NA	1.7 ~ 7.5	NA	5 ~ 22	0.063 ~ 0.269
Type of Reactor	Ozone/ membrane	Semibatch (stirred)	Bubble column	Bubble column	Bubble column	Hollow fiber
Diffuser Type	Symple Y mixer w/o diffuser	Fritted glass	Porous diffuser	Porous diffuser or venturi injector	Porous diffuser	Membrane
Bubble Size	NA	< 1mm	100 ~ 150μm	NA	1.75 ~ 5.25 mm	NA
pH	2.0	2.1	7 ~ 8	NA	7.5 ~ 8.1	2
Water Source (Volume)	DDI (3.2 L)	DDI (1.5 L)	DI or tap water (97 L)	Lagoon effluent (4 L)	Tap water (NA)	DI (1.5 L)
O_3 Dose (g/m^3)	1.5 ~ 36.0	46	8 ~ 60	0 ~ 134	10 ~ 60	7.86 ~ 9.97

3.5 CONCLUSIONS

1. Ozone gas was injected into the feed water stream of the tubular ceramic membrane to investigate its effect on the permeate flux. It was observed that an increase in permeate flux can be achieved by either increasing the gas flow rate or increasing the water flow rate. The increase in the permeate flux ranged from 5.0 to 63.3 %, depending on the system operating conditions. In addition, the effect of ozone addition on permeate flux at low water flow rate is more significant than that at high water flow rate.
2. The decomposition of dissolved ozone follows the first-order kinetics. The rate of ozone decomposition increased as the water temperature increased. The experimental results showed that the decomposition rate constant can not be neglected even at low pH level when using the ozonation/membrane system.
3. A mathematical model was developed and used to calculate the volumetric mass transfer coefficient of ozone in the ozonation/membrane system. This model was also verified to be able to predict the dissolved ozone concentration in the water tank.
4. The experimental results show that as the water flow rate increases, the volumetric mass transfer coefficient increases. The increase of ozone gas flow rate also increases the volumetric mass transfer coefficient of ozone.
5. Increases in the ozone dose resulted in an increase in the value of K_La. However, the K_La value first increased with increasing ozone doses and then decreased after it reached a maximum value.
6. The increase of K_La value is limited as the water temperature increased from 10 °C to 30 °C. This is probably due to the low ozone dose (2.5 g/m^3) applied in this experiment or the configuration of this bench-scale system.

7. Two different mixers, SYM and HEM, were used to investigate their effect on the performance of the system. The HEM produces finer bubbles than does the SYM, which resulted in greater values of K_La using the HEM. However, with the HEM, the dissolved ozone concentration was less than that obtained with the SYM. With the HEM, it was found that some bubbles accumulated on the top of the diffuser and did not mix with the feed water stream and pass into the membrane module. This design problem may result in the lower dissolved ozone concentrations observed.
8. Considering some important factors, such as gas flow rate, water flow rate, and the characteristics of the source water, which influence the K_La value, the ozonation/membrane system developed in this study can achieve reasonable ozone mass transfer by requiring lesser ozone dose, gas flow rate, and water flow rate than comparable systems. This system has the added advantage that it does not include diffuser thus reducing clogging problems.

3.6 REFERENCES

Amy, G. L., Kuo, C. J., and Sierka, R. A. (1988). "Ozonation of Humic Substances - Effects on Molecular-Weight Distributions of Organic-Carbon and Trihalomethane Formation Potential." *Ozone-Science & Engineering*, 10(1), 39-54.

Bablon, G., Bellamy, W. D., Bourbigot, M.-M., and et. al. (1991). "Fundamental Aspects." Ozone in Water Treatment: Application and Engineering, D. R. Brink, ed., Lewis Publishers, Chelsea, MI, 11-132.

Barberis, K., and Howarth, C. R. (1991). "Reactivity Studies in the Ozonolysis of Pollutants Using a Perforated Spinning Disk Reactor to Enhance Mass-Transfer." *Ozone-Science & Engineering*, 13(5), 501-519.

Bin, A. K., Duczmal, B., and Machniewski, P. (2001). "Hydrodynamics and ozone mass transfer in a tall bubble column." *Chemical Engineering Science*, 56(21-22), 6233-6240.

Bollyky, L. J. (1981). "The Mass-Transfer of Ozone into Water - Energy-Requirements State of the Art." *Ozone-Science & Engineering*, 3(3), 181-210.

Canale, R. P., and Weber, W. J. J. (1972). "Aeration and Gas Transfer." Physicochemical Processes - For Water Quality Control, W. J. Weber, ed., John Wiley & Sons., New York, 503-531.

Cheng, T. W., and Wu, J. G. (2003). "Quantitative flux analysis of gas - Liquid two-phase ultrafiltration." *Separation Science and Technology*, 38(4), 817-835.

Cipparone, L. A., Diehl, A. C., and Speitel, G. E. (1997). "Ozonation and BDOC removal: Effect on water quality." *Journal American Water Works Association*, 89(2), 84-97.

Cui, Z. F., and Wright, K. I. T. (1994). "Gas-Liquid 2-Phase Cross-Flow Ultrafiltration of Bsa and Dextran Solutions." *Journal of Membrane Science*, 90(1-2), 183-189.

Ducom, G., Matamoros, H., and Cabassud, C. (2002). "Air sparging for flux enhancement in nanofiltration membranes: application to O/W stabilised and non-stabilised emulsions." *Journal of Membrane Science*, 204(1-2), 221-236.

Faust, S. D., and Aly, O. M. (1999). *Chemistry of Water Treatment 2ND Edition*, Lewis Publishers, Ann Arbor, MI.

Gurol, M. D., and Singer, P. C. (1982). "Kinetics of Ozone Decomposition - a Dynamic Approach." *Environmental Science & Technology*, 16(7), 377-383.

Hashino, M., Mori, Y., Fujii, Y., Motoyama, N., Kadokawa, N., Hoshikawa, H., Nishijima, W., and Okada, M. (2000). "Pilot plant evaluation of an ozone-microfiltration system for drinking water treatment." *Water Science and Technology*, 41(10-11), 17-23.

Hoigne, J. (1988). "The Chemistry of Ozone in Water." Process Technologies for Water Treatment, Plenum Publishing Corp., New York.

Hsu, Y. C., Chen, T. Y., Chen, J. H., and Lay, C. W. (2002). "Ozone transfer into water in a gas-inducing reactor." *Industrial & Engineering Chemistry Research*, 41(1), 120-127.

Janknecht, P., Wilderer, P. A., Picard, C., Larbot, A., and Sarrazin, J. (2000). "Investigations on ozone contacting by ceramic membranes." *Ozone-Science & Engineering*, 22(4), 379-392.

Kim, J. O., Somiya, I., and Fujii, S. (1999). "Fouling Control of Ceramic Membrane in Organic Acid Fermenter by Intermittent Ozonation." Proceedings of the 14th Ozone World Congress, Dearborn, MI, 131-143.

Klijn, R. B., van der Meer, W. G. J., Vriezen, H., and van Ekkendonk, F. H. J. (2000). "Surface Water Treatment with Zenon Microfiltration Membranes: Minimisation of Energy and Chemical Use." Proceedings of the Conference on Membranes in Drinking and Industrial Water Production, L'Aquila, Italy, 557-563.

Laborie, S., Cabassud, C., Durand-Bourlier, L., and Laine, J. M. (1997). "Flux Enhancement by a Continuous Tangential Gas Flow in Ultrafiltration Hollow Fibres for Drinking Water Production: Effects of Slug Flow on Cake Structure." *Filtration & Separation*, 34(8), 887-891.

Laborie, S., Cabassud, C., Durand-Bourlier, L., and Laine, J. M. (1998). "Fouling Control by Air Sparging Inside Hollow Fibre Membranes-Effects on Energy Consumption." *Desalination*, 118(1-3), 189-196.

Ledakowicz, S., Maciejewska, R., Perkowski, J., and Bin, A. (2001). "Ozonation of Reactive Blue 81 in the bubble column." *Water Science and Technology*, 44(5), 47-52.

Mercier, M., Fonade, C., and Lafforgue-Delorme, C. (1995). "Influence of the Flow Regime on the Efficiency of a Gas-Liquid Two-Phase Medium Filtration." *Biotechnology Techniques*, 9(12), 853-858.

Mercier, M., Fonade, C., and Lafforgue-Delorme, C. (1997). "How slug flow can enhance the ultrafiltration flux in mineral tubular membranes." *Journal of Membrane Science*, 128(1), 103-113.

Richards, D. A., Fleischman, M., and Ebersold, L. P. (1976). "Mass Transfer Coefficients for the Ozone-Water System." *AIChE Symposium Series*, 73(166), 213-224.

Richardson, S. D., Thruston, A. D., Caughran, T. V., Chen, P. H., Collette, T. W., Floyd, T. L., Schenck, K. M., Lykins, B. W., Sun, G. R., and Majetich, G. (1999). "Identification of new ozone disinfection byproducts in drinking water." *Environmental Science & Technology*, 33(19), 3368-3377.

Roth, J. A., and Sullivan, D. E. (1981). "Solubility of Ozone in Water." *Industrial & Engineering Chemistry Fundamentals*, 20(2), 137-140.

Roustan, M., Duguet, J. P., Brette, B., Brodard, E., and Mallevialle, J. (1987). "Mass Balance Analysis of Ozone in Conventional Bubble Contactors." *Ozone Science & Engineering*, 9(3), 289-297.

Roustan, M., Wang, R. Y., and Wolbert, D. (1996). "Modeling hydrodynamics and mass transfer parameters in a continuous ozone bubble column." *Ozone-Science & Engineering*, 18(2), 99-115.

Shanbhag, P. V., Guha, A. K., and Sirkar, K. K. (1998). "Membrane-based ozonation of organic compounds." *Industrial & Engineering Chemistry Research*, 37(11), 4388-4398.

Sheffer, S., and Esterson, G. L. (1982). "Mass-Transfer and Reaction-Kinetics in the Ozone Tap Water- System." *Water Research*, 16(4), 383-389.

Shen, Z. S., Semmens, M. J., and Collins, A. G. (1990). "A Novel-Approach to Ozone Water Mass-Transfer Using Hollow Fiber Reactors." *Environmental Technology*, 11(7), 597-608.

Sotelo, J. L., Beltran, F. J., Benitez, F. J., and Beltranheredia, J. (1987). "Ozone Decomposition in Water - Kinetic-Study." *Industrial & Engineering Chemistry Research*, 26(1), 39-43.

Stankovic, I. (1988). "Comparison of Ozone and Oxygen Mass-Transfer in a Laboratory and Pilot-Plant Operation." *Ozone-Science & Engineering*, 10(3), 321-338.

Sugimitsu, H., Okazaki, S., and Moriwaki, T. "Decomposition of Ozone in Aqueous Solutions." *Ninth Ozone World Congress*, New York, 97-105.

Verberk, J. Q. J. C., Worm, G. I. M., Futselaar, H., and van Dijk, J. C. (2000). "Combined Air-Water Flush in Dead-End Ultrafiltration." Proceedings of the Conference on Membranes in Drinking and Industrial Water Production, L'Aquila, Italy, 655-663.

Weber Jr., W. J., and DiGiano, F. A. (1996). "Microtransport Processes." Process Dynamics in Environmental Systems, John Wiley & Sons., New York, 147-230.

Wright, P. C., Meeyoo, V., and Soh, W. K. (1998). "A study of ozone mass transfer in a cocurrent downflow jet pump contactor." *Ozone-Science & Engineering*, 20(1), 17-33.

Wu, J. J., and Masten, S. J. (2001). "Mass transfer of ozone in semibatch stirred reactor." *Journal of Environmental Engineering-Asce*, 127(12), 1089-1099.

Zhou, H. D., and Smith, D. W. (2000). "Ozone mass transfer in water and wastewater treatment: Experimental observations using a 2D laser particle dynamics analyzer." *Water Research*, 34(3), 909-921.

CHAPTER 4

THE EFFECT OF OZONATION/MEMBRANE PROCESS ON THE CHARACTERISTICS OF NATURAL ORGANIC MATTER

4.1 INTRODUCTION

Natural organic matter (NOM), which is made up of a heterogeneous mixture of organic compounds and occurs either as results of natural processes or human activities in the environment, is ubiquitous in aquatic systems. The composition of NOM can be divided into two fractions, humic substances, which consist of humin, fulvic acid and humic acid, and non-humic substances. Fractionation is accomplished based on the difference of the aqueous solubilities of the different components at different pH values (MacCarthy and Suffet 1989; Malcolm 1985). The molecular weight distribution of NOM ranges from a few hundred daltons for fulvic acids to tens of thousands daltons for the humic acids (Manahan 1993).

In water treatment, the presence of NOM is problematic because the reaction of NOM with disinfectants results in the formation of DBPs. Humic substances are recognized as the primary precursors of chlorination byproducts (Collins et al. 1986; Ichihashi et al. 1999; Manahan 1993; Reckhow et al. 1990). However, non-humic substances also result in the formation of a significant percentage of the regulated or potentially regulated DBPs. In addition, the non-humic fraction of NOM contributes to a higher fraction of BDOC, which may cause bacteria regrowth in water distribution systems (Mogren et al. 1990; Yavich 1998).

BDOC is a fraction of DOC that can be mineralized by heterotrophic microorganisms. The ozonation of water has been found to increase the regrowth potential of bacteria by converting part of the non-biodegradable carbon into BDOC

(Kuo et al. 1977; Narkis and Schneiderrotel 1980; Van der kooij et al. 1989; Yavich 1998). Moreover, the growth of bacteria in the distribution system may pose tastes, odor, color, and pipe corrosion problems (Levy et al. 1986).

The measurement of BDOC has been used predominantly to indicate the biostability of water and to evaluate the performance of biotreatment processes (e.g., biological filtration). One approach to measuring the biodegradability of water is to assess the AOC, which represents the regrowth potential of heterotrophic bacteria in water and was developed by van der Kooij, Visser, and Hijnen (1982). The other approach is based either on the reduction of DOC during incubation or on an estimate of the flux of organic matter utilized by bacteria and was developed by Servais, Billen, and Hascoët (1987). The correlation between BDOC and AOC depends predominately on the characteristics of the tested water (Charnock and Kjonno 2000; Siddiqui et al. 1997).

The application of ozonation prior to membrane filtration effectively reduces membrane fouling and enhances permeate flux (Hashino et al. 2000; Hyung et al. 2000; Kim et al. 1999). Ozonation of water containing NOM results in more lower molecular weight material, a decrease in the concentration of UV absorbing compounds, an increase in the biodegradability, a reduction in the formation of DBPs, and an increase in the formation of more polar compounds. In addition, membrane filtration provides a good physical barrier to turbidity, pathogens, and NOM, although the effectiveness of the filtration process depends very much on the size of the membrane filters employed. Based upon earlier research, we hypothesize that the ozonation/membrane process will effectively remove DBP precursors, reduce DBPs formation, and inactivate pathogens and produce biologically stable water if followed by biotreatment.

The objective of this study was to investigate the effect of the combined ozonation/membrane process on the characteristics of NOM and to evaluate the biodegradability of the treated water. Several experiments were conducted and their results are discussed. We considered: 1) the effect of ozonation on the permeate flux; 2) the effect of ozonation on DOC, UV-254, humic substances, non-humic substances, AOC, and BDOC; 3) the effect of biotreatment on the raw water and treated water quality following the ozonation/membrane process; 4) and the effect of operational parameters, such as water flow rate, gas flow rate, ozone dose, and water temperature, which affect the ozone mass transfer, on the efficacy of the ozonation/membrane system.

4.2 MATERIALS AND METHODS

4.2.1 Experimental Setup and Protocol

A specially designed ozonation/membrane system was used to investigate the permeate flux recovery as a result of ozonation and variation in the NOM resulting from the treatment process. NOM was assessed in terms of DOC, UV-254, humic substances, non-humic substances, AOC, and BDOC. A schematic diagram of this system is shown in Figure 4.1. Tubular ceramic membranes (Clover-leaf design (containing three channels), CéRAM Inside, Tami North America, St. Laurent, Québec, Canada) with a molecular weight cut-off of 15 kD were used in the system. The characteristics of the laboratory-scale ultrafiltration membrane are summarized in Table 4.1. Teflon tubing and stainless steel joints and valves were used throughout the system. Other components included: 3.5-liter and 1.5-liter water-jacked glass reservoirs made of Pyrex glass, and a simple Y inline mixer (Ozone Service, Burton, B.C., Canada).

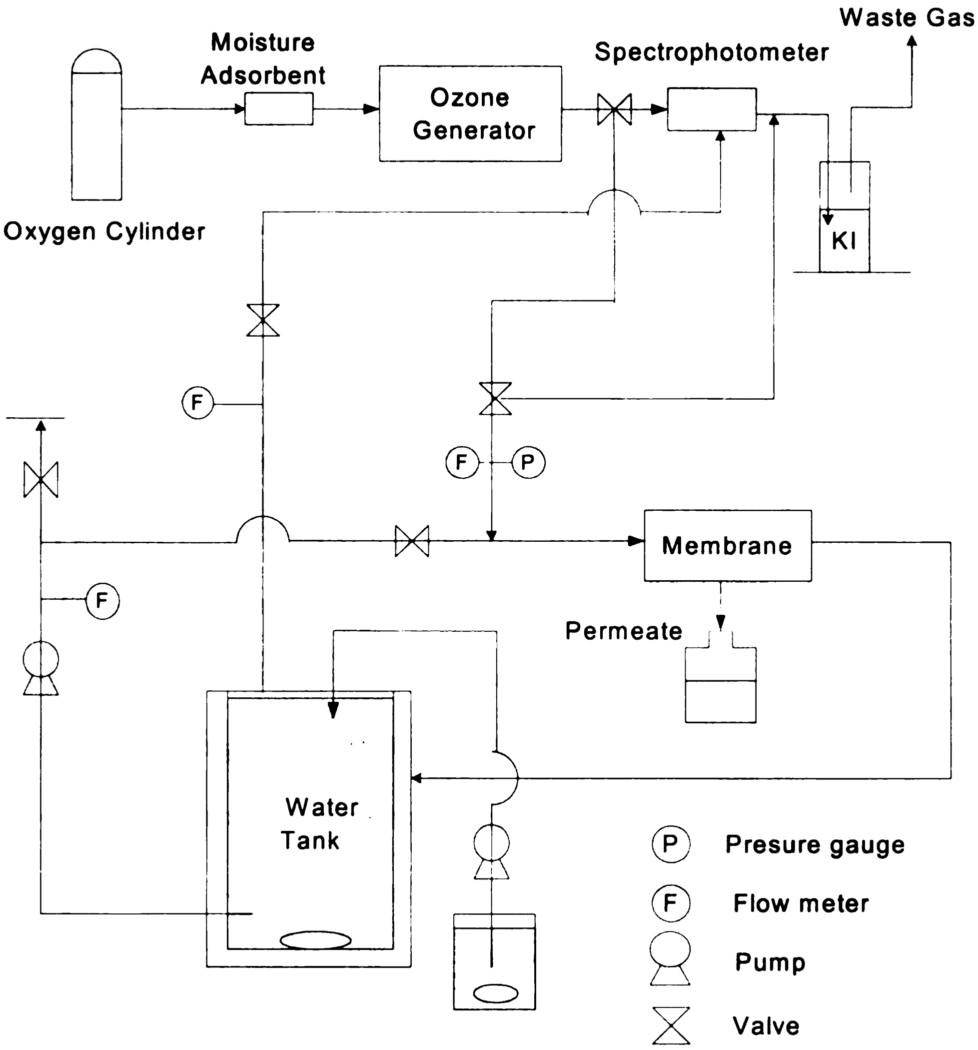

Figure 4.1 Experimental setup for the ozonation/membrane process.

Table 4.1 Details of the ceramic membrane.

External diameter (mm)	Active length (cm)	Filtering area (cm^2)	Number of channels	Operating pH range	Cut-off range (kD)
10	25.0	95.2	3	0-14	15

Ozone was generated by feeding pure oxygen gas from a gas cylinder to the ozone generator (Model OZ2PCS, Ozotech Inc., Yreka, Calif.). The oxygen gas stream was dried using a molecular sieve trap prior to ozone generation. The ozone gas concentration was controlled using the electric current of the ozone generator. The wasted ozone gas was vented after passing the gas through a 2% potassium iodide (KI) solution to destroy any residual ozone gas.

For the experiments investigating permeate flux recovery, a centrifugal pump (Model 4RH12, Dayton Electric Mfg. Co., Niles, Illinois) was used to inject water from the 3.5-liter water reservoir into the membrane module. A magnetic stirrer at the bottom of the reservoir was used to completely mix the water. The water flow rate was fixed at 2.75 L/min and the water temperature was maintained at 20 °C. The permeate flux was monitored by measurement of the flux in a volumetric cylinder over specified time intervals. A peristaltic pump (Masterflex Model 7520-35, Cole-Parmer Co., Chicago, Illinois) was used to continuously pump the water that was prepared in a 1.5-liter water tank into the 3.5-liter water reservoir to maintain the constant volume of water. The system was kept running under these operating conditions until the permeate flux decreased to 60% of the initial flux without ozonation. Then ozone gas was injected through the simple Y inline mixer into the feed water stream of the membrane module. The ozone gas flow rate was 100 mL/min and the ozone dose was 12.5 g/m^3. The system was stopped as soon as the permeate flux reached a constant value. Same experimental procedure was used to investigate the effect of oxygenation on the permeate flux. Pure oxygen was used instead of ozone and was injected into the feed water stream after the permeate flux decreased to 75% of the initial flux with out oxygenation.

The same system used in permeate flux recovery experiment was used to investigate the effect of the ozonation/filtration on the characteristics of NOM. Several operational factors, such as ozone concentration in the inlet gas phase, water flow rate, gas flow rate, and water temperature, which influence the ozone mass transfer and solubility, were investigated. Table 4.2. summarizes the experimental conditions used in this study.

Table 4.2. Experimental conditions.

Parameters	Values
Inlet ozone dose (g/m^3)	1.5, 2.5, 5.8
Water flow rate (L/min)	2.75
Ozone gas flow rate (mL/min)	50, 75, 100
Water temperature (°C)	10, 20, 30

The natural water and ozone gas were continuously fed into the membrane module. Prior to ozonation, raw water samples were pre-filtered through a 0.45 μm filter to remove coarse suspended solids. Since the collection of permeate from the membrane required several hours, a collection bottle with a cap was used and placed in an ice bath to chill and preserve the sample. The first 500 mL of permeate was collected and marked as "Permeate 1". The next 1.5 L of permeate was collected and marked as "Permeate 2". Permeate 1 and 2 represent the characteristics of the permeate collected at different time intervals and provide information of treated water quality on the performance of the ozonation/membrane system. The concentrate was recirculated back to the raw water reservoir. The filtered raw water and the Permeate 2 water were further treated by biofiltration to determine their biodegradability. Water samples were collected from the filtered raw water, the permeate, the water tank, and the filtrate of biofiltration columns. DOC, UV-254, humic substances, non-humic substances, AOC and BDOC were monitored. The dissolved ozone residual in collected samples was quenched by sparging the solution with a high purity helium gas (99.999 %) before analysis. Earlier studies show that quenching can be achieved in this manner in several seconds (Herner 1999).

4.2.2 Water Source

Experiments were carried out on Lake Lansing (Haslett, MI) water. Lake Lansing water samples were collected at the boat ramp at the Lake Lansing Park-South, Haslett, Michigan. Water quality characteristics of Lake Lansing are summarized in Table 4.3. Lake Lansing waters were collected in five-gallon tanks, properly labeled, and stored at 4°C. The maximum storage period was seven days. All waters were filtered through a 0.45-μm filter before testing.

4.2.3 Gas-phase Ozone Analysis

The concentration of ozone in gas phase was measured at UV 254 nm with a Milton Roy Genesis-5 spectrophotometer (Milton Roy, Inc., Rochester, NY) using a 2-mm quartz flow-through cell. An extinction coefficient of 3000 $M^{-1}cm^{-1}$ at 254 nm (Hoigné 1988) was used for calculating ozone concentrations.

Table 4.3 Typical quality characteristics of Lake Lansing water.

Parameters	Lake Lansing
TOC (mg/L)	8.6 ~ 11.0
pH	7.7 ~ 8.0
Alkalinity (mg/L as $CaCO_3$)	140
UV-254 (abs.)	0.160 ~ 0.180
SDS THM (μg/L)	240
SDS HAA (μg/L)	75
BDOC (mg/L)	1.0 ~ 4.0

4.2.4 UV-254 Absorption

UV absorption was measured at a wavelength of 254 nm with a Milton Roy Genesis-5 spectrophotometer (Milton Roy, Inc., Rochester, NY) at room temperature. A quartz cell providing a light path of 1 cm was used. Samples were prefiltered through a 0.45-μm filter before measurement.

4.2.5 TOC and DOC Analyses

TOC was determined by the heated-persulfate oxidation method (Standard Methods 1998) using an OI Analytical Model 101 analyzer with auto sampler. DOC was determined the same way but samples were prefiltered through a 0.45 μm glass-fiber filter before measurement.

Each sample was performed with three replicates. A blank (DDI water) and a standard calibration series of 2.5, 5.0, 7.5, and 10.0 mg C/L were prepared and run before analyzing water samples.

4.2.6 Humic Substances and Non-humic Substances Analyses

The concentrations of HS and NHS in water samples were measured by adsorption on XAD-8 resin using Method 5510C (Standard Methods 1998) with slight modification. The XAD-8 resin was prepared and cleaned following the procedure described in the Method 5510 C and then was packed in a 1.0 x 15-cm glass column.

A 100 mL water sample was first acidified to pH 2 with concentrated phosphoric acid and then pumped onto the top of the resin-packed column at a rate of 3 mL/min. The effluent from the column was collected and then analyzed for TOC, which represented the non-humic fraction of the dissolved organic matter in the water sample. Then the resin-packed column was back eluted with 100 mL of 0.1 N sodium hydroxide at a flow rate of 3 mL/min. The eluent was collected and acidified with concentrated phosphoric acid to a pH less than 4, purged with high-purity helium for 3 minutes to remove inorganic carbon, and analyzed for TOC. The organic content of the eluent represented the concentration of HS.

4.2.7 Biodegradable Dissolved Organic Carbon Analysis

BDOC was determined by recirculating raw and treated water through a biofiltration column that contains Lake Lansing water inoculum. The procedure described by Cipparone et al. (1997) was followed. The biofiltration system consisted of a glass chromatography column with a diameter of 2.5 cm and a total volume of 100 cm^3, a peristaltic pump (Masterflex Model 7553-50, Cole-Parmer Co., Chicago, Illinois), and a 1-liter glass water tank. Half of the column volume was filled with non-activated carbon. Untreated Lake Lansing water was used to seed the column and the organisms were acclimated by feeding ozonated Lake Lansing water into the column continuously over a period of four months before use of the column in this study. One liter of water sample in the feed water tank was recirculated at a rate of 10 mL/min at room temperature. The TOC concentration was monitored daily for seven days. The BDOC concentration was calculated as the difference between the initial TOC concentration in the sample and that in the final biodegradation sample.

4.2.8 Assimilable Organic Carbon Analysis

The concentration of AOC was measured using the Method 9217 of Standard Methods (1998). Water samples were collected in organic-carbon-free glass bottles, mixed well and poured into several test tubes. These test tubes were capped immediately and pasteurized in a 70 °C water bath for 30 minutes to inactivate bacteria originally present in the sample. After pasteurized samples cooled to room temperature, they were inoculated with 500 colony-forming units (CFU)/mL each of *Pseudomonas fluorescens* strain P17 and *Spirillum* strain NOX. The samples were incubated at room temperature (20 °C) for seven days, then a Heterotrophic Plate Count (HPC) was performed by distributing samples on predried R2A agar plates

(Standard Methods 1998). The colonies were counted on the plates after three days of incubation at room temperature and the concentration of AOC was calculated.

4.3 RESULTS AND DISCUSSION

4.3.1 Permeate Flux Recovery

The permeate fluxes with and without ozonation are shown in Figure 4.2. The permeate fluxes with and without oxygenation are presented in Figure 4.3. The prefiltered Lake Lansing water was used in the experiment. The ozonation/membrane system was operated at 2.75 L/min water flow rate and the water temperature was maintained at 20 °C. For the ozonation experiment, the initial permeate flux was 1.9 mL/min and gradually decreased to 1.15 mL/min (60% of the initial flux) in 12 hours. As soon as the permeate flux reached 60% of the initial flux, ozone gas was prepared from pure oxygen and injected into the water stream at 100 mL/min gas flow rate and 12.5 g/m^3 dose. It was observed that the permeate flux rebounded immediately and reached 1.85 mL/min (97% of the initial flux) in just one hour.

For the oxygenation experiment, the initial flux was 2.1 mL/min and decreased to 1.54 mL/min (75% of the initial flux) in 13.5 hours. After oxygen gas was injected to the feed water stream at 100 mL/min flow rate, the permeate flux increased immediately. The permeate flux reached 1.71 mL/min (84% of the initial flux) within just 10 minutes after the addition of oxygen gas and maintained at this flux level. Kim et al. (1999) observed similar results by using a ceramic membrane to investigate the effect of ozone and oxygen bubbling on permeate flux recovery. They found that ozone bubbling can result in recoveries up to 94% of the initial flux but oxygen bubbling resulted in recoveries up to 60%. The more efficient permeate flux recovery obtained with ozone compared to that with oxygen is thought to be due to the reaction of ozone with the organic matter that deposits on the membrane surface during normal operation. This reaction not only removes the deposition layer but also breaks down large molecular weight molecules. The injection of both oxygen and ozone is thought to increase the turbulence of the water stream thereby removing or thinning the deposition layer on the membrane surface and, with ozone, also breaking down large molecules and particles.

The hypothesis that organic substances are destroyed during ozonation is supported by atomic force microscope (AFM) scans obtained during this study (see Figures 4.4 to 4.7). The height images on the left mean topography and the phase images on the right show the phase difference between the resonance frequency of the cantilever and the altered oscillation frequency induced by the interaction of the tip with the sample. The phase image for the residuals of non-ozonation backwash (see Figure 4.5) is all one color. This implies that the residuals are basically the same substance, and that it doesn't have sharp edges. The phase images for the residuals of ozonation backwash (see Figures 4.6 and 4.7) show quite a bit of variation that resulted from the ozonation of NOM.

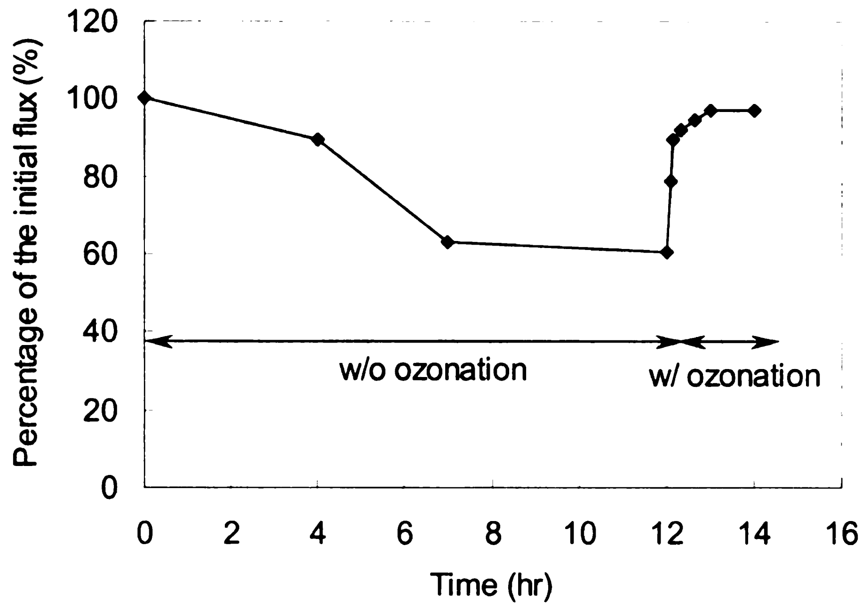

Figure 4.2 The variation of permeate flux with respect to operating time. Operating conditions: water flow rate, 2.75 L/min; ozone gas flow rate, 100 mL/min; ozone dose, 12.5 g/m^3; water temperature, 20 °C.

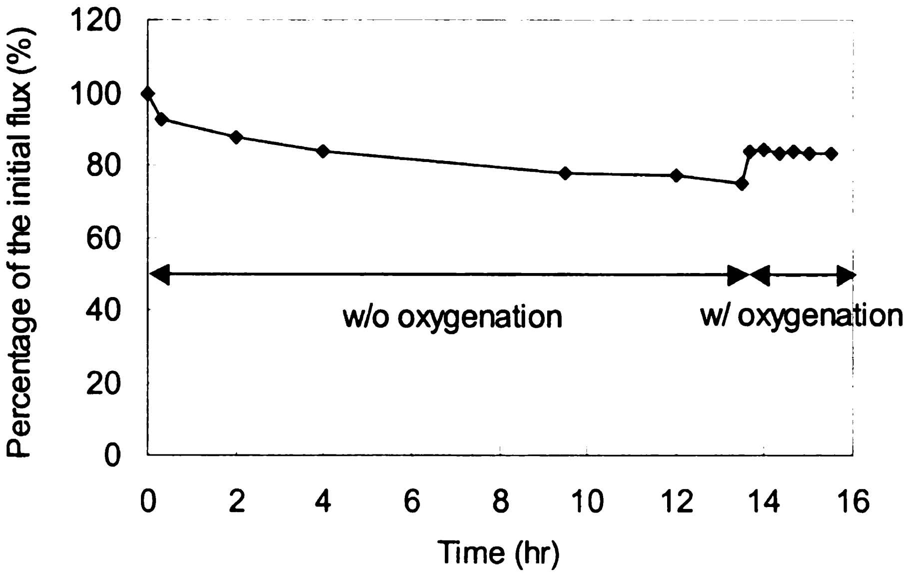

Figure 4.3 The variation of permeate flux with respect to operating time. Operating conditions: water flow rate, 2.75 L/min; oxygen gas flow rate, 100 mL/min; water temperature, 20 °C.

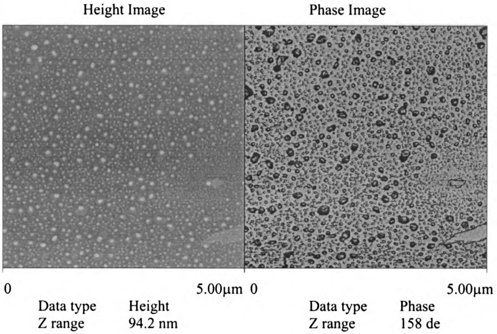

Figure 4.4 The atomic force microscope (AFM) scan of glass substrate with nothing on it. (Courtesy: Dr. Virginia Ayres, Michigan State University)

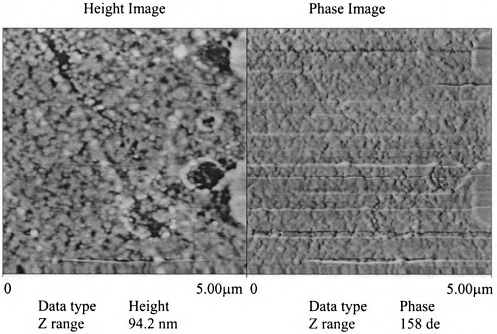

Figure 4.5 The atomic force microscope (AFM) scan of backwash of used ceramic membrane without ozonation of NOM. (Courtesy: Dr. Virginia Ayres, Michigan State University)

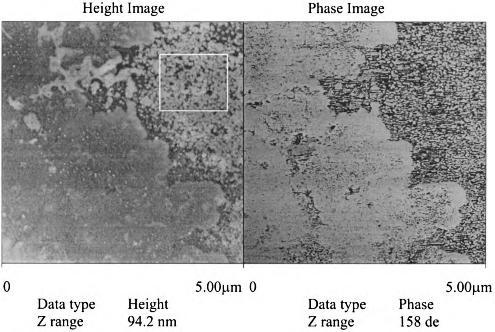

Figure 4.6 The atomic force microscope (AFM) scan of backwash of used ceramic membrane with ozonation of NOM. (Courtesy: Dr. Virginia Ayres, Michigan State University)

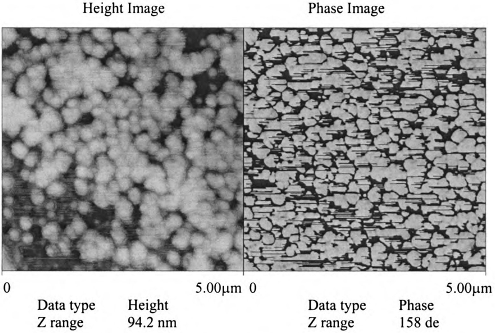

Figure 4.7 Close-up of area in white box in Figure 4.6. (Courtesy: Dr. Virginia Ayres, Michigan State University)

4.3.2 DOC

Before considering the removal of DOC in the ozonation/membrane system, it is important to recognize that the characteristics of NOM in the raw water can vary significantly every time when water samples are collected from Lake Lansing. This makes the direct comparison of treatment efficiency between different operational conditions challenging. Therefore, careful interpretation of the data obtained from this study is necessary.

The effect of water temperature on the DOC concentration is shown in Figure 4.8. Water samples were collected from filtered raw water (FRW), the first 500 mL of the permeate (P1), the next 1.5 liters of the permeate (P2), the 3.5-liter water tank (WT), and the filtrate (B-P2) of biofiltration column used to treat P2 water. The permeate flux of 10, 20, and 30 °C operating temperature was 1.9, 2.3, and 2.8 mL/min, respectively. It is apparent from Figure 4.4 that the DOC concentration decreased in P1, P2, and WT compared to that in the FRW water at 20 °C and 30 °C ($p < 0.01$). At 10 °C, the DOC concentration decreased by ca. 17% in P1 and P2 but only slightly decreased (2.5%) in WT. This suggests that, on one hand, ozonation partially removed DOC at all three temperatures, but that more organic matter was retained in the water tank at 10 °C because of low permeate yield. On the other hand, it has been established that the rate of ozone decomposition and the production of hydroxyl radical increase with increasing temperature (Sotelo et al. 1987). Consequently, the increased effectiveness of the process in degrading DOC in P2 and WT at higher temperatures may be due to the reaction of DOC with the hydroxyl radical, which is more powerful, faster, and relatively less selective oxidant than is molecular ozone.

Figure 4.9 presents the removal efficiency of DOC of P1, P2, and B-P2 at various water temperatures. For P2 water samples, about 15-33% of DOC was removed from the ozonation/membrane system. Since ozonation mainly converts humic to non-humic substances and higher- to lower-molecular weight, only a fraction of the DOC is oxidized. Galapate et al. (2001) used a semi-batch ozonation reactor to treat Minaga Reservoir water at ozone dose of 3 mg O_3/mg DOC and observed a 16% removal of DOC. Owen et al. (1995) used similar set up and observed DOC reduction up to 24% at ozone dose of 1 mg O_3/mg DOC.

The removal efficiency of DOC, as expected, achieved 70 to 80% when the biofiltration followed the ozonation/membrane system to treat P2 water (see Figure 4.9). This is because ozonation of water containing NOM can enhance the biodegradability of water due to the increase of BDOC (Volk et al. 1993; Volk et al. 1997; Yavich 1998). Siddiqui et al. (1997) observed a 40 to 50% removal of DOC at a ratio of O_3/DOC = 2 mg/mg by ozonation and biofiltration, regardless of the source of water or initial DOC. Similar results were reported by other researchers (Cipparone et al. 1997; Goel et al. 1995). Yavich (1998) compared the efficiency of two systems, fluidized bed treatment (FBT) /ozonation/biofiltration and ozonation/FBT, in the removal of DOC from Huron River water. He observed an up to 46% removal of DOC at an ozone dose of 3 mg/mg C. Comparing our results with reports mentioned above, the ozonation/membrane system followed by biofiltration used in this study seems to have higher DOC removal. The may be due to the extent of reaction resulting from the surface catalysis of ozone decomposition or the increased ozone contact time in our system.

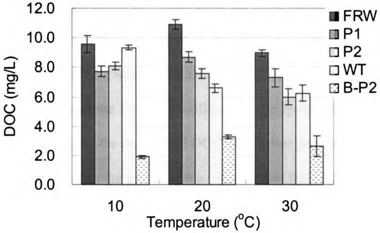

Figure 4.8 The variation of DOC concentration of different treatment stages at various water treatment temperatures. Operating conditions: water flow rate, 2.75 L/min; gas flow rate, 100 mL/min; ozone dose, 2.5 g/m^3.

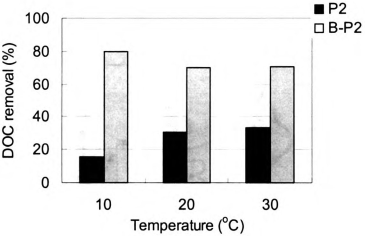

Figure 4.9 The percentage of DOC removal for permeate 2 (P2) and biotreated permeate 2 (B-P2) water at various water treatment temperatures. Concentrations are compared to those in the raw water. For temperatures 10, 20, 30 °C, the raw water DOC concentrations were 9.5, 10.9, 9.0 mg/L, respectively. Operating conditions: water flow rate, 2.75 L/min; gas flow rate, 100 mL/min; ozone dose, 2.5 g/m^3.

Figure 4.10 shows the concentration of DOC in the samples as a function of ozone gas flow rate. At all the flow rates used, the DOC concentration decreased in the permeate of the membrane. Figure 4.11 shows the percentage of DOC removal in the P2 and bio-treated B-P2 water. The efficiency of removal was essentially independent of gas flow rate. Without biofiltration, the system removed about 30% of DOC. With biofiltration, the removal of DOC was further increased to about 70%. These results indicate that the gas flow rate of ozone had little effect on the system performance in terms of DOC removal. This is thought to be due to the characteristics of the raw water quality or the long hydraulic retention time of this ozonation/membrane system.

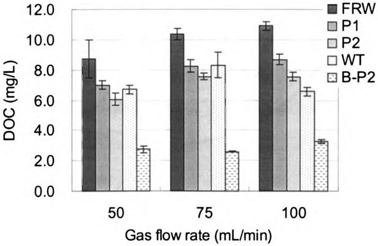

Figure 4.10 The variation of DOC concentration of different treatment stages at various ozone gas flow rates. Operating conditions: water flow rate, 2.75 L/min; ozone dose, 2.5 g/m^3; water temperature, 20 °C.

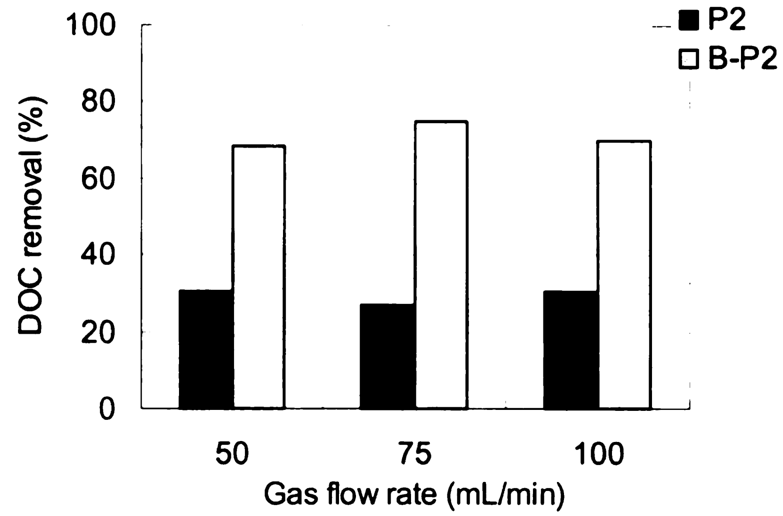

Figure 4.11 The percentage of DOC removal for permeate 2 (P2) and biotreated permeate 2 (B-P2) water at various ozone gas flow rates. Concentrations are compared to those in the raw water. For gas flow rates 50, 75, 100 mL/min, the raw water DOC concentrations were 8.7, 10.4, 10.9 mg/L, respectively. Operating conditions: water flow rate, 2.75 L/min; ozone dose, 2.5 g/m^3; water temperature, 20 °C.

The effect of ozone dose on the DOC removal is shown in Figure 4.12 and the removal efficiency is shown in Figure 4.13. The DOC concentration decreased in the permeate at all three ozone doses. As mentioned earlier, ozonation dose not remove much of the DOC but increases its biodegradability. Based on Figure 4.12, the DOC concentration in the permeate was not significantly reduced ($p > 0.05$), even at an ozone dose of 5.8 g/m^3. However, its DOC concentration after biofiltration was obviously less than those obtained at lower ozone doses (1.5 and 2.5 g/m^3). It indicates that even though the high ozone dose was not more effctive at removing DOC from the system than that observed at low ozone dose, more biodegradable organic material was produced at the 5.8 g/m^3 ozone dosage. Ozonation followed by biofiltration of P2 water removed 88% of DOC at 5.8 mg O_3/L but only removed 70% to 77% of DOC at 1.5 and 2.5 mg O_3/L (see Figure 4.13). This is consistent with the findings of Lee (2001) in terms of AOC.

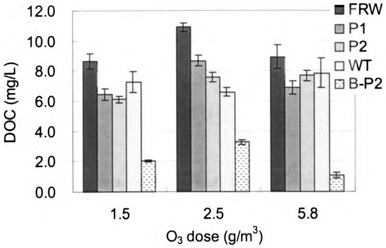

Figure 4.12 The variation of DOC concentration of different treatment stages at various ozone doses. Operating conditions: water flow rate, 2.75 L/min; gas flow rate, 100 mL/min; water temperature, 20 °C.

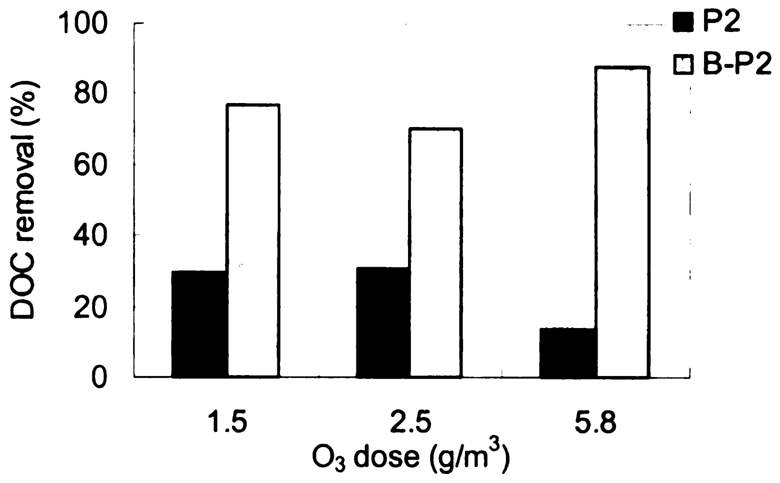

Figure 4.13 The percentage of DOC removal for permeate 2 (P2) and biotreated permeate 2 (B-P2) water at various ozone doses. Concentrations are compared to those in the raw water. For ozone doses 1.5, 2.5, 5.8 g/m^3, the raw water DOC concentrations were 8.7, 10.9, 8.9 mg/L, respectively. Operating conditions: water flow rate, 2.75 L/min; gas flow rate, 100mL/min; water temperature, 20 °C.

4.3.3 UV-254

The removal efficiency of UV-254 at various operational conditions is shown in Figures 4.14, 4.15 and 4.16. As expected, the UV-absorbing compounds were effectively removed, but not eliminated, at all tested conditions. The removal efficiencies for P1, P2, and WT ranged from 55% to 71%, 74 to 84%, and 75 to 85%, respectively. The maximum removal of UV-254 was 85% in our bench-scale system. No further removal was observed after the 85% removal efficiency was achieved.

The percentage removal of UV-254 of P1, which was the first 500 mL of collected permeate of membrane, was less than that of P2, which was the 1.5 L collection of permeate after P1. It appears that with increased ozone contact times, the removal efficiency of UV-254 increases. However, only minimal changes in the UV-254 removal efficiencies were observed between P2 and WT. This indicates that the contact time for P2 were sufficiently long to remove or break down most of the UV-254 absorbing compounds. Although the contact time of WT was longer than P2, only slight changes of UV-254 were observed, suggesting the remaining UV-254 absorbing substances are recalcitrant towards ozone.

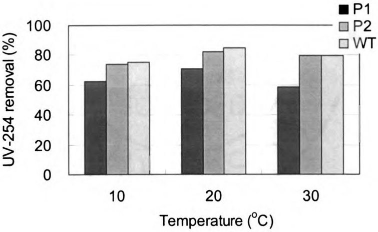

Figure 4.14 Efficiency of UV-254 removal at various water temperatures. Operating conditions: water flow rate, 2.75 L/min; gas flow rate, 100 mL/min; ozone dose, 2.5 g/m^3.

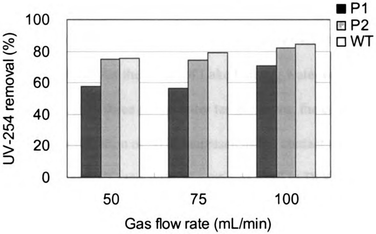

Figure 4.15 Efficiency of UV-254 removal at various ozone gas flow rates. Operating conditions: water flow rate, 2.75 L/min; ozone dose, 2.5 g/m^3; water temperature, 20 °C.

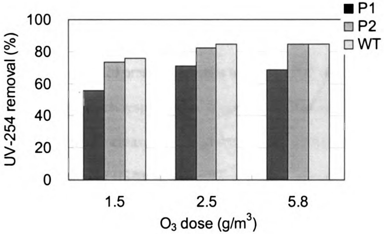

Figure 4.16 Efficiency of UV-254 removal at various ozone doses. Operating conditions: water flow rate, 2.75 L/min; gas flow rate, 100 mL/min; water temperature, 20 °C.

4.3.4 Humic and non-humic substances

The ratios of HS to DOC and of NHS to DOC for FRW, P1, P2, and WT water samples at various water temperatures are shown in Figures 4.17 and 4.18. The experimental results show that the NOM of Lake Lansing water originally consisted of about 60% of HS. At all three tested water temperatures, the concentration of HS decreased and the concentration of NHS increased as the contact time increased. As the water temperature at 20 °C and 30°C, the ratio of NHS to DOC first increased rapidly in P1 and then slightly increased in P2 and WT. In contrast, the ratio gradually increased in P1, P2, and WT at 10°C. This is thought to be because that the concentration of hydroxyl radicals increased with increasing water temperature due to rapid decomposition of ozone with increasing temperature. The OH radicals would react faster with HS than would molecular ozone, converting HS to NHS. However, at lower water temperature, fewer hydroxyl radicals were produced and the direct reaction between molecular ozone and HS was slower than that between hydroxyl radicals and HS.

Figures 4.19 and 4.20 present the ratios of HS to DOC and NHS to DOC at various ozone gas flow rates, respectively. It appears that the ratio of HS/DOC decreased as contact time increased for flowrates of 50 and 75 mL/min. At a flowrate of 100 mL/min, the ratio of HS/DOC in P1, P2, and WT were essentially constant at approximately 30%. Similarly, for gas flow rates of 50 and 75 mL/min, the ratios of NHS/DOC increased with contact time. With the 100mL/min samples, the results correspond well to those for the HS/DOC ratios: the greatest increase occurred in P1. A slight increase in NHS increased from P1 to P2 and the ratio was essentially equal (no statistical difference at $p = 0.05$ level) in P2 and WT samples.

The effect of ozone dose on the ratio of HS and NHS to DOC is shown in Figures 4.21 and 4.22, respectively. The ozone dose at 1.5 g/m^3 converted less HS to NHS comparing with that obtained at 2.5 and 5.8 g/m^3. However, the ratios of HS/DOC and NHS/DOC obtained for an ozone dose of 2.5 g/m^3 were very close to those of 5.8 g/m^3 at P1, P2, and WT. This may suggest that increasing the ozone dose over 2.5 g/m^3 does not further convert HS to NHS in the tested conditions.

Figure 4.23 shows the relationship between the concentration of HS at FRW, P1, P2, and WT and their UV-254 data for Lake Lansing water. As expected, the concentration of HS and the adsorption of UV-254 at different treatment stages and under various operational conditions were well correlated. This is because the aquatic HS contains aromatic functional groups and conjugated double bonds that absorb light at 254 nm in the ultraviolet wavelength region. The value of UV-254 increased as the concentration of HS increased (correlation is significant at the 0.01 level at 95% C.I.).

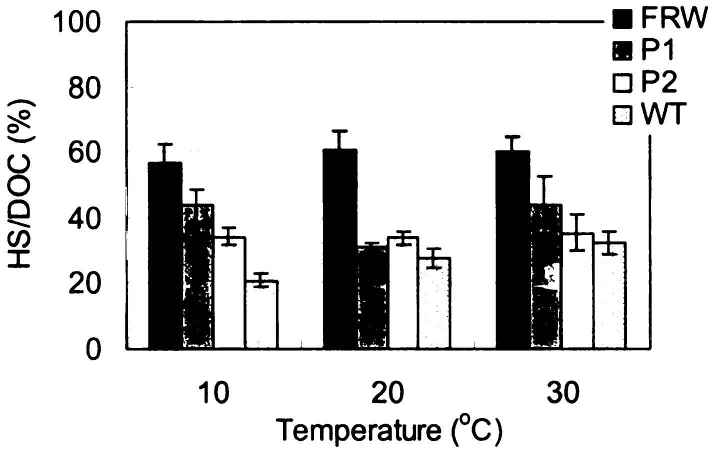

Figure 4.17 The ratio of HS/DOC of different treatment stages at various water treatment temperatures. Operating conditions: water flow rate, 2.75 L/min; gas flow rate, 100 mL/min; ozone dose, 2.5 g/m^3.

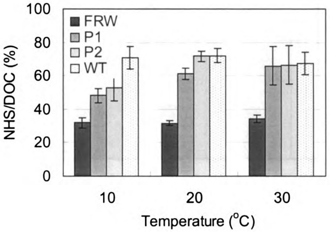

Figure 4.18 The ratio of NHS/DOC of different treatment stages at various water treatment temperatures. Operating conditions: water flow rate, 2.75 L/min; gas flow rate, 100 mL/min; ozone dose, 2.5 g/m^3.

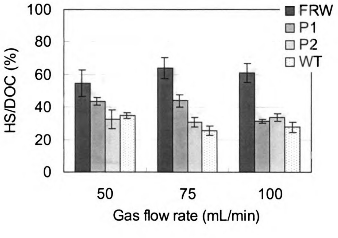

Figure 4.19 The ratio of HS/DOC of different treatment stages at various ozone gas flow rates. Operating conditions: water flow rate, 2.75 L/min; ozone dose, 2.5 g/m^3; water temperature, 20 °C.

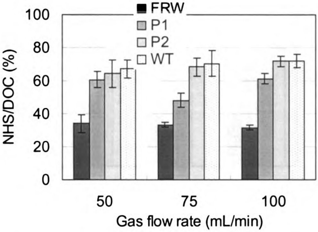

Figure 4.20 The ratio of NHS/DOC of different treatment stages at various ozone gas flow rates. Operating conditions: water flow rate, 2.75 L/min; ozone dose, 2.5 g/m^3; water temperature, 20 °C.

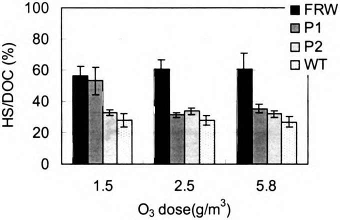

Figure 4.21 The ratio of HS/DOC of different treatment stages at various ozone doses. Operating conditions: water flow rate, 2.75 L/min; gas flow rate, 100 mL/min; water temperature, 20 °C.

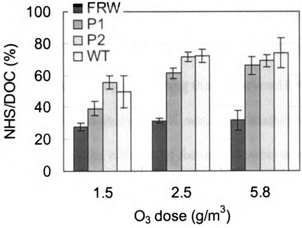

Figure 4.22 The ratio of NHS/DOC of different treatment stages at various ozone doses. Operating conditions: water flow rate, 2.75 L/min; gas flow rate, 100 mL/min; water temperature, 20 °C.

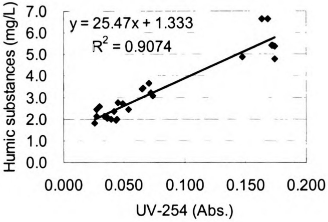

Figure 4.23 Correlation between the concentration of humic substances and UV-254 for Lake Lansing water. (Correlation is significant at the 0.01 level at 95% C.I.)

4.3.5 BDOC

For measuring the BDOC concentration, water samples were recirculated through a biofiltration column as described in Section 4.2.7. The BDOC concentration was measured by subtracting the day seven DOC from day zero DOC of the water sample. In this study, BDOC was only measured for FRW water, as the influent, and P2 water, as the effluent, of the ozonation/membrane system.

The percentages of BDOC to DOC of FRW and P2 water at various experimental conditions are shown in Figures 4.24, 4.25, and 4.26. As can be seen in these figures, the fraction of BDOC to DOC in the FRW ranged from 10 to 38%. After treated by the ozonation/membrane system, the percentage increased to 55 to 86%. A similar trend was observed by Escobar and Randall (2001) when they treated a low DOC raw water (1 mg/L) with ozone. They observed a 49% increment of the effluent BDOC when ozonation was used to treat the raw water.

The BDOC of permeate 2 water treated at 10 °C was approximately 77% of the DOC (see Figure 4.24). At 20 and 30 °C, the BDOC was only about 57% of the DOC. This may be due to the higher concentration of hydroxyl radicals at higher temperature than at lower temperature as was discussed in Section 4.3.2. The observation that the percentage of BDOC of the permeate 2 (B-P2) was lesser at the higher two temperatures is because one would expect that the OH radical would be less efficient than ozone at degrading the DOC into low molecular weight compounds that would provide substrate material for the microorganisms. On the other hand, the high percentage of BDOC in the FRW water at 10 °C may contribute to the higher percentage of BDOC in its P2 water.

The effect of ozone gas flow rate on the ratio of BDOC to DOC is shown in Figure 4.25. The ratio of BDOC:DOC of FRW water ranged from 14 to 35% and increased to 55 to 66% after treatment at various gas flow rates. The ozone gas flow rate did not have a significant influence on the BDOC:DOC ratio in the P2 water. This confirms the previous observations discussed in Sections 4.3.2.and 4.3.4. It also suggests that the conversion of non-BDOC to BDOC is as efficient at a gas flow rate of 50 mL/min as it is at gas flow rates of 75 and 100 mL/min.

Figure 4.26 shows the effect of ozone dose on the BDOC:DOC ratio. At an ozone dose of 5.8 g/m^3 most of the non-BDOC was converted to BDOC, with a BDOC:DOC of 86%. At ozone doses of 1.5 and 2.5 g/m^3, the BDOC:DOC ratios were only 67% and 57%, respectively. However, the ozone dose of 1.5 g/m^3 may be a better operational condition than the other two doses because of its lower cost of ozone production and acceptable efficiency in terms of conversion of non-BDOC.

The experimental results show that using the ozonation/membrane system can dramatically increase the percentage of BDOC in the permeate water, which can be easily removed by subsequent biotreatment. Urfer et al. (1997) suggest that ozonation and biofiltration should be considered as a coupled process rather than two independent process steps, since the ozonation results in the increase of BDOC and leads to regrowth problems in the water distribution system. Similar results were observed by Yavich and Masten (2003).

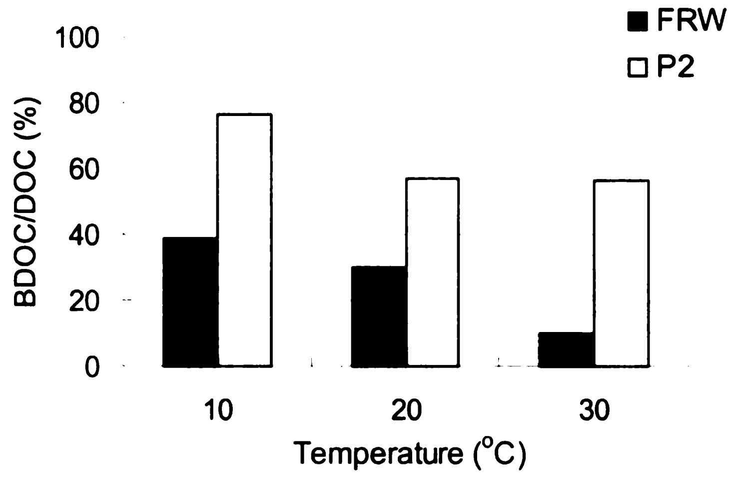

Figure 4.24 The percentages of BDOC to DOC of FRW and P2 water at various water treatment temperatures. Operating conditions: water flow rate, 2.75 L/min; gas flow rate, 100 mL/min; ozone dose, 2.5 g/m^3.

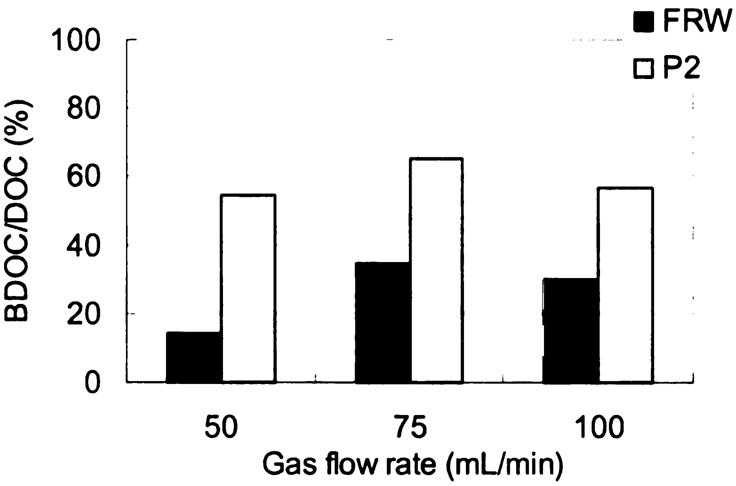

Figure 4.25 The percentages of BDOC to DOC of FRW and P2 water at various ozone gas flow rates. Operating conditions: water flow rate, 2.75 L/min; ozone dose, 2.5 g/m^3; water temperature, 20 °C.

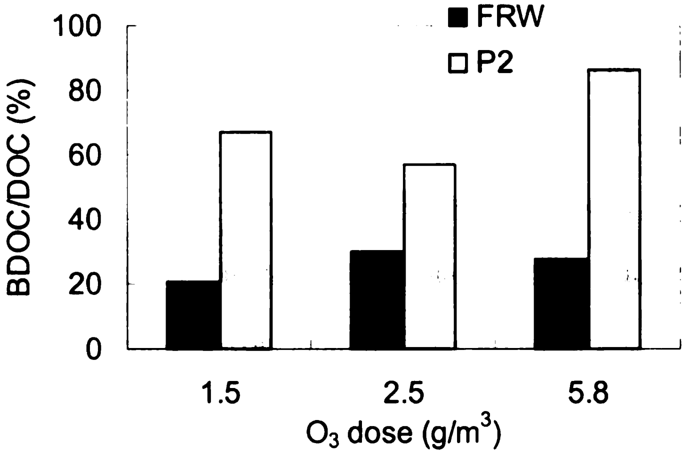

Figure 4.26 The percentages of BDOC to DOC of FRW and P2 water at various ozone doses. Operating conditions: water flow rate, 2.75 L/min; gas flow rate, 100 mL/min; water temperature, 20 °C.

4.3.6 AOC

Figures 4.27, 4.28, and 4.29 show the concentration of AOC of different treatment stages under various operational conditions. The abbreviation of B-FRW represents the filtrate of biofiltration column from the treatment of filtered raw water. Other notation is the same as described in Section 4.3.2. In this study, the AOC concentrations of FRW ranged from 110 to 470 μg/L and averaged 273 μg/L. After treatment by the ozonation/membrane system, the AOC concentration significantly increased in P1, P2 and WT waters. The average concentrations of AOC for P1, P2, and WT were 1038, 1365, and 1377 μg/L, respectively. The increase in the AOC concentration is thought to result from the conversion of large molecules to small molecules during ozonation. The smaller molecules are easily biodegraded, during ozonation (Escobar and Randall 2001; Volk et al. 1993; Volk et al. 1997). However, there were the formation of AOC could not be correlated to operational conditions used in our experimental results. Since it is well known that NOM is made up of a heterogeneous mixture of organic compounds and has complex composition, the amount and species of biodegradable compounds, which can be utilized by *Pseudomonas fluorescens* strain P17 and *Spirillum* strain NOX in terms of the measurement of AOC, may vary significantly after a long contact time with ozone under different operational conditions. Consequently, this induces that the AOC concentration and operational conditions are not correlated.

Although the ultrafiltration might be expected to remove some AOC, in our experiments we did not observe any significant removal of AOC by ultrafiltration, as measured by the difference in the AOC concentrations in P2 and WT waters. Several researchers found that membrane filtration is ineffective in reducing AOC concentrations. Escobar and Randall (1999; 2001) reported that nanofiltration (NF) effectively removed BDOC but no significant removal of AOC was observed. Charnock and Kjonno (2000) indicated that this is due to the fact that the AOC and BDOC analyses target different fractions of the biodegradable organic matter (BOM). Therefore, it is apparent that the ultrafiltration ceramic membrane used in our system did not effectively remove the AOC from the treated water.

Experiments of FRW and P2 water treated by biofiltration columns were conducted to evaluate the effect of biofiltration in reducing AOC concentrations. As expected, the AOC concentrations of B-FRW and B-P2 water decreased under most experimental conditions. The average concentration of AOC for B-FRW and B-P2 water was 106 and 77 μg/L, respectively. It suggests that biofiltration of FRW and P2 water can effectively remove much of the AOC concentration. The AOC concentration of B-P2 water was always less than that of B-FRW water, regardless the AOC concentration in P2 water. For FRW and P2 water samples, about 52 to 75%

and 91 to 97% of AOC were removed by biofiltration, respectively. Only one case of FRW water showed slight increase of AOC (from 139 to185 μg/L) after biofiltration.

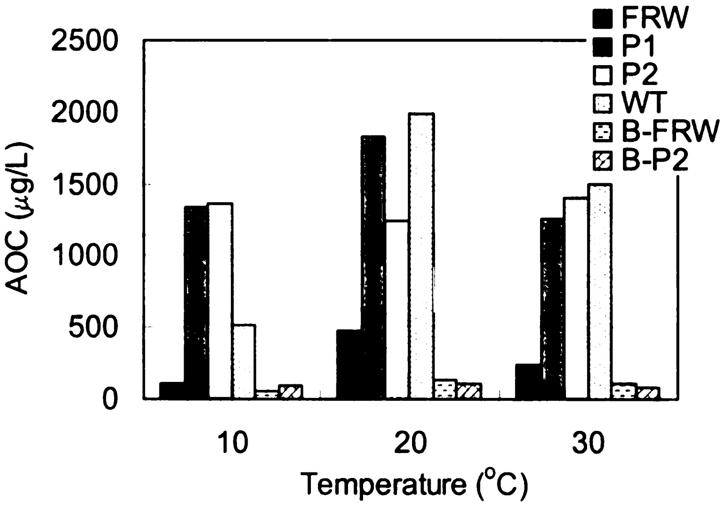

Figure 4.27 The concentration of AOC of different treatment stages at various water treatment temperatures. Operating conditions: water flow rate, 2.75 L/min; gas flow rate, 100 mL/min; ozone dose, 2.5 g/m^3.

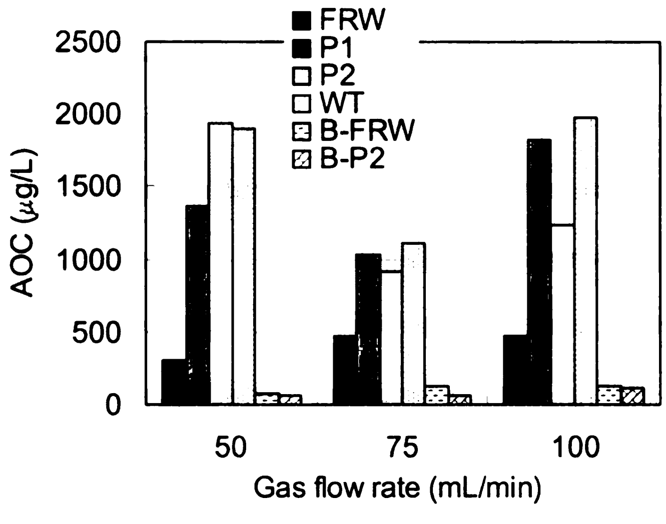

Figure 4.28 The concentration of AOC of different treatment stages at various ozone gas flow rates. Operating conditions: water flow rate, 2.75 L/min; ozone dose, 2.5 g/m^3; water temperature, 20 °C.

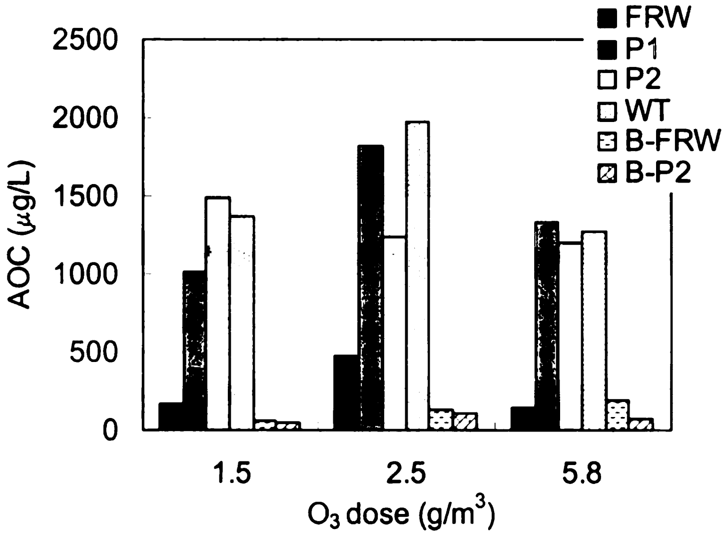

Figure 4.29 The concentration of AOC of different treatment stages at various ozone doses. Operating conditions: water flow rate, 2.75 L/min; gas flow rate, 100 mL/min; water temperature, 20 °C.

4.4 CONCLUSIONS

The characteristics of NOM changed in terms of DOC, UV-254, humic and non-humic substances, BDOC, and AOC when using the ozonation/membrane system to treat Lake Lansing water. The overall conclusions of the study are the following:

1. The addition of ozone in the feed water of membrane resulted in a recovery of the permeate flux from 60% to 97% of the initial flux. The increase in permeate flux may have been the result of an increase in the turbulence in the water stream as a result of the injection of ozone. The increased turbulence would be expected to remove or thin the deposition layer on the membrane surface. Additionally, the ozone would react and break down large molecules and particles. This latter phenomenon was important since ozone was more effective than air.
2. The water temperature influenced the DOC concentrations of permeate of the membrane. As the water temperature increased, the DOC concentration decreased. This may be due to the high permeate flux and/or the high concentration of hydroxyl radicals at elevated water temperatures.
3. The ozonation/membrane system removed 15 to 33% DOC. If followed by biofiltration, the percentage of DOC removal achieved 69 to 88% because the ozonation of NOM enhanced the biodegradability of water, measured as an increase in the BDOC.
4. The experimental results show that the gas flow rate of ozone had little effect on the system performance in terms of the removal of DOC, the conversion of humic and non-humic substances, and the production of BDOC.
5. There were no correlations between the formation of AOC and operational conditions found in our experimental results. This could be due to the amount and species of biodegradable compounds, which can be utilized by *Pseudomonas*

fluorescens strain P17 and *Spirillum* strain NOX in terms of the measurement of AOC, vary significantly after a long contact time with ozone under different operational conditions.

6. The concentration of UV-absorbing compounds decreased at all experimental conditions. The removal efficiency for the ozonation/membrane system ranged from 55 to 85% at various operating conditions. Increased ozone contact time resulted in an increase in the removal efficiency. The maximum removal of UV-254 was 85%.
7. The concentration of HS decreased and the concentration of NHS increased as the contact time increased. At water temperatures of 20°C and 30°C, the ratio of NHS/DOC first increased rapidly in P1 and then slightly increased in P2 and WT. In contrast, the ratio gradually increased in P1, P2, and WT at 10°C. This is thought to be because the higher concentration of hydroxyl radicals that were produced at higher water temperature reacted faster with HS than did molecular ozone to convert HS to NHS. However, at lower water temperature, fewer hydroxyl radicals were produced and the direct reaction between molecular ozone and HS was slower than that between hydroxyl radicals and HS.
8. The concentration of HS and the adsorption of UV-254 were well correlated at different treatment stages and various operational conditions.
9. Approximately 10 to 38% of the DOC in FRW was BDOC. After treatment using the ozonation/membrane system, the percentage increased, with ranges from 55 to 86%. The experimental results show that using ozonation/membrane system can dramatically increase the percentage of BDOC in the permeate water, which will improve performance of the subsequent biofilter.

10. The ozonation/membrane system increased the concentration of AOC significantly at all experimental conditions. The AOC concentration also decreased significantly after subsequent biotreatment, suggesting that a simple biotreatment of raw and ozonated water can effectively remove AOC concentration. The AOC concentration of the biotreated ozonated water was less than that of biotreated raw water, regardless the AOC concentration in ozonated water.
11. According to our experiment results, at operational conditions of 50 mL/min gas flow rate and an ozone dose of 1.5 g/m^3 effective removal of DOC, UV-254, and conversion of HS to NHS was possible. These conditions should reduce the cost of system operation over more extensive ozonation.

4.5 REFERENCES

Charnock, C., and Kjonno, O. (2000). "Assimilable organic carbon and biodegradable dissolved organic carbon in Norwegian raw and drinking waters." *Water Research*, 34(10), 2629-2642.

Cipparone, L. A., Diehl, A. C., and Speitel, G. E. (1997). "Ozonation and BDOC removal: Effect on water quality." *Journal American Water Works Association*, 89(2), 84-97.

Collins, M. R., Amy, G. L., and Steelink, C. (1986). "Molecular-Weight Distribution, Carboxylic Acidity, and Humic Substances Content of Aquatic Organic-Matter - Implications for Removal During Water-Treatment." *Environmental Science & Technology*, 20(10), 1028-1032.

Escobar, I. C., and Randall, A. A. (1999). "Influence of NF on distribution system biostability." *Journal American Water Works Association*, 91(6), 76-89.

Escobar, I. C., and Randall, A. A. (2001). "Assimilable organic carbon (AOC) and biodegradable dissolved organic carbon (BDOC): Complementary measurements." *Water Research*, 35(18), 4444-4454.

Galapate, R. P., Baes, A. U., and Okada, M. (2001). "Transformation of dissolved organic matter during ozonation: Effects on trihalomethane formation potential." *Water Research*, 35(9), 2201-2206.

Goel, S., Hozalski, R. M., and Bouwer, E. J. (1995). "Biodegradation of Nom - Effect of Nom Source and Ozone Dose." *Journal American Water Works Association*, 87(1), 90-105.

Hashino, M., Mori, Y., Fujii, Y., Motoyama, N., Kadokawa, N., Hoshikawa, H., Nishijima, W., and Okada, M. (2000). "Pilot plant evaluation of an ozone-microfiltration system for drinking water treatment." *Water Science and Technology*, 41(10-11), 17-23.

Herner, H. A. (1999). "The Reaction of Ozone with Pyrene: The By-products and Their Toxicological Implications.," Michigan State University, East Lansing.

Hoigne, J. (1988). "The Chemistry of Ozone in Water." Process Technologies for Water Treatment, Plenum Publishing Corp., New York.

Hyung, H., Lee, S., Yoon, J., and Lee, C. H. (2000). "Effect of preozonation on flux and water quality in ozonation- ultrafiltration hybrid system for water treatment." *Ozone-Science & Engineering*, 22(6), 637-652.

Ichihashi, K., Teranishi, K., and Ichimura, A. (1999). "Brominated trihalomethane formation in halogenation of humic acid in the coexistence of hypochlorite and hypobromite ions." *Water Research*, 33(2), 477-483.

Kim, J. O., Somiya, I., and Fujii, S. "Fouling Control of Ceramic Membrane in Organic Acid Fermenter by Intermittent Ozonation." *Proceedings of the 14th Ozone World Congress*, Dearborn, MI, 131-143.

Kuo, P. P. K., Chian, E. S. K., and Chang, B. J. (1977). "Identification of End Products Resulting from Ozonation and Chlorination of Organic-Compounds Commonly Found in Water." *Environmental Science & Technology*, 11(13), 1177-1181.

Lee, K.-H. (2001). "The effects of ozonation pathways on the formation of ketoacids and assimilable organic carbon (AOC) in drinking water," Michigan State University, East Lansing, MI 48823.

Levy, R. V., Hart, F. L., and Cheetham, R. D. (1986). "Occurrence and Public-Health Significance of Invertebrates in Drinking-Water Systems." *Journal American Water Works Association*, 78(9), 105-110.

MacCarthy, P., and Suffet, I. H. (1989). "Aquatic Humic Substances and Their Influence on the Fate and Treatment of Pollutants." Aquatic Humic Substances: Influence on Fate and Treatment of Pollutants, I. H. Suffet and P. MacCarthy, eds., American Chemical Society, Washington, DC., xvii-xxx.

Malcolm, R. L. (1985). "Geochemistry of Stream fulvic and Humic Substances." Humic Substances in Soil, Sediment, and Water, G. R. Aiken, D. M.

McKnight, R. L. Wershaw, and P. MacCarthy, eds., John Wiley & Sons., New York, 181-209.

Manahan, S. E. (1993). "Environmental Chemistry of Water." Fundamentals of Environmental Chemistry, Lewis Publisher, Chelsea, MI., 388-390.

Mogren, E. M., Scarpino, P., and Summers, R. S. (1990). "Measurement of Biodegradable Dissolved Organic Carbon in Drinking Water." Proc. 1990 AWWA Ann. Conf., Cincinnati, Ohio, 573.

Narkis, N., and Schneiderrotel, M. (1980). "Evaluation of Ozone Induced Biodegradability of Wastewater- Treatment Plant Effluent." *Water Research*, 14(8), 929-939.

Owen, D. M., Amy, G. L., Chowdhury, Z. K., Paode, R., McCoy, G., and Viscosil, K. (1995). "Nom - Characterization and Treatability." *Journal American Water Works Association*, 87(1), 46-63.

Reckhow, D. A., Singer, P. C., and Malcolm, R. L. (1990). "Chlorination of Humic Materials - by-Product Formation and Chemical Interpretations." *Environmental Science & Technology*, 24(11), 1655-1664.

Servais, P., Billen, G., and Hascoet, M. C. (1987). "Determination of the Biodegradable Fraction of Dissolved Organic-Matter in Waters." *Water Research*, 21(4), 445-450.

Siddiqui, M. S., Amy, G. L., and Murphy, B. D. (1997). "Ozone enhanced removal of natural organic matter from drinking water sources." *Water Research*, 31(12), 3098-3106.

Sotelo, J. L., Beltran, F. J., Benitez, F. J., and Beltranheredia, J. (1987). "Ozone Decomposition in Water - Kinetic-Study." *Industrial & Engineering Chemistry Research*, 26(1), 39-43.

Standard Methods. (1998). Standard Methods for the Examination of Water and Wastewater, A. E. Greenberg, L. S. Clesceri, and A. D. Easton, eds., APHA, AWWA, WEF, Washington, DC.

Urfer, D., Huck, P. M., Booth, S. D. J., and Coffey, B. M. (1997). "Biological filtration for BOM and particle removal: a critical review." *Journal American Water Works Association*, 89(12), 83-98.

Van der kooij, D., Hijnen, W. A. M., and Kruithof, J. C. (1989). "The Effects of Ozonation, Biological Filtration and Distribution on the Concentration of Easily Assimilable Organic-Carbon (Aoc) in Drinking-Water." *Ozone-Science & Engineering*, 11(3), 297-311.

Van der kooij, D., Visser, A., and Hijnen, W. A. M. (1982). "Determining the Concentration of Easily Assimilable Organic- Carbon in Drinking-Water." *Journal American Water Works Association*, 74(10), 540-545.

Volk, C., Renner, C., Roche, P., Paillard, H., and Joret, J. C. (1993). "Effects of Ozone on the Production of Biodegradable Dissolved Organic-Carbon (Bdoc) During Water-Treatment." *Ozone-Science & Engineering*, 15(5), 389-404.

Volk, C., Roche, P., Joret, J. C., and Paillard, H. (1997). "Comparison of the effect of ozone, ozone-hydrogen peroxide system and catalytic ozone on the biodegradable organic matter of a fulvic acid solution." *Water Research*, 31(3), 650-656.

Yavich, A. A. (1998). "The Use of Ozonation and Biological Fluidized Bed Treatment for the Control of NOM in Drinking Water," Ph.D. Dissertation, Michigan State University, East Lansing, MI.

Yavich, A. A., and Masten, S. J. (2003). "Use of Ozonation and FBT to Control THM Precursors." *Journal American Water Works Association*, 95(4), 159-171.

CHAPTER 5

THE USE OF OZONATION/MEMBRANE PROCESS FOR THE CONTROL OF DISINFECTION BY-PRODUCTS

5.1 INTRODUCTION

The production of disinfection by-products (DBPs) during the chlorination of drinking water is an important issue, arising from the discovery that some DBPs, such as trihalomethanes (THMs), are carcinogenic (Kool et al. 1985; Morris et al. 1992; Mughal 1992). Several oxidants, e.g. ozone, chloramines, and chlorine dioxide, may be used instead of chlorine to reduce the formation of chlorinated DBPs.

Ozone is a powerful oxidant and preferentially oxidizes electron-rich moieties and aromatic alcohols. It also acts as an electrophil reacting with molecular sites having a strong electronic density and as a nucleophil reacting with molecular sites with electronic deficiencies (Bablon et al. 1991). It was found that increasing the ozone dosage in water treatment processes decreases the formation of THMs and haloacetic acids (HAAs) (Cipparone et al. 1997; Lee 2001). Amy et al. (1988) also reported that in the presence of natural organic matter (NOM), ozonation results in the formation of partially oxidized compounds, which are less reactive with chlorine in forming THMs.

Ozone decomposes quickly when dissolved organic carbon (DOC) and hydroxyl radicals are present in water (Bablon et al. 1991; Hoigné and Bader 1975; Staehelin and Hoigné 1985). A secondary disinfectant is usually required when using ozone as the primary disinfectant because of the rapid disappearance of ozone residual (Oxenford 1996). The use of chlorine or chloramines as a secondary disinfectant following ozonation reduces the formation of THMs and HAAs compared to that observed when using only chlorine or chloramines (Richardson et al. 1999).

While ozonation can help to minimize the formation of THMs and HAAs, the reactions that occur during ozonation produce other by-products. Reported ozonation by-products include aldehydes (formaldehydes, acetaldehydes, glyoxal, and methylglyoxal), ketone, glyoxylic acid, and pyruvic acid (Paode et al. 1997; Weinberg and Glaze 1996). Although some of them are of particular concern due to their mutagenicity and carcinogenicity (Bull and McCabe 1984), these by-products are easily biodegradable and may serve as substrates for microbial regrowth in the distribution system. High removal efficiencies of aldehydes and ketoacids were observed when using ozonation-biological filtration processes to treat ozonated water (Griffini et al. 1999).

The purpose of this study was to evaluate the effect of ozonation/membrane process on the formation of DBPs by treating Lake Lansing water under various operational conditions. Chlorine residual and the concentration of THMs, HAAs, aldehydes, ketone, and ketoacids were monitored at different treatment stages. Biofiltration followed the ozonation/membrane system, allowing for a study of the effect of biotreatment on the formation of DBPs.

5.2 MATERIALS AND METHODS

5.2.1 Experimental Setup and Protocol

A specially designed ozonation/membrane system was used to investigate the formation of several DBPs (i.e., THMs, HAAs, aldehydes, ketones, and ketoacids) resulting from the treatment process. The system was the same one that was described in Chapter 4 and a schematic diagram of this system is shown in Figure 4.1.

Tubular ceramic membranes (Clover-leaf design (containing three channels), CéRAM Inside, Tami North America, St. Laurent, Québec, Canada) with a molecular weight cut-off of 15 kD were used in the system. The characteristics of the laboratory-scale ultrafiltration membrane are summarized in Table 4.1. Teflon tubing and stainless steel joints and valves were used throughout the system. Other components included: 3.5-liter and 1.5-liter water-jacked glass reservoirs made of Pyrex glass, and a simple Y inline mixer (Ozone Service, Burton, B.C., Canada).

Ozone was generated by feeding pure oxygen gas from a gas cylinder to the ozone generator (Model OZ2PCS, Ozotech Inc., Yreka, Calif.). The oxygen gas stream was dried using a molecular sieve trap prior to ozone generation. The ozone gas concentration was controlled using the electric current of the ozone generator. The wasted ozone gas was vented after passing the gas through a 2% potassium iodide (KI) solution to destroy any residual ozone gas.

Several operational factors, such as ozone concentration in the inlet gas phase, gas flow rate, and water temperature, which influence the ozone mass transfer and solubility, were investigated. Table 5.1. summarizes the experimental conditions used in this study.

Table 5.1 Experimental conditions.

Parameters	Values
Inlet ozone dose (g/m^3)	1.5, 2.5, 5.8
Water flow rate (L/min)	2.75
Ozone gas flow rate (mL/min)	50, 75, 100
Water temperature (°C)	10, 20, 30

Lake Lansing water and ozone gas were continuously fed into the membrane module of the ozonation/membrane system. Prior to ozonation, the raw water was pre-filtered through a 0.45 μm filter to remove coarse suspended and colloidal solids. Since the collection of permeate from the membrane required several hours, a collection bottle with a cap was used and placed in an ice bath to chill and preserve the sample. The first 500 mL of permeate was collected and marked as "Permeate 1". The next 1.5 L of permeate was collected and marked as "Permeate 2". Permeate 1 and 2 represent the characteristics of the permeate collected at different time intervals and provide information on the performance of the ozonation/membrane system. The concentrate was recirculated back to the raw water reservoir. Herein, the water samples from filtered raw water, permeate 1, and permeate 2 are noted as FRW, P1, and P2, respectively. After the system was stopped, the water remained in the water reservoir, denoted as WT. The FRW and the P2 water were further treated by biofiltration at room temperature for seven days to investigate the efficiency of biotreatment on the removal of DBPs. Water samples collected from the filtrate of biofiltration columns are noted as B-FRW and B-P2. The concentrations of DOC, humic substances (HS), non-humic substances (NHS), chlorine residual, simulated distribution system (SDS) THMs, SDS HAAs, aldehydes (formaldehyde, acetaldehyde, propionaldehyde, glyoxal, and methyl glyoxal), ketones (acetone and 2-butanone), and ketoacids (glyoxylic acid, pyruvic acid, and ketomalonic acid) were monitored. The dissolved ozone residual in collected samples was quenched by sparging the solution with a high purity helium gas (99.999 %) before analysis. Earlier studies show that quenching can be achieved in this manner in several seconds (Herner 1999).

5.2.2 Water Source

Experiments were carried out on Lake Lansing (Haslett, MI) water. Water quality characteristics of Lake Lansing are summarized in the previous chapter (see Table 4.3). Lake Lansing waters were collected in five-gallon tanks, properly labeled, and stored at 4°C. The maximum storage period was seven days. All waters were filtered through a 0.45-µm filter and warmed to room temperature before testing.

5.2.3 Chlorine Residual

The chlorine residual was determined by the iodometric method as described in Standard Methods 4500B (Standard Methods 1998). A 50 mL water sample was acidified with the addition of 2.5 mL of acetic acid. After approximately 1 g of KI and a few drops of starch indicator were added, the solution turned blue. Then the solution was titrated against 0.01 N sodium thiosulfate ($Na_2S_2O_3$). Titration was continued until the blue color became colorless. The titration volume was recorded and the chlorine residual was determined.

5.2.4 SDS THMs

Four THM compounds, chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$), and bromoform ($CHBr_3$), were monitored in this study. These compounds were measured in chlorinated FRW, P1, P2, WT, B-FRW, and B-P2 waters. The analysis of SDS THMs used Method 5710 (Standard Methods 1998). Water samples were dosed a chlorine concentration that allowed residual chlorine concentration in the range of 0.5 to 2 mg/L after 48 hours incubation at room temperature according to the procedures in Method 2350 (Standard Methods 1998). Then samples were prepared according to the THMFP method in Method 5710 (Standard Methods 1998). THMs were extracted by hexane and analyzed by a gas chromatography (Hewlett-Packard 5890 Series II) that was equipped with ^{63}Ni electron capture detector (ECD). A 30 m, 0.53 mm I.D. DB-624 column (J&W Scientific, Folsom, CA) was used. The oven temperature was programmed from 50 °C increasing to 150 °C with a rate of 10 °C/min. The flow rate of the carrier gas (N_2) was 12.0 mL/min. The injector temperature and detector temperature were 275 and 350 °C, respectively.

5.2.5 SDS HAAs

HAAs were determined using USEPA Method 552.2. The compounds determined were monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), bromochloroacetic acid (BCAA), trichloroacetic acid (TCAA), and dibromoacetic acid (DBAA). These compounds were measured in FRW, P1, P2, WT, B-FRW, and B-P2 waters chlorinated according to the procedures in Method 2350 (Standard Methods 1998). A Perkin Elmer Autosystem gas chromatograph equipped with an ECD, an autosampler, and a DB-1 column (J&W Scientific, Folsom, CA) was used for the analysis. The oven temperature was programmed to hold 15 minutes at 32 °C, then increase to 75 °C with a rate of 5 °C/min and hold 5 minutes, then increase to 100 °C with a rate of 5 °C/min. The carrier flow was 1.0 mL/min. The injector temperature and detector temperature were 200 and 260 °C, respectively.

5.2.6 Aldehydes and Ketones

Measured aldehydes and ketones included formaldehyde, acetaldehyde, propionaldehyde, glyoxal, methyl glyoxal, acetone, and 2-butanone. These compounds were measured in FRW, P1, P2, WT, B-FRW, and B-P2 waters. The method used followed the instructions in USEPA Method 556 (Munch et al. 1998). A Perkin Elmer Autosystem gas chromatograph equipped with an ECD, an autosampler, and a DB-5 column (J&W Scientific, Folsom, CA) was used in the analysis. The oven temperature was programmed to hold 1 minute at 50 °C, then increase to 220 °C at a rate of 4 °C/min, then increase to 250 °C at a rate of 20 °C/min and hold for 5 minutes. The carrier flow was 1.0 mL/min. The injector temperature and detector temperature were 180 and 300 °C, respectively.

5.2.7 Ketoacids

Glyoxylic acid, pyruvic acid, and ketomalonic acid were monitored in this study. In a 30 mL vial containing 20 mL water sample, 200 mg potassium hydrogen phthalate (KHP) and 1 mL of a 15 mg/mL freshly prepared aqueous 0-(2,3,5,6-Pentafluorobenzyl)-hydroxylamine hydrochloride (PFBHA) reagent were added. After incubation at 45 C for 1.75 hours, the sample was cooled to room temperature. Following the addition of 0.05 mL of concentrated sulfuric acid, 4 mL of methyl-tert-butyl ether (MTBE) containing 3 mg/L of dibromopropane was added and the sample was shaken by hand for 3 minutes. After allowing the phases to separate for approximately 5 minutes, approximately 3 mL of the upper MTBE layer was transferred to a 15 mL glass vial and 2 mL 10% sulfuric acid in methanol was added. The vial was capped with PTFE faced septa and a screw cap, then placed in a heating block at 50 C and maintained for 1.5 hours. After cooling to room temperature, 4 mL of 10% sodium sulfate (Na_2SO_4) solution was added and the tube was shaken by hand for 3 minutes. After allowing the phases to separate for approximately 5 minutes, the upper MTBE layer was then submitted for analysis. A Perkin Elmer

Autosystem gas chromatograph equipped with an ECD, an autosampler, and a DB-5 column (J&W Scientific, Folsom, CA) was used in the analysis. The settings of GC were the same as used in aldehydes analyses (see Section 5.2.5).

5.2.8 Other Analyses

The concentration of gas-phase ozone, DOC, UV-254, humic substances, and non-humic substances were measured by using the same method as described in Section 4.2.

5.3 RESULTS AND DISCUSSION

5.3.1 Chlorine Demand

Chlorine demand values and DOC concentrations for water samples that were collected at various treatment stages under different experimental conditions are summarized in Table 5.2. The value of chlorine demand was calculated by subtracting the concentration of chlorine residual from the initial chlorine dosage. Figures 5.1 to 5.3 show the variation of chlorine demand of different treatment stages at various experimental conditions. According to the experimental results shown in Table 5.2, it is interesting to find that the levels of chlorine demand and DOC concentrations for water samples of FRW, P1, P2 and WT fluctuate between 7.0 ~ 8.5 mg/L and 6.0 ~ 10.9 mg/L, respectively. The maximum reduction of the chlorine demand was less than 10% (see the P1 water sample at water temperature 30 °C) and the demand increased over its initial value in some water samples (see the P2 and WT samples at water temperature 30 °C, the WT samples at 75 mL/min gas flowrate, and the WT sample at 5.8 g/m^3 O_3 dose). The removal of chlorine demand by the ozonation/membrane system was limited in this study. An explanation for this observation is that two competing reactions were occurred during ozonation. One reaction is the attack of nucleophilic sites on DOC by molecular ozone, thereby decreasing the reactivity of DOC with chlorine. On the contrary, ozone can generate new chlorine-consuming sites by the hydroxylation of aromatic moieties in humic material. Jadashecart et al. (1991) observed a significant increase of chlorine demand when fulvic acid was ozonated at pH 8 and in the absence of bicarbonate, i.e., at conditions where the radical-type pathway (hydroxyl radical reactions) predominates. However, they also found that the ozonation of fulvic acid in the presence of bicarbonate led to a small decrease in the chlorine demand, as a result of the direct reaction with molecular ozone. Thus it is reasonable to presume that the competition of these two reactions resulted in the limited increase and decrease of chlorine demand in our study. The variation of DOC concentration has been discussed in the previous chapter (see Section 4.3.2, Chapter 4).

Figures 5.1 to 5.3 also show that the biotreatment can effectively remove the chlorine demand of water. Biofiltration alone without pre-ozonation (i.e., B-FRW waters) removed 30 to 55% of chlorine demand. The removal efficiency of chlorine demand with biofiltration following the ozonation/membrane system ranged from 60% up to 90% for B-P2 waters. This indicates that a large fraction of the chlorine-consuming material was biodegradable and combining ozonation and biotreatment processes can reduce the chlorine demand of water.

Figure 5.4 presents the correlation between the concentration of DOC and chlorine demand of Lake Lansing water tested in this study. According to the experimental results, chlorine demand and DOC were positively and linearly correlated under the conditions we tested. The correlation is statistically significant ($p = 0.01$ at 95% C.I.).

Table 5.2 Chlorine demands and DOC concentrations for samples collected at various treatment stages under different experimental conditions.

Temp. (°C)^1	FRW		P1		P2		WT		B-FRW		B-P2	
	DOC	CD	DOC	CD	DOC	CD	DOC	CD	DOC	CD	DOC	CD
10	9.6	8.5	7.7	8.2	8.1	8.5	9.3	8.3	5.8	4.5	1.9	1.4
20	10.9	7.5	8.7	7.3	7.6	7.4	6.6	7.3	7.6	5.2	3.3	3.1
30	9.0	7.7	7.3	7.0	6.0	7.9	6.3	7.9	8.0	4.4	2.6	2.0
Gas flowrate^2	FRW		P1		P2		WT		B-FRW		B-P2	
	DOC	CD	DOC	CD	DOC	CD	DOC	CD	DOC	CD	DOC	CD
50	8.7	7.4	7.0	7.2	6.1	7.0	6.7	7.2	7.5	3.4	2.8	0.7
75	10.4	7.5	8.3	7.5	7.6	7.2	8.3	7.6	6.8	5.2	2.6	2.4
100	10.9	7.5	8.7	7.3	7.6	7.4	6.6	7.3	7.6	5.2	3.3	3.1
O_3 dose^3	FRW		P1		P2		WT		B-FRW		B-P2	
	DOC	CD	DOC	CD	DOC	CD	DOC	CD	DOC	CD	DOC	CD
1.5	8.7	8.0	6.4	7.9	6.1	7.4	7.3	7.5	6.9	4.0	2.0	1.5
2.5	10.9	7.5	8.7	7.5	7.6	7.2	8.3	7.6	6.8	5.2	2.6	2.4
5.8	8.9	8.0	6.9	7.9	7.7	7.9	7.9	8.2	6.4	4.5	1.1	1.7

1. Water flow rate, 2.75 L/min; gas flow rate, 100mL/min; O3 dose, 2.5 g/m^3.
2. Water flow rate, 2.75 L/min; O3 dose, 2.5 g/m^3; water temperature, 20 °C.
3. Water flow rate, 2.75 L/min; gas flow rate, 100mL/min; water temperature, 20 °C.
4. DOC, CD (chlorine demand), and O_3 dose: g/m^3; Gas flow rate: mL/min.
5. FRW: filtered raw water; P1: permeate 1; P2: permeate 2; WT: samples from the water tank; B-FRW: biofiltrated FRW water; B-P2: biofiltrated P2 water.

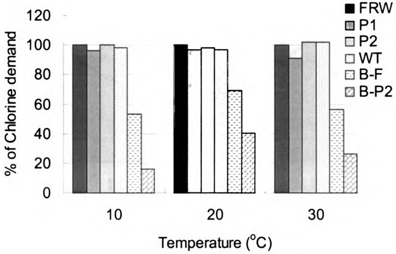

Figure 5.1 The percentage variation of chlorine demand (CDi/CD$_0$) of different treatment stages at various water temperatures. (Operating conditions: water flow rate, 2.75 L/min; gas flow rate, 100 mL/min; O_3 dose, 2.5 g/m^3)

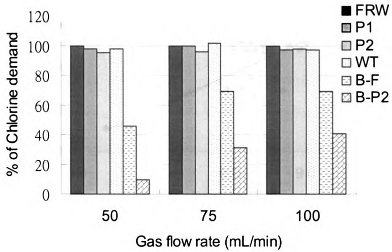

Figure 5.2 The percentage variation of chlorine demand (CDi/CD_0) of different treatment stages at various gas flow rates. (Operating conditions: water flow rate, 2.75 L/min; O_3 dose, 2.5 g/m^3; water temperature, 20 °C)

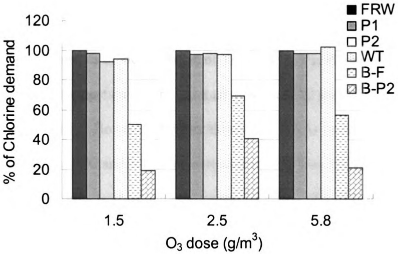

Figure 5.3 The percentage variation of chlorine demand (CDi/CD_0) of different treatment stages at various ozone doses. (Operating conditions: water flow rate, 2.75 L/min; gas flow rate, 100 mL/min; water temperature, 20 °C)

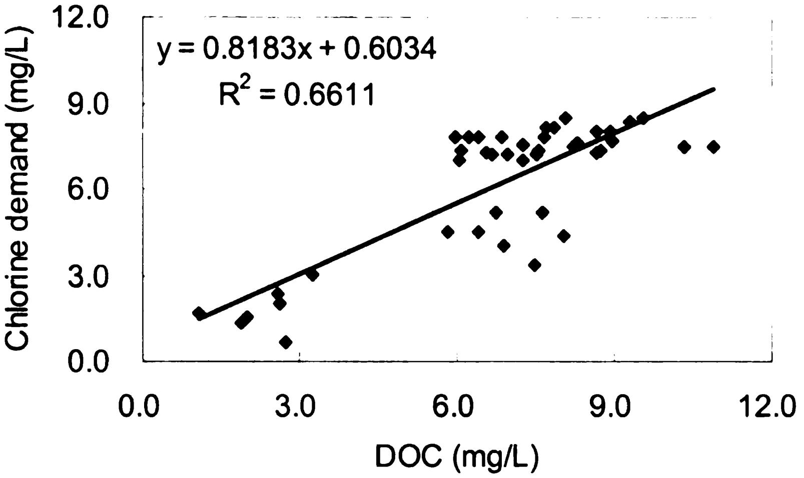

Figure 5.4 Correlation between chlorine demand and the concentration of DOC of Lake Lansing water treated by the ozonation/membrane/biofiltration system. (Correlation is statistically significant at 95% C.I.)

5.3.2 THMs and HAAs

The effects of water temperature on the concentration of THMs and HAAs of different treatment stages are shown in Figures 5.5 and 5.6, respectively. As seen in Figure 5.5, the decreases of the formation of THMs in the P1, P2, and WT water at 10 °C water treatment temperature were less than those at 20 °C and 30 °C water treatment temperature. However, the concentration of HAAs in the P1, P2, and WT water decreased at 20 °C and 30 °C but increased at 10 °C (see Figure 5.6). In a previous work, the effects of temperature on the formation of THMs and HAAs of Lake Lansing water were investigated by using a continuous stirred reactor. Its results are summarized in Table 5.3. It was observed that the THMs and HAAs concentrations increased slightly as the temperature increased from 5 °C to 35 °C. However, the experimental results in this study show that the THMs concentrations under all three operating conditions and the HAAs concentrations of treated water at 20 °C and 30 °C decreased significantly as the water temperature increased ($p < 0.01$). This was probably the result of a longer hydraulic retention time used in this study, and higher ozone mass transfer rate into the water and higher reaction rate constant at higher water temperature. Similar observations were reported by Zhang et al. (2001).

The measured concentrations of HAAs in P1, P2, and WT water were greater than that of FRW water when Lake Lansing water was treated at 10 °C (Figure 5.6). It may be that HAAs precursors were generated by the partial oxidation of humic substances more quickly than they were destroyed by ozonation. On the other hand, the increase in HAA concentrations could result from reactions of ozone, exposing more active sites in the NOM matrix when ozonation broke down large molecules. Some researchers observed the same trend when measuring THM concentration during ozonation. Yamada et al. (1986) observed that the THM formation potential (THMFP) increased in the initial stage of low ozone dose and then gradually decreased with respect to the increase in the amount of ozone consumed when humic acids were ozonated. Rice (1980) explained that ozone can destroy some types of THM precursors and produce THM precursors from some types of naturally occurring humic and fulvic materials. Several researchers reported similar observations (Duguet et al. 1985; Glaze et al. 1982; Wallace et al. 1988).

Biotreatment alone or following ozonation before chlorination effectively reduced the formation of THMs and HAAs. From Figures 5.5 and 5.6, it can be seen that the concentrations of THMs and HAAs decreased significantly in biotreated FRW waters (B-FRW) (except the HAAs concentration of B-FRW water at 10 °C) and biotreated P2 waters (B-P2) ($p < 0.01$). The removal efficiency of THMs precursors by ozonation/membrane/biofiltration (B-P2 water) increased as the water temperature increased ($p < 0.05$), however, that of HAAs increased as the water temperature increased from 10 °C to 20 °C but decreased as the water temperature further increased from 20 °C to 30 °C ($p < 0.01$). The experimental results indicates that biological filtration following ozonation can effectively decrease the formation of THMs and HAAs, but the removal efficiency of HAAs precursors by biofiltration (either alone or following ozonation/membrane system) was independent to the treated water temperature and may depend on the characteristics of raw water, the characteristics of P2 water, or the condition of microorganisms in the biofilter.

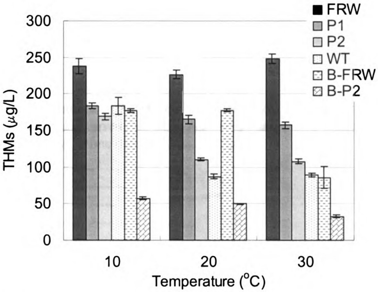

Figure 5.5 Concentrations of THMs of different treatment stages at various water treatment temperatures. (Operating conditions: water flow rate, 2.75 L/min; gas flow rate, 100 mL/min; O_3 dose, 2.5 g/m^3)

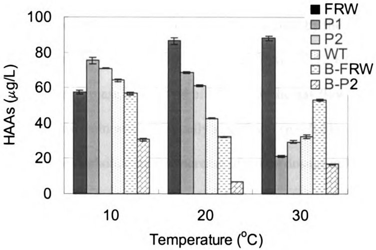

Figure 5.6 Concentrations of HAAs of different treatment stages at various water treatment temperatures. (Operating conditions: water flow rate, 2.75 L/min; gas flow rate, 100 mL/min; O_3 dose, 2.5 g/m^3)

Table 5.3 Concentrations of THMs and HAAs for Lake Lansing water treated by continuous stirred reactor. (Operating conditions: hydraulic retention time, 12.5 min; ozone dosage, 1 mg O_3/mg C)

Temperature (°C)	THMs (μg/L)	HAAs* (μg/L)
5	154.0	102.6
15	166.9	106.5
35	173.6	108.5

* including: monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), and dibromoacetic acid (DBAA).

The effects of ozone gas flowrate on the concentration of THMs and HAAs of different treatment stages are shown in Figures 5.7 and 5.8, respectively. As seen from Figure 5.7, the THMs concentrations in water treated by the ozonation/membrane system (P2 water) decreased from 177.52 ± 6.67 μg/L to 110.24 ± 1.96 μg/L and the increase in removal efficiency as the gas flow rate increased from 50 mL/min to 100 mL/min was statistically significant ($p < 0.01$). The decrease of THMs levels can be explained by the increase of ozone dosage at high gas flowrate. Figure 5.8 shows that HAAs concentrations of P2 water decreased with increasing the gas flowrate. However, the removal efficiency with increasing the gas flow rate was not statistically significantly decreased ($p > 0.05$). The THM precursors may have higher reaction rates with ozone than those of HAAs, which results in the different effect of ozone on the removal efficiencies.

The data in Figures 5.7 and 5.8 also illustrate the performance of the biotreatment on the removal of THMs and HAAs precursors. The experimental results showed that biological filtration alone or following ozonation/membrane decreased the formation of THMs and HAAs. The percent removal of THMs by biofiltration alone and following ozonation/membrane system ranged from 22% to 33% and 78% to 89%, respectively. For HAAs, the removal efficiency ranged 16% to 63% for biofiltration alone and 79% to 92% for following the ozonation/membrane system.

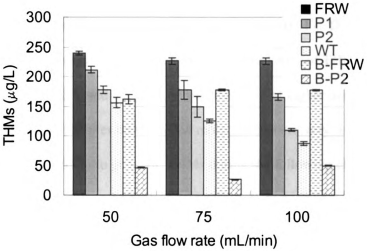

Figure 5.7 Concentrations of THMs of different treatment stages at various gas flow rates. (Operating conditions: water flow rate, 2.75 L/min; O_3 dose, 2.5 g/m^3; water temperature, 20 °C)

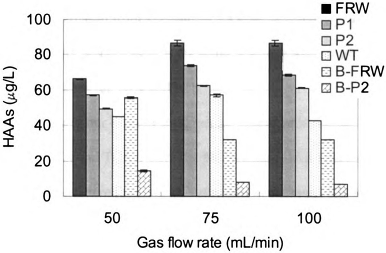

Figure 5.8 Concentrations of HAAs of different treatment stages at various gas flow rates. (Operating conditions: water flow rate, 2.75 L/min; O_3 dose, 2.5 g/m^3; water temperature, 20 °C)

Figures 5.9 and 5.10 show the effects of ozone dose on the formation of THMs and HAAs, respectively. As expected, the removal efficiency of THMs precursors significantly increased as the ozone dose increased ($p < 0.01$). The ozonation/membrane system removed 28%, 51%, and 60% of THMs precursors at ozone dose of 1.5, 2.5, and 5.8 g/m^3, respectively. If, at higher ozone doses, more ozone reacted with the sites on the NOM molecule that are very reactive to chlorine, a reduction in their ability to generate THMs during the following chlorination would occur. The indirect action, being less selective, will degrade certain molecular sites very reactive to chlorine, but will also react on other sites not very reactive to chlorine. However, the removal of HAAs precursors did not follow the same trend. Although ozonation decreased the formation of HAAs, the removal efficiency of HAAs precursors was independent of ozone doses and ranged between 29% and 48%. The biofiltration following ozonation/membrane significantly decreased the formation of THMs. The removal efficiency of THMs ranged from 65% to 89% and increased as the ozone dose increased from 1.5 g/m^3 to 5.8 g/m^3 ($p < 0.01$). However, the removal efficiency of HAAs precursors of B-P2 water was independent of ozone doses ($p = 0.29$) and ranged between 86% and 92%.

According to our experimental results, chloroform was the predominant THM species and DCAA and TCAA were the predominant HAA species in all water samples, including filtered raw water, ozonation/membrane effluent and biotreated water. Increases in the percentage of bromodichloromethane, dibromochloromethane, BCAA, and DBAA were observed in biotreated water. This was probably caused by the increase of bromide-to-DOC ratio in the water sample after biofiltration. This observation is consistent with the finding of other researchers (Coleman et al. 1992; Miltner et al. 1992; Wobma et al. 2000).

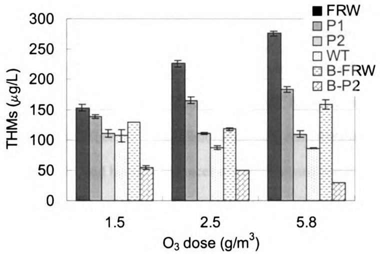

Figure 5.9 Concentrations of THMs of different treatment stages at various ozone doses. (Operating conditions: water flow rate, 2.75 L/min; gas flow rate, 100 mL/min; water temperature, 20 °C)

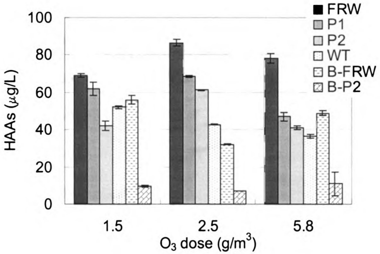

Figure 5.10 Concentrations of HAAs of different treatment stages at various ozone doses. (Operating conditions: water flow rate, 2.75 L/min; gas flow rate, 100 mL/min; water temperature, 20 °C)

The correlation between THMs and HAAs based on the data obtained from this study is shown in Figure 5.11. The relationship between THMs and HAAs was statistical significance (at $p = 0.01$ level at 95% C.I.). Several researchers have indicated that surrogate parameters such as TOC, UV-254, humic substances can be used as indicators of DBP precursors (Chiang et al. 2002; Edzwald et al. 1985; Nieminski et al. 1993). Therefore, the relationships between DBPs and surrogates such as DOC, UV-254, and humic substances of Lake Lansing water tested in this study were also investigated. Figures 5.12 to 5.14 show the relationships between THMs and surrogates and Figures 5.15 to 5.17 present that of HAAs. As seen from the experimental results, both THMs and HAAs were positively correlated with surrogate parameters under the conditions we tested. They are all linearly related and the correlations are statistical significance (at $p = 0.01$ level at 95% C.I.).

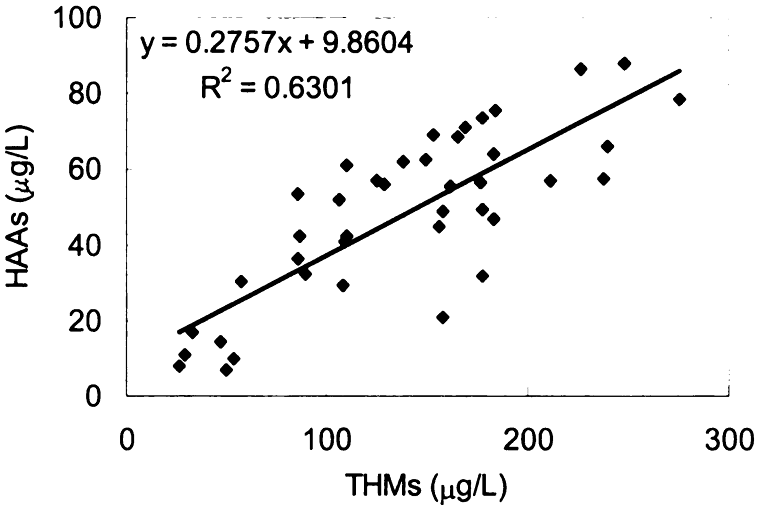

Figure 5.11 Correlation between the THMs and HAAs of Lake Lansing water treated by the ozonation/membrane/biofiltration system. (Correlation is statistically significant at 95% C.I.)

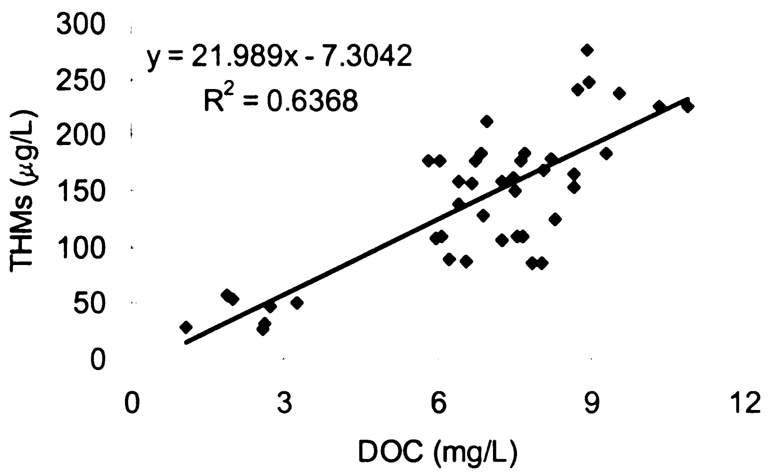

Figure 5.12 Correlation between THMs and the concentration of DOC of Lake Lansing water treated by the ozonation/membrane/biofiltration system. (Correlation is statistically significant at 95% C.I.)

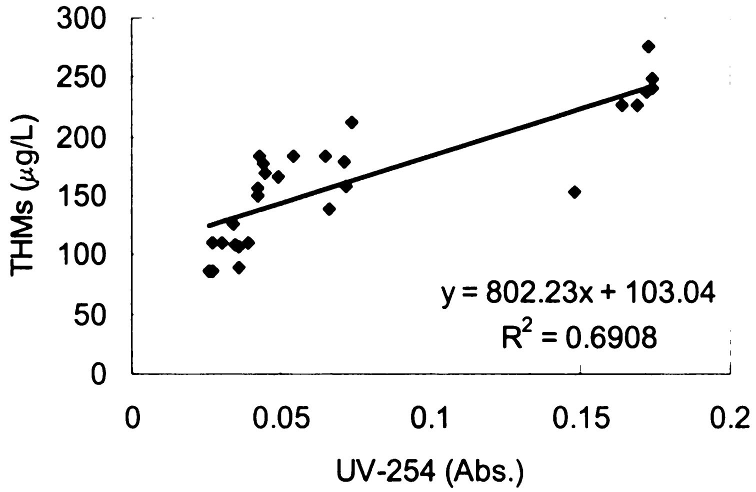

Figure 5.13 Correlation between THMs and the absorbance of UV-254 of Lake Lansing water treated by the ozonation/membrane system. (Correlation is statistically significant at 95% C.I.)

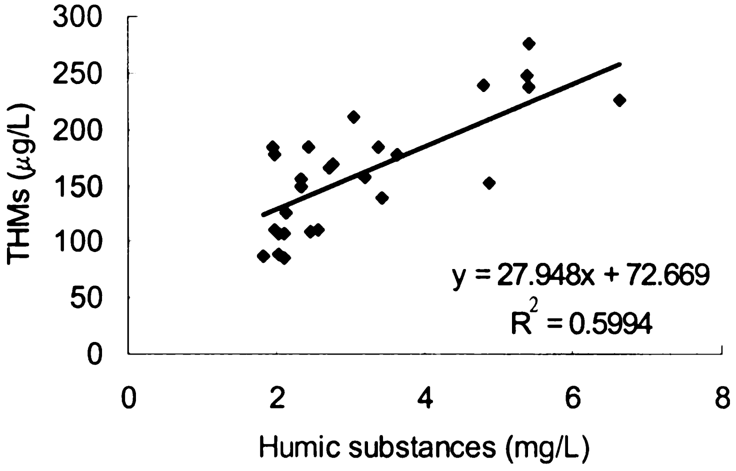

Figure 5.14 Correlation between THMs and the concentration of humic substances of Lake Lansing water treated by the ozonation/membrane system. (Correlation is statistically significant at 95% C.I.)

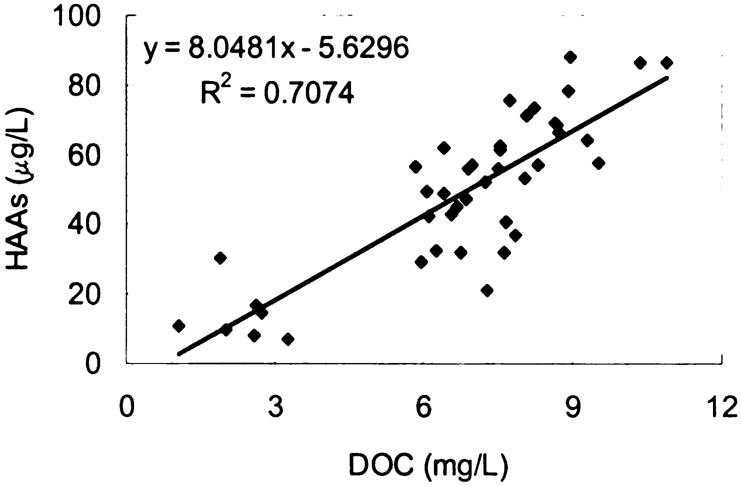

Figure 5.15 Correlation between HAAs and the concentration of DOC of Lake Lansing water treated by the ozonation/membrane/biofiltration system. (Correlation is statistically significant at 95% C.I.)

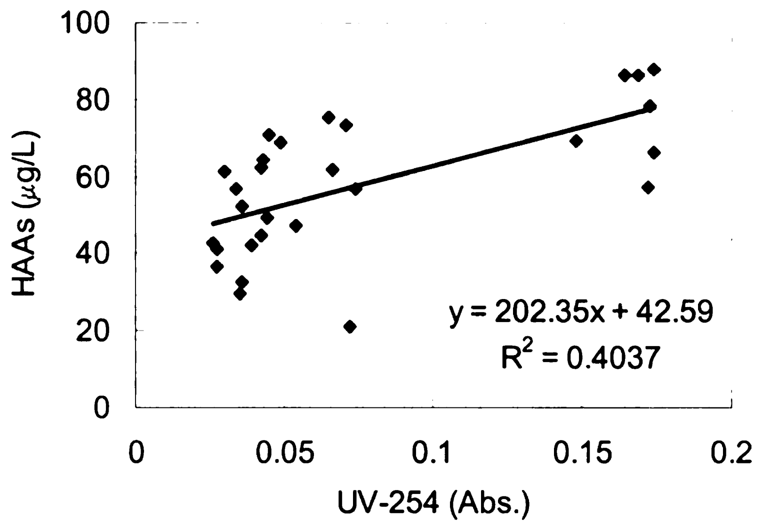

Figure 5.16 Correlation between HAAs and the absorbance of UV-254 of Lake Lansing water treated by the ozonation/membrane system. (Correlation is statistically significant at 95% C.I.)

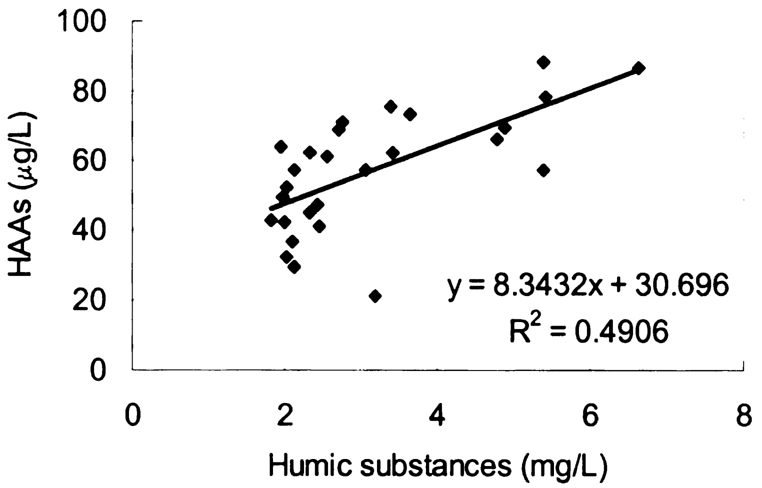

Figure 5.17 Correlation between HAAs and the concentration of humic substances of Lake Lansing water treated by the ozonation/membrane system. (Correlation is statistically significant at 95% C.I.)

5.3.3 Aldehydes, Ketones, and Ketoacids

Five aldehydes (formaldehyde, acetaldehyde, propionaldehyde, glyoxal, and methyl glyoxal), two ketones (acetone and 2-butanone) and three ketoacids (glyoxylic acid, pyruvic acid, and ketomalonic acid) were monitored in this study. Among these compounds, acetaldehyde, propionaldehyde, and acetone were not detected in all water samples and the concentrations of 2-butanone were too variable to allow firm conclusions. These more volatile compounds may have been lost when ozonated sample were purged with high purity nitrogen to quench residual ozone and stop the reactions. Alternatively, their loss could have been the result of volatilization during the lengthy times required to collect samples of the P1 and P2 waters. Acetaldehyde, propionaldehyde, and acetone were also not detected in all non-ozonated water samples such as FRW and B-FRW. Therefore, only the experimental results of total aldehydes including formaldehyde, glyoxal, and methyl glyoxal and total ketoacids are discussed in this section.

Formaldehyde and pyruvic acid were the two principal products of ozonation in our study. This observation was consistent with the findings of Coleman et al. (1992) in studies where they ozonated model humic acid solutions and of Schechter and Singer (1995) and Paode et al. (1997) in studies where they ozonated raw surface waters. Figures 5.18 and 5.19 show the effects of water temperature on the concentrations of aldehydes and ketoacids, respectively. Aldehydes levels and ketoacids concentrations increased significantly as a result of ozonation at all three experimental conditions ($p < 0.01$). Interestingly, the variations in the aldehyde and ketoacid levels with time were different. The formation of aldehydes increased to a maximum then was followed by a gradual decrease with the progress of ozonation time in all three water temperatures. Ko et al. (1998) and Yamada and Somiya (1980) reported the same observation. It is assumed that the production of aldehydes during the early stages of ozonation is greater than the rate of their decomposition by oxidation. The aldehydes are slowly destroyed by molecular ozone or the hydroxyl radical. As a result of the complicated production/decomposition reactions, the concentration of aldehydes reached a maximum then declines. However, the formation of ketoacids increased with the progress of ozonation time, i.e., the ketoacids concentrations in the FRW < P1 < P2 < WT. It is likely that the methyl glyoxal was oxidized to pyruvic acid and the decomposition rate of pyruvic acid was lower than that of methyl glyoxal (Weinberg and Glaze 1996; Yamada and Somiya 1980). The concentrations of ketoacids were much higher than those of the aldehydes in ozonated water samples. This is consistent with other reports (Carlson and Amy 1997; Griffini et al. 1999; Xie and Reckhow 1992).

The concentration of total aldehydes in P2 water increased from 154.8 ± 15.3 μg/L at 10 °C water temperature to 211.3 ± 5.0 μg/L at 20 °C and then decreased to 123.0 ± 4.9 μg/L at 30 °C. The correlation between water temperature and aldehydes level was not significant ($p > 0.05$). Hoigné (1982) indicated that the direct reaction of molecule ozone is the primarily pathway for the formation of aldehydes. Schechter and Singer (1995) also reported this observation. It is reasonable to assume that more molecular ozone is involved in the direct reaction pathway at low water temperature. Also, at low water temperatures, the permeate flux of the membrane system was smaller than that at high temperatures which resulted in a longer retention time at low temperatures than high temperatures. At low water temperatures, the aldehyde concentration reached a maximum earlier, followed by the destruction of aldehydes, resulting in the lower aldehyde levels in water. In contrast, at higher water temperatures, it is hypothesized that the production of aldehydes through direct reaction was less significant (than at lower temperatures) and the destruction of aldehydes by the hydroxyl radical was more significant than at lower temperatures. This could explain the experimental results in Figure 5.18.

The correlation between water temperature and ketoacids level was also not significant ($p > 0.05$) (see Figure 5.19). The effects of water temperature on the formation of ketoacids may be explained as the same reason of aldehydes. Yamada and Somiya (1980) observed that pyruvic acid, which was the principle species of ketoacids in our experiments, gradually increased to a maximum and then very slowly decreased. They also reported that pyruvic acid increased with reaction time and did not react appreciably with ozone. According to our data, the rate of production of ketoacids appeared to be faster than its destruction, which resulted in the accumulation of ketoacids in WT water. The variation of initial FRW water quality may also contribute to the difference in ketoacids formation at different water temperature.

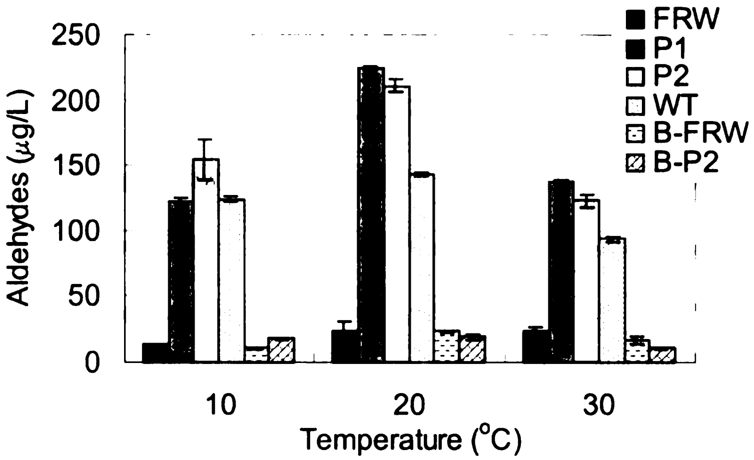

Figure 5.18 Concentrations of aldehydes of different treatment stages at various water treatment temperatures. (Operating conditions: water flow rate, 2.75 L/min; gas flow rate, 100 mL/min; O_3 dose, 2.5 g/m^3)

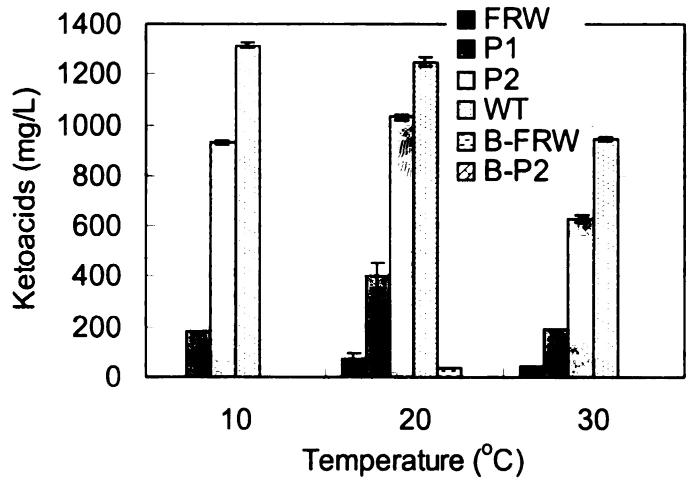

Figure 5.19 Concentrations of ketoacids of different treatment stages at various water treatment temperatures. (Operating conditions: water flow rate, 2.75 L/min; gas flow rate, 100 mL/min; O_3 dose, 2.5 g/m^3)

The effects of ozone gas flow rate on the formation of aldehydes and ketoacids are shown in Figures 5.20 and 5.21, respectively. When a gas flow rate of 100 mL/min was used, the formation of aldehydes reached a maximum at the P1 stage. Under these conditions a greater amount of ozone was delivered than that at 75 and 50 mL/min. As less gas flow rate was applied, the aldehydes level reached its maximum later. According to Figure 5.20, the maximum aldehyde concentration increased significantly as the ozone gas flow rate increased ($p < 0.01$). The formation of ketoacids also significantly increased as the gas flow rate increased ($p < 0.01$) (see Figure 5.21).

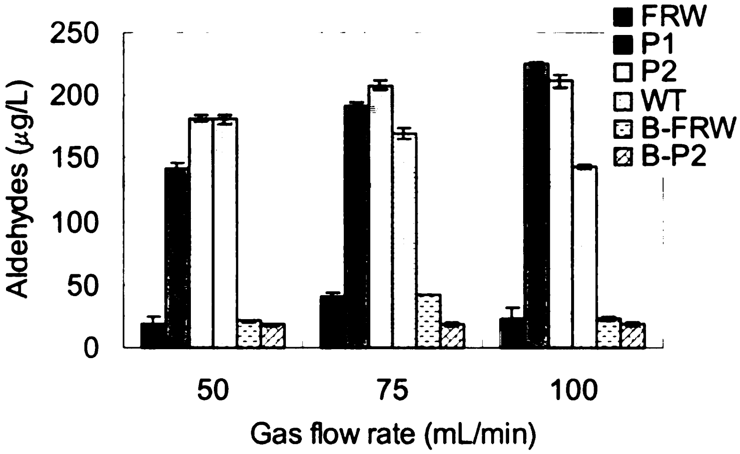

Figure 5.20 Concentrations of aldehydes of different treatment stages at various gas flow rates. (Operating conditions: water flow rate, 2.75 L/min; O_3 dose, 2.5 g/m^3; water temperature, 20 °C)

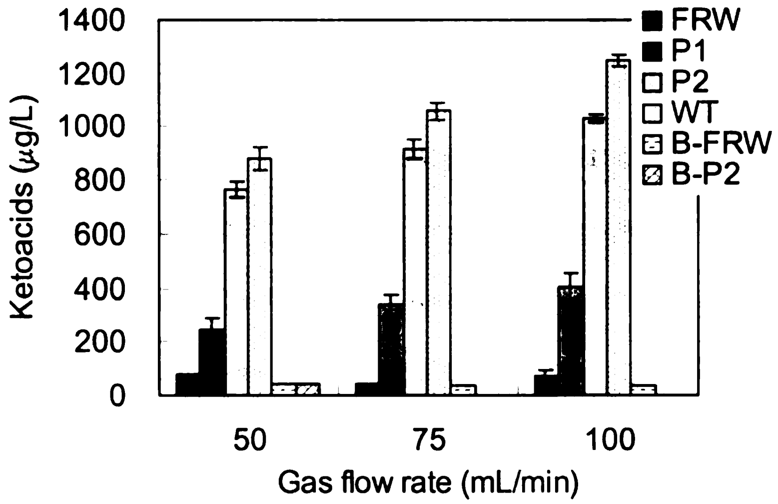

Figure 5.21 Concentrations of ketoacids of different treatment stages at various gas flow rates. (Operating conditions: water flow rate, 2.75 L/min; O_3 dose, 2.5 g/m^3; water temperature, 20 °C)

Figure 5.22 presents the effects of ozone dose on the formation of aldehydes at different treatment stages. The maximum concentration of aldehydes increased as the ozone dose increased from 2.5 to 5.8 g/m^3 ($p < 0.01$), but the difference of the level between ozone doses of 1.5 g/m^3 and 2.5 g/m^3 was not significant ($p > 0.05$). This probably was due to the characteristics of the FRW water. However, the time needed for aldehydes to reach maximum was shorter at higher ozone doses than at lower ones.

The effects of ozone dose on the ketoacids concentrations are shown in Figure 5.23. The maximum concentration of ketoacids significantly increased as the ozone dose increased ($p < 0.01$).

The concentrations of biotreated P2 water (B-P2) of aldehydes and ketoacids are also illustrated in Figures 5.18 to 5.23. The removal efficiency by biofiltration of aldehydes is shown in Table 5.4. It appears that very high removal efficiency, ranged between 85.4% and 94.8%, was achieved in the biofilter, which followed the ozonation/membrane system. The biotreatment process also removed ketoacids very effectively. Only two samples were found to have residual ketoacids concentrations. The concentration of ketoacids in P2 waters ranged between 632 μg/L and 1476 μg/L and the ketoacids residuals in B-P2 waters were 38.1 μg/L and 42.6 μg/L. The percent removal of ketoacids by biofiltration was between 94.1% and 100%. Several researchers have reported that both aldehydes and ketoacids are very biodegradable, with removal efficiencies between 80 and 100% (Griffini et al. 1999; Price et al. 1993; Wobma et al. 2000).

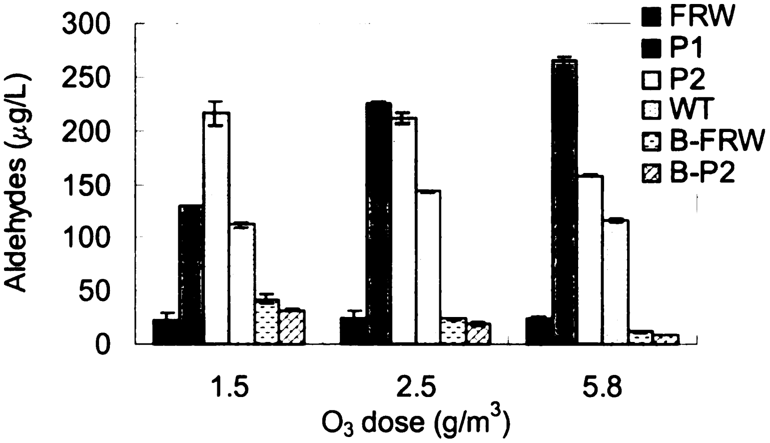

Figure 5.22 Concentrations of aldehydes of different treatment stages at various ozone doses. (Operating conditions: water flow rate, 2.75 L/min; gas flow rate, 100 mL/min; water temperature, 20 °C)

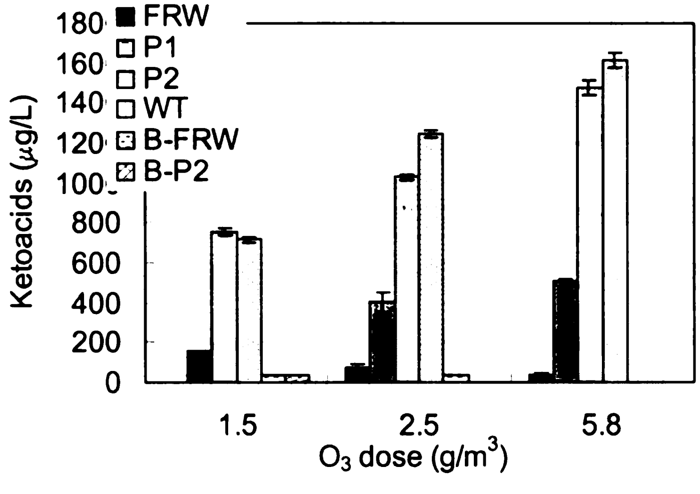

Figure 5.23 Concentrations of ketoacids of different treatment stages at various ozone doses. (Operating conditions: water flow rate, 2.75 L/min; gas flow rate, 100 mL/min; water temperature, 20 °C)

Table 5.4 Removal efficiencies of aldehydes by ozonation/membrane/biofiltration.

Temperature (°C)	Efficiency (%)	Gas flowrate (mL/min)	Efficiency (%)	Ozone dose (g/m^3)	Efficiency (%)
10	88.6	50	89.9	1.5	85.4
20	90.9	75	91.1	2.5	90.9
30	91.0	100	90.9	5.8	94.8

The relationships between aldehydes, ketoacids, and several parameters were also investigated in this study. Figure 5.24 shows the correlation between aldehydes and ketoacids. The relationship between aldehydes and ketoacids was statistical significance (at $p = 0.01$ level at 95% C.I.) in the early stage of ozonation (see Line 1 in Figure 5.24). However, as we discussed earlier, the concentrations of aldehydes decreased as the ozone contact time increased but the formation of ketoacids increased with increasing the ozone contact time. The decrease of aldehydes and the increase of ketoacids also depended on the operational conditions as described earlier. Thus, the correlation between aldehydes and ketoacids was not statistically significant ($p > 0.05$) after long contact time (see Line 2 in Figure 5.24). Griffini et al. (1999) reported that a strong relationship between aldehydes and ketoacids was observed. They also found that the formation of aldehydes and ketoacids was proportional to the DOC concentration. However, in our study, neither aldehydes nor ketoacids were correlated with DOC at a significant level ($p > 0.05$). This may be due to variations in the production of aldehydes and ketoacids as the raw water quality changed with season and environmental conditions.

The relationships between ozonation byproducts (aldehydes and ketoacids) and surrogate parameters (UV-254, humic substances, and non-humic substances) are plotted in Figures 5.25 to 5.30. Correlations are statistically significant at 95% C.I. UV-254 and humic substances are negatively correlated with aldehydes and ketoacids and the non-humic substances are correlated positively with them. This is because the aromatic moieties of DOC were degraded by ozone, which resulted in the reduction of the UV-254 absorbance, and the humic substances decreased as they were converted to non-humic substances during ozonation. In addition, the formation of aldehydes and ketoacids increased due to the decomposition of large molecules of DOC by ozonation.

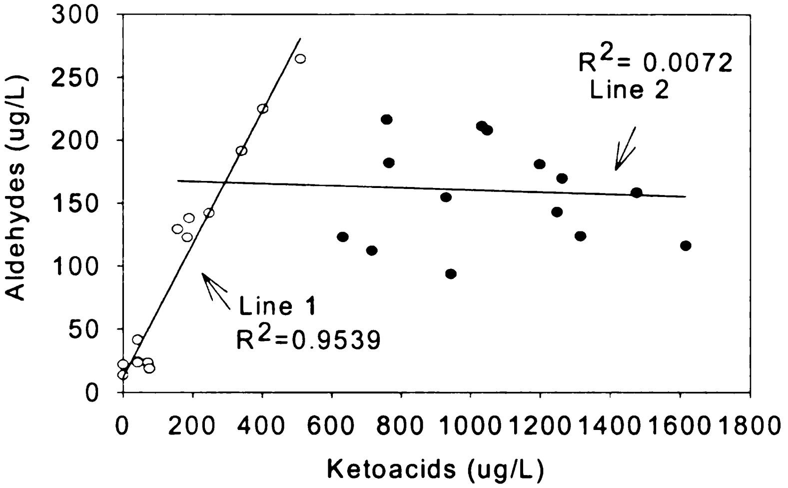

Figure 5.24 Correlations between the aldehydes and ketoacids of Lake Lansing water treated by the ozonation/membrane/biofiltration system. (Line 1 represents the correlation during the earlier stage of ozonation containing FRW and P1 data; Line 2 represents the correlation during the later stage of ozonation containing P1, P2, and WT data. Correlation is statistically significant at 95% C.I. for Line 1 only.)

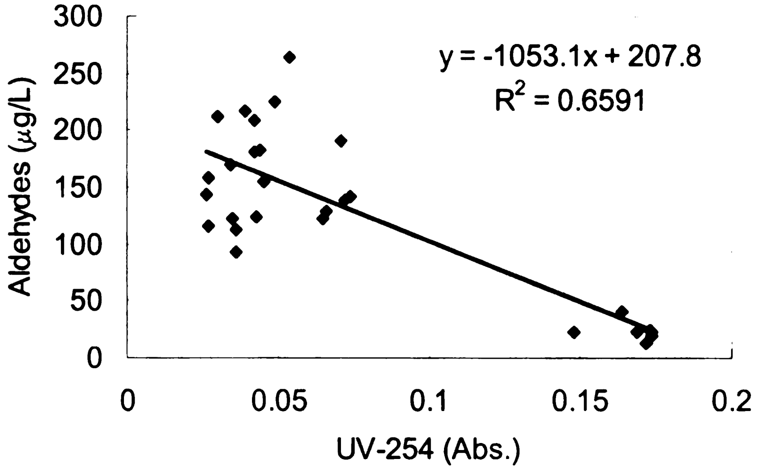

Figure 5.25 Correlation between aldehydes and the absorbance of UV-254 of Lake Lansing water treated by the ozonation/membrane system. (Correlation is statistically significant at 95% C.I.)

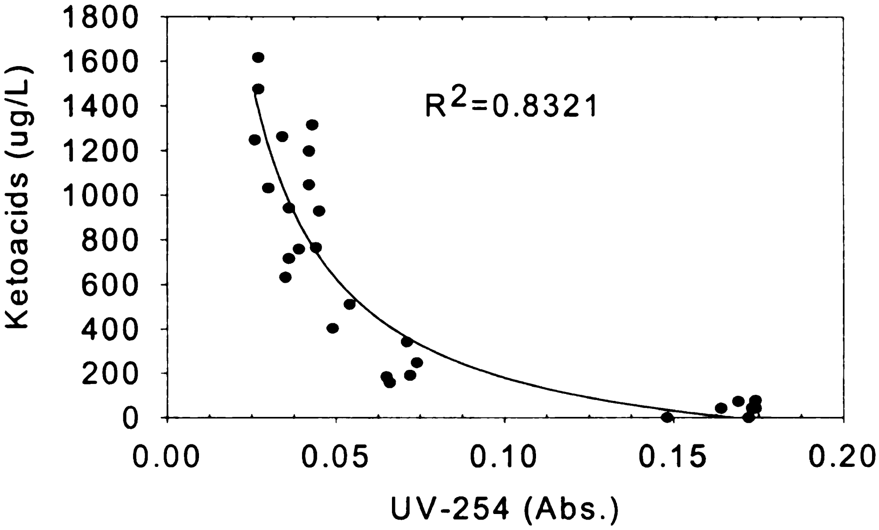

Figure 5.26 Correlation between ketoacids and the absorbance of UV-254 of Lake Lansing water treated by the ozonation/membrane system. (Correlation is statistically significant at 95% C.I.)

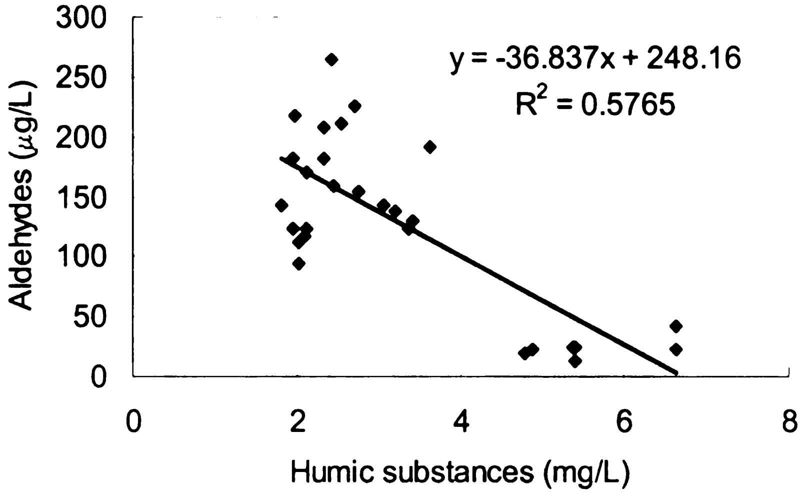

Figure 5.27 Correlation between aldehydes and the concentration of humic substances of Lake Lansing water treated by the ozonation/membrane system. (Correlation is statistically significant at 95% C.I.)

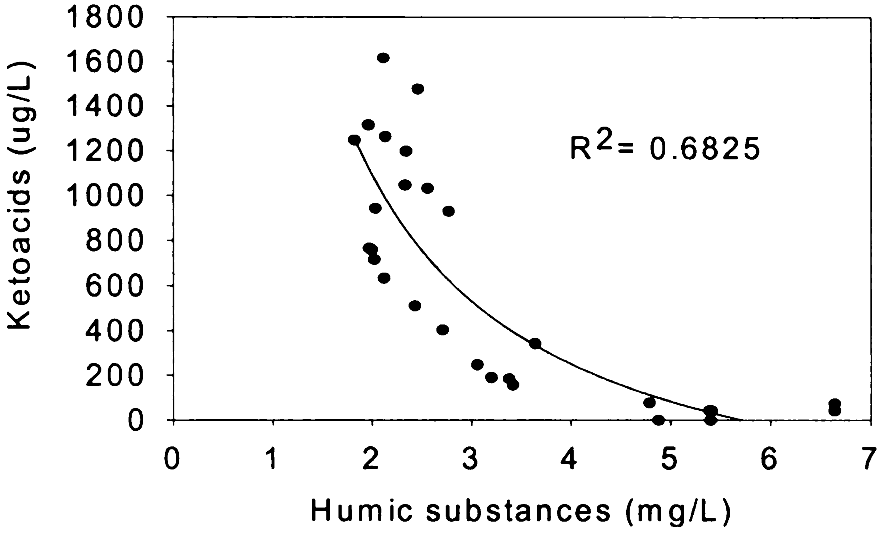

Figure 5.28 Correlation between ketoacids and the concentration of humic substances of Lake Lansing water treated by the ozonation/membrane system. (Correlation is statistically significant at 95% C.I.)

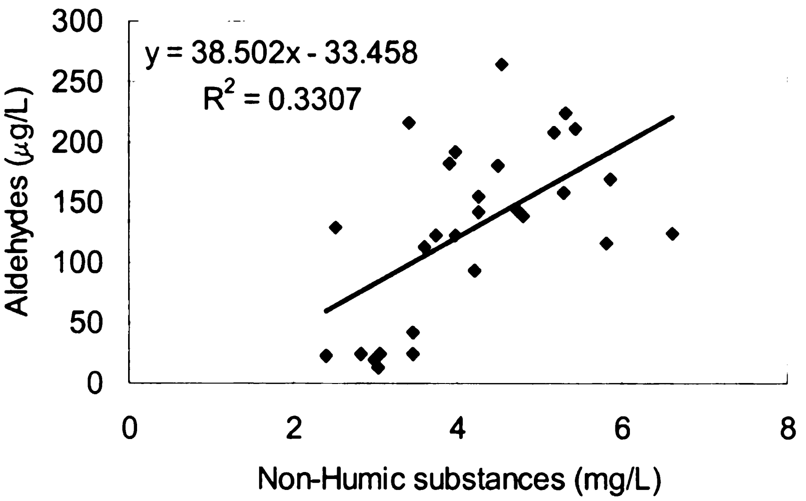

Figure 5.29 Correlation between aldehydes and the concentration of non-humic substances of Lake Lansing water treated by the ozonation/membrane system. (Correlation is statistically significant at 95% C.I.)

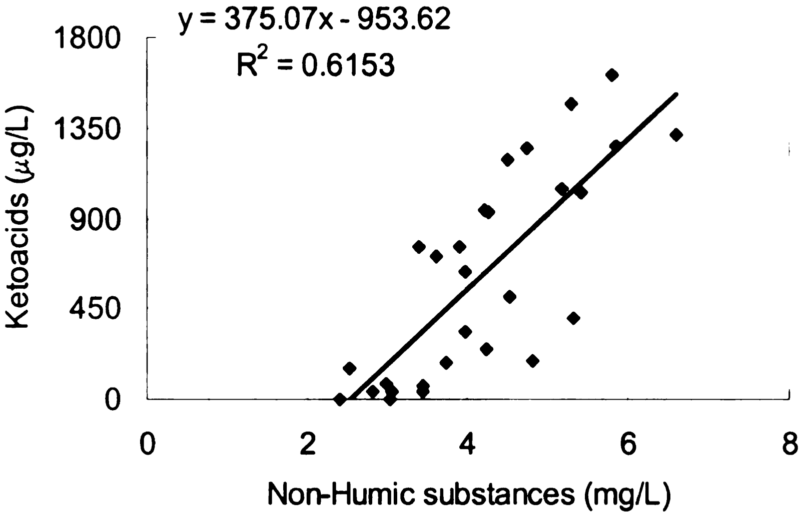

Figure 5.30 Correlation between ketoacids and the concentration of non-humic substances of Lake Lansing water treated by the ozonation/membrane system. (Correlation is statistically significant at 95% C.I.)

5.4 CONCLUSIONS

1. The ozonation/membrane system resulted in limited decreases in chlorine demand. In some cases, the treated water had a greater chlorine demand than that of the initial filtered raw water. Two competing reactions may have contributed to this phenomena. First, a decrease in the number of chlorine-consuming sites may have occurred as a result of reactions of NOM with molecular ozone, by direct reaction pathway. Secondly and simultaneously to the first reaction, new chlorine-consuming sites may have been generated through direct or radical pathway involving hydroxyl radicals and other radical species produced by the decomposition of molecular ozone. The competition of these two reactions resulted in the variations in the chlorine demand observed in this study.
2. Biofiltration alone decreased 30 to 55% of chlorine demand from Lake Lansing water. The percent removal of chlorine demand with biofiltration following the ozonation/membrane system ranged from 60% up to 90%. This indicates that a great fraction of chlorine-consuming material was biodegradable and combining ozonation and biotreatment processes can significantly reduce the level of chlorine demand of water.
3. The THMs concentrations decreased significantly as the water temperature increased. The HAAs concentrations in the treated water decreased significantly as the water temperature increased from 20 °C to 30 °C. This was probably the result of a longer hydraulic retention time used in this study, and higher ozone mass transfer rate into the water and higher reaction rate constants at higher water temperature. When treating the water at 10 °C, the observed concentrations of HAAs in treated water were greater than that in the filtered raw water. HAAs precursors generated by partial oxidation of humic substances may have reacted

were more quickly than they were destroyed by ozonation. On the other hand, this observation could have been the result of the exposure of additional active sites in the NOM matrix when ozonation decomposed large molecules.

4. Biological filtration following ozonation can effectively decrease the formation of THMs and HAAs. The removal efficiency of THMs precursors increased as the water temperature increased. But the removal efficiency of HAAs precursors by biofiltration (either alone or following ozonation/membrane system) was independent to the treated water temperature and may depend on the characteristics of raw water, the characteristics of water treated by ozonation/membrane system, or the condition of microorganisms in the biofilter.
5. The removal efficiency of THMs precursors by ozonation/membrane system or subsequent biofiltration increased as the gas flow rate or the ozone dose increased. HAAs concentrations under the same experimental conditions decreased with increasing the gas flow rate and ozone dose. However, decreases in their removal efficiency were not statistically significant. As such, precursors of THMs may have greater reaction rates with ozone and secondary radicals than those of HAAs, resulting in differences in the removal efficiencies.
6. Aldehydes and ketoacids concentrations increased significantly during ozonation under all experimental conditions. The concentrations of ketoacids were much greater than those of aldehydes in ozonated water samples. The formation of aldehydes increased to a maximum, followed by a gradual decrease with ozonation time. However, the formation of ketoacids consistently increased with ozonation time.
7. The correlations between ketoacids and ozone gas flowrate, ketoacids and ozone dose, and aldehydes and ozone gas flowrate were significant, which indicates that

as these control parameters increased the formation of aldehydes and ketoacids increased. However, it was found that the formation of aldehydes was not significantly correlated with either water temperature or ozone dose. The formation of ketoacids and water temperature were also not significantly correlated. This was probably due to the variations in the characteristics of the DOC in the tested water (since water was collected over the fall and winter seasons) or because of the competitive reactions involving the generation and destruction of aldehydes and ketoacids in the ozonation/membrane system.

8. Very high removal efficiencies of aldehydes and ketoacids were achieved by the biofiltration following the ozonation/membrane system. It was observed that the concentrations of aldehyde were reduced by 85.4% to 94.8% using the ozonation/membrane/biofiltration system. In the entire study, only two of nine samples were found to have ketoacids residual. The percent removal of ketoacids by biofiltration was between 94.1% and 100%.
9. The relationship between THMs and HAAs was statistically significant (at $p = 0.01$ level at 95% C.I.). The concentrations of aldehydes and ketoacids were also statistically related. THMs and HAAs were positively correlated with surrogate parameters (DOC, UV-254, and humic substances) under the experimental conditions tested. The correlctions between ozonation byproducts (aldehydes and ketoacids) and surrogate parameters (UV-254, humic substances, and non-humic substances) were also found to be statistically related. However, neither aldehydes and DOC nor ketoacids and DOC were significantly correlated in this study. This may be due to variations in the production of aldehydes and ketoacids in the different raw waters.

10. According to these experimental results, chloroform was the predominant species of THMs. DCAA and TCAA were the predominant species of HAAs, and formaldehydes and pyruvic acid were two principal products of ozonation in all water samples in this study. Increases in the percentage of bromodichloromethane, dibromochloromethane, BCAA, and DBAA were observed in biotreated water.

5.5 REFERENCES

Amy, G. L., Kuo, C. J., and Sierka, R. A. (1988). "Ozonation of Humic Substances - Effects on Molecular-Weight Distributions of Organic-Carbon and Trihalomethane Formation Potential." *Ozone-Science & Engineering*, 10(1), 39-54.

Bablon, G., Bellamy, W. D., Bourbigot, M.-M., and et. al. (1991). "Fundamental Aspects." Ozone in Water Treatment: Application and Engineering, B. Langlais, D. A. Reckhow, and D. R. Brink, eds., Lewis Publishers, Chelsea, MI, 11-132.

Bull, R. J., and McCabe, L. J. (1984). "Risk Assessment Issues in Evaluating the Health Effects of Alternate Means of Drinking Water Disinfection." Water Chlorination: Chemistry, Environmental Impact, and Health Effects, R. L. Jolley and e. al., eds., Lewis Publishers, Chelsea, Mich.

Carlson, K., and Amy, G. (1997). "The formation of filter-removable biodegradable organic matter during ozonation." *Ozone-Science & Engineering*, 19(2), 179-199.

Chiang, P. C., Chang, E. E., and Liang, C. H. (2002). "NOM characteristics and treatabilities of ozonation processes." *Chemosphere*, 46(6), 929-936.

Cipparone, L. A., Diehl, A. C., and Speitel, G. E. (1997). "Ozonation and BDOC removal: Effect on water quality." *Journal American Water Works Association*, 89(2), 84-97.

Coleman, W. E., Munch, J. W., Ringhand, H. P., Kaylor, W. H., and Mitchell, D. E. (1992). "Ozonation Post-Chlorination of Humic-Acid - a Model for Predicting Drinking-Water Disinfection by-Products." *Ozone-Science & Engineering*, 14(1), 51-69.

Duguet, J. P., Brodard, E., Dussert, B., and Mallevialle, J. (1985). "Improvement in the Effectiveness of Ozonation of Drinking-Water through the Use of Hydrogen-Peroxide." *Ozone-Science & Engineering*, 7(3), 241-258.

Edzwald, J. K., Becker, W. C., and Wattier, K. L. (1985). "Surrogate Parameters for Monitoring Organic-Matter and Thm Precursors." *Journal American Water Works Association*, 77(4), 122-132.

Glaze, W. H., Peyton, G. R., Lin, S., Huang, R. Y., and Burleson, J. L. (1982). "Destruction of Pollutants in Water with Ozone in Combination with Ultraviolet-Radiation .2. Natural Trihalomethane Precursors." *Environmental Science & Technology*, 16(8), 454-458.

Griffini, O., Bao, M. L., Barbieri, K., Burrini, D., Santianni, D., and Pantani, F. (1999). "Formation and removal of biodegradable ozonation by-products during ozonation-biofiltration treatment: Pilot-scale evaluation." *Ozone-Science & Engineering*, 21(1), 79-98.

Herner, H. A. (1999). "The Reaction of Ozone with Pyrene: The By-products and Their Toxicological Implications.," Michigan State University, East Lansing.

Hoigne, J. (1982). "Mechanisms, Rates and Selectivities of Oxidation of Organic Compounds Initiated by Ozonation of Water." Handbook of Ozone Technology and Applications, R. G. Rice and A. Netzer, eds., Ann Arbor Science, Ann Arbor, MI, 307-379.

Hoigne, J., and Bader, H. (1975). "Ozonation of Water: Role of Hydroxyl Radicals as Oxidizing Agents." *Science*, 190, 782-784.

Jadashecart, A., Ventresque, C., Legube, B., and Dore, M. (1991). "Effect of Ozonation on the Chlorine Demand of a Treated Surface-Water and Some Macromolecular Compounds." *Ozone-Science & Engineering*, 13(2), 147-160.

Ko, Y. W., Chiang, P. C., and Chang, E. E. (1998). "Ozonation of p-hydroxybenzoic acid solution." *Ozone-Science & Engineering*, 20(5), 343-360.

Kool, H. J., van Kreijl, C. F., and Hrubec, J. (1985). "Mutagenic and Carcinogenic Properties of Drinking Water." Water Chlorination: Chemistry, Environmental Impacts, and Health Effects, R. L. Jolley, W. A. Brungs, and R. B. Cumming, eds., Lewis Publ., Chelsea, Mich.

Lee, K.-H. (2001). "The effects of ozonation pathways on the formation of ketoacids and assimilable organic carbon (AOC) in drinking water," Michigan State University, East Lansing, MI 48823.

Miltner, R. J., Shukairy, H. M., and Summers, R. S. (1992). "Disinfection by-Product Formation and Control by Ozonation and Biotreatment." *Journal American Water Works Association*, 84(11), 53-62.

Morris, R. D., Audet, A. M., Angelillo, I. F., Chalmers, T. C., and Mosteller, F. (1992). "Chlorination, Chlorination by-Products, and Cancer - a Metaanalysis." *American Journal of Public Health*, 82(7), 955-963.

Mughal, F. H. (1992). "Chlorination of Drinking Water and Cancer: A Review." *Jour. Envir. Pathol., Toxicol. & Oncol.*, 11(5,6), 287-292.

Munch, J. W., Munch, D. J., Winslow, S. D., Wendelken, S. C., and Pepich, B. V. (1998). "Determination of Carbonyl Compounds in Drinking Water by Pentafluorobenzylhydroxylamine Derivatization and Capillary Gas Chromatography with Electron Capture Detection." USEPA, Cincinnati, Ohio.

Nieminski, C. E., Chaudhuri, S., and Lamoreaux, T. (1993). "The Occurrence of Dbps in Utah Drinking Waters." *Journal American Water Works Association*, 85(9), 98-105.

Oxenford, J. L. (1996). "Disinfection By-Products: Current Practices and Future Directions." Disinfection By-products in Water Treatment, R. A. Minear and G. L. Amy, eds., Lewis Publisher, Boca Raton, FL., 3-16.

Paode, R. D., Amy, G. L., Krasner, S. W., Summers, R. S., and Rice, E. W. (1997). "Predicting the formation of aldehydes and BOM." *Journal American Water Works Association*, 89(6), 79-93.

Price, M. L., Bailey, R. W., Enos, A. K., Hook, M., and Hermanowicz, S. W. (1993). "Evaluation of Ozone Biological Treatment for Disinfection by- Products Control and Biologically Stable Water." *Ozone-Science & Engineering*, 15(2), 95-130.

Rice, R. G. (1980). "The Use of Ozone to Control Trihalomethanes in Drinking-Water Treatment." *Ozone-Science & Engineering*, 2(1), 75-99.

Richardson, S. D., Thruston, A. D., Caughran, T. V., Chen, P. H., Collette, T. W., Floyd, T. L., Schenck, K. M., Lykins, B. W., Sun, G. R., and Majetich, G. (1999). "Identification of new ozone disinfection byproducts in drinking water." *Environmental Science & Technology*, 33(19), 3368-3377.

Schechter, D. S., and Singer, P. C. (1995). "Formation of Aldehydes During Ozonation." *Ozone-Science & Engineering*, 17(1), 53-69.

Staehelin, J., and Hoigne, J. (1985). "Decomposition of Ozone in Water in the Presence of Organic Solutes Acting as Promoters and Inhibitors of Radical Chain Reactions." *Environmental Science & Technology*, 19(12), 1206-1213.

Standard Methods. (1998). Standard Methods for the Examination of Water and Wastewater, A. E. Greenberg, L. S. Clesceri, and A. D. Easton, eds., APHA, AWWA, WEF, Washington, DC.

Wallace, J. L., Vahadi, B., Fernandes, J. B., and Boyden, B. H. (1988). "The Combination of Ozone Hydrogen-Peroxide and Ozone Uv- Radiation for Reduction of Trihalomethane Formation Potential in Surface-Water." *Ozone-Science & Engineering*, 10(1), 103-112.

Weinberg, H. S., and Glaze, W. H. (1996). "An Overview of Ozonation Disinfection By-Products." Disinfection By-products in Water Treatment, R. A. Minear and G. L. Amy, eds., Lewis Publisher, Boca Raton, FL., 165-186.

Wobma, P., Pernitsky, D., Bellamy, B., Kjartanson, K., and Sears, K. (2000). "Biological filtration for ozone and chlorine DBP removal." *Ozone-Science & Engineering*, 22(4), 393-413.

Xie, Y. F., and Reckhow, D. A. (1992). "Formation of Ketoacids in Ozonated Drinking-Water." *Ozone-Science & Engineering*, 14(3), 269-275.

Yamada, H., and Somiya, I. (1980). "Identification of Products Resulting from Ozonation of Organic- Compounds in Water." *Ozone-Science & Engineering*, 2(3), 251-260.

Yamada, H., Somiya, I., and Inanami, F. (1986). "The Effect of Preozonation on the Control of Trihalomethane Formation." *Ozone-Science & Engineering*, 8(2), 129-150.

Zhang, X. Z., Ni, Y., and van Heiningen, A. (2001). "Effect of temperature on the kinetics of pulp ozonation." *Journal of Pulp and Paper Science*, 27(8), 279-283.

CHAPTER 6

CORRELATIONS BETWEEN THE FORMATION OF ASSIMILABLE ORGANIC CARBON AND OZONATION BY-PRODUCTS

6.1 INTRODUCTION

The use of ozone as a disinfectant results in a decrease in the concentration of halogenated disinfectant by-products (DBPs) (Amy et al. 1988; Cipparone et al. 1997). However, the ozonation of water containing natural organic matter (NOM) can increase the concentration of biodegradable organic matter (BOM) by decomposing larger molecules, resulting in the formation of lower molecular weight material and more polar and hydrophilic compounds (e.g., see Amy et al. 1988; Amy et al. 1992; Flogstad and Odegaard 1985; Kaastrup and Halmo 1989; Koechling et al. 1996; Owen et al. 1995). The presence of BOM in treated water can result in the formation of biofilms in water distribution systems, unpleasant taste, odors, and color, in biologically mediated corrosion and in interferences with microbiological monitoring (Lee et al. 1980; Miltner et al. 1992; Schechter and Singer 1995).

Assimilable organic carbon (AOC) is one approach to estimating the concentration of BOM. It represents the degradable fraction of BOM that can be consumed by microorganisms. A significant correlation between the AOC concentration and the level of regrowth of heterotrophic bacteria in water distribution systems has been reported (Vanderkooij 1992). Several researchers found that the correlation between AOC and ozonation by-products such as aldehydes was significant (Paode et al. 1997; Schechter and Singer 1995). Therefore, the objective of this study was to determine whether significant correlations exist between the concentration of AOC and ozonation by-products.

6.2 MATERIALS AND METHODS

6.2.1 Experimental Setup and Protocol

A specially designed ozonation/membrane system and four biofiltration columns were used to investigate the formation of AOC and ozonation DBPs (i.e., aldehydes, ketones, and ketoacids) resulting from the treatment process. The system was the same one that was described in Chapter 4. A schematic diagram of this system is shown in Figure 4.1. Operational and experimental conditions were described in Section 5.2.1. AOC, aldehydes (formaldehyde, acetaldehyde, propionaldehyde, glyoxal, and methyl glyoxal), ketones (acetone and 2-butanone), and ketoacids (glyoxylic acid, pyruvic acid, and ketomalonic acid) were monitored in all water samples in this study.

6.2.2 Water Source

Experiments were carried out on Lake Lansing (Haslett, MI) water. Water quality characteristics of Lake Lansing are summarized in the previous chapter (see Table 4.3). Lake Lansing waters were collected in five-gallon tanks, properly labeled, and stored at 4°C. The maximum storage period was seven days. All waters were filtered through a 0.45-µm filter and warmed to room temperature before testing.

6.2.3 Analytical Methods

The measurement of AOC followed the Method 9217 of Standard Methods (1998) as described in Section 4.2.8. Aldehydes and ketones were measured by using the USEPA Method 556 (Munch et al. 1998) as described in Section 5.2.5. The concentration of ketoacids was measured by using the same method as described in Section 5.2.6.

6.3 RESULTS AND DISCUSSION

6.3.1 Ozonation By-products

The experimental results describing total aldehydes and ketoacids were presented in the previous chapter. As mentioned in Chapter 5, acetaldehyde, propionaldehyde, and acetone were not detected in all water samples. Therefore, only the results of three species of aldehydes (formaldehyde, glyoxal, and methyl glyoxal) and one species of ketone (2-Butanone) were discussed in this section. All species were found to be significantly correlated with AOC in our study (at $p = 0.01$ level at 95% C.I.).

The concentrations of formaldehyde, which is the principle aldehydes species, were determined at different treatment stages under various experimental conditions. These results are shown in Figures 6.1 to 6.3. Although the maximum concentration of formaldehyde was different at different experimental conditions, likely due to the varying composition of NOM in the raw water and the different operating conditions, the level of formaldehyde usually reached a maximum level in P1 or P2, and then decreased in WT. This indicates that the formation of formaldehyde in the early stages of ozonation was faster than its decomposition by oxidation, but it was gradually destroyed by molecular ozone or hydroxyl radical after all its precursors were converted to formaldehyde. Similar results were reported by several researchers (Ko et al. 1998; Yamada and Somiya 1980). Correlations between the maximum level of formaldehyde and ozone gas flow rate and between the maximum level of formaldehyde and ozone dose were significant ($p < 0.01$). As the gas flow rate or ozone dose increased, the formation of formaldehyde increased. However, the correlation between the formation of formaldehyde and water temperature was not significant ($p > 0.05$). This observation is the same as that observed for total aldehydes.

Figures 6.4 to 6.6 show the concentrations of glyoxal at various treatment stages under different experimental conditions. Figures 6.7 to 6.9 show of the variations in the concentrations of methyl glyoxal. The formation of glyoxal and methyl glyoxal follow similar trends to that observed for formaldehyde. The concentrations of glyoxal and methyl glyoxal increased early during treatment and then decreased after reaching the maximum level. At 10 °C water temperature, glyoxal concentration of different treatment stage increased as the ozonation time increased. It appears that the difference in the formation and decomposition potentials of glyoxal were higher at lower water temperature. It could be due to the direct reaction of molecular ozone is the primarily pathway that favors the formation of aldehydes (Hoigné 1982).

The maximum concentration of glyoxal and methyl glyoxal increased as the gas flowrate increased but decreased as the water temperature increased ($p < 0.01$). Their concentrations also increased as the ozone dose increased but the correlations between concentration and ozone dose were not statistical significance ($p > 0.05$).

Figures 6.1 to 6.9 also illustrate the performance of the biotreatment on the removal of ozonation by-products. Biofiltration effectively and significantly removed the concentrations of all aldehydes species in P2 water, which was treated by ozonation/membrane system ($p < 0.01$). The percentage of formaldehyde, glyoxal, and methyl glyoxal removed ranged between 72.9% and 88.3%, 93.0% and 100%, and 93.2% and 98.1%, respectively.

Table 6.1 summarizes the concentration of 2-butanone measured in waters from the different treatment stages at various experimental conditions. It shows that the concentrations of 2-butanone increased significantly during ozonation ($p < 0.01$) except for one raw water sample treated at ozone gas flowrate of 75 mL/min. However, no firm conclusions can be made for the relationships between 2-butanone concentrations and experimental conditions because of the variability of the results. The vapor pressure of 2-butanone is 90.6 mmHg at 25 °C, and the Henry's law constant is 5.77×10^{-5} atm m^3/mol at 25 °C (Agency for Toxic Substances and Disease Registry 1992). This suggests that volatilization may result in losses of 2-butanone to the air during the purging ozonated water (to quench ozone). Moreover, the variations in the composition of NOM in FRW water (the concentration of 2-butanone in FRW water varied between 2.6 μg/L and 297.7 μg/L) and the complex competing reactions during ozonation in the water may also result in the variability of 2-butanone concentrations.

The results obtained after biotreatment of 2-butanone (B-FRW and B-P2) were also highly variable. The highest removal efficiency was over 99% but the level of 2-butanone was also found to increase from 2.6 μg/L to 646.0 μg/L in one sample after biofiltration. The 2-butanone concentration decreased in 9 out of 14 biotreated samples ($p < 0.01$) but increased in the other 5 ones ($p < 0.01$). Several researchers have studied the biodegradation of 2-butanone and reported that biofiltration can remove 2-butanone (Agathos et al. 1997; Amanullah et al. 2000; Deshusses 1997; Deshusses et al. 1995; Edwards et al. 1994). Several factors may result in the variation of 2-butanone concentration: 1) the decomposition rate of 2-butanone by the microorganisms in the biofiltration column, 2) the losses of 2-butanone from the biofiltration system to the air, and 3) the sample handling during analysis. Therefore, further studies on the biodegradation of 2-butanone by using ozonation/membrane and subsequent biofiltration should be conducted.

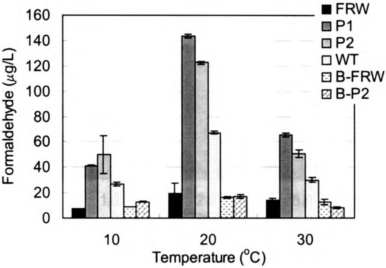

Figure 6.1 Concentrations of formaldehyde of different treatment stages at various water treatment temperatures. (Operating condition: water flowrate, 2.75 L/min; gas flowrate, 100 mL/min; O_3 dose, 2.5 g/m^3)

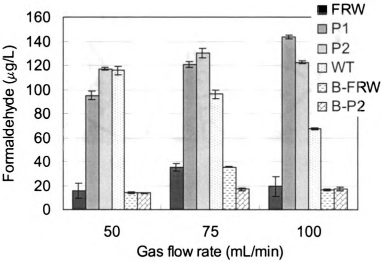

Figure 6.2 Concentrations of formaldehyde of different treatment stages at various gas flowrates. (Operating condition: water flowrate, 2.75 L/min; O_3 dose, 2.5 g/m^3; water temperature, 20 °C)

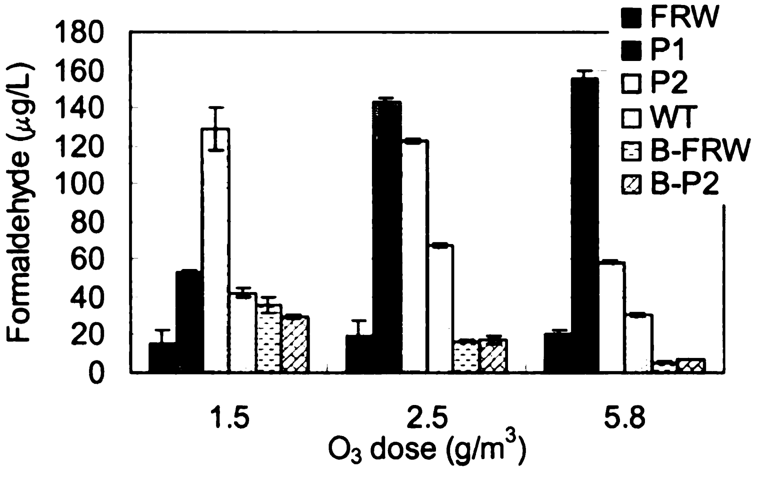

Figure 6.3 Concentrations of formaldehyde of different treatment stages at various ozone doses. (Operating condition: water flowrate, 2.75 L/min; gas flowrate, 100 mL/min; water temperature, 20 °C)

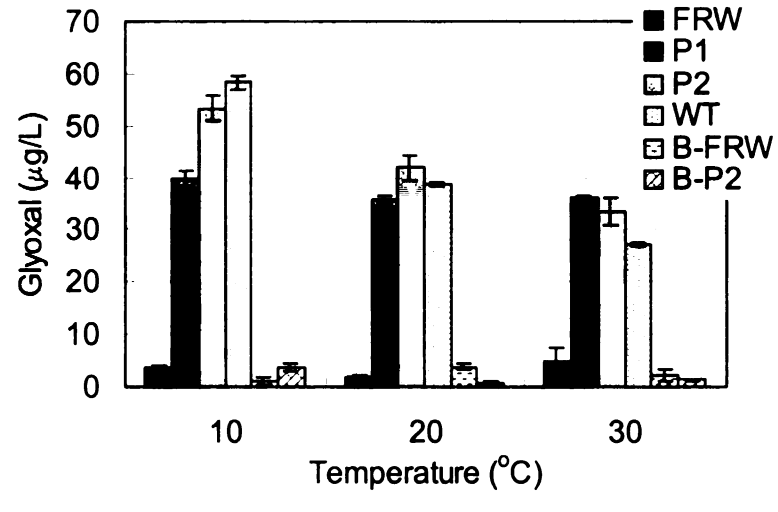

Figure 6.4 Concentrations of glyoxal of different treatment stages at various water treatment temperatures. (Operating condition: water flowrate, 2.75 L/min; gas flowrate, 100 mL/min; O_3 dose, 2.5 g/m^3)

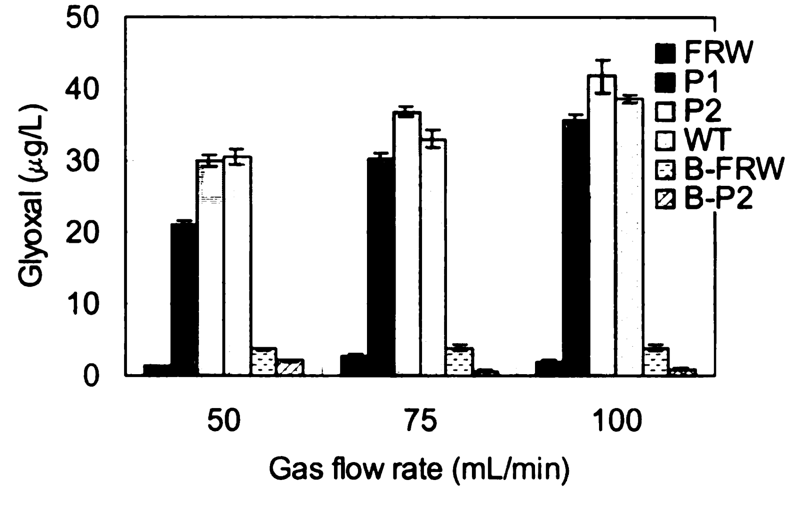

Figure 6.5 Concentrations of glyoxal of different treatment stages at various gas flow rates. (Operating condition: water flowrate, 2.75 L/min; O_3 dose, 2.5 g/m^3; water temperature, 20 °C)

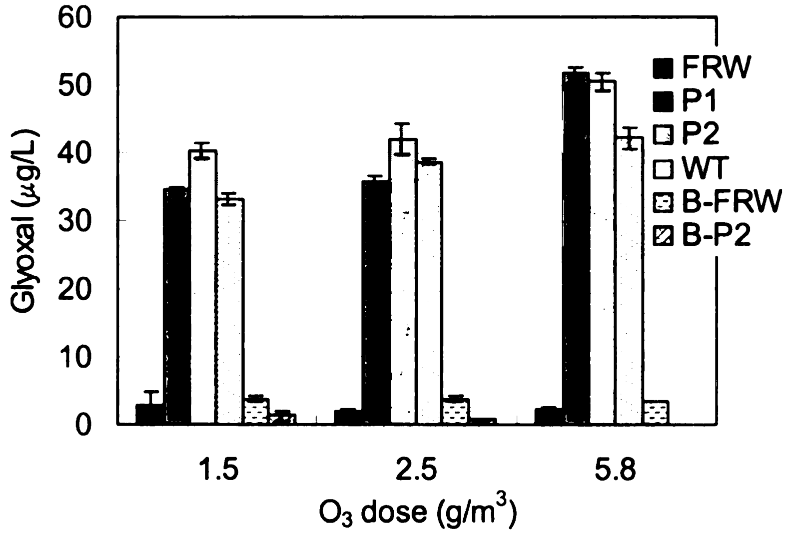

Figure 6.6 Concentrations of glyoxal of different treatment stages at various ozone doses. (Operating condition: water flowrate, 2.75 L/min; gas flowrate, 100 mL/min; water temperature, 20 °C)

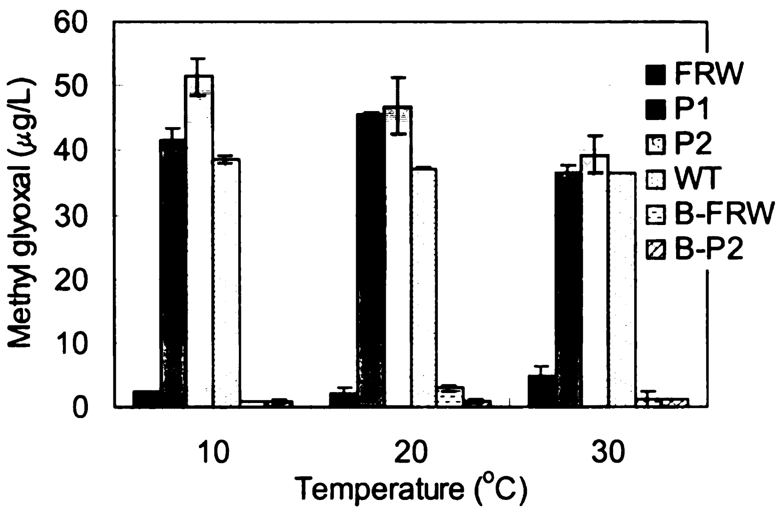

Figure 6.7 Concentrations of methyl glyoxal of different treatment stages at various water treatment temperatures. (Operating condition: water flowrate, 2.75 L/min; gas flowrate, 100 mL/min; O_3 dose, 2.5 g/m^3)

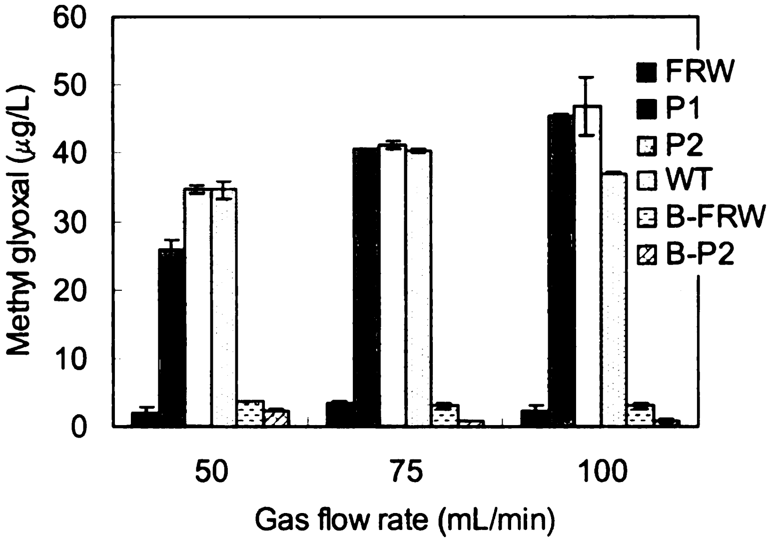

Figure 6.8 Concentrations of methyl glyoxal of different treatment stages at various gas flow rates. (Operating condition: water flowrate, 2.75 L/min; O_3 dose, 2.5 g/m^3; water temperature, 20 °C)

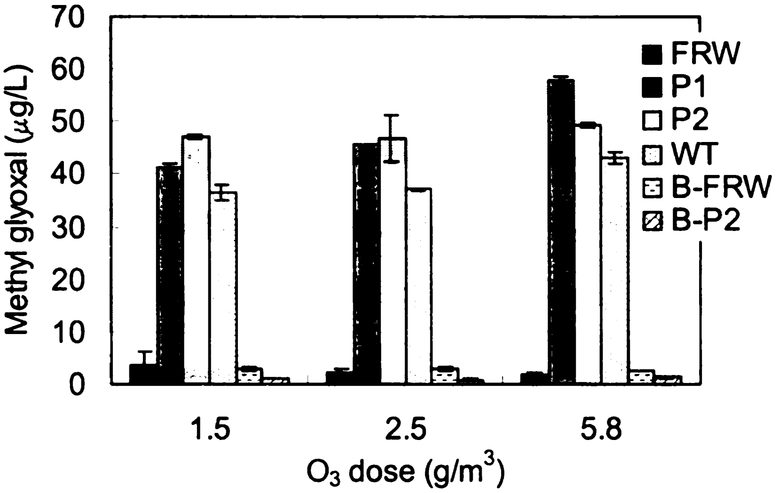

Figure 6.9 Concentrations of methyl glyoxal of different treatment stages at various ozone doses. (Operating condition: water flowrate, 2.75 L/min; gas flowrate, 100 mL/min; water temperature, 20 °C)

Table 6.1 Concentrations of 2-Butanone for Lake Lansing water measured in different treatment stages at various experimental conditions in this study. (μg/L)

Temperature[1]	FRW	P1	P2	WT	B-FRW	B-P2
10	195.9	1048.2	112.8	179.0	115.8	448.9
20	179.1	599.6	906.7	1105.4	484.8	1.3
30	114.0	261.0	580.9	873.2	60.7	33.9
Gas flowrate[2]	FRW	P1	P2	WT	B-FRW	B-P2
50	297.7	832.9	982.1	1427.7	288.7	256.7
75	297.5	158.7	224.9	229.6	475.5	3.3
100	179.1	599.6	906.7	1105.4	484.8	1.3
Ozone dose[3]	FRW	P1	P2	WT	B-FRW	B-P2
1.5	208.8	382.7	198.2	158.6	484.8	112.6
2.5	179.1	599.6	906.7	1105.4	484.8	1.3
5.8	2.6	245.4	405.8	300.5	646.0	594.6

1. unit: °C
2. unit: mL/min
3. unit: g/m^3

6.3.2 Correlations Between AOC and Ozonation By-products

The Pearson correlation coefficient of similarity (r value) is used to investigate the correlations between AOC(total), AOC(P17), and AOC(NOX) and ozonation by-products. The AOC(total) means that the density of viable cells of *Pseudomonas fluorescens* strain P17 and *Spirillum* strain NOX was converted to AOC concentrations. The AOC(P17) and AOC(NOX) mean that only the density of viable cells of *Pseudomonas fluorescens* strain P17 and only that of *Spirillum* strain NOX was converted to AOC concentrations, respectively. The Pearson coefficient was generated by using the statistical software, SPSS for Windows (Release 10.0, SPSS Inc.). The absolute value of the Pearson coefficient indicates the strength of the linear relationship between AOC and ozonation by-products, with larger absolute values indicating stronger relationships. The experimental results for formaldehyde, glyoxal, methyl glyoxal, and 2-butanone were discussed in the previous section. The results for AOC(total), aldehydes and ketoacids were presented in Chapters 4 and 5.

Table 6.2 summarizes the Pearson correlation coefficients of AOC(total), AOC(P17), and AOC(NOX) that were determined by using ozonation by-products as independent variables. Significant and positive correlations were found between independent variables and AOC(total), AOC(P17), AOC(NOX) at the $p = 0.01$ level (n=38, at 95% C.I.). According to the Pearson coefficients in Table 6.2, total concentration of ozonation by-products (aldehydes + 2-butanone + ketoacids) and the concentration of AOC behaved similarly in the treatment system in this study and the total concentration of ozonation by-products could be used as a surrogate of AOC(total). It also shows the same for AOC(P17) and AOC(NOX). Figures 6.10 to 6.12 show correlations between AOC(total), AOC(P17), AOC(NOX) and the sum of aldehydes, 2-butanone, and ketoacids treated by the ozonation/membrane and biofiltration system in our study.

Schechter and Singer (1995) reported that the concentration of aldehydes could be used as a surrogate for the more complex AOC analysis. The concentration of aldehydes is the sum of formaldehyde, glyoxal, and methyl glyoxal in our study. Our results confirmed their observation. The concentration of methyl glyoxal was another good candidate as a surrogate for AOC(total), AOC(P17), and AOC(NOX).

However, it should be noted that the correlation between AOC and ozonation by-products would be affected by the nature of NOM. Small differences in the composition of NOM might result in a significant difference of the formation of ozonation by-products. Therefore, waters obtained from different sources might react differently in the treatment system. As such, further investigation is necessary to assess the more general correlations between the formation of AOC and ozonation by-products.

Table 6.2 Correlations between AOC(total), AOC(P17), AOC(NOX) and ozonation by-products.

Independent variables	AOC(total) (r value)	AOC(P17) (r value)	AOC(NOX) (r value)
Aldehydes	0.863	0.850	0.850
Formaldehyde	0.722	0.684	0.716
Glyoxal	0.821	0.873	0.794
Methyl glyoxal	0.885	0.902	0.865
2-Butanone	0.780	0.641	0.796
Ketoacids	0.752	0.783	0.731
Aldehydes + 2-Butanone +Ketoacids	0.899	0.856	0.892
Aldehydes + 2-Butanone	0.860	0.736	0.871
Aldehydes + Ketoacids	0.804	0.841	0.781
2-Butanone + Ketoacids	0.876	0.829	0.870

* n = 38, the correlation is significant at the 0.01 level at 95% C.I.

** r is the correlation between the observed and predicted values of AOC(total), AOC(P17), and AOC(NOX).

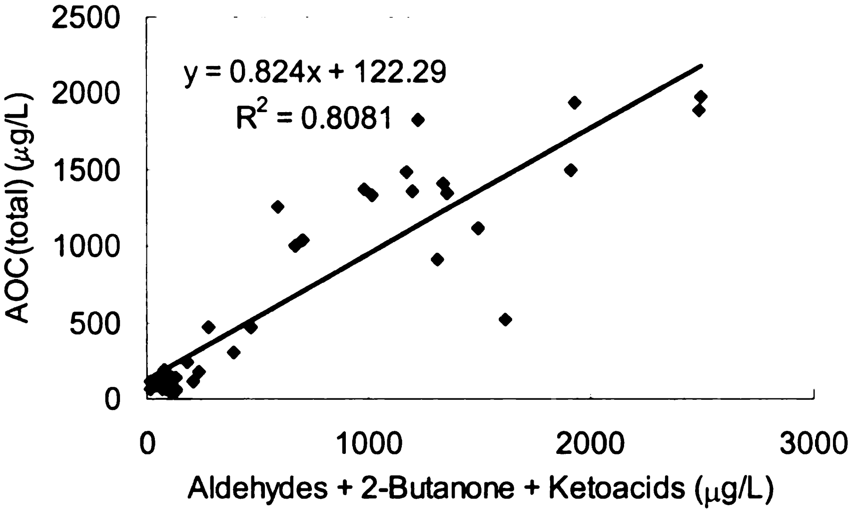

Figure 6.10 Correlation between AOC(total) and the sum of aldehydes, 2-butanone, and ketoacids of Lake Lansing water treated by the ozonation/membrane and biofiltration system. (Correlation is significant at the 0.01 level.)

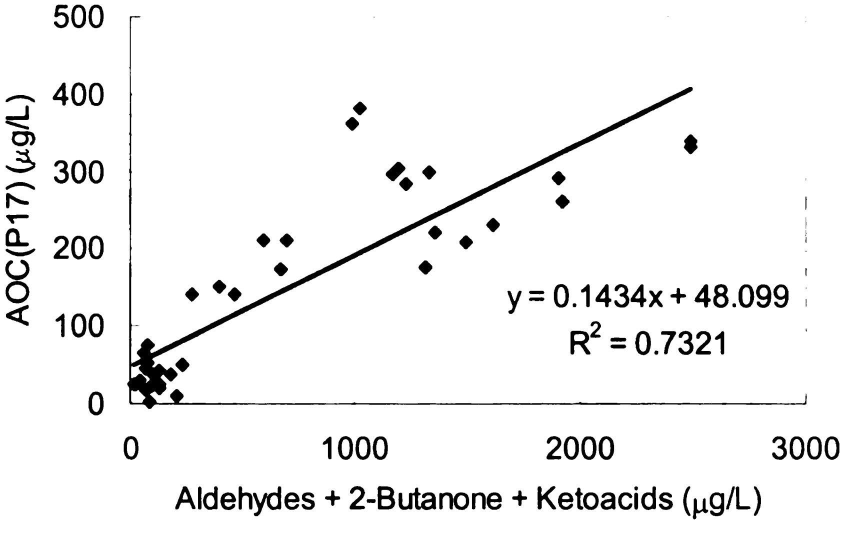

Figure 6.11 Correlation between AOC(P17) and the sum of aldehydes, 2-butanone, and ketoacids of Lake Lansing water treated by the ozonation/membrane and biofiltration system. (Correlation is significant at the 0.01 level.)

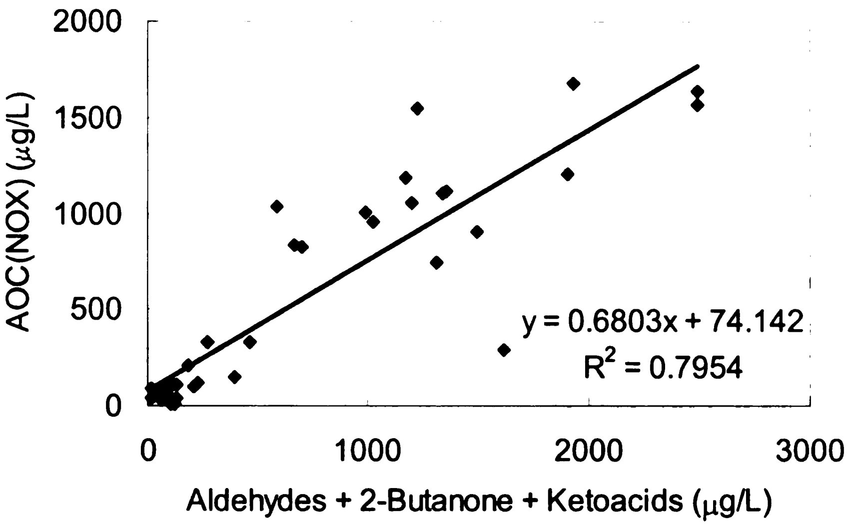

Figure 6.12 Correlation between AOC(NOX) and the sum of aldehydes, 2-butanone, and ketoacids of Lake Lansing water treated by the ozonation/membrane and biofiltration system. (Correlation is significant at the 0.01 level.)

6.4 CONCLUSIONS

1. The concentrations of formaldehyde, glyoxal, and methyl glyoxal decreased after they reached their maximum level, which indicated that their formation in the early stages of ozonation was faster than their decomposition by oxidation. However, these ozonation by-products were gradually destroyed by ozonation after the precursors were oxidized.
2. As the gas flow rate or ozone dose increased, the maximum concentration of formaldehyde increased. However, the correlation between the maximum level of formaldehyde and water temperature was not significant. On the other hand, the maximum concentration of glyoxal and methyl glyoxal increased as the gas flow

rate increased but decreased as the water temperature increased. The maximum concentrations of glyoxal and methyl glyoxal also increased as the ozone dose increased but the increases were not statistical significance.

3. Biofiltration effectively removed the concentrations of all aldehydes in water treated by ozonation/membrane system.
4. The biotreatment of 2-butanone shows variable results. Further studies on the biodegradation of 2-butanone by using ozonation/membrane and subsequent biofiltration should be conducted.
5. Significant and positive correlations were found between ozonation by-products and AOC(total), AOC(P17), and AOC(NOX).
6. The total concentration of ozonation by-products (aldehydes + 2-butanone + ketoacids), aldehydes, and methyl glyoxal are three good surrogates for AOC(total), AOC(P17), and AOC(NOX) for Lake Lansing water treated by ozonation/membrane system and biofiltration under experimental conditions tested in this study.

6.5 REFERENCES

Agency for Toxic Substance and Disease Registry (1992). *Toxicological Profile for 2-Butanone*, Agency for Toxic Substances and Disease Registry, U.S. Public Health Service.

Agathos, S. N., Hellin, E., Ali-Khodja, H., Deseveaux, S., Vandermesse, F., and Naveau, H. (1997). "Gas-phase methyl ethyl ketone biodegradation in a tubular biofilm reactor: microbiological and bioprocess aspects." *Biodegradation*, 8(4), 251-264.

Amanullah, M., Viswanathan, S., and Farooq, S. (2000). "Equilibrium, kinetics, and column dynamics of methyl ethyl ketone biodegradation." *Industrial & Engineering Chemistry Research*, 39(9), 3387-3396.

Amy, G. L., Kuo, C. J., and Sierka, R. A. (1988). "Ozonation of Humic Substances - Effects on Molecular-Weight Distributions of Organic-Carbon and Trihalomethane Formation Potential." *Ozone-Science & Engineering*, 10(1), 39-54.

Amy, G. L., Sierka, R. A., Bedessem, J., Price, D., and Tan, L. (1992). "Molecular-Size Distributions of Dissolved Organic-Matter." *Journal American Water Works Association*, 84(6), 67-75.

Cipparone, L. A., Diehl, A. C., and Speitel, G. E. (1997). "Ozonation and BDOC removal: Effect on water quality." *Journal American Water Works Association*, 89(2), 84-97.

Deshusses, M. A. (1997). "Transient behavior of biofilters: Start-up, carbon balances, and interactions between pollutants." *Journal of Environmental Engineering-Asce*, 123(6), 563-568.

Deshusses, M. A., Hamer, G., and Dunn, I. J. (1995). "Behavior of Biofilters for Waste Air Biotreatment .2. Experimental Evaluation of a Dynamic-Model." *Environmental Science & Technology*, 29(4), 1059-1068.

Edwards, D. E., Adams, W. J., and Heitkamp, M. A. (1994). "Laboratory-Scale Evaluation of Aerobic Fluidized-Bed Reactors for the Biotreatment of a Synthetic, High-Strength Chemical- Industry Waste Stream." *Water Environment Research*, 66(1), 70-83.

Flogstad, H., and Odegaard, H. (1985). "Treatment of Humic Waters by Ozone." *Ozone-Science & Engineering*, 7(2), 121-136.

Hoigné, J. (1982). "Mechanisms, Rates and Selectivities of Oxidation of Organic Compounds Initiated by Ozonation of Water." Handbook of Ozone Technology and Applications, R. G. Rice and A. Netzer, eds., Ann Arbor Science, Ann Arbor, MI, 307-379.

Kaastrup, E., and Halmo, T. M. (1989). "Removal of Aquatic Humus by Ozonation and Activated Carbon Adsorption." Aquatic Humic Substances: Influence on Fate and Treatment of Pollutants, I. H. Suffet and P. MacCarthy, eds., American Chemical Society, Washington, DC., 697-726.

Ko, Y. W., Chiang, P. C., and Chang, E. E. (1998). "Ozonation of p-hydroxybenzoic acid solution." *Ozone-Science & Engineering*, 20(5), 343-360.

Koechling, M. T., Shukairy, H. M., and Summers, R. S. (1996). "Effect of Ozonation and Biotreatment on Molecular Size and Hydrophilic Fractions of Natural Organic Matter." Water Disinfection and Natural Organic Matter: Characterization and Control, R. A. Minear and G. L. Amy, eds., American Chemical Society, Washington, DC., 196-210.

Lee, S. H., Oconnor, J. T., and Banerji, S. K. (1980). "Biologically Mediated Corrosion and Its Effects on Water- Quality in Distribution-Systems." *Journal American Water Works Association*, 72(11), 636-645.

Miltner, R. J., Shukairy, H. M., and Summers, R. S. (1992). "Disinfection by-Product Formation and Control by Ozonation and Biotreatment." *Journal American Water Works Association*, 84(11), 53-62.

Munch, J. W., Munch, D. J., Winslow, S. D., Wendelken, S. C., and Pepich, B. V. (1998). "Determination of Carbonyl Compounds in Drinking Water by Pentafluorobenzylhydroxylamine Derivatization and Capillary Gas Chromatography with Electron Capture Detection." USEPA, Cincinnati, Ohio.

Owen, D. M., Amy, G. L., Chowdhury, Z. K., Paode, R., McCoy, G., and Viscosil, K. (1995). "Nom - Characterization and Treatability." *Journal American Water Works Association*, 87(1), 46-63.

Paode, R. D., Amy, G. L., Krasner, S. W., Summers, R. S., and Rice, E. W. (1997). "Predicting the formation of aldehydes and BOM." *Journal American Water Works Association*, 89(6), 79-93.

Schechter, D. S., and Singer, P. C. (1995). "Formation of Aldehydes During Ozonation." *Ozone-Science & Engineering*, 17(1), 53-69.

Standard Methods. (1998). Standard Methods for the Examination of Water and Wastewater, A. E. Greenberg, L. S. Clesceri, and A. D. Easton, eds., APHA, AWWA, WEF, Washington, DC.

Vanderkooij, D. (1992). "Assimilable Organic-Carbon as an Indicator of Bacterial Regrowth." *Journal American Water Works Association*, 84(2), 57-65.

Yamada, H., and Somiya, I. (1980). "Identification of Products Resulting from Ozonation of Organic- Compounds in Water." *Ozone-Science & Engineering*, 2(3), 251-260.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 CONCLUSIONS

A novel ozonation/membrane system was used in this study to investigate its ability to control NOM and DBPs in drinking water under various operating conditions. This research was conducted by using a bench-scale system to determine the efficiency of ozone mass transfer in the system, to investigate the effect of the system followed by biofiltration on the characteristics of NOM and the formation of DBPs, and to establish the correlation between NOM, DBPs, and AOC. Considering important factors such as gas flow rate and water flow rate which influence the K_La value, the ozonation/membrane system can achieve reasonable ozone mass transfer by requiring lesser ozone dose, gas flow rate, and water flow rate than comparable systems. This system has the added advantage that it does not include diffuser thus reducing clogging problems.

7.1.1 Mass Transfer of Ozone in the System

The volumetric mass transfer coefficient of ozone was determined under different operating conditions. Water flow rate, gas flow rate, inlet gaseous ozone concentration, and water temperature were the operational parameters controlled in this study. The K_La value of ozone increased with increasing the water flow rate and gas flow rate over the range of operating conditions studied. However, as the ozone dose increased, the K_La value first increased to a maximum value and then decreased.

The water temperature was found to have little effect on the K_La value over the temperature range from 10 °C to 30 °C.

A mathematical model was developed to describe the concentration profiles of dissolved ozone in the ozonation/membrane system. The simulations fit reasonably well with the experimental data under different operating conditions. Although the DDI water used in the mass transfer study was acidified to pH 2 to avoid ozone decomposition in the water, the ozone decomposition rate constant, k, was considered in the model because the ozone decomposition experiment showed that the k value is not negligible when using the ozonation/membrane system.

7.1.2 Characteristics of NOM

The characteristics of NOM in terms of DOC, UV-254, humic and non-humic substances, BDOC, and AOC were monitored in the treatment process of the ozonation/membrane system. The DOC concentration in the permeate water of the membrane decreased as the temperature increased and 15 to 33% of DOC was removed. Ozonation effectively decreased the absorbance of UV-254 by 55 to 85%, converted humic substances to non-humic substances, and significantly increased the biodegradability of water in terms of BDOC and AOC. A good correlation was established between the humic substances and UV-254.

After biofiltration, the removal efficiency of DOC increased to between 69 and 88%. Between 91 to 97% of the AOC was also removed by ozonation/membrane filtration/biofiltration. This suggests that biotreatment following the ozonation/membrane system can maximize the removal of organic carbon, which may react with chlorine and result in the formation of DBPs or result in the bacteria regrowth problem in the distribution system if remains in the treated water.

Adding ozone gas at the membrane inlet resulted in a recovery of the permeate flux from 60% to 97% of the initial flux. The experimental results also show that effective removal of DOC, UV-254 and conversion of humic substances to non-humic substances can be achieved at low gas flow rate and low ozone dose. Therefore, these conditions should reduce the cost of system operation over more extensive ozonation and decrease the frequency of membrane cleaning or replacement, which should also, indirectly, reduce the cost of maintenance.

7.1.3 Control of DBPs

The decrease in chlorine demand was not significant for the range of operating conditions studied by using the ozonation/membrane system. Some experimental results even show an increase in the chlorine demand. This implies that ozonation create chlorine-reacting sites on DOC. Biotreatment was shown to decrease the chlorine demand effectively. The removal efficiency ranged from 60% to 90% in the ozonation/membrane system followed by biofiltration. This indicates that the chlorine reactive material is biodegradable.

The formation of THMs decreased with increasing temperature, gas flow rate, and ozone dose regardless of whether or not biofiltration followed the bench-scale system. Similarly, the level of HAAs decreased with increasing the gas flow rate or the ozone dose, regardless of whether or not biofiltration followed ozonation/membrane filtration. On the contrary HAAs was independent of the water temperature. The formation of ozonation by-products, i.e., aldehydes and ketoacids, significantly increased after ozonation under all operating conditions. Aldehydes and ketoacids are easily biodegradable. The use of biofiltration following ozonation/membrane system resulted in an 85 to 95% reduction in aldehydes concentrations and a 94 to 100% reduction in ketoacids levels.

Chlorine demand and DOC, THMs and HAAs, aldehydes and ketoacids, THMs and surrogate parameters (DOC, UV-254, HS), HAAs and surrogate parameters (DOC, UV-254, HS), aldehydes and NHS, ketoacids and NHS were positively correlated and their correlations were statistically significant. Aldehydes and surrogate parameters (UV-254, HS), ketoacids and surrogate parameters (UV-254, HS) were negatively correlated and their correlations were statistically significant.

7.1.4 Correlations Between AOC and Ozonation By-products

The level of formaldehyde, glyoxal, and methyl glyoxal increased in the early stage of ozonation and then decreased after they reached their maximum level. It was observed that the maximum concentration of formaldehyde increased with increasing gas flow rate and ozone dose. The maximum concentration of glyoxal and methyl glyoxal increased as the gas flow rate increased but decreased as the water temperature increased.

There exists statistically significant and positive correlations between ozonation by-products and AOC. The experimental results also show that the total concentration of ozonation by-products (aldehydes + 2-butanone + ketoacids), aldehydes, and methyl glyoxal are three good surrogates for AOC, P17, and NOX for Lake Lansing water treated by ozonation/membrane system and biofiltration under experimental conditions studied in this research.

7.2 RECOMMENDATIONS FOR FUTURE RESEARCH

Based upon the experimental results of this study, the ozonation/membrane system followed by biotreatment should be able to effectively decrease the concentrations of DOC, AOC, BDOC, and UV-254-absorbing compounds, reduce the formation of THMs and HAAs, remove most of the aldehydes and ketoacids, decrease the chlorine demand of water, and reduce the bacteria regrowth potential in the distribution system. Recommendations for future research include:

1. Tubular ceramic membranes with a molecular weight cut-off of 15 kD were used in this study. Ceramic membranes with different molecular weight cut-offs and different types of ceramic membranes (when they are available) should be investigated to determine their effect on the treated water quality.
2. Only a simple membrane flux recovery test was conducted in this study. In order to better understand the mechanism of the fouling process, the prevention of membrane fouling by ozonation should be investigated. In addition, the transmembrane pressure, which is an operational parameter that influences permeate flux and can be an indicator of membrane fouling, should be monitored.
3. Carboxylic acids, such as formic acid and acetic acid, need to be monitored in order to better understand their formation and transformation of ozonation by-products.
4. The Lake Lansing water contains low bromide concentration. As bromide not only reacts with ozone and forms bromate, but also affects the formation of other DBPs, it is important to investigate the applicability of this system on waters containing high bromide concentrations.
5. The economic analysis needs to be conducted when cost related information of ceramic membrane is available.