

LIBRARY
Michigan State
University

PLACE IN RETURN BOX
 to remove this checkout from your record.
TO AVOID FINES return on or before date due.

DATE DUE	DATE DUE	DATE DUE
SEP 30 2000 122200		
OCT 16 2003		

**THE USE OF OZONATION AND BIOLOGICAL FLUIDIZED BED TREATMENT
FOR THE CONTROL OF NOM IN DRINKING WATER**

By

Alexander Anatoly Yavich

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

1998

ABSTRACT

THE USE OF OZONATION AND BIOLOGICAL FLUIDIZED BED TREATMENT FOR THE CONTROL OF NOM IN DRINKING WATER

By

Alexander A. Yavich

Bench-scale and pilot-scale studies were conducted using Huron River water taken at the Ann Arbor Water Treatment Plant. The major water quality parameters that were monitored in this study included TOC, BDOC, UV-254 absorption, THMFP, AMW distribution, humic and non humic fractions of NOM, turbidity, pH and alkalinity.

A combination of factors, including ozone dose, hydraulic retention time, and the concentration of dissolved ozone was identified, which controlled both the destruction of organic carbon and the production of low-molecular weight organic compounds and biodegradable organic matter during ozonation. The relationships between properties of THM precursors, including TOC, UV-254, humic substances, and THMFP were established and used to investigate the efficacy of the ozonation and biological fluidized bed treatment (FBT). A mathematical model that described the transformation of NOM during ozonation was developed and verified over a range of ozone doses of up to 3 mg/mg C, temperatures of up to 25°C, and hydraulic retention times of up to 20 minutes.

The biodegradable organic matter in Huron River water consisted of rapidly and slowly biodegrading fractions ("fast" and "slow" BDOC). The biodegradability of raw and treated waters was characterized by the maximum biodegradation rate of "fast" BDOC ($R_{\max}$), the minimum biodegradation time that required to eliminate "fast" BDOC

($EBCT_{min}$), and by the minimum concentration of “slow” BDOC that remained in the water after biodegradation at $EBCT_{min}$ ($BDOC_{slow}$).

The following treatment processes that included ozonation and FBT were investigated: (1) single-pass ozonation/FBT; (2) ozonation/FBT with recycle; (3) single-pass FBT/ozonation with biofiltration; (4) recirculating FBT/ozonation with biofiltration; (5) single-pass FBT/ozonation/biofiltration with the addition of acetate to the FBT column (“stimulated” FBT); and (6) recirculating “stimulated” FBT/ozonation with biofiltration. Among these processes, the recirculating “stimulated” FBT/ozonation process followed by biofiltration was most efficient in terms of the removal of NOM relative to ozone consumption and biodegradation time. The removal of NOM was comparable to that achieved at the Ann Arbor Water Treatment Plant, that uses lime softening, flocculation/sedimentation, ozonation and GAC filtration. For a design capacity of 1 MGD, the cost of treatment by the FBT/ozonation process followed by biofiltration was estimated to be at least 40 percent lower than that by a conventional flocculation/sedimentation process with ozonation and GAC filtration.

Copyright by
Alexander Anatoly Yavich
1998

ACKNOWLEDGEMENTS

I wish to express my sincere thanks to Dr. Masten for the opportunity to start and complete this research and for her guidance and support during all these years I have been in graduate program. I also wish to thank Dr. Rajan and Dr. Hickey for the time they spent discussing with me this work. Those discussions were extremely helpful. I am grateful to my committee members Dr. Davies, Dr. Davis, once again Dr. Rajan, and Dr. Zabik for technical and moral support and for the time they invested in reviewing this work. My thanks are also extended to Dr. Amy and Dr. Collins for support of the ideas that were realized in this research.

I am thankful to Jeff Cook and Dan Wagner who helped me in building and operating the pilot-scale system. My thanks are also due to my fellow graduate students Ajay Kasarabada, Jullie Mellema, and Yvonne Chang who took part in this research. I also would like to thank Janice Scadsen of the Ann Arbor Water Treatment Plant for technical support. I am grateful to the EPA Fellowship office and NSF for financial support.

The completion of this work would have not been possible without help of my wife, Yelena, my daughter Dina, and my parents. I wish to thank them for their love and patience.

TABLE OF CONTENTS

TABLES	ix
FIGURES	xi
ABBREVIATIONS	xv
1. INTRODUCTION	1
1.1. Significance.....	1
1.2. Objectives	4
1.3. Project Outline	6
2. BACKGROUND	7
2.1. Characterization of NOM	7
2.1.1. Humic Substances.....	8
2.1.2. Organic Carbon Content	11
2.1.3. UV Absorption.....	11
2.1.4. THMFP	12
2.1.5. Molecular Weight Distribution	13
2.1.6. BDOC	14
2.2. Review of Treatment Processes	16
2.2.1. Slow Sand Filtration	16
2.2.2. Chemical Coagulation.....	17
2.2.3. Carbon adsorption.....	19
2.2.4. Membrane separation.....	20
2.2.5. Ozonation.....	22
2.2.6. Combined ozonation/biotreatment.....	25
2.2.7. Proposed Ozonation/FBT Process	29
3. MATERIALS AND METHODS.....	33
3.1. Water Source.....	33
3.2. Experimental Systems.....	34
3.2.1. Bench-Scale Ozonation System.....	34
3.2.2. Ozonation/FBT System.....	36
3.2.3. FBT/Ozonation System.....	40
3.2.4. FBT System	41
3.2.5. Biofiltration system.....	41
3.3. Analytical Methods.....	44
3.3.1. Organic carbon	44
3.3.2. UV-254	45
3.3.3. Humic Substances.....	45
3.3.4. AMW Distributions	46
3.3.5. THMFP.	47
3.3.6. BDOC	48
3.3.7. Other parameters.....	48
3.4. Quality Assurance and Control	49
3.4.1. Data Management	49
3.4.2. Sample Collection and Analysis	50

3.4.3. Data Analysis	51
4. PRELIMINARY EVALUATION OF THE OZONATION/FBT PROCESS	53
4.1. Introduction.....	53
4.2. Potential of Ozonation/FBT System	54
4.3. Effect of Ozonation and FBT on Transformation of NOM	63
4.4. Fractionation of NOM by Ultrafiltration	68
4.5. Confirmation Study.....	75
4.6. Ozonation/FBT with Recycle	80
4.7. Summary	82
5. SURROGATE CHARACTERIZATION OF NOM.....	84
5.1. Introduction.....	84
5.2. UV-254 and TOC.....	86
5.3. HS and UV-254.....	94
5.4. THMFP and TOC	97
5.5. THMFP and UV-254	100
5.6. Summary	101
6. OZONATION OF NOM.....	102
6.1. Introduction.....	102
6.2. Effect of Operational Parameters.....	104
6.2.1. Effect of Gas Flow Rate.....	104
6.2.2. Effect of Hydraulic Retention Time	110
6.2.3. Effect of Ozone Dose on BDOC.....	123
6.3. Ozonation Kinetics.....	126
6.3.1. Introduction.....	126
6.3.2. Model Development.....	130
6.3.2.1. Model Based on the Specific Ozone Consumption Rate	130
6.3.2.2. Model Based on HS and nonHS.....	133
6.3.3. Rate of Ozone Consumption.....	133
6.3.3.1. Spectroscopic Method	134
6.3.3.2. Method Based on Ozone Consumption Model	141
6.3.3.3. The Use of Ozone Consumption Rate to Evaluate the Efficacy of Ozonation	144
6.3.4. Reaction of Ozone with Humic Substances.....	152
6.3.4.1. Stoichiometric Coefficient	152
6.3.4.2. Reaction Rate Coefficient.....	155
6.3.5. Reaction of Ozone with Nonhumic Substances.....	159
6.3.5.1. Stoichiometric Coefficient	159
6.3.5.2. Reaction rate coefficient.....	161
6.3.6. Mass Transfer Coefficient.....	164
6.3.7. Ozonation Model	165
6.3.8. Model Validation	167
6.4. Summary	180
7. BIODEGRADATION OF NOM	183
7.1. Introduction.....	183
7.2. Approach.....	184
7.3. FBT vs. Biofiltration.....	186

7.4. Effect of Temperature	191
7.5. Biodegradation of Ozonated Water	195
7.6. Summary	198
8. EVALUATION OF COMBINED OZONATION AND FBT PROCESS	199
8.1. Introduction.....	199
8.2. Single Pass FBT/Ozonation Process.....	202
8.3. FBT/Ozonation Process with Recycle	212
8.4. Stimulated FBT/Ozonation Process.....	219
8.5. Stimulated FBT/Ozonation Process with Recycle.....	224
8.6. BIODEGRADATION KINETICS	228
8.7. Summary	232
9. ECONOMIC ANALYSIS	234
10. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH....	241
10.1. Conclusions.....	241
10.1.1. General Conclusions.....	241
10.1.2. Surrogate Characterization of NOM.....	242
10.1.3. Ozonation Studies	243
10.1.4. Biodegradation Studies	245
10.1.5. Pilot-Scale Study of the Combined Ozonation and FBT Process.....	246
10.2. Recommendations for Future Research	248
APPENDICES	250
Appendix A. List of formulas.....	251
Appendix B. Annual cost analysis.....	254
Appendix C. Control charts.....	262
Appendix D. Spreadsheet Formats.....	267
REFERENCES	275

TABLES

Tables

3.1	Typical quality characteristics of Huron River water.....	33
3.2	QA/QC summary.....	52
4.1	Performance of the ozonation/FBT system.....	62
4.2	Comparison of recycle and single pass modes of ozonation/FBT operation.....	81
5.1	Characteristics of surrogate parameters... ..	84
6.1	Experimental conditions for bench- and pilot-scale systems.....	112
6.2	Effect of quenching on UV-254 and TOC after ozonation.....	135
6.3	Experimental data for v_{nonHS}	160
6.4	Experimental data for k_{nonHS}	162
6.5	Experimental data for k_{La}	164
6.6	Kinetic parameters for ozonation model	166
6.7	Experimental and calculated data for ozonation of raw water (ozone dose 1 mg/mg C, HRT = 7 minutes)	178
6.8	Experimental and calculated data for ozonation of raw water (ozone dose 1 mg/mg C, HRT = 20 minutes)	179
7.1	Operational biodegradation characteristics for FBT and biofiltration effluents	190
7.2	Effect of temperature on biodegradation characteristics of raw water	195
7.3	Effect of ozonation on biodegradation characteristics of water	197
8.1	Efficiency of FBT/ozonation/biofiltration and ozonation/FBT	211
8.2	Biodegradation characteristics of FBT/ozonation effluent.....	212
8.3	Biodegradation characteristics of stimulated FBT/ozonation effluent....	224
8.4	Biodegradation characteristics of recirculating stimulated FBT/ozonation effluent	228

9.1	Values for major cost, design and operating parameters	236
9.2	Cost breakdown for the combined ozonation and FBT process	239
9.3	Costs of selected treatment systems.....	239

FIGURES

Figures

2.1	Comparison of FBT and biofilter operations	30
3.1	Schematic of the bench-scale ozonation system	35
3.2	Schematic of the ozonation/FBT system	38
3.3	Schematic of a downflow ozone contactor.....	39
3.4	Schematic of the FBT/ozonation system	40
3.5	Schematic of the recirculating FBT system	42
3.6	Schematic of the biofiltration system	43
4.1	Simplified schematic of the ozonation/FBT system.....	56
4.2	Time plot of TOC removal during acclimation period.....	57
4.3	Removal of TOC from untreated Huron River water by FBT.....	58
4.4	Variations in TOC concentrations with time and ozone doses	60
4.5	Variations in TOC concentrations with time and ozone doses	61
4.6	Effect of ozone dose on TOC removal after ozonation and FBT	65
4.7	Effect of ozone dose on UV-254 removal after ozonation and FBT	66
4.8	Effect of ozone dose on HS removal after ozonation and FBT	67
4.9	AMW distribution after FBT	71
4.10	AMW distribution after ozonation and FBT (ozone dose=0.5 mg/mg C).....	72
4.11	AMW distribution after ozonation and FBT (ozone dose=1.0 mg/mg C).....	73
4.12	AMW distribution after ozonation and FBT (ozone dose=2.0 mg/mg C).....	74
4.13	Effect of ozone dose on TOC removal after ozonation and FBT	77
4.14	Effect of ozone dose on UV-254 removal after ozonation and FBT	78
4.15	AMW distribution after ozonation and FBT (ozone dose=7.0 mg/mg C).....	79
5.1	Seasonal variations of TOC and UV-254 in Huron River water.....	87

5.2	Correlation between TOC and UV-254 for ozonated water	88
5.3	Correlation between TOC and UV-254 for biotreated water	89
5.4	Correlation between TOC and UV-254 for ozonated and biotreated water	90
5.5	Ozone-dose averaging linear correlation between TOC and UV-254	92
5.6	Exponential relationship between TOC and UV-254.....	93
5.7	Correlation between HS and UV-254	95
5.8	Correlation between average values of HS and UV-254	96
5.9	Correlation between THMFP and TOC.....	98
5.10	Correlation between average values of THMFP and TOC.....	99
5.11	Correlation between average values of THMFP and TOC.....	100
6.1	c_g^{in} requirements for various gas flow rates.....	106
6.2	Dissolved ozone concentrations for various flow rates.....	107
6.3	Effect of ozone dose on TOC concentrations for various gas flow rates...	108
6.4	Effect of ozone dose on UV-254 for various gas flow rates.....	109
6.5	Effect of ozone dose on TOC concentrations for various HRTs.....	114
6.6	Effect of ozone dose on UV-254 for various HRTs.....	115
6.7	c_g^{in} requirements for various HRTs.....	116
6.8	Dissolved ozone concentrations for HRTs.....	117
6.9	Efficiency of ozone utilization in the bench-scale ozone contactor.....	118
6.10	c_g^{in} requirements for bench- and pilot-scale systems.....	119
6.11	Dissolved ozone concentrations for bench- and pilot-scale systems.....	120
6.12	Removal of TOC during ozonation in bench- and pilot-scale systems.....	121
6.13	Removal of UV-254 during ozonation in bench- and pilot-scale systems.	122
6.14	Removal of UV-254 during ozonation at low HRTs.....	124
6.15	Effect of ozone dose on BDOC concentration.....	125
6.16	Kinetic curve of ozone depletion based on UV-254.....	138
6.17	Kinetic curve of ozone depletion based on UV-254 using base-line correction.....	139
6.18	Correlation between dissolved ozone concentrations measured spectrophotometrically and by Indigo method.....	140

6.19	Correlation between k_{O_3} s determined by different methods.....	143
6.20	Effect of ozone dose on k_{O_3} for various gas flow rates.....	146
6.21	Correlation between UV-254 and k_{O_3} for various gas flow rates.....	147
6.22	Correlation between TOC and k_{O_3} for various gas flow rates.....	148
6.23	Effect of ozone dose on k_{O_3} for various HRTs.....	149
6.24	Correlation between UV-254 and k_{O_3} for various HRTs.....	150
6.25	Correlation between TOC and k_{O_3} for various HRTs.....	151
6.26	Transformation of organic matter during ozonation.....	154
6.27	Relationship between HS and k_{HS} for various temperatures.....	157
6.28	The plot of Arrhenius' equation for the reaction of ozone with HS.....	158
6.29	The plot of Arrhenius' equation for the reaction of ozone with HS	163
6.30	Rate of ozone utilization.....	169
6.31	Experimental and calculated data for c_g^{out} ($t=20^\circ\text{C}$, HRT=7 min).....	170
6.32	Experimental and calculated data for c_L ($t=20^\circ\text{C}$, HRT=7 min).....	171
6.33	Experimental and calculated data for HS ($t=20^\circ\text{C}$, HRT=7 min).....	172
6.34	Experimental and calculated data for nonHS ($t=20^\circ\text{C}$, HRT=7 min).....	173
6.35	Experimental and calculated data for c_g^{out} ($t=20^\circ\text{C}$, HRT=20 min).....	174
6.36	Experimental and calculated data for c_L ($t=20^\circ\text{C}$, HRT=20 min).....	175
6.37	Experimental and calculated data for HS ($t=20^\circ\text{C}$, HRT=20 min).....	176
6.38	Experimental and calculated data for nonHS ($t=20^\circ\text{C}$, HRT=20 min).....	177
7.1	Biodegradabale and nonbiodegradable fraction of NOM.....	185
7.2	Removal of UV-254 by FBT and biofiltration.....	187
7.3	Removal of TOC by FBT and biofiltration.....	188
7.4	Removal of BDOC by FBT and biofiltration.....	190
7.5	Removal of TOC by FBT for various temperatures.....	192
7.6	Removal of UV-254 by FBT for various temperatures.....	193
7.7	Removal of BDOC by FBT for various temperatures.....	194
7.8	Biodegradation of ozonated samples.....	197
8.1	Simplified schematic of the FBT/ozonation system.....	204
8.2	Removal of UV-254 during ozonation of raw water and FBT effluent....	208
8.3	Removal of TOC during ozonation of raw water and FBT effluent.....	209

8.4	AMW distribution of NOM after FBT and ozonation.....	210
8.5	Biodegradation kinetics of the FBT/ozonation effluent.....	211
8.6	Simplified schematic of the FBT/ozonation system with recycle.....	213
8.7	Effect of recycle on the removal of TOC by FBT/ozonation.....	214
8.8	Effect of ozone dose on the removal of TOC by FBT/ozonation.....	216
8.9	Effect of recycle on the removal of UV-254 by FBT/ozonation.....	217
8.10	Biofiltration of the FBT/ozonation effluent.....	218
8.11	Effect of acetate dose on the removal of TOC by FBT/ozonation.....	221
8.12	Biofiltration of effluents from FBT/ozonation and enhanced FBT/ozonation.....	222
8.13	Biodegradation kinetics of enhanced FBT/ozonation effluent.....	223
8.14	Biofiltration of effluents from enhanced FBT/ozonation with recycle.....	226
8.15	Biodegradation kinetics of effluents from enhanced FBT/ozonation with recycle.....	227
8.16	Relationship between BDOC concentration and biodegradation rate.....	231
9.1	Simplified schematic of the FBT/ozonation process with recycle.....	235
9.2	Effect of recycle on treatment cost.....	240

ABBREVIATIONS

SDWA	Safe Drinking Water Act
DBP	Disinfection by-products
THM	Trihalomethanes
THMFP	Trihalomethane formation potential
HAA	Haloacetic acids
TOC	Total organic carbon
UV-254	Ultraviolet absorbance measured at 254 nm
HS	Humic substance concentration
NonHS	Nonhumic substance concentration
AMW	Apparent molecular weight
FBT	Fluidized bed treatment
EBCT	Empty-bed contact time
HRT	Hydraulic retention time
MWCO	Molecular weight cutoff
mg C/L	Milligram carbon / L
RSD	Relative standard deviation

1. INTRODUCTION

1.1. SIGNIFICANCE

A significant portion of the water treatment industry will face major technical and financial hurdles in meeting the disinfection by-product (DBP) requirements of the Safe Drinking Water Act (SDWA) reauthorization. Under the Disinfectants/Disinfection By-products (D/DBP) rule, the United State Environmental Protection Agency (U.S. EPA) has recently approved legislation to reduce the maximum allowable trihalomethane (THM) concentrations in finished waters from 100 to 80 µg/L (Arrora, LeChevallier, and Dixon, 1997; Pontius, 1995)¹. This criterion will be difficult to meet for many water utilities, especially those that use surface water supplies. In compliance with the SDWA amendments the U.S. EPA would also be required to identify technologies that are technically and economically feasible for small systems serving up to 10,000 people (National Research Council, 1997). Therefore, a major concern of water utilities is identifying suitable economical treatment processes that will reduce the levels of DBP precursors in finished drinking waters.

The addition of ozone prior to chlorination has been identified as an important pretreatment step in the minimization of THM formation to meet the current and future U.S. EPA standards (U.S. EPA Drinking Water Regulations, 1997). Past regulatory actions by the U.S. EPA resulted in an increase in the acceptance of ozone by US water

¹ The U.S. EPA is currently considering the revision of the Disinfection/Disinfection Byproducts Rule (D/DBP), which may result in changes in the maximum allowable THM concentrations in drinking water (Federal Register, V. 63, No. 61, pp. 15673-15692, March 31, 1998).

utilities. Since the early 1980s, the number of U.S. drinking water treatment plants employing ozone has risen rapidly from about 10 to more than 200. The number is expected to reach at least 300 plants by the year 2000 (U.S. EPA Drinking Water Regulations, 1997). It is anticipated that current and future EPA regulatory actions will increase the acceptance of ozone even further (U.S. EPA Drinking Water Regulations, 1997).

This research project investigated the use of ozonation in combination with biological-fluidized-bed treatment (FBT) to control natural organic matter (NOM) and THM precursors in drinking water. The proposed ozonation/FBT process has several potential advantages over conventional ozonation/biofiltration processes, including:

- (1) The ozonation/FBT process uses a fluidized bed reactor (in place of biofilters) in which clogging is virtually impossible, and, therefore, no additional pretreatment is required.
- (2) The efficiency of the removal of biodegradable organic matter by FBT is expected to be greater than that obtained by biofiltration. This is because the attached biomass concentration is expected to be greater in the FBT system as compared to those in the conventional biofilter due to greater specific surface area and no-clogging operation. Also, because of greater specific surface area, if activated carbon is used as a support medium, the use of FBT will result in significant saving in activated carbon.
- (3) The ozonation/FBT process can be operated in a cyclic mode, in which the water alternately passes through ozonation and biodegradation steps. In this way, ozonation is expected to degrade only those compounds that are not

biodegradable, thus reducing ozone consumption and, therefore, capital and operating and maintenance costs.

- (4) The ozonation/FBT units will be standard-size units. The process performance of the unit can be optimized for different sources of water supplies. The system is also expected to meet future effluent standards through process parameter optimization without process expansion or modification.
- (5) Finally, FBT systems have a considerably smaller footprint than biofilters, and therefore may be very useful for applications where space for retrofitting or expansion is limited.

Over the last ten years, the biological component of this proposed system has been developed and used in several applications for the biological treatment of process waters and for the bioremediation of volatile organic compounds and chlorinated solvents in groundwaters (Hickey, Wagner, and Mazewski, 1991). Because of low operational costs (power, GAC, oxygen), these systems have proved a competitive advantage over aqueous carbon adsorption and air stripping/vapor carbon adsorption in bioremediation applications. These systems can also be monitored and controlled from remote locations using advanced telemetry, thus reducing staffing requirements and O&M costs (Hickey, Wagner, and Mazewski, 1991).

Skid-mounted biological FBT systems (with single pass flow capacities ranging from 30 gpm to 1850 gpm) are available off-the-shelf, from a leading U.S. manufacturer of water and wastewater treatment equipment/processes (*Envirex, Ltd.*). These systems could

serve communities ranging from 500 to 50,000 people. Using multiple FBT units in one system, their applications can be further expanded.

If technical and economical merits are established, the ozonation/FBT process will be a very attractive alternative to both conventional coagulation and ozonation/biofiltration processes, especially for small water treatment utilities and for larger utilities where space for retrofitting or expansion is limited.

1.2. OBJECTIVES

The ultimate goal of the project was to develop an efficient and simple processing system that could be used in both small and larger drinking water treatment facilities to control THM precursors. An additional goal was to better understand the transformation of NOM during ozonation and biotreatment to allow for the optimization of the developed process. The specific aims of this project were:

- (1) To assess the impact of ozonation and FBT on the properties of NOM, including total organic carbon (TOC), ultraviolet absorption measured at 254 nm (UV-254), humic and nonhumic content, molecular weight transformations, and trihalomethane formation potential (THMFP).
- (2) To establish the relationships between various properties of NOM and to assess the role of these parameters in the evaluation and optimization of the proposed ozonation/FBT process.
- (3) To test the hypothesis that the efficiency of FBT increases with ozone dose.

- (4) To investigate the effect of control variables, including ozone dose and retention time on the efficacy of ozonation and FBT for the removal of NOM.
- (5) To determine if the humic and nonhumic fractions of NOM can be used to model the kinetics of ozone reactions with NOM. If so, to develop a kinetic model of ozone reactions with NOM using these parameters.
- (6) To compare the efficiency of FBT to that of biofiltration for the removal of NOM.
- (7) To test the hypothesis that the recycle of a portion of system effluent back to the ozonation stage increases the efficiency of the proposed ozonation/FBT for the removal of NOM relative to ozone consumption.
- (8) To test the hypothesis that the use of FBT prior to ozonation increases the efficiency of the combined ozonation/FBT process for the removal of NOM relative to ozone consumption.
- (9) To assess the role of biofiltration as the final stage of the ozonation/FBT process for the control of THM precursors and biodegradable organic matter in finished water.
- (10) To assess the impact of adding an easily biodegradable carbon source to the FBT system in order to increase process efficiency in terms of the removal of NOM and biodegradation time.
- (11) To estimate the cost of treatment by combined ozonation and FBT and compare this cost with the cost of conventional treatments.

Several other hypotheses were developed and tested in the course of this study.

They will be discussed in the appropriate chapters or sections.

1.3. PROJECT OUTLINE

Chapter 2 provides the background information relevant to the project. This includes characterization of NOM and its impact on water quality and treatment and the processes available for the treatment of drinking water. Additional background information relevant to the topics of the discussion is provided in each chapter that follows. Chapter 3 describes experimental systems and analytical methods used in this research project. Chapter 4 evaluates the potential of the ozonation/FBT process to remove NOM and to control THM precursors. Chapter 5 identifies surrogate parameters that are subsequently used for the investigation of the ozonation and biodegradation of NOM and for the optimization of the proposed ozonation/FBT process. Studies of the ozonation and biodegradation of NOM are presented in Chapters 6 and 7, respectively. Chapter 8 investigates several approaches for the optimization of the proposed process. Chapter 9 presents a preliminary economic analysis of the proposed process and compares it with that of conventional treatment processes. Conclusions and recommendations for future research are given in Chapter 10.

2. BACKGROUND

This chapter presents background information relevant to the matter of this dissertation. Section 1.2 provides general information about natural organic matter (NOM) and methods for its characterization. Section 2.3 describes the impact of NOM on water quality and treatment. Section 2.4 discusses treatment methods for the removal of NOM from water.

2.1. CHARACTERIZATION OF NOM

Natural organic matter (NOM) is a complex matrix of organic materials present in natural waters. A major concern of water utilities with respect to NOM is in that that it can impart color, tastes, and odors to the water and react with disinfectant to form disinfection by-products.

NOM consists of humic and nonhumic fractions. The humic fraction is more hydrophobic than the nonhumic fraction (Manahan, 1991; Liao et al., 1982, Schnitzer and Kahn, 1972). The nonhumic fraction includes hydrophilic acids, proteins, aminoacids, and carbohydrates (Manahan, 1991). Nonhumic substances have been considered to present less of drinking water quality problems than humic substances (Bablon et al. 1991a).

NOM can be characterized by nonspecific parameters based on their ability to absorb UV light, by their organic carbon composition, or by their potential to form

trihalomethanes (THMFP). A molecular weight characterization of NOM provides valuable information on the transformation of NOM and is a powerful tool in evaluating potential treatment strategies. NOM can also be characterized by its biodegradability potential. The latter characterization can provide information on the efficacy of biological treatment or to predict the possibility of bacterial growth in the distribution system.

2.1.1. Humic Substances

Humic substances, which comprise 40-60% of the dissolved organic carbon (DOC) in natural waters, are the largest fraction of NOM in water. They are normally present in concentrations > 1 mg of C/L (Vik and Eikebrokk, 1989).

Humic substances represent a unique category of natural products in which the essence of the materials appears to be its heterogeneity. Although these materials are known to result from the decomposition of biological material, the precise biochemical and chemical pathways by which they are formed have not been elucidated. Because of their complex, multicomponent nature, humic substances cannot be described in specific molecular terms. Thus, when dealing with humic substances, researchers are forced, by circumstances, to express the amount of material in terms of organic matter or as dissolved organic carbon (MacCarthy & Suffet, 1989).

Humic substances are defined operationally by the methods used to extract them from water or soil. Typically they are divided into more soluble fulvic acids and the less soluble humic acids, with fulvic acids predominating in most waters (Manahan, 1991). The

humic acid and fulvic acid do not refer to single compounds, but to a wide range of compounds of generally similar origin.

Aquatic humic acids differ from aquatic fulvic acids in average molecular weight, elemental and functional group composition, and in other characteristics. Aquatic fulvic acid usually has a molecular weight of less than 2000 daltons (Thurman, 1985). Humic acids have a molecular weight of 2000-5000 daltons or greater (Thurman, 1985), and is, therefore, considered colloidal. As, in natural waters, humic acid is associated with various metal ions and clays, it may have a larger molecular weight than that determined with purified free acid.

Humic substances are polyelectrolytes with various functional groups attached to the hydrocarbon skeleton (Manahan, 1991). Trussel and Umphres (1978) described the structure of humic substance as a huge amorphous mass containing a polyheterocondensate center to which certain functional groups, such as carboxyl acid, phenolic groups, alcohols, methoxyl groups, carbonyl groups, ethers, and esters are attached. The carboxyl and phenolic functional groups are primarily responsible for the acid-base and complexation characteristics of humic substances (Manahan, 1989). Humic acid contains fewer carboxyl and hydroxyl functional groups than does the fulvic acid fraction, making it less soluble in water (Vik & Eikebrokk, 1989). Liao et al. (1982) concluded that humic acid contains longer fatty acid chains than does fulvic acid. This finding may help to explain the hydrophobic properties of humic acid. Thurman (1985) found that phenolic content of humic acid is greater than that of fulvic acid, and there are more color centers on the humic acid molecule.

Humic substances can be measured by separating them from nonhumic materials by the adsorption on XAD-8 resin. In fact, the ability of humic substances to adsorb on XAD-8 resin represents their operational definition.

The main physicochemical properties of humic substances, which arise from the presence of several functional groups, are a strong reactivity with halogens, complexation with metals, and the association of humic substances with organic micropollutants (Bablon et al. 1991a). Humic substances also produce aesthetically undesirable problems such as color. Humic substances can reduce the capacity and effectiveness of activated carbon by competing with other organic contaminants for active sites on activated carbon. Humic substances may reduce the bioavailability of hydrophobic substances, thereby, reducing the rate at which the biodegradation of organic compounds occurs (MacCarthy and Suffet, 1989).

Among the adverse effects that humic substances have on water quality and treatment, the most important is the reaction of humic substances with chlorine. This reaction results in the formation of chlorinated organic compounds, such as chloroform, other low-molecular-weight disinfection by-products (e.g., haloacetonitriles, haloacids, haloaldehydes, haloketones, chlorophenols, chloropicrin, and others) and complex high-molecular-weight chlorinated compounds (Stevens et al., 1989). In fact, it is owing to the discovery of trihalomethanes (THMs) in water supplies, that humic substances have been given special attention. It is now generally accepted that these suspected carcinogens can be formed in the presence of humic substances during the disinfection of water by chlorination (Manahan, 1991). Trussell and Umphres (1978) suggested that the halogenation of aquatic humic substances occurs via alternate hydrolysis and

halogenation steps. Several factors, such as the nature of humic substances, chlorine dose, and pH, have been found to affect the formation of THMs.

2.1.2. Organic Carbon Content

As a result of their heterogeneous and ill-defined character, there are no direct analytical techniques to measure NOM. One way is to define NOM by its organic carbon content .

About 50 percent of the organic carbon in surface water of the United States consists of humic substances. The humic substances are from 40 to 65% carbon by weight (Manahan, 1990; McCarthy and Suffet, 1989). Many workers use the terms organic carbon contents and humic substances interchangeably (McCarthy and Suffet, 1989). Although such usage is not entirely correct, in general there is a good correlation between organic carbon contents and humic substance concentration (Krasner et al., 1996).

2.1.3. UV Absorption

Organic compounds that are aromatic or have conjugated double bonds absorb light in the ultraviolet (UV) wavelength region. UV absorption, thus, is a good technique for measuring the presence of NOM, such as humic substances, because they contain aromatic moieties and are the dominant form of organic matter in natural waters (Edzwald, Becker, and Wattier, 1985). Strong correlation may exist between UV

absorption and organic carbon content and THM precursors (Eaton, 1995; Edzwald, Becker, and Wattier, 1985). In some cases, UV-254 absorbance may be a better indicator than TOC concentration for DBP formation (Najm et al., 1994; Edzwald, Becker, and Wattier, 1985). UV absorption has also been used to evaluate organic removal by various water treatment processes (Eaton, 1995; Edzwald, Becker, and Wattier, 1985). The use of spectroscopic measurements coupled with organic carbon monitoring can provide information about the nature and variability of NOM. Specific absorption, the ratio of UV absorption to organic carbon concentration, has also been used to characterize natural organic matter (Krasner et al., 1996; Eaton, 1995).

Under the Information Collection Rule (ICR), water utilities across the United States will be required to monitor UV absorption in an attempt to correlate this parameter with DBP precursors. A wavelength of 254 nm has been used to characterize the aromatic portion of NOM (Masten, 1991). This wavelength has also been selected for the purpose of ICR (Eaton, 1995).

2.1.4. THMFP

THMs (chloroform, dichlorobromomethane, chlrodibromomethane, and bromoform) are the dominant DBP species formed during chlorination. THMs are increasingly regulated by U.S. EPA and is one of the major parameters that needs to be controlled by a treatment process. Therefore methods to determine the potential for forming THMs are useful in evaluating water treatment processes or water sources or for predicting THM concentrations in a distribution systems.

There has been extensive research relating to factors that influence the creation of THMs. Trussel and Umphres (1978) reported that factors that might be responsible for the formation of THMs include (1) TOC concentration, (2) inorganic chemistry of water (e.g., pH, bromide concentration), (3) contact time of chlorine with NOM, and (4) chlorine/TOC ratio. THM formation is stimulated by elevated temperature and alkaline pH and by increasing concentration of free chlorine residual. A longer contact time generally increases THM formation. Therefore, in order to be able to analyze and compare the results from different sources, the control of such variables as temperature, reaction time, chlorine dose and residual, and pH is essential. The standard reaction conditions have been identified as follows: free chlorine residual at least 3 mg/L and not more than 5 mg/L at the end of 7 day reaction period, with sample incubation temperature of 25°C, and pH controlled at 7 with phosphate buffer (*Standard Methods*, 1992).

It should be noted that THMFP determined under standard reactions conditions is not intended to simulate water treatment processes but are most useful for estimating the concentration of THM precursors, as well as for evaluating water-treatment options for reducing levels of THM precursors in the raw water.

2.1.5. Molecular Weight Distribution

The performance of many water treatment processes is related to size distribution of NOM (Jackson, Hong, and Summers, 1993; Collins, Amy, and Steelink, 1986). Different processes have been cited as being amenable to removing certain size molecules. For example, higher molecular weight matter was found to be generally more

amenable to the removal by coagulation (Amy et al., 1992, Chadik and Amy, 1983). A water source with medium molecular weight materials can be effectively treated by activated carbon adsorption (Pirbazary et al., 1989). High molecular weight materials may be difficult to treat by activated carbon adsorption, because large molecules are unable to enter smaller pores of activated carbon (Pirbazary et al., 1989). Ozonation partially oxidizes higher molecular weight compounds leading to the formation of lower molecular weight compounds, which are more biodegradable (Amy, Kuo, and Sierka, 1988). Other researchers (Anderson, Johnson, and Christman, 1986) observed loss of carbon from high and low molecular weight fractions during ozonation.

In this study, molecular weight fractionation was used to evaluate the ozonation/FBT process and to better understand the transformation of NOM during ozonation and biotreatment.

2.1.6. BDOC

Biodegradable organic carbon (BDOC) is the portion of organic carbon in water that can be mineralized by heterotrophic microorganisms. One characteristic of ozonation is its tendency to increase the biodegradability of aquatic organic matter. Increased biodegradability can lead to improved performance of subsequent biological processes. However, if left uncontrolled, it can also encourage the regrowth of bacteria in distribution systems (Reckhow et al., 1993).

Several methods for measuring potentially biodegradable organic matter have been developed in recent years. A method for measuring assimilable organic carbon

(AOC) was developed by van der Kooij, Visser, and Hijnen (1982). However, this method attempted to measure bacterial regrowth potential rather than a change in organic carbon.

Another method was developed by Servais and colleagues (Servais, Billen, and Hascoet, 1987). The method includes the inoculation of a sample with a mixed bacterial culture and measuring DOC at the beginning and end of incubation period. The sample is incubated at room temperature for approximately four weeks. This methods gives no information on the kinetics of biodegradation.

Fixed-biofilm biodegradation to measure BDOC was introduced by Joret and Levy (1988) and Morgen, Scarpino, and Summers (1990). The first method (Joret and Levy, 1988) involves the addition of sand with acclimated biofilm to water samples and incubation at room temperature under aerated conditions. Daily measurements of DOC are made until there is no further change. BDOC is taken as the decrease in DOC. The method raises the possibility of release of organic matter from biomass.

The second method (Morgen, Scarpino, and Summers, 1990) involves recirculation of the sample through a biofiltration column. The methods is representative of biotreatment processes and is currently widely used for measuring BDOC when the concern is the reduction of DBP formation potential through a biological processes (Cipparone, Diehl, and Speitel, 1997; Huck, 1990). The procedure will be discussed in greater detail in Section 3.3.6.

2.2. REVIEW OF TREATMENT PROCESSES

Since the late 1970s much work has focussed on the development of processes to reduce the formation of THM precursors in drinking waters. Among the processes which have been most extensively investigated are slow sand filtration, coagulation, activated carbon adsorption, membrane separation, ozonation, and ozonation combined with biological granular activated carbon adsorption (GAC) or biofiltration. The review of these major processes is given below.

2.2.1. Slow Sand Filtration

Slow sand filtration was the original form of water treatment used in nineteenth century and is now considered a low-technology approach to water treatment (National research Council, 1997). Although not originally conceived as a biological process, its value in that role has been recognized over the years. Removal mechanisms in slow sand filtration are both physical and biological: biological action breaks down some organic matter, and some inert suspended particles are physically removed from the water (Cleasby, 1990).

The process usually involves passage of raw water through a bed of sand at low velocity (usually less than 0.4 m/h). With extended use of the filter, a biological ecosystem grows in the sand bed. On the top of the filter media, a biologically active organic layer (so-called Scmutzdecke layer) builds up and assists filtration. The water then enters the top layer of sand, where more biological action occurs (Cleasby, 1990).

The use of this process is limited to waters having low turbidity and organic carbon content (Cleasby, 1991; Cleasby et al., 1984; Fox et al., 1984). Slow sand filtration is not very effective at removing THM precursors or color. Therefore, only high quality waters (low in turbidity, algae, and color) are suitable for application to slow sand filters without pretreatment.

2.2.2. Chemical Coagulation

Evidence available in the literature indicates that chemical coagulation removes DBP precursors and lowers level of DBPs formed upon chlorination of settled water (Najm et al., 1994; Chadik and Amy, 1983; Semmens and Field, 1980). Alum has commonly used for the removal of organic matter, including DBP precursors (Najm, 1994). Alum coagulation at a dosage of 50 mg/L has been reported to reduce THMFP at values of up to 70 percent (Reckhow and Singer, 1990). The use of coagulation with metal salts and polymers has also been proven successful for the removal of humic substances (Babcock and Singer (1979), Vik and Eikebrokk (1989), and Bottero and Bersillon (1989)). Babcock and Singer (1979) showed that up to 90% of TOC can be removed by the coagulation of humic acid, whereas the coagulation of fulvic acid removed only 20% of TOC. Similar results have been reported by Perdue and Lytle (1983). Vik and Eikebrokk (1989) pointed out that the main parameters affecting the coagulation of humic substances were the initial concentration of humic substances, the coagulant dosage, and the pH at which the coagulation were carried out. They also showed that the removal of humic substances by alum coagulation was efficient only over a narrow range of pH (4.5-5). Glazer and Edzwald

(1979) achieved approximately 40% removal of TOC by the coagulation of humic acid using cationic polyelectrolytes.

Although coagulation is one of the most common processes used in water treatment, one must recognize the problems associated with this process. The effectiveness of chemical coagulation for DBP precursors removal strongly depends on the type and concentration of organic material present in the raw water, the coagulant type and dosage, and pH (Najm, 1994).

Coagulation of humic substances has been shown to be effective only over a narrow range of pH, with optimum-removal occurring at a pH in the range of 5-6 (Reckhow and Singer, 1990; Dempsey, Ganho, and O'Melia, 1984; Chadik and Amy, 1983). Higher pH would require considerably higher coagulant dosages for effective coagulation (Vik and Eikerbrokk, 1989). The coagulation of humic substances with alum, which has been shown to be most effective coagulant, may cause a particle separation problem (Vik and Eikerbrokk, 1989). Turbidity created by colloidal destabilization may be difficult to remove.

Morris and Knocke (1984) showed that temperature had a great impact on coagulation with alum. In some typical tests, residual turbidity increased from 0.5 NTU at 25°C to 2.4 NTU at 5°C. Some of the reasons suggested for the decreased efficiency of coagulation at lower temperatures is increased viscosity and its effect on sedimentation (Armirtharajah and O'Melia, 1990). Among the most challenging conditions for treatment by coagulation are very cold water, approximately 5°C and colder, and turbidities of approximately 10 NTU and lower. When the amount of particulate matter in the water is low, sedimentation is not very effective (National Research Council, 1997). Another

difficult condition for water treatment is the combination of high color and moderate to high turbidity. The pH that is best for color removal may be different from the pH that is best for turbidity removal (National Research Council, 1997).

2.2.3. Carbon adsorption

Historically, activated carbon adsorption was used primarily to remove tastes and odors from water, but its use as an adsorbent for toxic and carcinogenic compounds has increased steadily and is a primary application (National Research Council, 1997).

Activated carbon adsorption has also been used for the removal of humic substances. Kaastrup and Halmo (1989) found that the nature of humic substances and the pore-size distribution of the activated carbon were the most important factors in determining the absorbability of humic substances. The authors noted the poor absorbability of humic substances, which was reflected in unfavorable adsorption isotherms, slow adsorption kinetics, and immediate breakthrough of color-imparting substances from the adsorption column. The absorption capacities for smaller fulvic acid molecules were seen to be higher than that observed for humic acid. McCreary and Snoeyink (1980) obtained similar results. The adsorption capacities for humic acid were observed to be directly related to the fraction of large pores in the carbon. They also found that the adsorption rate of humic acid was inversely related to carbon-pore size. By studying the adsorption of humic and fulvic acids onto activated carbon, McCreary and Snoeyink (1980) found that the lower-molecular weight species were more readily adsorbed. Lee et al. (1981) did not achieve satisfactory results for the removal of humic acid when activated carbon was used alone.

Competitive adsorption is an important consideration in the design of an activated carbon system for drinking water treatment. NOM in water may compete with contaminants for adsorption sites on the carbon, thus increasing the amount of carbon needed to remove the target contaminants. Pirbazary et al. (1989) showed that humic substances reduced the adsorption capacity of the activated carbon for other organic pollutants normally present in water. Competing organic contaminants can also displace the contaminants already adsorbed to the carbon.

Lykins and Clark (1989) showed that activated carbon adsorption alone was unlikely to be the process of choice for the removal of humic substances and pretreatment would be required to decrease the molecular weight of humic substances before activated carbon could be applied effectively. GAC use also requires removing particulate matter from untreated water to avoid clogging of the treatment column.

2.2.4. Membrane separation

Once considered a viable technology only for desalination, membrane filtration is increasingly employed for the removal of NOM. Several membrane filtration technologies appropriate for water treatment are distinguished by their nominal molecular weight cutoff (MWCO), which is an estimate of the smallest size molecule that will be retained by the membrane in a filtration process. By these guidelines, membrane filtration technologies are classified as employing microfiltration, ultrafiltration, or nanofiltration (National Research Council, 1997).

Microfiltration uses membranes with an MWCO of greater than 100,000 daltons and is effective for the removal of some bacterial species, but is not capable of removing most humic materials. Ultrafiltration uses membranes with an MWCO of approximately 10,000 to 100,000 daltons and can remove some humic materials. Nanofiltration membranes have an MWCO of 1,000 to 10,000 daltons and are very effective towards the removal of humic materials (National Research Council, 1997).

Although membrane filtration is effective for the removal of THMFP and greatly reduces the need for disinfectant, several potential disadvantages with respect to the application in water treatment must be recognized (National Research Council, 1997; Weiesner et al. 1994):

- Membrane filtration is sensitive to particulate matter, turbidity, and some NOM that can foul the membrane. To avoid this, water must be pretreated by a more conventional treatment process prior to polishing by membrane filtration.
- As nanofiltration also removes alkalinity, the product water can be corrosive and adding alkalinity may be needed to reduce corrosivity.
- Membrane filtration may exert high operating costs associated with module replacement costs, pressure requirements, and cleaning.
- Choosing the most appropriate membrane material for a given application still remains an art, since many different factors, including both water quality and operational conditions, can greatly affect the membrane performance.
- Unlike conventional treatment processes, in which approximately 5 to 10 percent of the water is discharged as waste, membrane processes produce waste streams amounting to as much as 15% of the total water volume.

2.2.5. Ozonation

Since early 1980s, the number of U.S. drinking water treatment plants employing ozone has risen rapidly from about 10 to more than 200. The number is expected to reach at least 300 plants by the year 2000 (U.S. EPA Drinking Water Regulations, 1997). The increasing acceptance of ozone in U.S. water treatment plants has been affected positively by past EPA regulatory actions. It is anticipated that current and future EPA regulatory actions will increase the acceptance of ozone even further (U.S. EPA Drinking water Regulations, 1997).

Ozonation, at doses used in conventional water treatment practice (1 mg ozone/mg C or less), is anticipated to bring about only slight reduction (< 10 percent) in organic carbon (Amy, Kuo, and Sierka., 1988). Masten (1991) and Bablon et al. (1991b) also observed only a minor reduction in the concentration of organic matter during ozonation of humic substances. However, it has been established that ozone oxidizes humic substances leading to the formation of lower molecular weight species. . Flogstad and Odegaard (1985) showed that, in drinking water, the concentration of high-molecular-weight humic substances was reduced after ozonation and a nearly corresponding amount of low-molecular-weight compounds was produced. They also showed that increased ozone dosage led to an increase in the biological degradability. There have, however, been some conflicting reports relating to the transformation of molecular weight fractions. Edwards and Benjamin (1992), for example, observed the reduction in low-molecular weight compounds

after ozonation at doses less than 1 mg/mg C. Similar results were obtained by Anderson, Johnson, and Christman (1986).

Meijers (1976) showed that waters containing humic substances could be efficiently using ozone. The degradation of color has been found to be almost total when ozone dosages between 1 and 3 mg O₃/mg C were applied (Masten, 1991; Killops, 1986; Watts, 1985). This suggests that ozone reacted efficiently with the aromatic portion of the humic substances. The effect of ozone on the aromatic portion of the humic substance has also been shown to occur by following the decrease in the UV absorbance during and after ozonation (Masten, 1991; Kruithof et al., 1989; Reckhow et al., 1986; Anderson, Johnson, and Christman, 1986). The decrease in the UV absorbance is also an indicator of the changing character of humic substances during ozonation. For example, Masten (1991) showed that during ozonation of humic acid the greatest change in the UV absorbance spectra occurred at a wavelength of 254 nm, indicating a significant change in the aromaticity of the humic acid. Legube et al. (1989) showed that ozone consumption increased with increasing the initial UV absorbance of the humic substances, which may be attributed to both the higher initial concentration of humic substance and the higher content of aromatic functional groups. Masten (1991) also observed similar results.

Complete ozonation of humic substances to carbon dioxide and water is too expensive to be feasible for water treatment. At typical ozone dose-to-carbon ratios, the oxidation of humic materials is incomplete and some ozonation by-products are formed. The by-products, which are formed, may result either from the direct reaction of the humic substance with molecular ozone or from indirect reactions involving free radicals formed during the decomposition of ozone. The nature of parental organic matter can vary widely,

as can the pH and the aqueous concentration of free radical scavengers, such as bicarbonate and carbonate ions. For this reason, the character and concentration of ozone by-products will vary significantly from water to water (Bablon et al., 1991b). It appears, that aldehydes are ubiquitous products formed from ozonation of NOM (Glaze et al., 1989). Other compounds identified in ozonated waters and humic substance solutions include mono- and dicarboxylic acids, mono- and diketones and alkanes (Glaze et al., 1989; Killips, 1986; Lawrence et al. 1980). Watts (1985) also identified aromatic acids in ozonated humic substance solutions.

Several investigators have studied the effect of ozonation on the reactivity of humic substances with chlorine. Using an aquatic fulvic acid, Reckhow et al. (1986) showed that ozonation at a neutral pH (phosphate buffer solution) resulted in a decrease in THMFP, total organic halides (TOX), trichloroacetic acid, and dichloroacetonitrile. Using fulvic acids extracted from numerous surface waters, Legube et al. (1989), obtained the results comparable to those obtained by Reckhow et al. (1986) under similar reaction conditions. They suggested that the reaction of molecular ozone with humic substances could lead to the degradation of aromatic sites, which are thought to be the precursors of organochlorinated by-products. On the contrary, hydroxyl radicals appear to react with humic substances, resulting in the hydroxylation of sites. As a result of that, new THM precursors may form (Legube et al., 1989). As the presence of bicarbonate ions in the system will tend to scavenge the hydroxyl radicals, the formation of new THM precursors will be reduced and the degradation of existing ones will be increased by the action of molecular ozone (Reckhow et al., 1986). Although the effect of ozonation on the reactivity of NOM with chlorine is not well understood, there has been a general agreement regarding the effect of

ozonation of the reduction of THMFP. Amy, Kuo, and Sierka (1988) observed 15–40% reduction in THMFP during ozonation at doses up to 2.5 mg/mg C. Reckhow and Singer (1990) observed a 15% THMFP reduction at an ozone dose of 1 mg/mg C. Similar results of THMFP were reported by Singer and Chang (1990), who conducted tests at ten water utilities.

2.2.6. Combined ozonation/biotreatment

It is generally recognized that ozonation converts nonbiodegradable organic matter to biodegradable organic carbon (BDOC) by breaking the structure of NOM and enhancing the transformation of higher molecular weight compounds to lower molecular weight compounds. The removal of biodegradable organic matter during subsequent treatment is particularly important because this matter has been linked to the growth of microorganisms within distribution systems (Ahmad, 1998).

Biological treatment is one method of removing biodegradable organic matter. As was stated earlier, the primary interest in biological processes stems from the recognition that after ozonation, biological activity is stimulated whether it is a specific design objective or not. All biological processes used in drinking water treatment are the biofilm type. Most commonly used systems in water treatment are biological filters or GAC filters. Slow sand filtration is still used at some plants in European countries and is able to adequately remove organic matter (Ahmad, 1998).

An increase in the biological degradability of NOM after ozonation is described elsewhere (Goel, Hozalski, & Bouwer, 1995; Flogstad and Odegaard, 1985). Cipparone,

Diehl, and Speitel (1997) established that the rate and extent of biodegradation of organic matter increased with ozone dose. Shukairy and Summers (1992) conducted batch ozonation and biodegradation studies to remove organic halides from surface waters and groundwaters containing humic substances. The authors reported that the combined treatment removed 47% of purgable organic halogen formation potential (POXFP) and dissolved organic halogen formation potential (DOXFP) from Ohio River water versus 25 and 10%, respectively, when ozonation was used alone. For groundwater humic substances, the removal of POXFP increased from 40% (ozonation alone) to 80% (combined ozonation and biodegradation) and the removal of DOXFP increased from 25 to 70%. In all experiments, a dosage of 2 mg/mg TOC was applied. In further studies, increased ozone dosage was shown to result in an increased removal of THMFP (Shukairy and Summers, 1996). A similar effect was established by Speitel et al. (1993). The study showed that the percentage removal of THMFP in natural water by ozonation and biodegradation steadily increased with ozone dosage, up to a maximum of about 60% at a dose of 5 mg/mg TOC. The contribution of ozonation to the removal of THMFP was about half that of biodegradation at ozone doses of 2 mg/mg TOC. At an ozone dose of 3 mg/mg TOC, the contributions of ozonation and biodegradation were approximately equal, whereas at an ozone dose of 5 mg/mg TOC, the contribution of ozonation was about twice that due to biodegradation (Speitel et al., 1993).

The general approach to the removal of THM precursors from drinking waters by combined ozonation and biotreatment has been to first oxidize humic substances and other NOM to a biodegradable form, and then to use biological treatment to remove any biodegradable organic matter. It was shown that the production of AOC and BDOC starts

at low levels of ozone dosage and increases with ozone dosage (Speitel et al., 1993). The maximum removal of THMFP and HAAFP by ozonation followed by biodegradation was observed at an ozone dosage of approximately 5 mg/mg C, which was the maximum ozone dose used in the experiments (Speitel et al. 1993). The high dosage of ozone required can be attributable to the fact that a portion of ozone is consumed by the ozonation products that could have been degraded biologically. This conclusion is supported by the data obtained by Speitel et al. (1993), which showed that at large ozone doses, THMFP removal occurs largely through ozonation, rather than biodegradation.

Combining ozonation and biological activated carbon (BAC) has been successfully used at many water works in Great Britain, France, Germany, and other European countries (Ahmad, 1998; Rachwal, Foster, and Holmes, 1992; Venteresque, Bablon, and Jadar-Hecart, 1991; Sontheimer and Hublele, 1986) for more than two decades. In recent years, there has also been increasing interest in the combined ozonation/biofiltration in the United States (Price et al., 1993; Malley et al.1993; Krasner et al., 1993).

The Swinford Water Treatment Works (Oxford, England) built a demonstration plant that incorporated preozonation, chemical coagulation/flocculation, rapid gravity filtration, main ozonation and biologically active GAC to treat Thames River water having TOC from 2 to 7 mg/L (Rachwal, Foster, and Holmes, 1992). The total ozone dose for preozonation and main ozonation was approximately 1 mg/mg C. Nominal contact times of 5 and 15 minutes was used for preozonation and main ozonation, respectively. The GAC filters had an EBCT of 15-30 minutes. Overall TOC removal

through the plant was approximately 40%. The process was capable of eliminating of approximately 65% of THMFP, which correlated well with UV-254 absorbance.

The Metropolitan Water District of Southern California (MWD) conducted a pilot-scale study of ozonation and high-rate filtration using California state water and Colorado River water with TOC levels of 3.5 and 2.5 mg/L, respectively (Krasner et al., 1993). The pilot plant included ozonation at a dose of approximately 0.5 mg/mg C, coagulation with alum, followed by flocculation and sedimentation, and high-rate biofiltration using GAC-sand. The biofilter was operated at a low EBCT of 4.2 minutes. The pilot-plant testing showed that the process did not adequately remove TOC. Nearly 90% of TOC passed through the filter. However, the process was effective towards the removal of aldehydes, with nearly 80% of formaldehyde, glyoxal, and methylglyoxal that was formed during ozonation being removed through biofiltration. It should be noted that the temperature during pilot plant testing varied from 15 to 25°C.

East Bay Municipal Water District (EBMUD) conducted similar pilot testing at the Sobrante Filter plant using water having a TOC concentration of 2.2-3.2 mg/L (Price et al., 1993). The pilot plant testing consisted of taking water after flocculation/sedimentation from the full-scale facility, ozonating it at a dose of approximately 0.7 mg/mg C, and passing it through a GAC/sand filter. The filtration rate corresponded to an EBCT of 4.5 minutes. The temperature was 10-22°C during the experiments. The pilot testing showed that ozonation removed approximately 18% of TOC and 30% of THMFP, however, very little removal of TOC and THMFP was observed during biofiltration.

Pilot-plant studies of combined ozonation and slow sand filtration were conducted at the Andover Water Treatment plant (Andover, Mass.) (Malley et al., 1993). The raw water had a low turbidity (approximately 1 NTU) and an average TOC concentration of 4.3 mg/L, a UV-254 absorbance of 0.1 cm^{-1} , and a THMFP of $200 \text{ }\mu\text{g/L}$. An ozone dose of approximately 2 mg/mg C was used in all experiments and the EBCT in the biofilter was 2.8 hours. The pilot-plant testing was conducted at a temperature of 23-27°C. The removal of TOC and THMFP in the entire treatment process was 30-70% and 50-68%, respectively. It was shown that ozone increased the BDOC content in water. However, ozone also reduced filter run times as a result of increased clogging of the filter media via biofilm development.

2.2.7. Proposed Ozonation/FBT Process

The use of biological filtration systems utilizing GAC and other media has been well documented. Multi-step physical treatment and biological filtration are used in many European countries. It appears that the approach to including biological processes in drinking water treatment practice in this country is to combine biofiltration with an existing physiochemical unit operation.

In this project, a different approach to the problem has been proposed and investigated. It includes using ozonation in combination with biological-fluidized-bed treatment (FBT).

Figure 2.1 demonstrates the differences in operation of a biofilter and FBT column. In biofilters, water flows downwards through a packed medium, which is

colonized by microorganisms. Biological action breaks down some organic materials, and some inert suspended particles are physically removed from the water. In FBT columns, a bed of small particles is fluidized by the upward flow of water. Very high specific surface area can be achieved without introducing the problem of clogging.

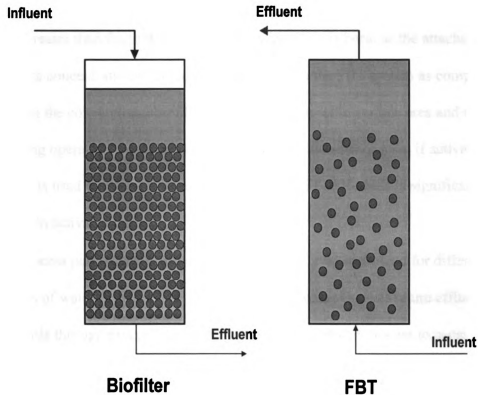


Figure 2.1 Comparison of FBT and biofilter operations

The proposed ozonation/FBT process has several potential advantages over conventional ozonation/biofiltration processes, which are:

- The ozonation/FBT process uses a fluidized-bed reactor (in place of biofilters) in which clogging is virtually impossible, and, therefore, no additional pretreatment may be required.
- The efficiency of the removal of biodegradable organic matter by FBT is expected to be greater than that obtained by biofiltration. This is because the attached biomass concentration is expected to be greater in the FBT system as compared to those in the conventional biofilter due to greater specific surface area and no-clogging operation. Also, because of greater specific surface area, if activated carbon is used as a support medium, the use of FBT will result in significant saving in activated carbon.
- The process performance of the unit can potentially be optimized for different sources of water supplies. The system is also expected to meet future effluent standards through process parameter optimization without process expansion or modification.
- Finally, FBT systems have a considerably smaller footprint than biofilters, which may be very useful for the application where space for retrofitting or expansion is limited.

Over the last ten years, the biological component of this system has been developed and used in several applications for the biological treatment of process waters and for the bioremediation of volatile organic compounds and chlorinated solvents in groundwaters (Hickey, Wagner, and Mazewski, 1991). The low operational costs of these

systems (power, GAC, oxygen) have proved their competitive advantage in bioremediation applications. These systems can also be monitored and controlled from remote locations using advanced telemetry, thus reducing manpower requirements and O&M costs. Integrated ozonation-biotreatment that used a FBT system has also been investigated for the treatment of bleaching effluents from pulp and paper industry (Heinzle et al., 1992).

Commercial fluidized bed systems are currently marketed by Ecolotrol, Biothane, DorrOliver, and Envirex. Skid-mounted biological FBT systems (with single pass flow capacities ranging from 30 gpm to 1850 gpm) are available off-the-shelf. These systems could serve communities ranging from 500 to 50,000 people, which can be further expanded using multiple FBT units in one system.

If technical and economical merits are established, the ozonation/FBT process will be a very attractive alternative to both conventional coagulation and ozonation/biofiltration processes, especially for small water treatment utilities and for larger utilities where space for retrofitting or expansion is limited.

3. MATERIALS AND METHODS

3.1. WATER SOURCE

The study was conducted with Huron River water collected at the pump station to the Ann Arbor Water Treatment Plant. Typical characteristics of Huron River water are summarized in Table 3.1. Huron River water contains relatively high concentrations of TOC and THMFP and, hence, was well suited to evaluate the ability of the ozonation/FBT system to remove TOC and THM precursors from water and to sustain turbidity without pretreatment. The raw water has a low bromide concentration.

Table 3.1 Typical Quality Characteristics of Huron River Water

Parameter	Raw water
TOC, mg/L	5.8 – 8.3
pH	7.8 - 8.2
Alkalinity, mg/L as CaCO ₃	350-420
Turbidity, NTU	0.9 – 3.4
UV absorbance @ 254 nm, cm ⁻¹	0.152 - 0.228
Bromide, µg/L	70
THMFP, µg/L	340 - 460

It should be noted that it was essential to focus our efforts on a single water source, rather than using multiple water sources. The latter approach would have altered our objective of better understanding the transformation of NOM during ozonation and

FBT to simply a feasibility study. The study of the applicability of the process to various water sources is the next logical step upon completion of this project.

3.2. EXPERIMENTAL SYSTEMS

3.2.1. Bench-Scale Ozonation System

A schematic of the system used to study the ozonation of NOM is shown in Figure 3.1. The water was pumped by a peristaltic pump (feed pump) from a holding tank into the ozone reactor. The ozone contactor was a 360 mL water jacketed gas-washing bottle, which was operated as a completely-stirred tank reactor (CSTR). The reactor was equipped with a fritted glass gas diffuser near the base, a vent-gas exit port, and water entrance and exit ports. The diffuser was used to sparge the ozone/oxygen mixture into the contactor. Additional mixing was provided with a magnetic stirring bar. All fittings and tubings were made of either PTFE or stainless steel.

A second pump was installed downstream of the ozone contactor, which was synchronized with the feed pump in order to maintain a constant liquid level in the contactor. This effluent pump pumped water either into an effluent collection tank or into a purging flask from where water flowed by gravity into the effluent collection tank. The purging flask was used to quench the ozone reaction by purging the reactor effluent with helium to remove unreacted ozone. The residual ozone in the gas phase was destroyed by passing the gas through a potassium iodide solution.

Ozone was generated from pure, dry oxygen using an air-cooled Ozotech Model OZ1PCS/V ozone generator (Ozotech, Inc., Yreka, Ca). The gas flow rate to the reactor was controlled by a Sierra Instrument Model 900 mass flow controller (Sierra Instruments, Inc., Monterey, CA), installed upstream of the ozone contactor. A check valve was installed downstream of the flow controller to prevent water in the ozone contactor from cycling back into the flow controller and the ozone generator. Influent and effluent ozone gas concentrations were measured spectrophotometrically at 254 nm using 0.2-cm flow-through quartz cells with the Milton Roy Spectronic Genesys-5 spectrophotometer (Milton Roy, Inc., Rochester, NY). An extinction coefficient of 3000 $\text{LM}^{-1}\text{cm}^{-1}$ was used to convert absorbance reading $\text{mg O}_3/\text{L}$. Aqueous ozone concentrations were measured using the Indigo method (Standard Methods, 1992).

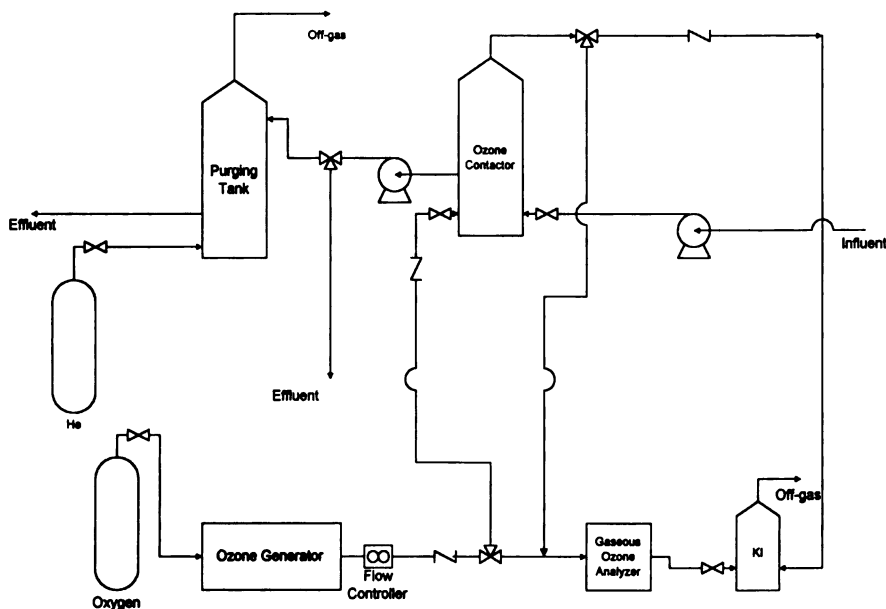


Figure 3.1. Schematic of the bench-scale ozonation system

3.2.2. Ozonation/FBT System

A schematic of the pilot-scale ozonation/FBT system is shown in Figure 3.2. The system included an ozone contactor, retention tank, and a FBT column. The water was pumped by a peristaltic pump from a holding tank into the ozone contactor. The ozone contactor was a downflow injector-type bubble contactor. The contactor consisted of a downflow vertical tube and an expanding cross section hood, as shown in Figure 3.3. Water and gas entered at the top of the contactor and flowed concurrently downward through the tube into the expanding hood, and exited at the bottom of the contactor. The contactor was designed so that the inlet velocity was greater and the exit velocity was lower than the buoyant velocity of the bubbles. Thus, the bubbles were trapped inside the hood. At the bottom of the downward tube, the velocity changed rapidly which created significant swirling and turbulence at the top of hood. This resulted in a high gas-liquid interfacial area and a high mass transfer rate.

A retention tank was installed downstream of the ozone contactor. The pressure head that developed in the hood of the contactor moved water out of the contactor into the middle of a retention tank. The retention tank was a 1L water jacketed glass column. Periodically, gas, which had accumulated in the contactor, was released through the retention tank. This gas was analyzed for ozone and then passed through a potassium iodide trap to destroy residual ozone prior to discharge of the gas. The tank was also used to collect samples of ozonated water. Since the flow rate of influent flow was significantly lower than that required to maintain sufficient turbulence in the ozone contactor, an additional pump was installed (not shown in Figure 3.2) to recirculate water

from the bottom of the retention tank back to the ozone contactor. A recycle pump was installed to provide the recycle of a portion of system effluent back to the ozone contactor.

From the retention tank, water flowed by gravity into a small recirculation tank from where it was recirculated through the FBT column with a peristaltic pump at a rate sufficient to fluidize the bed. The FBT column was a jacketed glass column 2 inches in diameter and 60 inches in height. Non-activated carbon, termed “baker product” by the manufacturer (Calgon Co., Pittsburgh, Pa), was the same material as granular activated carbon (GAC) except that it had not undergone the activation step in the manufacturing process and had, therefore, little sorptive capacity (Voice et al., 1992). It was essential to use a non-adsorbent material as a support media in the FBT column in order to separate microbial removal of BDOC from sorptive removal.

During the first stage of the study, the height of the fluidized bed was maintained at 35 inches. This corresponded to an EBCT of approximately 180 minutes at a water flow of 10 mL/min. Later, two-third of the acclimated material was removed from the column, a portion of which was transferred to the biofiltration column, described in Section 3.5. The remaining fluidized bed provided an EBCT of 30 minutes at a water flow of 20 mL/min.

Ozone was generated from pure, dry oxygen using an Ozotech Model OZ1PCS/V ozone generator (Ozotech, Inc., Yreka, Ca). The gas flow rate to the reactor was controlled by a Sierra Instrument Model 900 mass flow controller, which was installed between the ozone generator and the ozone contactor. A check valve was installed downstream of the flow controller to prevent water in the ozone contactor from cycling

back into the flow controller and the ozone generator. Influent and effluent ozone gas concentrations were measured spectrophotometrically at 254 nm in 0.2-cm flow-through quartz cells with the Milton Roy Spectronic Genesys-5 spectrophotometer and amperimetrically with the Orbisphere MOCA ozone analyzer (Orbisphere Laboratories, Geneva, Switzerland). Aqueous ozone concentrations were measured amperimetrically with the Orbisphere ozone analyzer.

It should be noted that since the design capacity of the system was greater than the operating influent flow, additional recirculation loops were provided in the FBT column and ozone contactor in order to maintain the fluidization of the bed in the FBT column and the inlet velocity in the ozone contactor, respectively. Since these recirculating flowrates were several orders of magnitude greater than the influent flowrate, both FBT column and the ozone contactor could be considered as completely-mixed reactors.

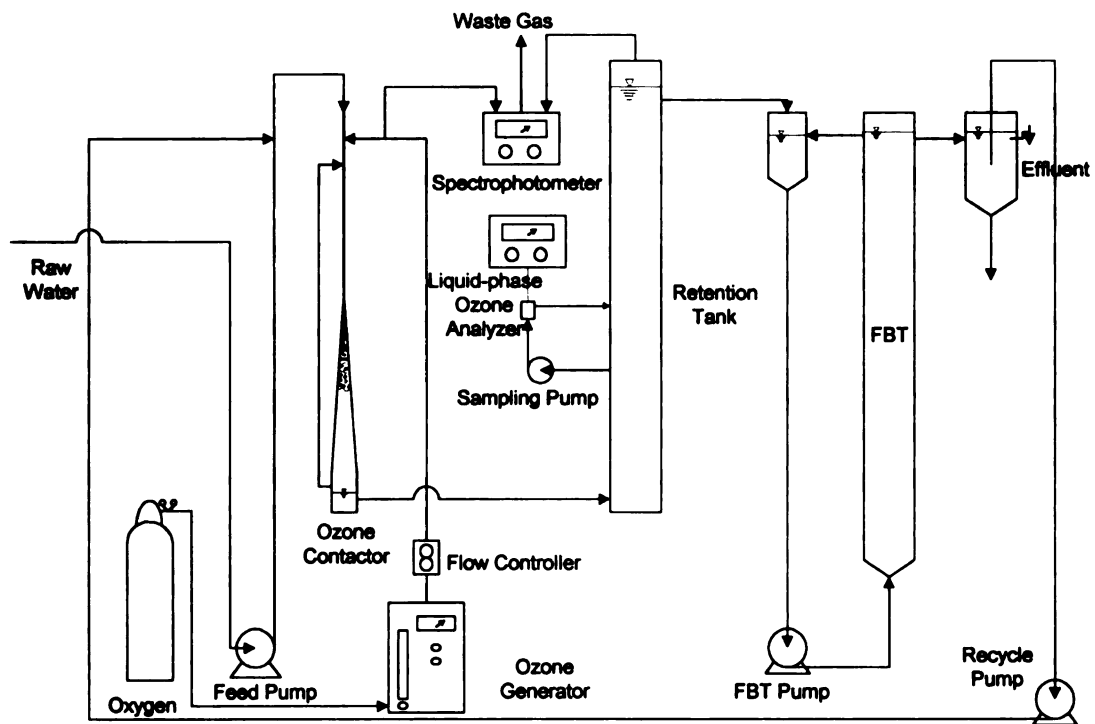


Figure 3.2. Schematic of the ozonation/FBT system

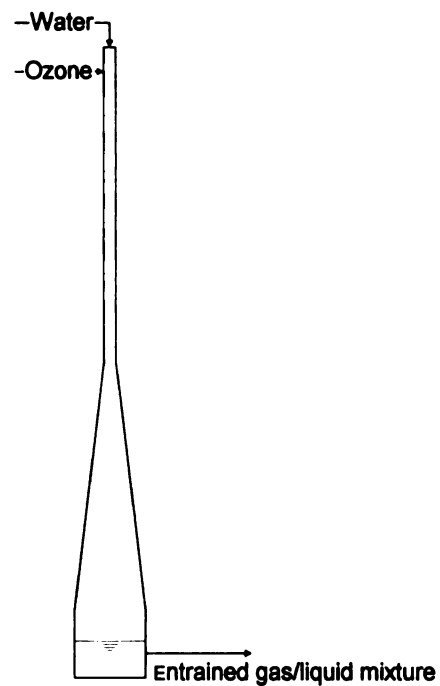


Figure 3.3. Schematic of a downflow ozone contactor

3.2.3. FBT/Ozonation System

The FBT/ozonation system, shown in Figure 3.4, was essentially the same as that described in Section 1.2.2 with the exception that raw water was pumped first to the FBT column. The water from the FBT column flowed by gravity to the ozone contactor. Water from the ozonation retention tank flowed by gravity to a holding tank from where it was directed to the biofiltration column described in Section 3.2.5. A recycle line was provided to recycle water from the ozonation system to the FBT column.

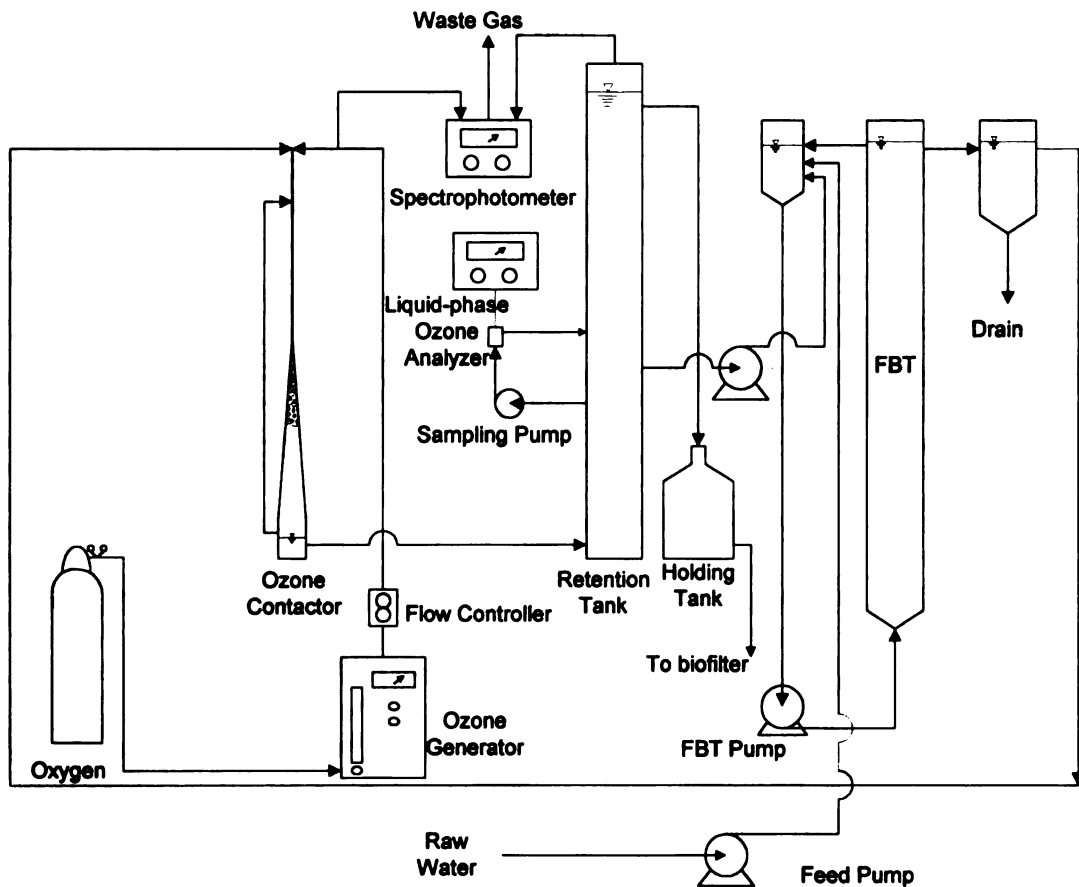


Figure 3.4. Schematic of the FBT/ozonation system

3.2.4. FBT System

The biodegradation of NOM was studied using a recirculating FBT system shown in Figure 3.5. The recirculating FBT system used the same FBT column employed in the FBT/ozonation system. In this configuration all lines connected to the ozonation system were shut off.

Water was continuously pumped from a holding tank to the bottom of the FBT column by a peristaltic pump. The fluidization of the bed was maintained by recirculating water from the top of the reactor to the bottom by a second peristaltic pump. The effluent flowed by gravity into the collection vessel from where samples were taken for analyses.

3.2.5. Biofiltration system

The biofiltration system (see Figure 3.6) included a glass chromatography column with a diameter of 2.5 cm and a total volume of 100 cm³, a peristaltic pump, and feed and collection reservoirs. All fittings and tubing were of stainless steel or PTFE. An acclimated biofilm media were taken from the FBT system and packed into the biofiltration column. The system was operated at room temperature.

The system operated in either single-pass or recirculating modes. In the single-pass mode, water was passed from the feed tank through the biofilter and collected in the collection reservoir. The EBCT in the column was controlled by varying the flow rate of

the influent flow. The samples were taken for analyses from the system influent and effluent.

When the recirculating mode was employed, water was circulated from the feed reservoir through the column and back to the reservoir. The operation is described in more detail in Section 3.3.6. Between the experiments, the biofilm was maintained by recirculating ozonated water through the filter.

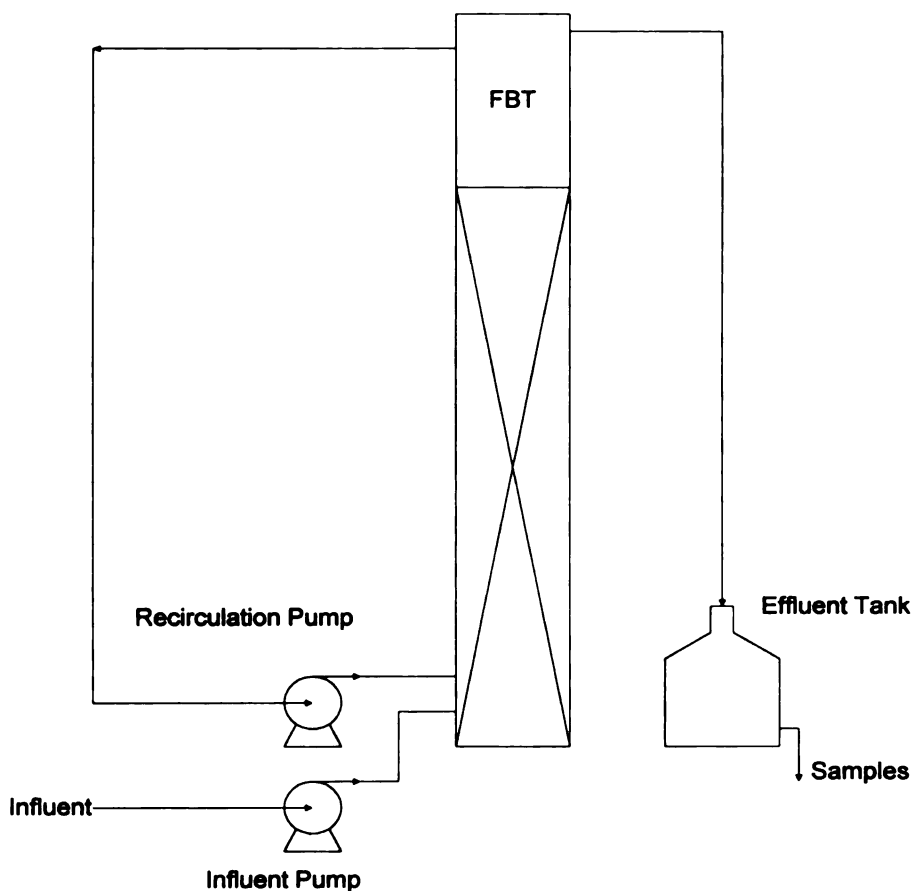


Figure 3.5. A schematic of the recirculating FBT system

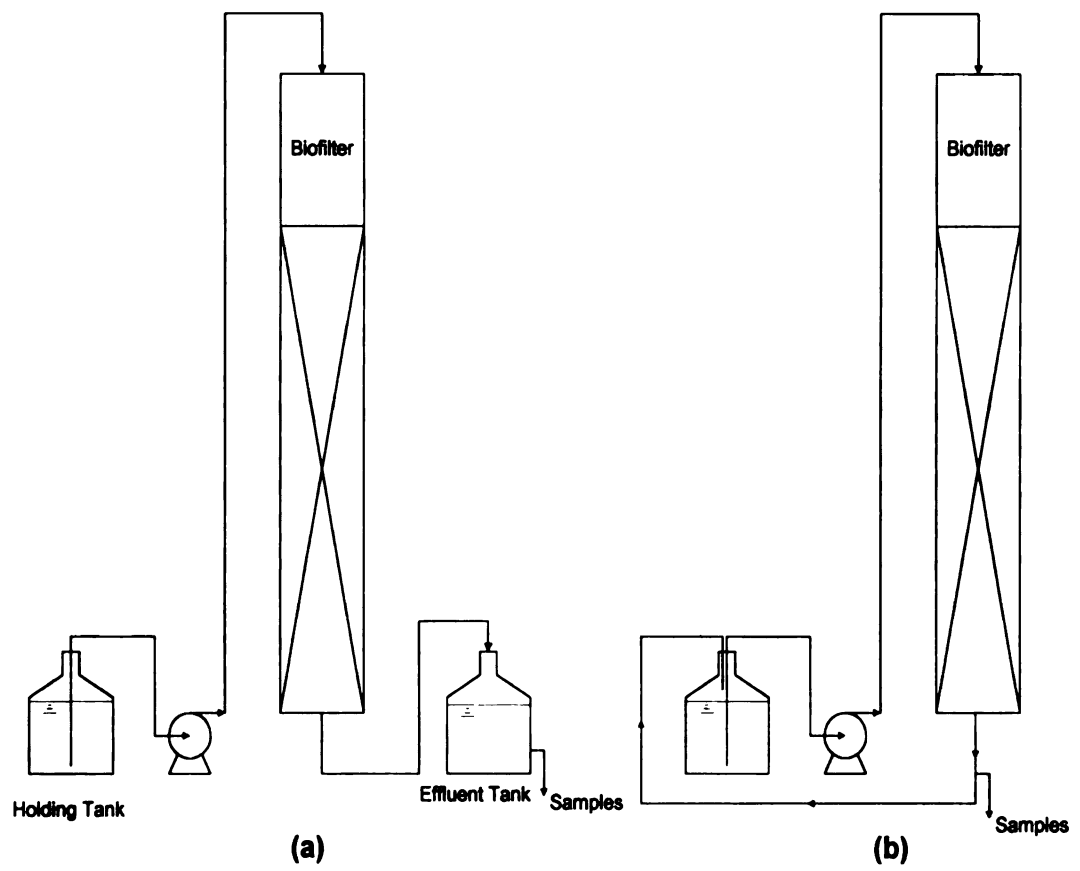


Figure 3.6. A schematic of the biofiltration system

3.3. ANALYTICAL METHODS

3.3.1. Organic carbon.

Total and dissolved organic carbon were determined using a Dohrmann Model DC-190 carbon analyzer (Dohrmann, Santa Clara, Calif) that uses the combustion method and an OI Analytical Model 1010 analyzer that uses the UV/persulfate method (Standard Methods, 1992). A 5 mL sample loop was employed in the OI Analytical analyzer. A 40 mL sample was used with the OI Analytical analyzer, and a 10 mL sample was used with the DC-190 analyzer. When it was necessary to measure dissolved organic carbon (DOC), samples were prefiltered through a 0.45 μm glass-fiber filter before analysis.

All samples were acidified to pH less than 4.0 and purged with high purity helium for three minutes. Each run was performed with four replicates. The first replicate was usually greater than the three subsequent replicates and, when it was the case, the first replicate was eliminated. The average relative analytical accuracy was approximately 1.5% for the DC-190 analyzer and 0.6% for the OI Analytical analyzer. To ensure the reliability of results, the blank (Milli-Q water) and 2.5, 5, 7.5, and 10 ppm standards were run before running the samples.

3.3.2. UV-254

UV absorption was measured at a wavelength of 254 nm with a Milton Roy Genesis-5 spectrophotometer (Milton Roy, Inc., Rochester, NY) using a 1 cm quartz cell. Samples of treated and untreated natural waters were analyzed without pH adjustment.

3.3.3. Humic Substances.

The concentration of humic substances in water samples was measured by adsorption on XAD-8 resin using a slightly modified procedure of Method 5510C (Standard Methods, 1992). The resin was packed in a 1.0 x 15-cm glass column. The resin preparation and cleaning procedures were followed as described in the *Standard Methods*. The fractionation procedure was as follows. A 100 mL sample acidified to pH 2 with concentrated phosphoric acid, was pumped onto the top of the resin bed at a rate of 2-3 mL/min. The effluent was collected at the bottom of the column. The first 3 mL of the column effluent were discarded. After the sample passed through the column, 3 mL of Milli-Q water were pumped onto the column to displace the portion of the sample remaining in the column and to remove water soluble organic acids that may be retained by the resin. The column effluent was analyzed for DOC, which represented the non-humic fraction of the dissolved organic matter. The column containing adsorbed organic materials was back eluted with 100mL of 0.1N NaOH at a rate of 0.8-1.0 mL/min. The eluent was immediately acidified with concentrated phosphoric acid to a pH of 2-4. After collection, the eluent was purged with high-purity helium to remove inorganic carbon,

and analyzed for DOC. The organic content of the eluent represented the humic substance concentration. The average mass balance for humic and nonhumic fractions of NOM in Huron River water ranged from 92 to 99% with an average of 95%.

3.3.4. AMW Distributions

Apparent molecular weight (AMW) distributions were determined by an ultrafiltration membrane technique. Molecular weight separations were performed using a pressurized cell apparatus (Amicon Corp, Danvers, Mass.) using 200-mL stirred cells and YM and YC series ultrafiltration membranes characterized by nominal molecular weight cutoffs of 500, 1000, 3000, 10000, and 30000 AMW units (Collins and Vaughan, 1993; Amy et al., 1992). The ultrafiltrations were performed in parallel, therefore, the procedure did not provide a discrete AMW fraction, but rather the accumulation of organic matter below the given AMW cutoff of the membrane. The UF membranes were prepared according to the manufacturer's recommendations by rinsing with Milli-Q water for one hour and alternate soaking in a 0.1N NaOH solution and Milli-Q water at least twice. The cleaning removed the glycerine and any absorbing materials coating the UF membranes. Prior to sample filtration, 200 mL of Milli-Q water was filtered and tested for TOC to assure that there was no contamination. To avoid a dilution effect from the rinse water, the first 20 mL of the permeate was wasted, then the sample was collected. All permeates obtained were characterized according to organic carbon content. The detail analytical protocols are presented in Mellema (1998).

3.3.5. THMFP.

THMs were determined using EPA Method 3810 (US EPA, 1988) and the *Standard Method 6232 (Standard Methods, 1992)*. Chlorine demand and THMFP were determined using *Standard Methods 2350 and 5710, respectively (Standard Methods, 1992)*.

Method 3810 is a static headspace technique for extracting volatile organic compounds from samples. It is a simple method that allows for a large number of samples to be screened in a relatively short period of time and is well suited for comparative analysis (Kolb, Auer, and Pospisil, 1983).

A Model 8700 Autosystem gas chromatograph (Perkin Elmer Corporation, Norwalk, Connecticut) with an HS 40 automated head space sampler (Perkin Elmer Corporation, Norwalk, Connecticut) was used. The gas chromatograph was equipped with a ^{63}Ni electron capture detector (ECD) with a 30 m x 0.53 mm DB-624 column (J & W Scientific, Folsom, California). The detector temperature was set at 350 °C. The injector temperature was 200°C. The column temperature was initially set at 80 °C, then increased at a rate of 10 °C/min to 200 °C, held for 0 minutes. The flow rate of the carrier gas (H_2) is 10 mL/min.

For quality control, samples were periodically analyzed using the liquid-liquid extraction method. Detail analytical protocols for the head-space and liquid-liquid extraction methods and quality control procedures are presented in Kasarabada (1997). The methods produced similar results and were found to be statistically equivalent (Kasarabada, 1997).

3.3.6. BDOC

The BDOC was determined by recirculating raw or treated water through the biofiltration column described in Section 3.2.3. The procedure described by Cipparone, Diehl, and Speitel (1997) was followed except for slight modifications. Briefly, before starting the sample analysis, 2 L of the water sample were pumped through the column and discarded. Upon completion of this step, the volume of the water in the feed reservoir was adjusted to 4 L and recirculation of the sample began at a rate of 10-12 mL/min. The TOC concentration was monitored until no further removal of TOC was observed, which indicated the completion of the biodegradation. Biodegradation was usually completed after 5 or 6 days, but recirculation was continued for seven days in most cases to ensure complete biodegradation. The BDOC concentration was calculated as the difference between the TOC concentration in the sample before the analysis and that in final biodegradation sample.

3.3.7. Other parameters

Other physical-chemical parameters, including pH, alkalinity, turbidity were determined according to *Standard Methods* (1992).

3.4. QUALITY ASSURANCE AND CONTROL

3.4.1. Data Management

Considering the large volume of data collected in this research, it was important to develop and maintain a cross-referenced database for all data, interfaced with graphical and statistical software. The spreadsheet formats are presented in Appendix D. The main spreadsheets for the pilot ozonation/FBT system and for bench-scale ozonation system, shown in Table D.1 and D.2, included the following information:

- date of the collection of water batch
- date of sample collection (for the pilot system)
- date of bench experiments (for the bench system)
- mode of operation (for the pilot system)
- the operating conditions
- analytical data.

The measured parameters (e.g., gas flow, ozone concentrations, temperature) and parameters that were analyzed immediately upon collection, including pH, alkalinity, turbidity, UV-254, were hand written on a blank spreadsheet and then transferred to an appropriate electronic file, which automatically calculated ozone dose, retention time (for the bench system) and EBCT (for the pilot system). Other analytical data could be accessed through the appropriate spreadsheets (see Tables D.3-D.5), which shared information with the main spreadsheet.

Since many analytical parameters, including TOC, HS, nonHS, and MWD, involved TOC measurements, a separate spreadsheet was maintained for all TOC data

collected on a specific day. The TOC spreadsheet shown in Table D.6, contained complete sample description and could be accessed by the date of analysis, which in all cases was performed on the day of sampling.

All graphs presented in this research are interfaced with appropriate spreadsheet data, the reference of which is displayed by clicking on the graph. All raw data were filed and could be accessed by the date of analysis.

3.4.2. Sample Collection and Analysis

Samples were collected in the appropriate containers and were labeled to provide complete sample identification. To minimize cross-contamination, containers were designated to specific types of samples by the type of analyte and sampling location. To avoid contamination, samples for TOC analyses were collected to TOC vials that were also designated to specific locations (e.g., samples collected from the retention tank were collected in the same set of vials). All glassware was cleaned according to *Standard Methods* (1992). Most samples were analyzed within several hours after collection and all samples were analyzed with 24 hours after collection.

Proper instrument operation was assessed before each sample analysis and blanks were run to ensure that system components were clean. To ensure the quality of the results the standards with known concentration of compounds were run before each analysis. All standards solutions were stored for no longer than recommended by the manufacturer. For TOC analyses using the Dorhmann analyzer, the calibration was conducted before each run. The calibration of the OI Analytical analyzer was performed

when fresh standards were prepared. The standards of 0, 2.5, 5, and 7.5 mg/L were run before each set of analysis and proper operation was assessed by maintaining a control chart. For humic substance and MWD analyses, the blanks were run through the XAD-8 columns and ultrafiltration membranes to ensure that the systems were clean. The glassware used in these analyses was designated to specific samples.

3.4.3. Data Analysis

Analytical quality control procedures were applied to properly qualify the results obtained from this research. Statistical tests for comparison of variances and means were based on 95% confidence levels. Up to five replicates were used for assessment of precision at different levels of processing/analyses. Accuracy controls included comparison to standards or spikes, where appropriate. The summary of QA/QC results are presented in Table 3.8.

Table 3.8. QA/QC Summary

Parameter	Limit of Detection	Accuracy % recovery	Precision Range or % RSD
TOC, mg/L	0.07	98-101	0.8 rsd
UV-254, 1/cm	0.002	-	0.001- 0.002 range
THMs ¹ , µg/L ¹	5	85-120	10.9±1.1 rsd
BDOC, mg/L	0.2	-	-
HS, mg C/L	n/d	95±3	2.4 ± 1.5rsd
MW500, mg C/L	n/d	95±2.7	4.0 ± 3 rsd

¹ Kasarabada (1997)

4. PRELIMINARY EVALUATION OF THE OZONATION/FBT PROCESS

4.1. INTRODUCTION

The objectives of the study presented in this section were to

- assess the impact of ozonation and FBT on the properties of NOM, including TOC, UV-254, humic substances, molecular weight distribution, and THMFP.
- evaluate the ability of the system to sustain turbidity without pretreatment.
- assess the role of ozonation and FBT in the transformation of NOM.
- evaluate the effect of the recycle of a portion of system effluent on the efficiency of the ozonation/FBT process.

The hypotheses that were tested in this portion of the study are described in each section that follows. Section 4.2 presents the results of the experiments that assessed the impact of ozonation and FBT on the properties of NOM. These experiments also tested the hypothesis that the efficiency of the ozonation/FBT process would increase with ozone dose. Sections 4.3 - 4.5 present the results of the experiments that assessed the role of ozonation and FBT in the transformation of NOM. These experiments also attempted to reconcile conflicting reports regarding the effect of ozonation on the production of biodegradable organic matter and low-molecular weight organic matter (less than 1,000 daltons).

4.2. POTENTIAL OF OZONATION/FBT SYSTEM

The experiments described in this section assessed the impact of the ozonation/ FBT process on the properties of NOM. It was expected that ozone would oxidize NOM, rendering it more amenable to the removal by subsequent biodegradation. As such, the efficiency of the ozonation/ FBT system towards the removal of NOM was expected to increase with ozone dose.

This study was conducted using the pilot-scale ozonation/ FBT system described in Section 3.2 (see Figure 3.2.2). A simplified schematic of the treatment train with sampling locations is shown in Figure 4.1. The experiments were conducted at room temperature. Ozone dose was varied from 0 to 2 mg/mg C. The parameters that were monitored in this study included TOC concentration, UV-254 absorbance, HS, turbidity, chlorine demand, THMFP, and AMW distribution. pH and alkalinity were also measured along the treatment train. Sampling was started after four months of acclimation period (from July to November 1996). During that period water was ozonated with an ozone dose of 2 mg/mg C. As can be seen in Figure 4.2, no removal of TOC in the FBT column occurred during the first two months of the acclimation period. During the next two months, the removal steadily increased reaching a plateau at the end of November.

The experiments described in this chapter were conducted in the period from November 1996 to March 1997. For each ozone dose, the system was operated for approximately one month. After all three dosages were evaluated, experiments were repeated using ozone doses of 1 and 2 mg/mg C for another two to three weeks. This experimental design was used to determine if seasonal variations of water quality and

changes in biofilm growth during prolonged experimental time would affect the process performance.

The FBT alone resulted in the maximum removal of about 16 percent of organic carbon from untreated Huron River water. As can be seen in Figure 4.3, the TOC removal steadily increased with EBCT reaching a plateau at an EBCT of approximately 180 minutes. Subsequently, the ozonation/FBT system was operated at a flow rate of 10 mL/min, which corresponded to an empty-bed contact time (EBCT) in the FBT column of 180 minutes. This flow rate was selected for the following reasons:

- (1) several operational conditions could be investigated using the same batch of water;
- (2) the biodegradability potential of Huron River water could be evaluated; and
- (3) the transformation of NOM during FBT could be better understood.

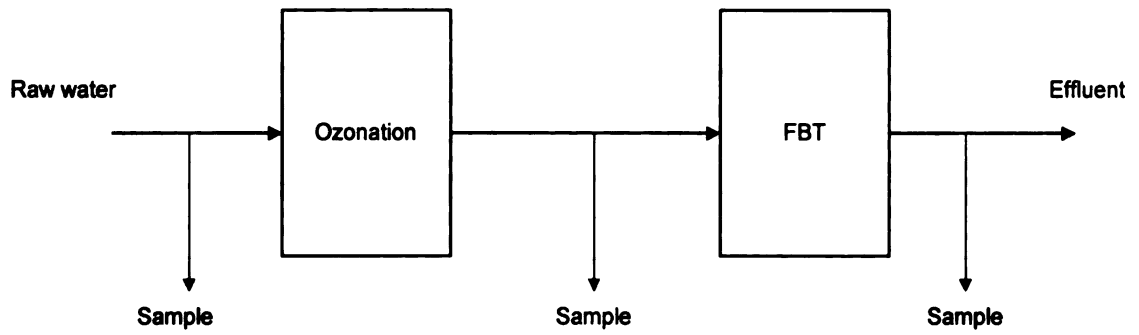


Figure 4.1. Simplified schematic of the ozonation/FBT system

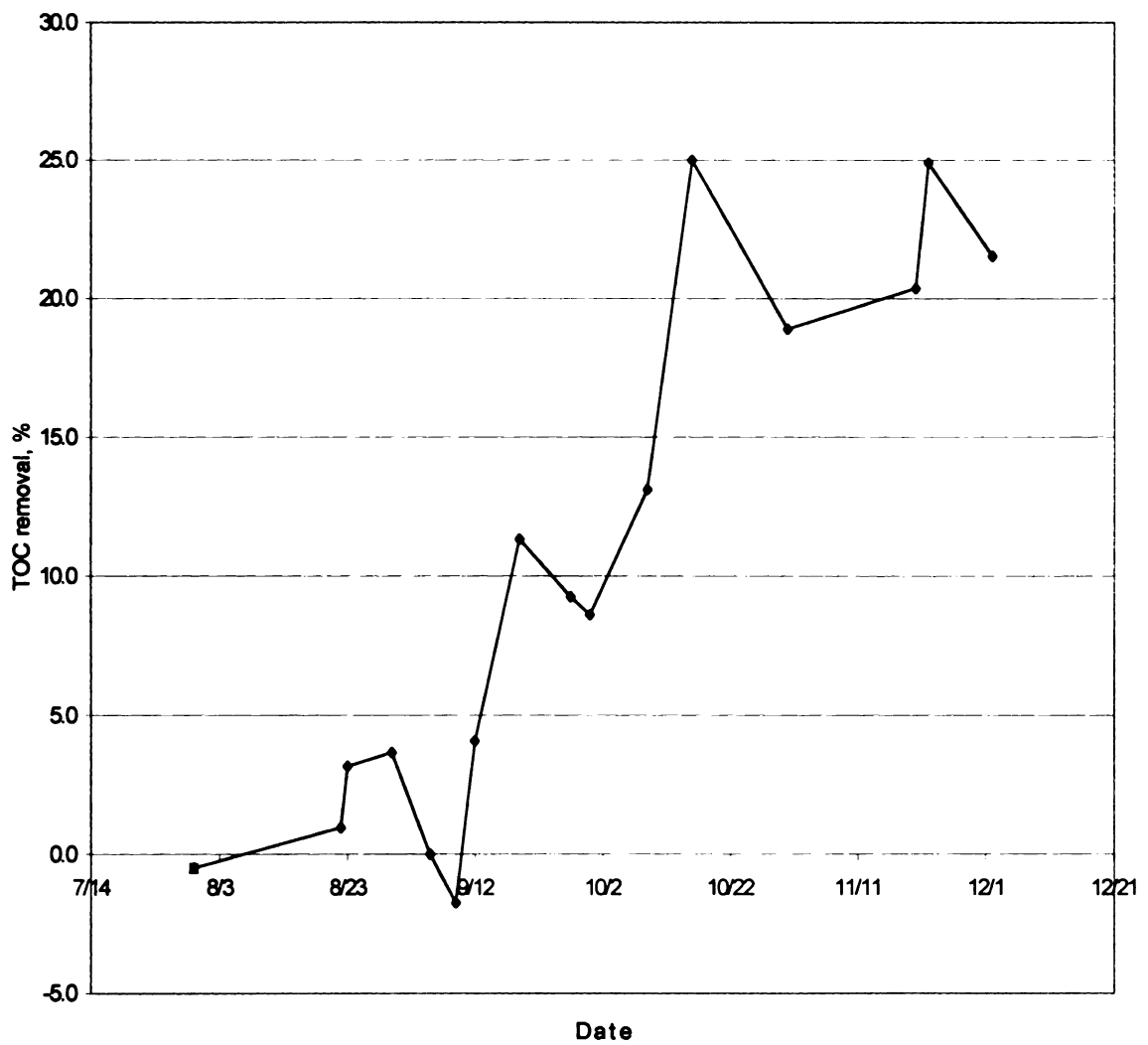


Figure 4.2. Time plot of TOC removal from ozonated water by FBT during acclimation period (ozone dose - 2 mg/mg C, EBCT – 180 min)

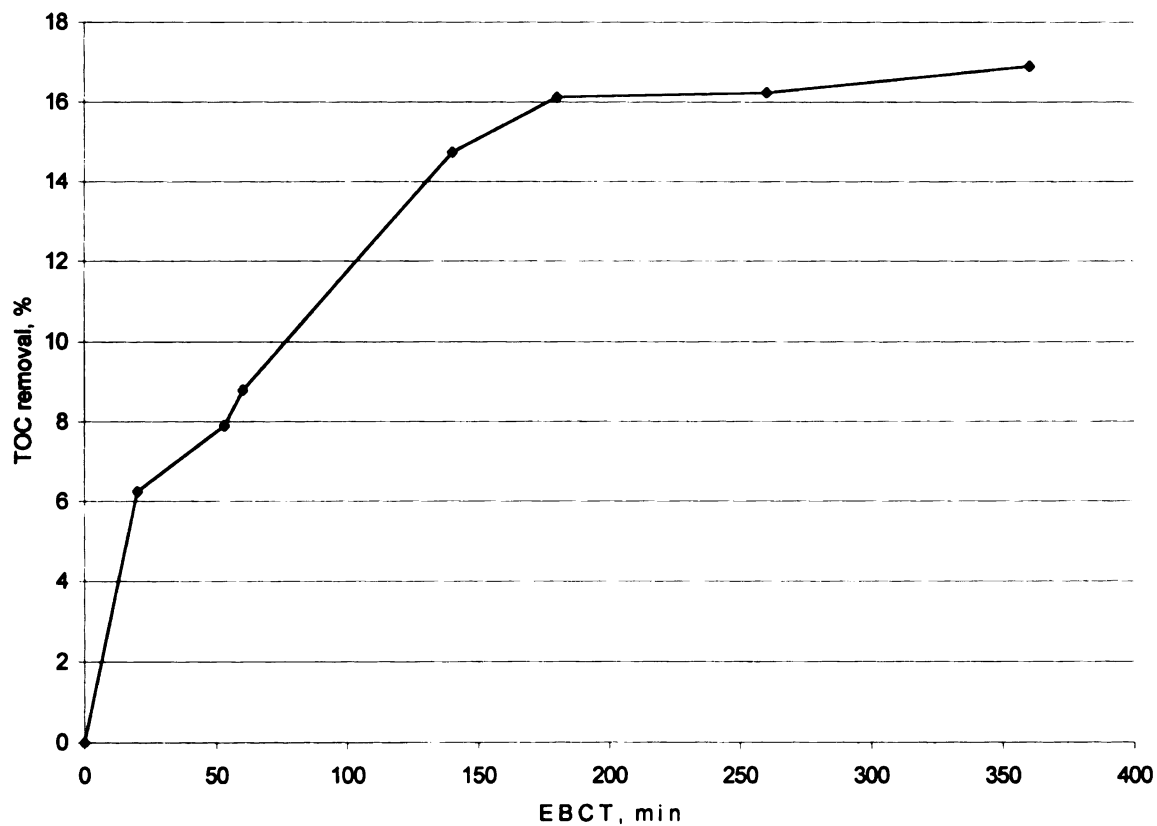


Figure 4.3. Removal of TOC from untreated Huron River water by FBT

Figures 4.4-4.5 show time plots of TOC and UV-254. The results for THMFP were presented by Kasarabada (1997) and are summarized in Table 4.1. TOC followed expected trends, with both ozonation and FBT contributing to the reduction of TOC (see Figure 4.4). The TOC removal increased with ozone dose. The lowest TOC concentration after ozonation/FBT was approximately 3 mg/L, which was achieved at an ozone dose of 2 mg/mg C. The results for winter and spring testing were essentially the same. Figure 4.5 shows a time plot of UV-254. The UV-254 reduction occurred mostly through ozonation, rather than through biodegradation. The removal of UV-254 increased with ozone dose. When no ozone dose was applied FBT resulted in the reduction in UV-254 from 0.160 to approximately 0.135 cm⁻¹.

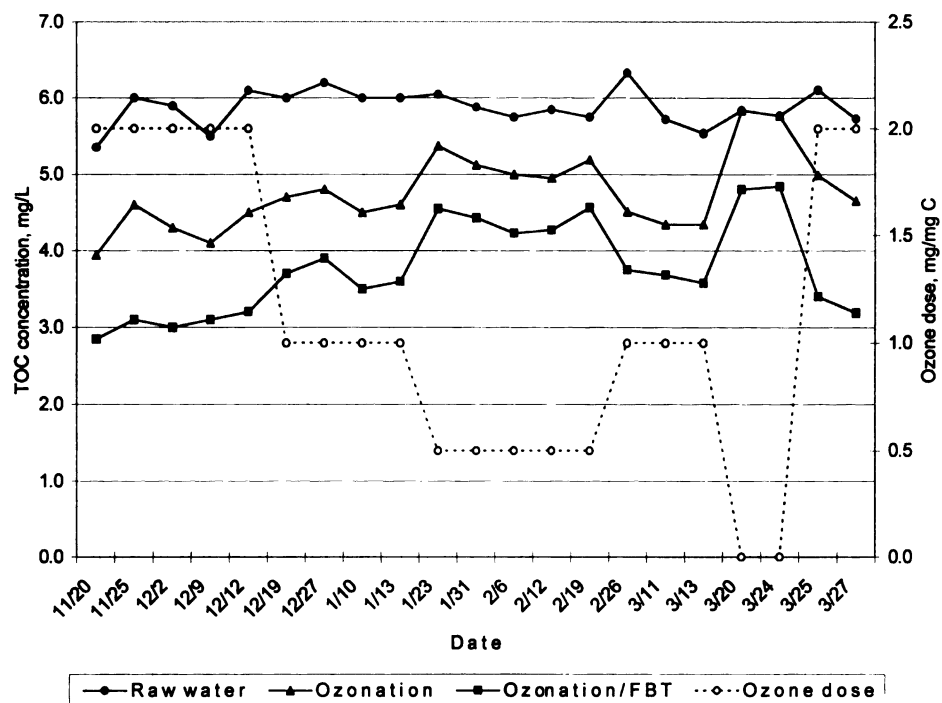


Figure 4.4. Variations in TOC concentration with time and ozone doses in raw water and along the treatment train (FBT EBCT = 180 minutes)

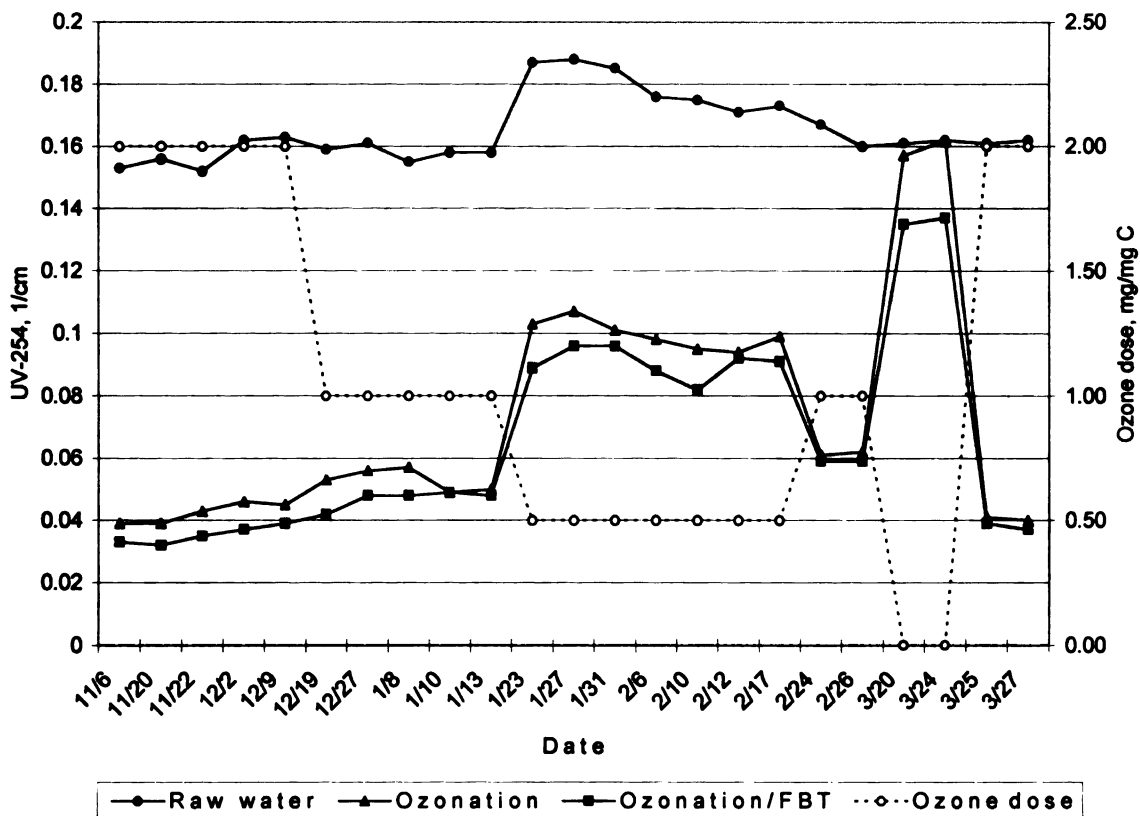


Figure 4.5. Variations in UV-254 with time and ozone doses in raw water and along the treatment train (FBT EBCT = 180 minutes)

Table 4.1 summarized the effect of ozonation/FBT on major water quality parameters. The removal of TOC increases with ozone dose reaching approximately 48 percent at a dose of 2 mg/mg C. FBT alone resulted in a reduction in turbidity to some extent. The removal of turbidity increased with ozone dose reaching nearly 80 percent at a dose of 2 mg/mg C. It should be noted that breakthrough of turbidity was not observed during the operation of the ozonation/FBT system. FBT alone resulted in approximately 20 percent decrease in the concentration of UV-254 absorbing compounds. This suggests that FBT was able to break down some aromatic portion of NOM. As was the case with TOC and turbidity, the removal of UV-254 increased with ozone dose reaching nearly 80 percent at a dose of 2 mg/mg C. It is worth noting that FBT alone was able to remove approximately 16 percent of TOC and UV254-absorbing compounds. The removal of THMFP also increased with ozone dose. The difference in the concentration of THMFP for ozone doses of 1 and 2 mg/mg C was not statistically significant at 5 percent level.

Table 4.1. Performance of the ozonation/FBT system

Parameter	Raw water (system influent)	System effluent			
		Ozone dose, mg/mg C			
		0	0.5	1.0	2.0
TOC, mg/L	6.04±0.32	4.82±0.02	4.44±0.14	3.71±0.10	3.04±0.12
Turbidity, NTU	1.33±0.24	1.05±0.15	0.77±0.20	0.49±0.16	0.28±0.11
UV-254, cm ⁻¹	0.166±0.007	0.139±0.009	0.091±0.005	0.051±0.008	0.035±0.003
Cl ₂ demand, mg/L	6.95±1.36	5.45±0.49	2.47±0.41	1.53±0.5	1.7±0.41
THMFP, µg/L	403±46	351±29	164±26	135±34	116±28

4.3. EFFECT OF OZONATION AND FBT ON TRANSFORMATION OF NOM

The results of the experiments described in the previous section agreed with the hypothesis that the efficiency of the ozonation/FBT system to remove NOM increased with ozone dose. The ozonation/FBT was also able to control turbidity. The next important question that needed to be answered was whether or not the efficiency of FBT would increase with ozone dose.

There have been conflicting reports on the effect of ozone doses on the production of biodegradable organic. Miltner et al. (1992) who studied the ozonation of Ohio River water reported that BDOC increased with an increase in ozone dose to up to 3 mg/mg C. Volk et al. (1993) determined that the ozonation of Seine River and Oise River waters resulted in a maximum production of BDOC at a dose of 0.5 mg/mg C. BDOC then decreased with higher ozone dosages. The authors also showed that an addition of hydrogen peroxide resulted in a decrease in the production of BDOC compared to ozonation alone. Cipparone, Diehl, and Speitel (1997) observed an increase in BDOC concentration during ozonation of Lake Austin water. BDOC leveled off at a dose of 1 mg/mg C. This study attempted to reconcile these differences.

Figure 4.6 summarizes TOC removal for all ozone doses, categorized by the type of removal. Ozonation at an ozone dose of 0.5 mg/mg C resulted in the removal of approximately 16 percent of TOC. The following FBT resulted in the removal of additional 12 percent of TOC, compared to 16 percent of TOC that was removed from nonozonated water (the difference was statistically significant at 5 percent level). The removal of TOC via ozonation increased with ozone dose and appeared to reach a plateau

at a dose of approximately 1 mg/mg C. Ozonation at doses of less than 1 mg/mg C did not result in an increase in the production of BDOC. Ozonation at a dose of 2 mg/mg C resulted in an increase in the production of BDOC, which was removed by the following FBT. The removal of TOC after ozonation and FBT reached a maximum of 50 percent at an ozone dose of 2 mg/mg C, with approximately 20 percent of that being removed via FBT.

As can be seen in Figure 4.7, FBT alone resulted in an approximately 16 percent reduction of UV-254 in the raw water. However, when ozone was applied, the removal of the UV-254 occurred mostly through ozonation rather than the FBT. This is not surprising considering the fact that ozone is especially effective towards the oxidation of UV254-absorbing organics, i.e. the aromatic fraction of NOM (Masten, 1991). The removal of UV-254 during ozonation increased with ozone dose. Ozonation with an ozone dose of 1 mg/mg C resulted in the removal of 65 percent of UV-254. An increase in an ozone dose to 2 mg/mg C contributed only an additional 10 percent to UV-254 removal. Only slight removal of UV-254 was observed after the FBT of ozonated water.

The HS concentrations decreased with an increase in ozone dose. The FBT, as expected, did not affect HS concentration. Figure 4.8 shows that the most noticeable changes in HS concentrations occurred when ozone dose increased to 1 mg/mg C, with only minor changes occurring with an increase in ozone dose from 1 to 2 mg/mg C. This correlates very well with the UV-254 trends.

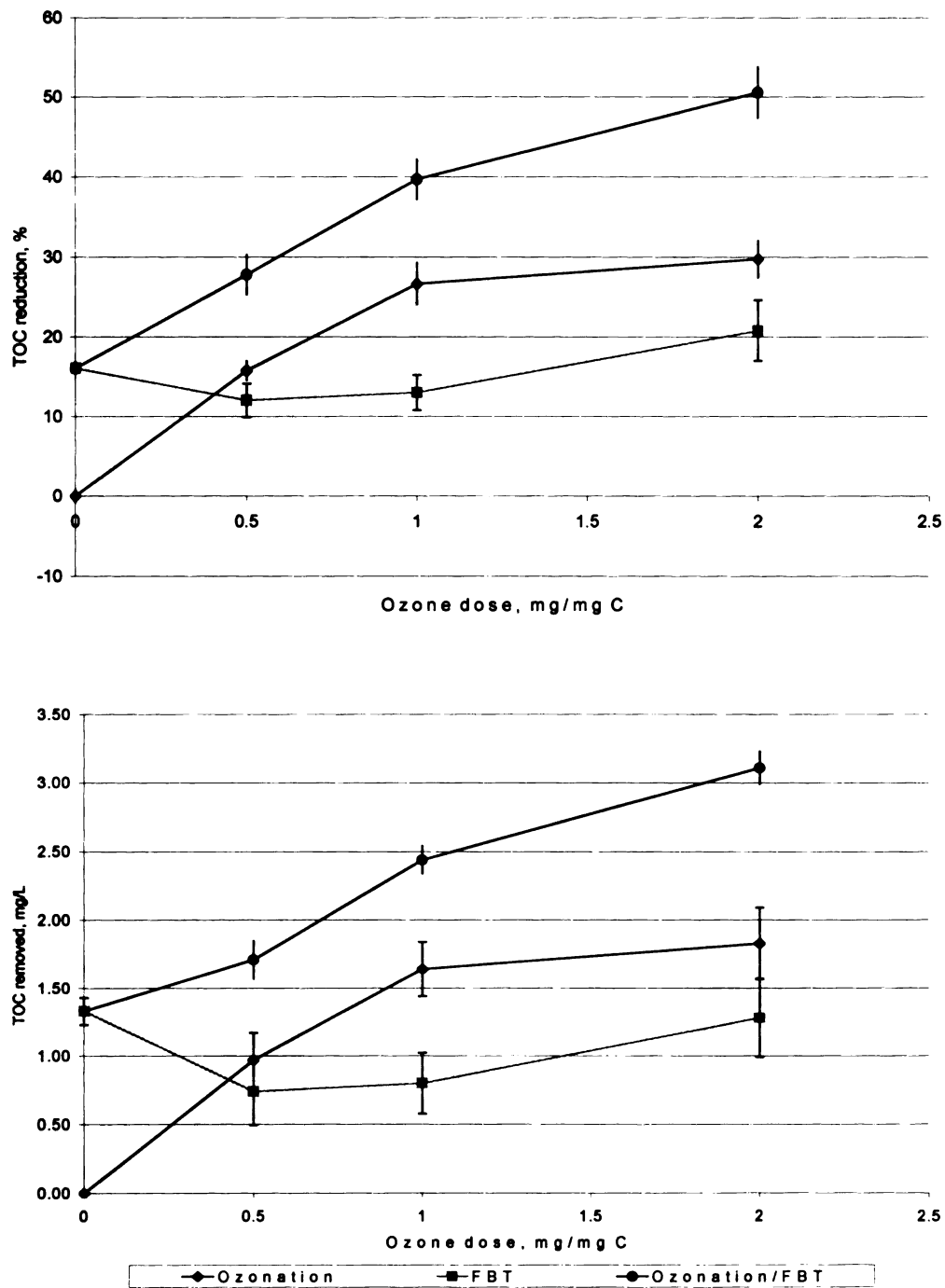


Figure 4.6. Effect of ozone dose on the removal of TOC after ozonation and FBT

(EBCT = 180 min, RT in ozone contactor = 100 min, liquid flow = 10 mL/min, gas flow 15 mL/min)

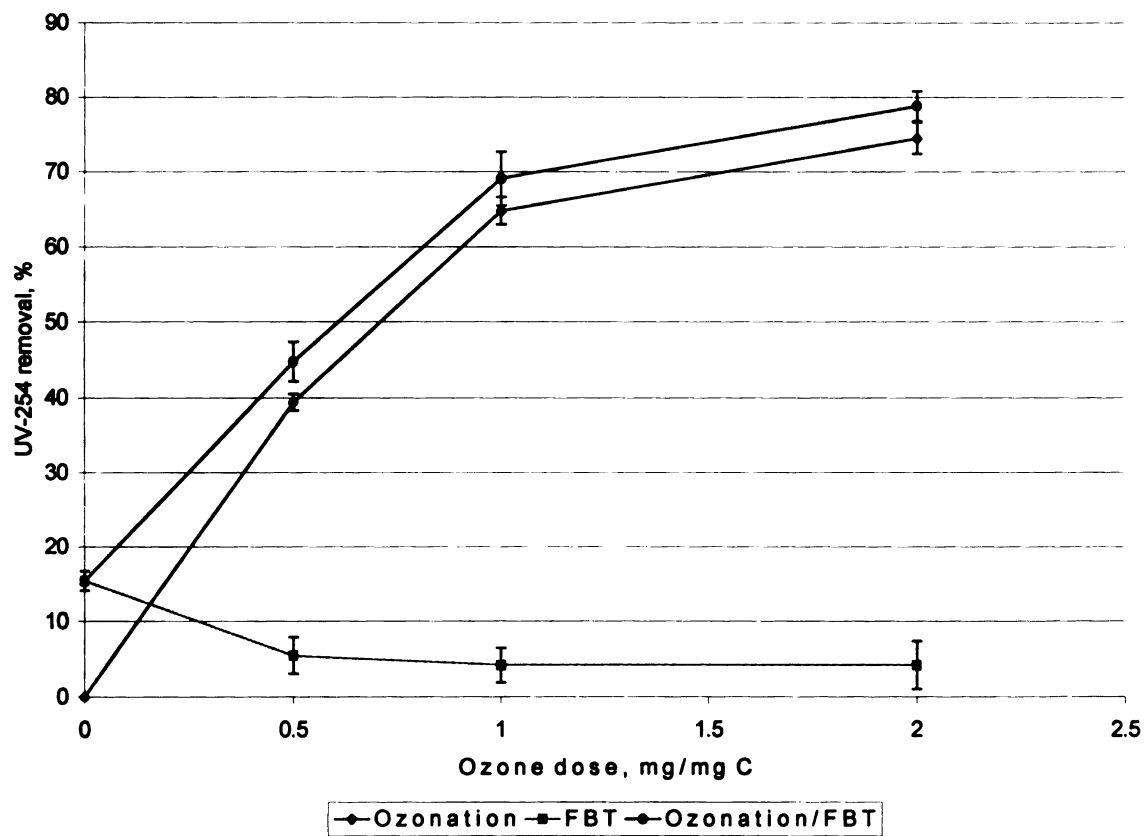


Figure 4.7. Effect of ozone dose on the removal of UV-254 after ozonation and FBT
(EBCT = 180 min, RT in ozone contactor = 100 min, liquid flow = 10 mL/min, gas flow 15 mL/min)

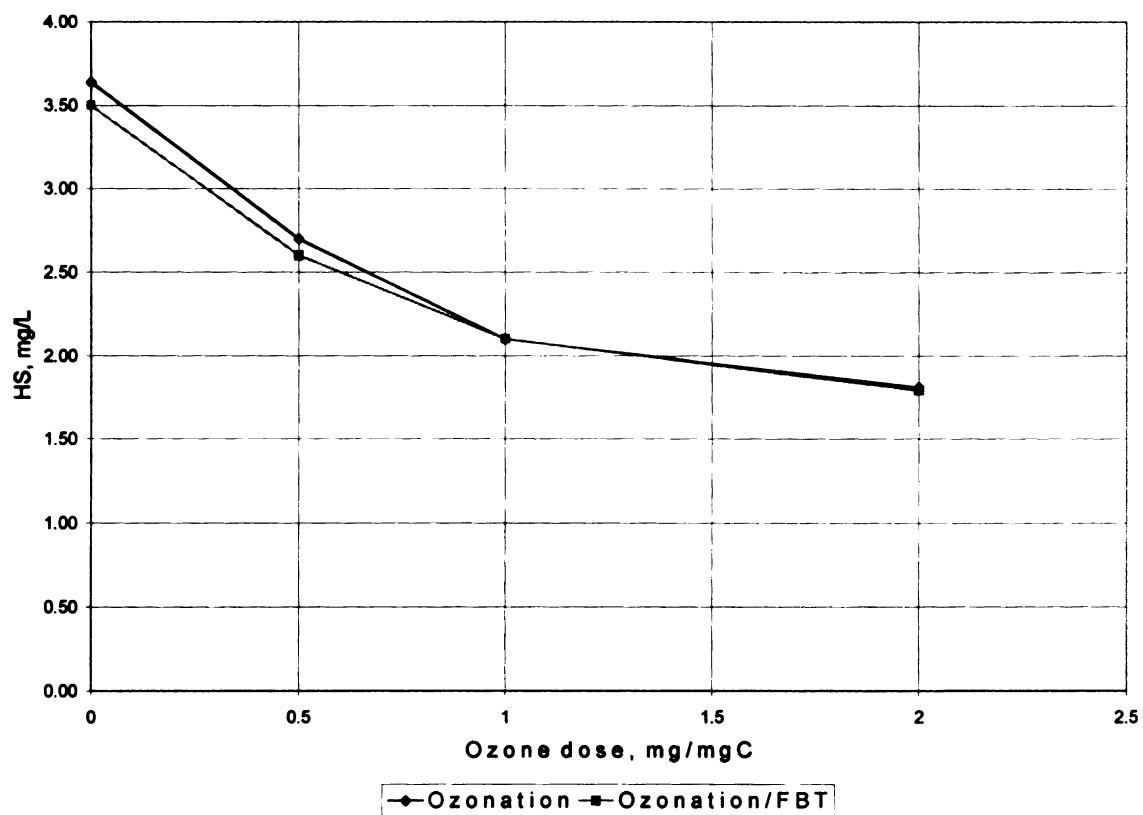


Figure 4.8. Effect of ozone dose on the removal of HS after ozonation and FBT

(EBCT = 180 min, RT in ozone contactor = 100 min, liquid flow = 10 mL/min, gas flow 15 mL/min)

4.4. FRACTIONATION OF NOM BY ULTRAFILTRATION

The results of the experiments described in Section 4.3 showed that under operational conditions studied ozone appeared to oxidize some organic matter that could, otherwise, be degraded biologically. This finding was further explored using fractionation of NOM by ultrafiltration, which provided additional information on the transformation of organic matter during ozonation and FBT.

There have been conflicting reports on the transformation of molecular weight fractions during ozonation. Several investigators observed the destruction of high-molecular weight compounds and a corresponding increase in lower molecular weight compounds upon ozonation (Hongve et al., 1989; Flogstad and Odegaard, 1985; Veenstra et al., 1985), while others saw a reduction of low molecular weight compounds (Amy, Kuo, and Sierka, 1988; Anderson, Johnson, and Christman, 1986). No correlations between these changes and ozone dose was found. This study attempted to reconcile these differences.

The results are described in detail by Mellema (1998). Briefly, Figures 4.9-4.12 show AMW distribution of organic matter in raw water and in water after ozonation and FBT for various ozone doses. The FBT of raw water appears to reduce, to some extent, higher molecular weight organic matter (greater than 1,000 daltons), except for the fraction with a molecular cutoff greater than 30,000 daltons (see Fig. 4.9). The low molecular weight compounds (AMW < 1,000) were only slightly reduced after FBT. This is thought to be because the FBT broke down some higher molecular weight compounds into smaller constituents, thus, contributing to low molecular weight fractions. An

increase in the concentration of organic carbon in the fraction with an AMW of greater than 30,000 daltons has yet to be explained.

As expected, ozonation with an ozone dose of 0.5 mg/mg C resulted in a decrease in the concentration of higher molecular weight organic matter (see Figs. 4.10). However, a corresponding increase in the concentration of organic carbon in lower-molecular weight fractions, which were thought to be potentially biodegradable, was not observed. This suggests that along with higher molecular weight compounds, ozone simultaneously oxidized low molecular weight compounds, thus reducing the amount of substrate available to microorganisms during subsequent FBT. This correlates well with the results of the experiments presented in Section 4.3, which showed a decrease in BDOC concentration after ozonation (see Figure 4.5).

Ozonation with an ozone dose of 1 mg/mg C resulted in further removal of higher molecular weight compounds (see Fig 4.11). Once again, an increase in the concentration of low molecular weight fractions was not observed. Based on the results of earlier experiments (see Fig. 4.10) and the TOC trends (see Fig. 4.6), this already was expected.

Ozonation with an ozone dose of 2 mg/mg C did result in an increase in the concentration of low-molecular-weight organics (see Fig. 4.12). The result correlates well with the data presented in Figure 4.6, which showed an increase in BDOC when ozone dose was increased from 1 to 2 mg/mg C.

As was the case with raw water, the FBT of ozonated water broke down a portion of high molecular weight organic matter (see Figures 4.9-4.11). It should be noted that this partial removal of high molecular weight compounds could not be attributed only to the adsorption of these materials to the biofilm support media. This is because very little

TOC removal in the FBT column was observed during acclimation period (see Figure 4.2).

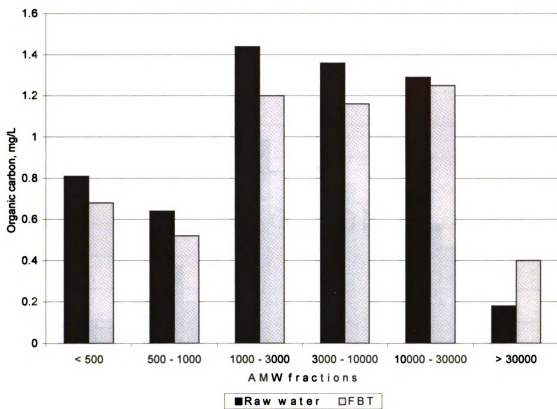


Figure 4.9. AMW distribution after FBT

(EBCT - 180 min)

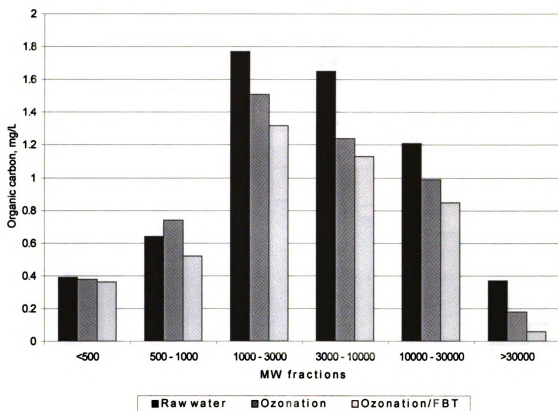


Figure 4.10. AMW distribution after ozonation and FBT
(ozone dose -0.5 mg/mg C, EBCT – 180 min)

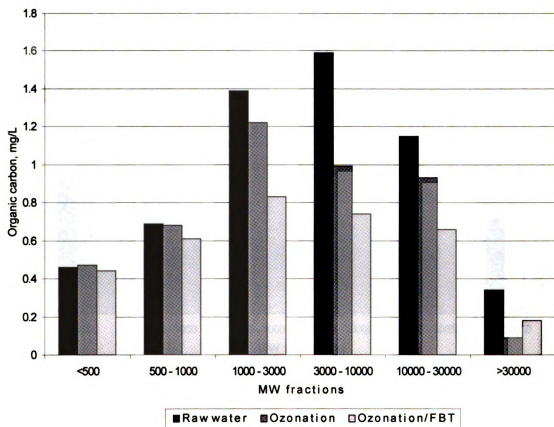


Figure 4.11. AMW distribution after ozonation and FBT
(ozone dose -1 mg/mg C, EBCT – 180 min)

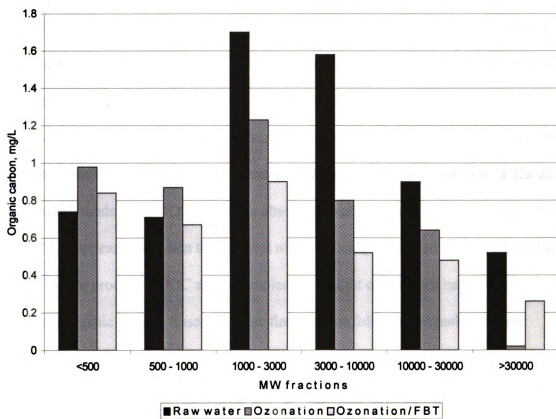


Figure 4.12. AMW distribution after ozonation and FBT
(ozone dose –2 mg/mg C, EBCT – 180 min)

4.5. CONFIRMATION STUDY

The results of the experiments presented in Sections 4.3 and 4.4 showed that TOC removal during ozonation increased with ozone dose and appeared to reach a plateau at a dose of approximately 1 mg/mg C. Ozonation with ozone doses of 0.5 and 1 mg/mg did not appear to result in an increase in the concentration of low molecular weight compounds. A decrease in BDOC concentration was observed. An increase in ozone dose from 1 to 2 mg/mg C did result in an increase in the concentration of both low molecular weight compounds and BDOC. From the observation of the trends shown in Figures 4.6, 4.10-4.12, it appears that when the removal of TOC during ozonation leveled off, ozone was utilized to produce BDOC and low molecular weight compounds rather than to mineralize organic carbon. Based on these findings, the following hypotheses were formulated:

- under the operational conditions studied and for ozone doses greater than 1 mg/mg C, increasing ozone dose would not affect TOC removal;
- under the operational conditions studied and for ozone doses greater than 1 mg/mg C, the production of biodegradable organic matter would increase with ozone dose; and
- under the operational conditions studied and for ozone doses greater than 1 mg/mg C, the concentration of low molecular weight compounds would increase after ozonation.

This section describes the results of the experiments that were conducted under the same conditions as described in Sections 4.3 and 4.4 with the exception that ozone dose was varied from 0 to 7 mg/mg C. Although ozone doses greater than 2 mg/mg C are not practical from economic standpoint, this experimental design was used to verify hypotheses described above.

As can be seen in Figures 4.13 and 4.14, the trends for TOC and UV-254 were remarkably similar to those obtained earlier (see Figures 4.6 and 4.7). Ozonation could potentially remove approximately 23% of organic carbon (see Fig. 4.13). As expected, this also resulted in the oxidation of some potentially biodegradable organic matter. The removal of TOC increased with ozone dose and reached a plateau at a dose of 1 mg/mg C, which agreed with our previous findings. Further increases in ozone dose resulted in an increased production of BDOC, which reached nearly 40 percent at an ozone dose of 7 mg/mg C.

Figure 4.14 shows that ozonation was able to remove up to 80 percent of UV254-absorbing compounds at an ozone dose of approximately 2 mg/mg C. Further removal of UV-254 was difficult to achieve even at higher ozone doses.

Figure 4.15 shows AMW distribution after ozonation and FBT for an ozone dose of 7 mg/mg C. As expected, ozonation resulted in a decrease in higher molecular weight compounds and in a dramatic increase in the concentration of low molecular weight organic matter. The FBT resulted in significant removal of both low and high molecular weight compounds.

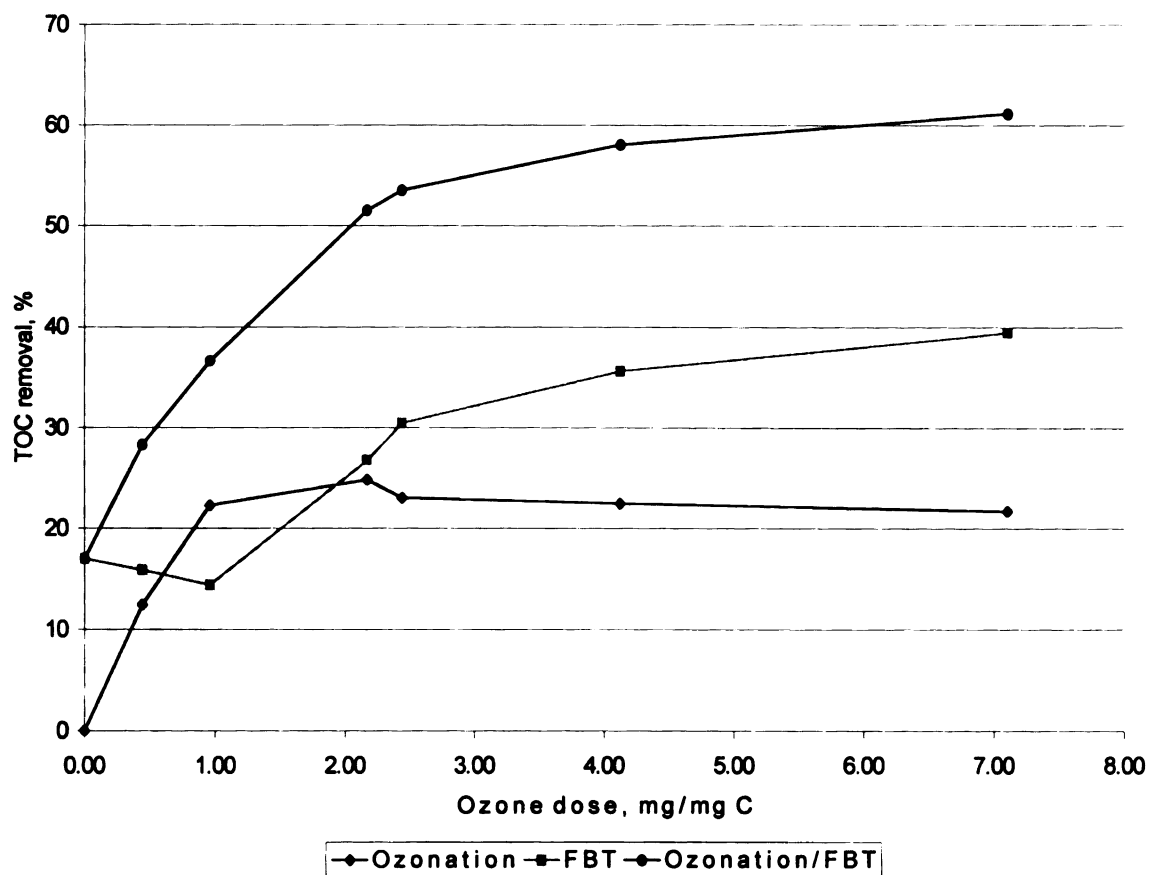


Figure 4.13. Effect of ozone dose on the removal of TOC after ozonation and FBT
(EBCT = 180 min, RT in ozone contactor = 100 min, liquid flow = 10 mL/min, gas flow 15 mL/min)

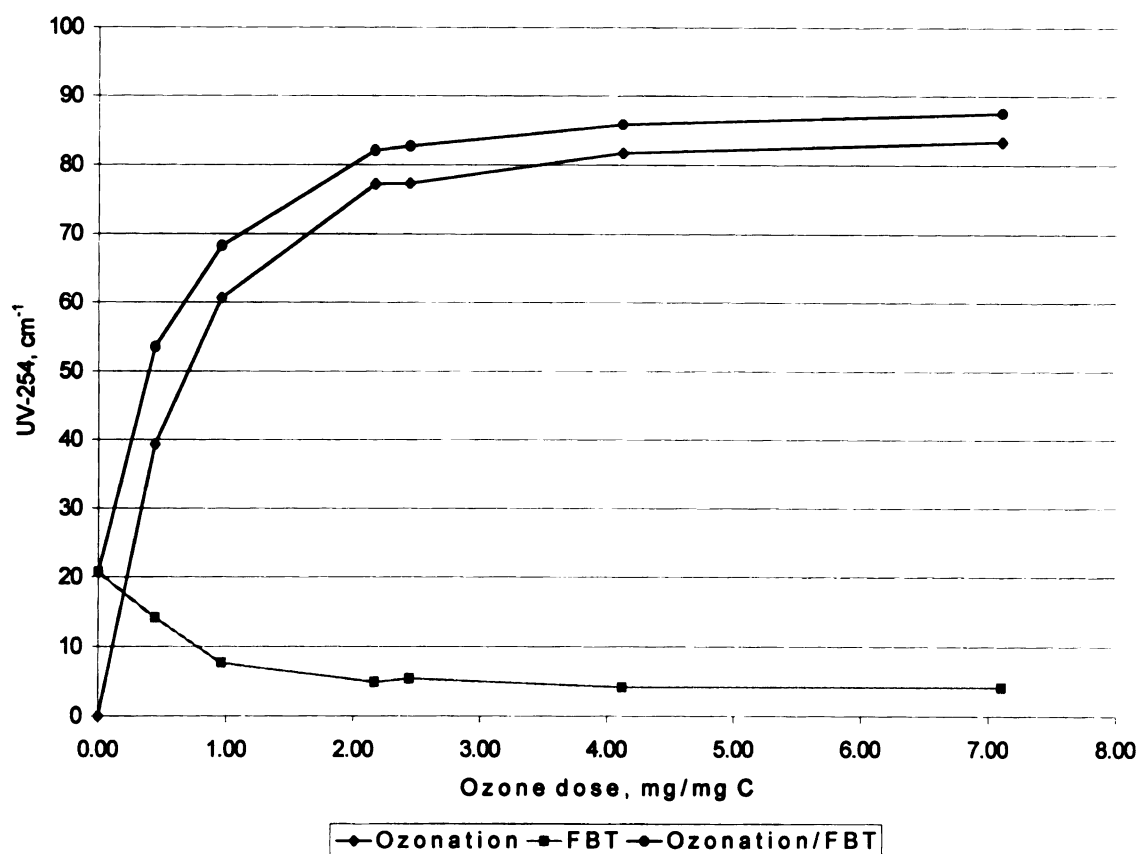


Figure 4.14. Effect of ozone dose on the removal of UV-254 after ozonation and FBT
(EBCT = 180 min, RT in ozone contactor = 100 min, liquid flow = 10 mL/min, gas flow 15 mL/min)

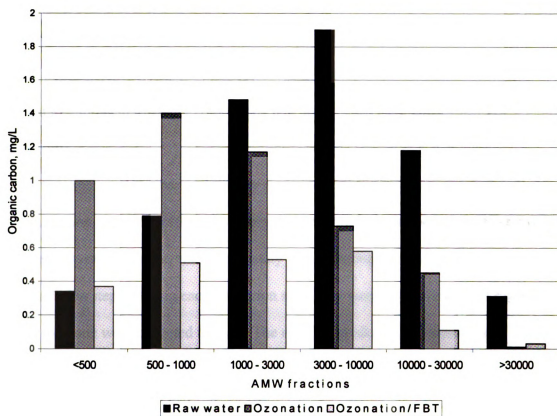


Figure 4.15. AMW distribution after ozonation and FBT
(ozone dose -7 mg/mg C, EBCT – 180 min)

4.6. OZONATION/FBT WITH RECYCLE

The results of the study presented in the previous sections showed that, under operational conditions studied, ozone was utilized inefficiently in the ozonation/FBT system: ozone broke down higher molecular weight compounds and simultaneously oxidized low molecular weight compounds that could, otherwise, be degraded biologically.

This section describes preliminary evaluation of the recycle mode of operation in which a portion of system effluent was recycled back to the ozonation step. By recycling a portion of system effluent, water alternately passed through ozonation and biodegradation steps. During each ozonation step, only those compounds with highest affinity to ozone were expected to react. The reaction products and nonreacted compounds would pass to the biodegradation step, which would remove biodegradable portion of organic matter. Nonbiodegradable organic materials would be recycled back to the ozonation step for further ozonation. In this way, ozonation was expected to degrade only those compounds that were not biodegradable. This approach was successfully utilized for the treatment of bleaching effluents in pulp and paper industry, which resulted in increased biodegradation efficiency relative to the amount of ozone consumed (Heinzle, Fahmy, and Kut, 1992).

The experimental results for the ozonation/FBT process with recycle at a recycle ratio (recycle flow to influent flow ratio) and an ozone dose of 1 mg/mg C are presented in Table 4.2. As was shown in the previous sections, at an ozone dose of 1 mg/mg C the lowest level of BDOC concentration was achieved after ozonation, which is thought to

be because of the mineralization of organic carbon during ozonation. The results for single-pass ozonation/FBT process using the same raw water are given for comparison.

Table 4.2. Comparison of recycle and single-pass modes of ozonation/FBT operation

Parameter	Raw water	Single-pass ozonation/FBT	Ozonation/FBT with recycle
TOC, mg/L	5.96±0.23	3.67±0.07	3.49±0.03
Turbidity, NTU	1.17±0.13	0.62±0.06	0.40±0.07
UV-254, cm ⁻¹	0.163±0.002	0.049±0.001	0.048±0.001
THMFP, µg/L	425±15	120±34	75

The recycle mode of operation resulted in a slight increase in the removal of TOC and UV-254 compared to the single-pass mode. The effect was more noticeable for turbidity. Due to the malfunction of the gas chromatograph, only one data point was obtained THMFP and it was not possible to determine if the difference was statistically significant.

Although the recycle mode of operation appears to result in a greater removal of organic matter and THM precursors than did the single-pass process, the effect was less than expected. This is thought to be because of slow biodegradation of organic matter.

4.7. SUMMARY

The study presented in this chapter confirmed the hypothesis that the efficiency of the combined ozonation/FBT process increased with ozone dose. The FBT efficiency however, appeared to decrease when ozone dose increased from 0 to 1 mg/mg C. Further increase in ozone dose did result in an increased FBT efficiency. This is thought to be because along with breaking down high molecular weight compounds, ozone oxidized some low molecular weight, potentially biodegradable, organic matter. Fractionation of NOM by ultrafiltration confirmed this finding. The study also showed that FBT was able to break down some high molecular weight compounds into smaller constituents.

The results of the experiments partially explained conflicting information reported in different sources on the effect of ozone doses on production of biodegradable organic matter and low molecular weight organic compounds. It appears that when ozonation is conducted under conditions that encourage the mineralization of organic carbon, a decrease in the concentration of BDOC and low molecular weight organic compounds may occur. When no TOC removal is observed during ozonation, an increase in ozone dose is likely to result in an increased production of biodegradable organic matter and low molecular weight organic compounds. The operating conditions that affect the mineralization of organic matter are investigated in Chapter 6.

The study presented in this chapter demonstrated a good potential of the ozonation/FBT process to control THM precursors in drinking water. At an EBCT of 180 minutes and an ozone dose of up to 2 mg/mg C, the process was able to remove up to 50 percent of TOC and humic substances, up to 80 percent of UV-254, up to 70 percent of

THMFP, and up to 80 percent of turbidity. The pH and alkalinity did not significantly change during the treatment. The removal of TOC was comparable to that achieved at Ann Arbor Water Treatment plant (Scadsen, 1997), which included softening, flocculation/sedimentation, ozonation, and activated carbon adsorption. Although the recycle mode of operation resulted in increased process efficiency, the effect was less than expected.

5. SURROGATE CHARACTERIZATION OF NOM

5.1. INTRODUCTION

The parameters that were used to evaluate the transformation of NOM during ozonation and FBT included TOC, UV-254, humic substances and THMFP (see Chapter 4). Table 5.1 presents major characteristics of these parameters. (They were described in more detail in Chapter 2.)

Table 5.1. Characteristics of surrogate parameters

Parameter	Characteristics	Ease of measurement
TOC	Collective measure of NOM present in water	easy to measure; can be measured in-line
UV - 254	characterizes the aromatic portion of NOM	easy to measure; can be measured in-line
HS	heterogeneous organic materials that include most of the naturally occurring organic matter in water; precursors for THMs	difficult to measure
THMFP	potential of water to produce THMs on chlorination; any treatment process must be evaluated on the basis of how effectively it can reduce THMFP	difficult to measure

The humic substance and THMFP analyses were laborious and time-consuming and only four to six samples per week could be analyzed. This would limit the progress of the study. Therefore, it was important, at that early stage of the project, to establish the relationships between TOC, UV-254, HS, and THMFP, which could be used to substitute

one parameter for the others during further investigation of the ozonation and FBT processes. The objectives of the study presented in this chapter were:

- to test the hypothesis that there exists a correlation between TOC and UV-254; the relationships between these parameters may, however, be different for ozonation, FBT, or combined ozonation/FBT effluents;
- to test the hypothesis that there exists a correlation between UV-254 and HS and this correlation does not vary for waters at different treatment stages;
- to test the hypothesis that there exists a correlation between TOC and THMFP and, if so, to determine if this correlation varies for waters at different treatment stages;
- to test the hypothesis that there exists a correlation between UV-254 and THMFP and, if so, to determine if this correlation varies for waters at different treatment stages;
- to determine if the relationships between surrogate parameters are functions of ozone dose.

The experimental data used to develop the correlations between surrogate parameters were generated from the pilot-scale ozonation/FBT system for ozone doses ranging from 0 to 2 mg/mg C and an EBCT of 30 and 180 minutes. In the experiment using FBT alone, the EBCT was varied from 15 to 360 min. The experiments were conducted at room temperature. All experimental data generated during the period from November 1996 to July 1997 were included in the analysis except for four data points which appeared to be in error or because the paired datum was not obtained in the same day.

5.2. UV-254 AND TOC

An important characteristic of the raw water quality observed during the period when the data were generated was seasonal variations in TOC and UV-254. Figure 5.1 shows that TOC and UV-254 were relatively constant during the fall-winter period and increased rapidly in the spring, which was probably the result of runoff from snowmelt. The peak of TOC was approximately 6.9 mg/L in May and then decreased in summer period.

Figures 5.2-5.4 show the relationships between TOC concentration and UV-254 for ozonated water, water treated by FBT alone, and water treated by combined ozonation and FBT, respectively. Equations representing the least-square linear fit through the data are included in each plot. Visual evaluation of the quality of fit between the data and the straight lines and the values of the correlation coefficients, r^2 , show that there exist good correlations between TOC concentration and UV-254 for each treatment stage. The slope of the correlation lines was, however, different, for different treatments. The slope was the lowest for the ozonation and the greatest for the FBT, with the slope for the ozonation/FBT being in the middle. This was not surprising considering the fact that ozonation had greater effect on the removal of UV254-absorbing compounds rather than on the removal of organic carbon, whereas biotreatment appears to be more effective towards the removal of nonaromatic (nonUV-254 absorbing) portion of organic matter. The results, thus, confirmed the hypothesis that although there exists good linear correlations between UV-254 and TOC concentration, the relationships were different for

waters at different treatment stages. Therefore, it does not appear that either of these parameters can be substituted for the other when evaluating various treatment strategies.

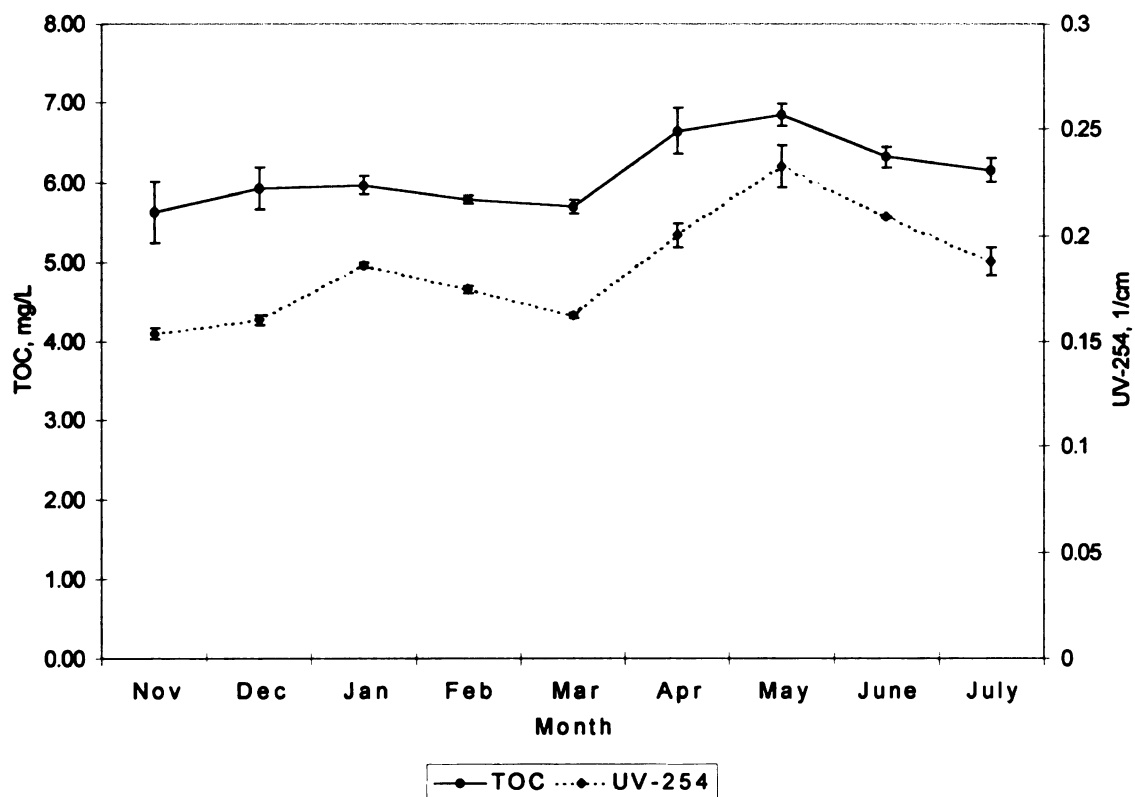


Figure 5.1. Seasonal variations of TOC and UV-254 in Huron River

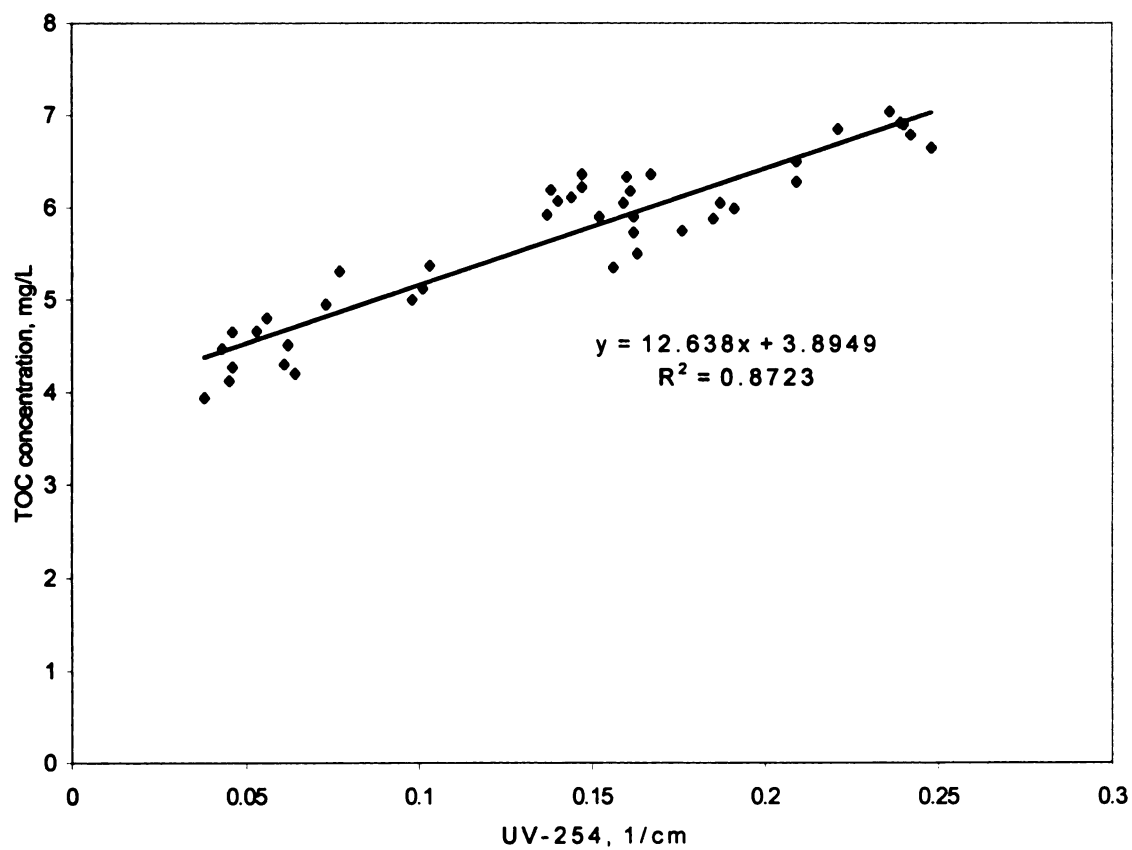


Figure 5.2. Correlation between TOC concentration and UV-254 for ozonated water (ozone dose – 0-2 mg/mg C)

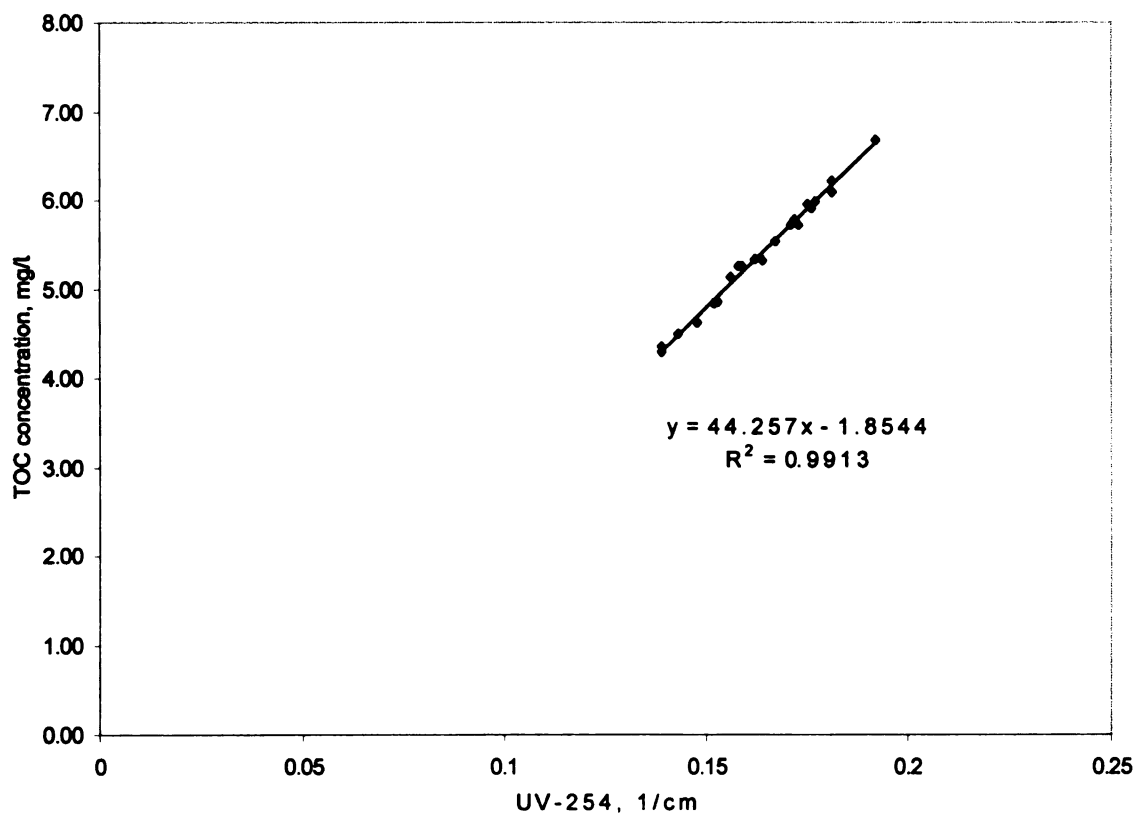


Figure 5.3. Correlation between TOC concentration and UV-254 for biotreated water
(EBCT – 15-360 min)

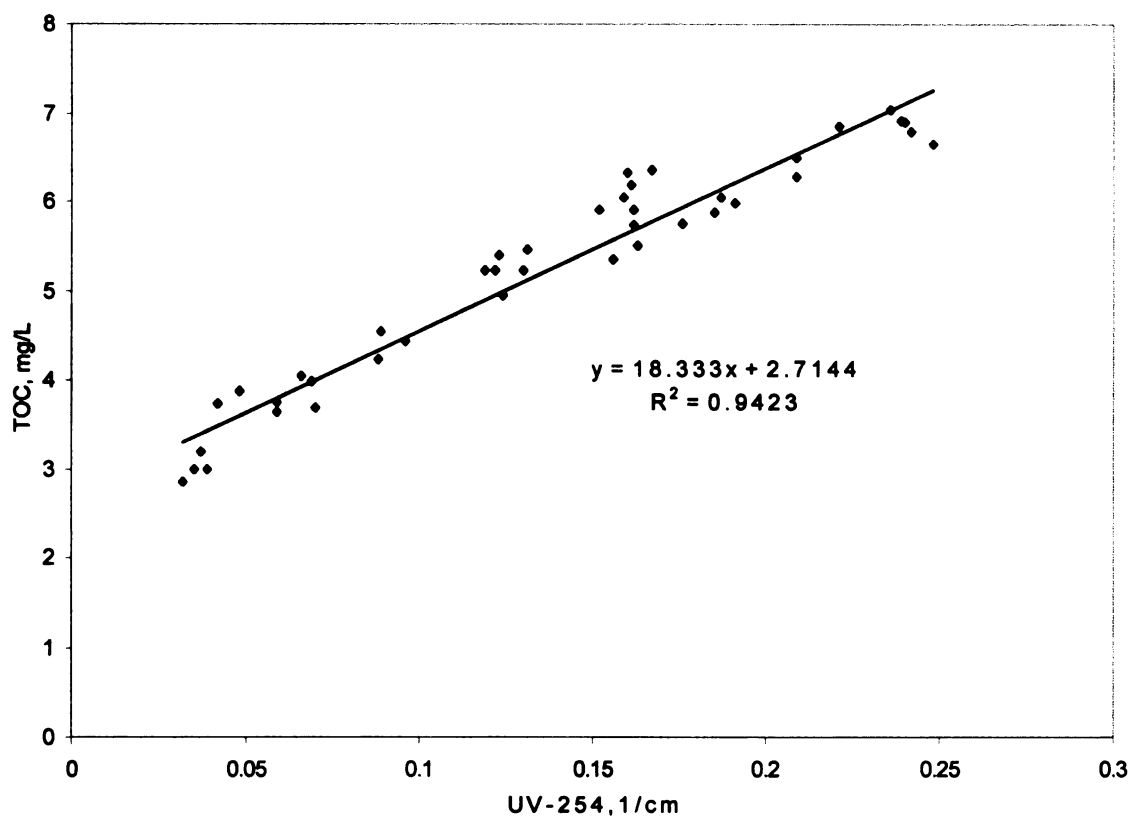


Figure 5.4. Correlation between TOC concentration and UV-254 for ozonated and biotreated water (ozone dose 1-2 mg/mg C, EBCT – 180 min)

An attempt was made to determine if the relationships between TOC concentration and UV-254 were functions of ozone dose. This was done by plotting average TOC concentration versus average UV-254 for each ozone dose. Figure 5.5 shows the correlations between average TOC concentrations and average UV-254 for ozonation and ozonation/FBT effluents. The ozone-dose averaging technique produced good linear correlations between TOC concentration and UV-254 despite the fact that the data had relatively high standard deviations due to seasonal water quality variations.

From the plots in Figures 5.2, 5.4, and 5.5, ozone-dose averaging of the data did not significantly alter the relationships between TOC concentration and UV-254. The advantage of the technique, however, is in that it links the relationships to ozone dose. For example, by observing the plots in Figure 5.5 one can conclude that most significant changes in TOC concentration and UV-254 occurred when ozone dose increased from 0 to 1 mg/mg C. An increase in ozone dose to 2 mg/mg C did not result in a significant removal of either TOC concentration or UV-254.

It is worth to note that, an exponential relationship appears to better describe the relationship between TOC and UV-254 (see Figure 5.6). Additional studies would be, however, required to confirm this. This was beyond the scope of this study, since it did not appear that TOC-UV relationships could be used for the evaluation of the ozonation and biodegradation processes.

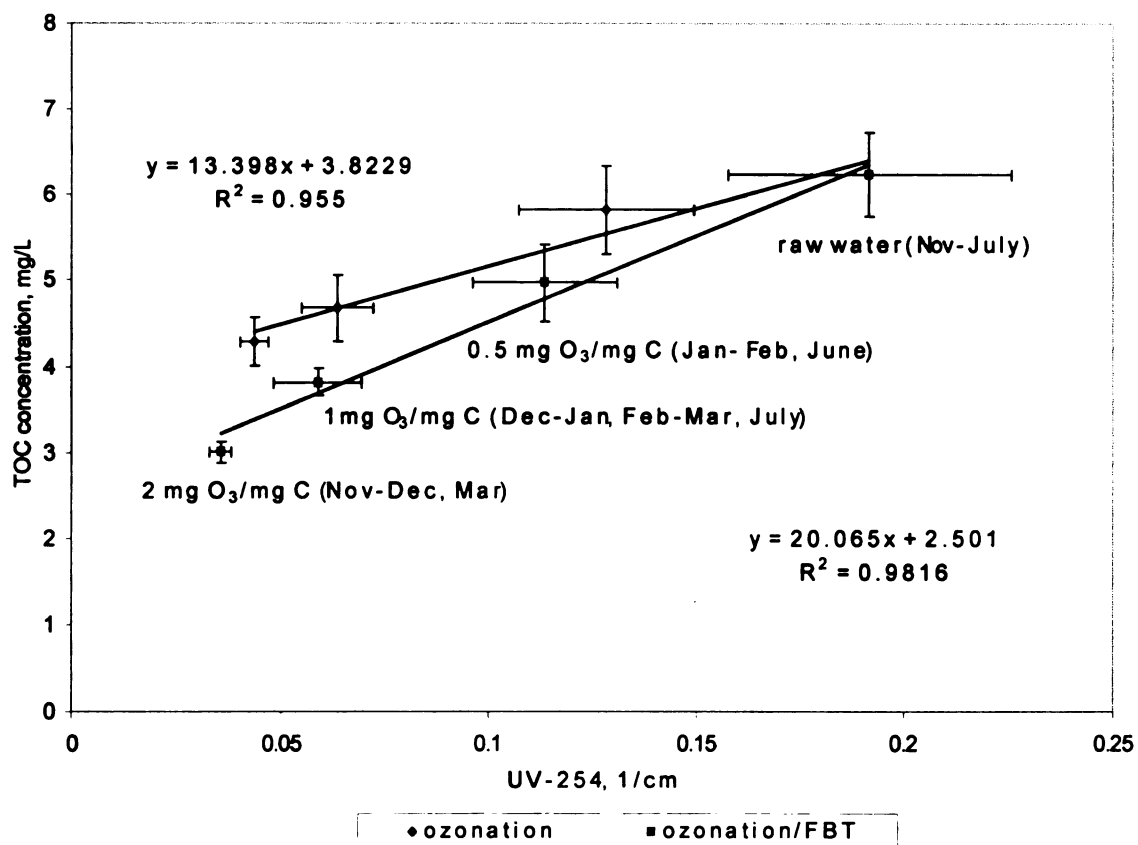


Figure 5.5. Ozone-dose averaging linear correlation between TOC and UV-254

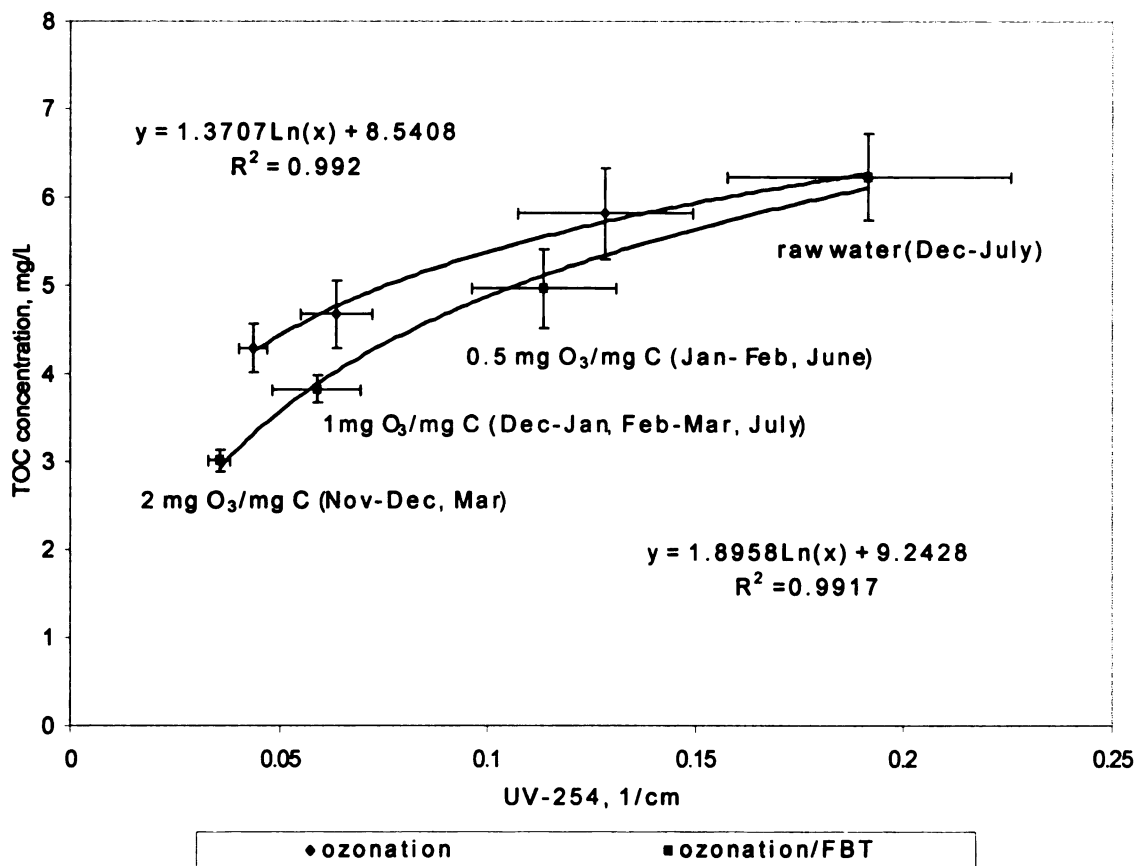


Figure 5.6. Exponential relationship between TOC and UV-254

5.3. HS AND UV-254

In order to establish the relationship between HS and UV-254 the data for raw water, ozonated water, and water after ozonation and FBT, were plotted on the same graph, shown in Figure 5.7. Visual observation of the plot suggests that the relationship between HS and UV-254 appears to be the same for waters at different treatment stages. A straight line fitted well all HS and UV-254 data for raw and treated water.

The ozone-dose averaging technique was applied to HS and UV-254 data. Figure 5.8 shows excellent correlation between HS and UV-254 when the average data for each ozone dose were plotted. The relationship was essentially the same as the one that was established in Figure 5.7. The visual observation of the plot in Figure 5.8 shows that most significant changes of HS and UV-254 occurred when ozone dose increased from 0 to 1 mg/mg C. Further increase in ozone dose to 2 mg/mg C did not result in a significant removal of either HS concentration or UV-254.

The results of the study demonstrated that there exists a good UV-254 is a very good linear correlation between HS and UV-254, which did not appear to vary for waters at different treatment stages. The relationship did not appear to be dependent on ozone doses either.

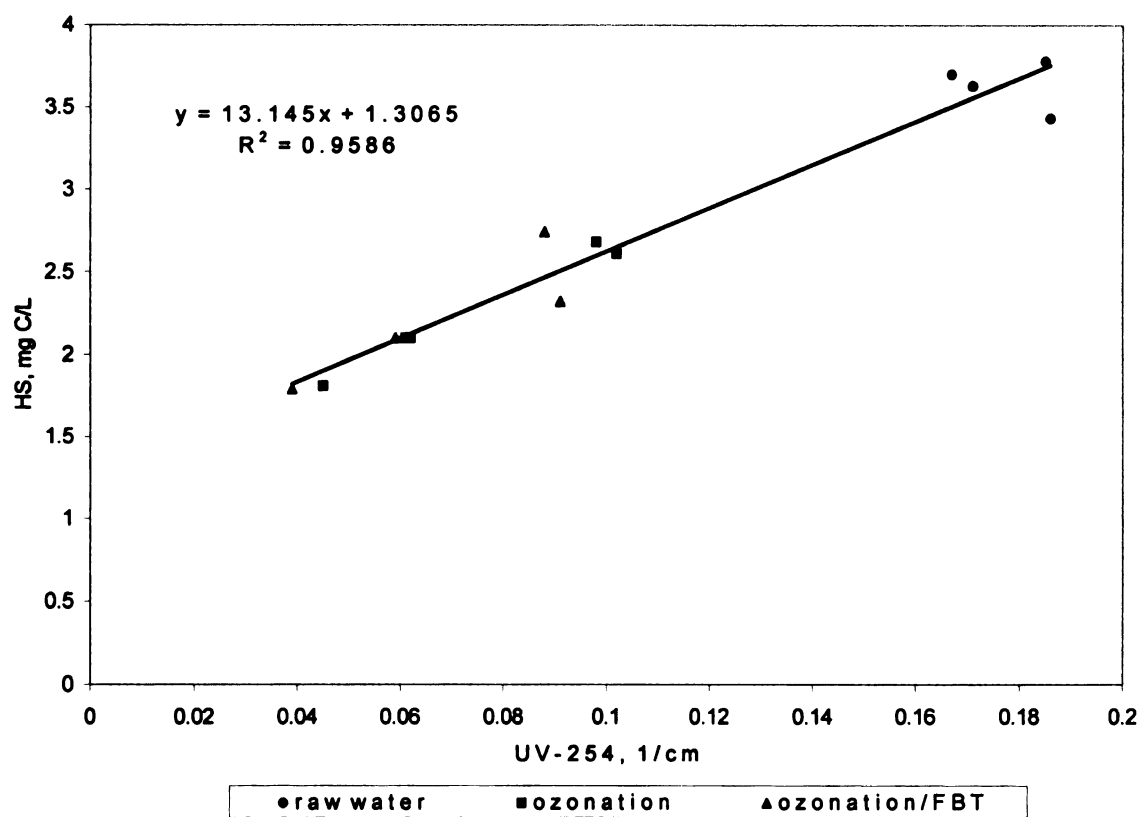


Figure 5.7. HS versus UV-254 (ozone dose – 0.2 mg/mg C, EBCT – 180 min)

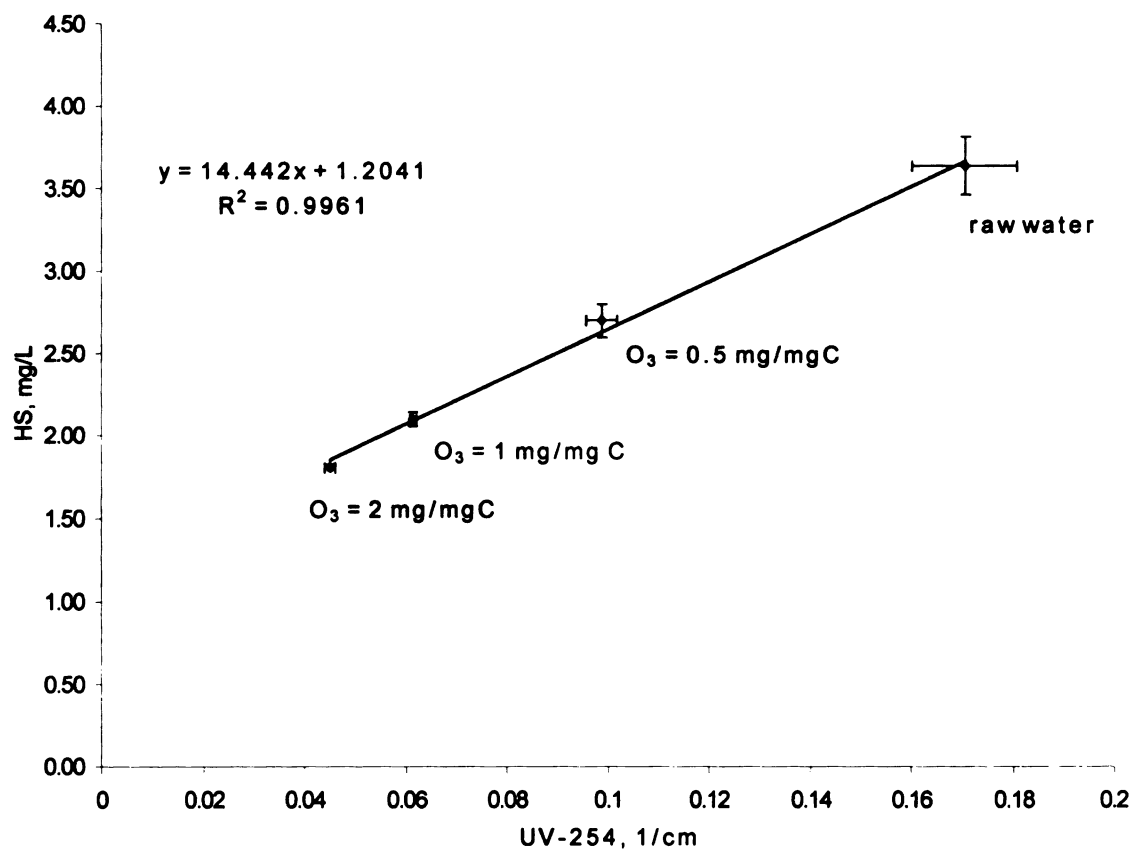


Figure 5.8. Correlation between average HS and UV-254 at each ozone dose

5.4. THMFP AND TOC

The relationship between THMFP and TOC was established using the data for raw water, ozonated water, and water after ozonation and FBT, which were plotted on the same graph. As can be seen in Figure 5.9, there exists an exponential relationship between THMFP and TOC. The relationship appears to be the same for waters at different treatment stages. The plot using average THMFP and UV-254 data categorized by treatment and ozone doses (see Figure 5.10) also suggests that this regression line could be applied for waters at different treatment stages. The averaging approach, presented in Figure 5.10, could also be used to evaluate the effect of ozonation and FBT on the removal of THMFP. For example, the removal of THMFP after ozonation with doses of 1 and 2 mg/mg C was not statistically different from that obtained after ozonation/FBT at an ozone dose of 0.5 mg/mg C. The removal of THMFP after ozonation/FBT at an ozone dose of 1 mg/mg C was greater than that obtained after ozonation with a dose of 2 mg/mg C (the difference was statistically significant at 95% confidence interval). This suggests that the use of ozonation in combination with FBT for the removal of THMFP was more efficient than ozonation alone with respect to ozone consumption.

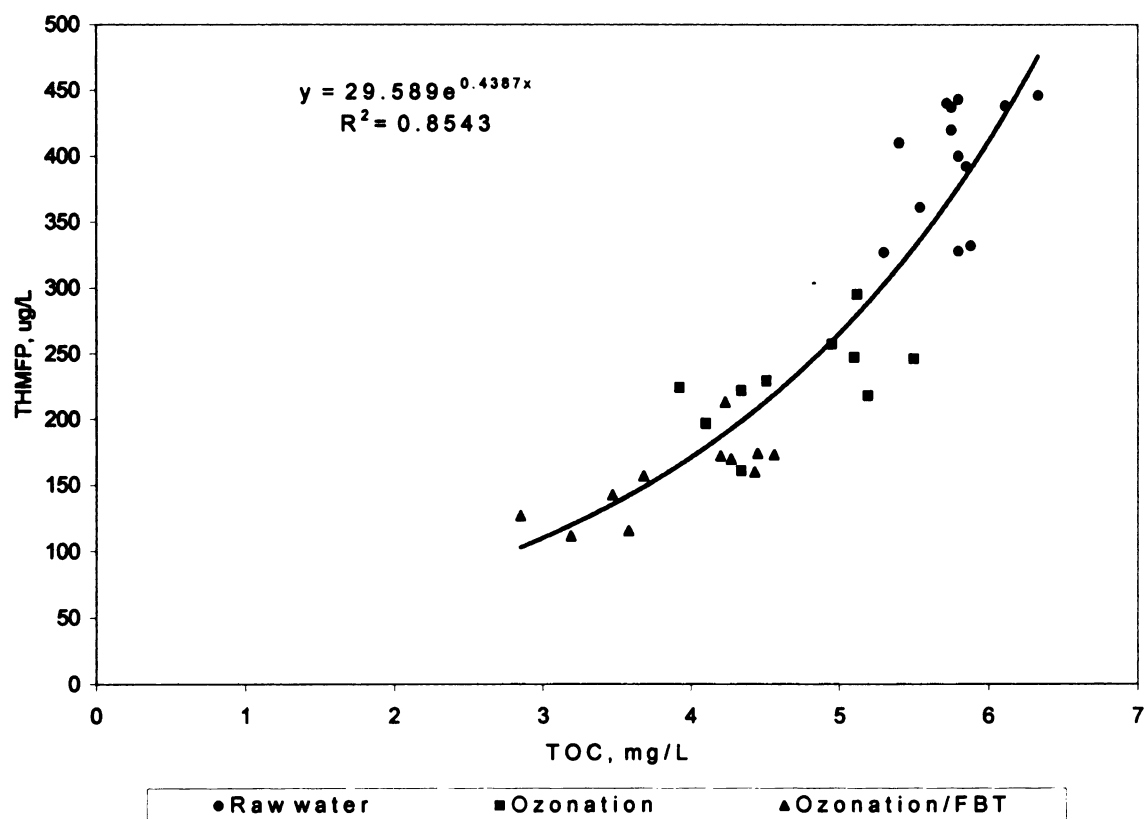


Figure 5.9. THMFP versus TOC concentration
(ozone dose – 0.2 mg/mg C, EBCT = 180 min)

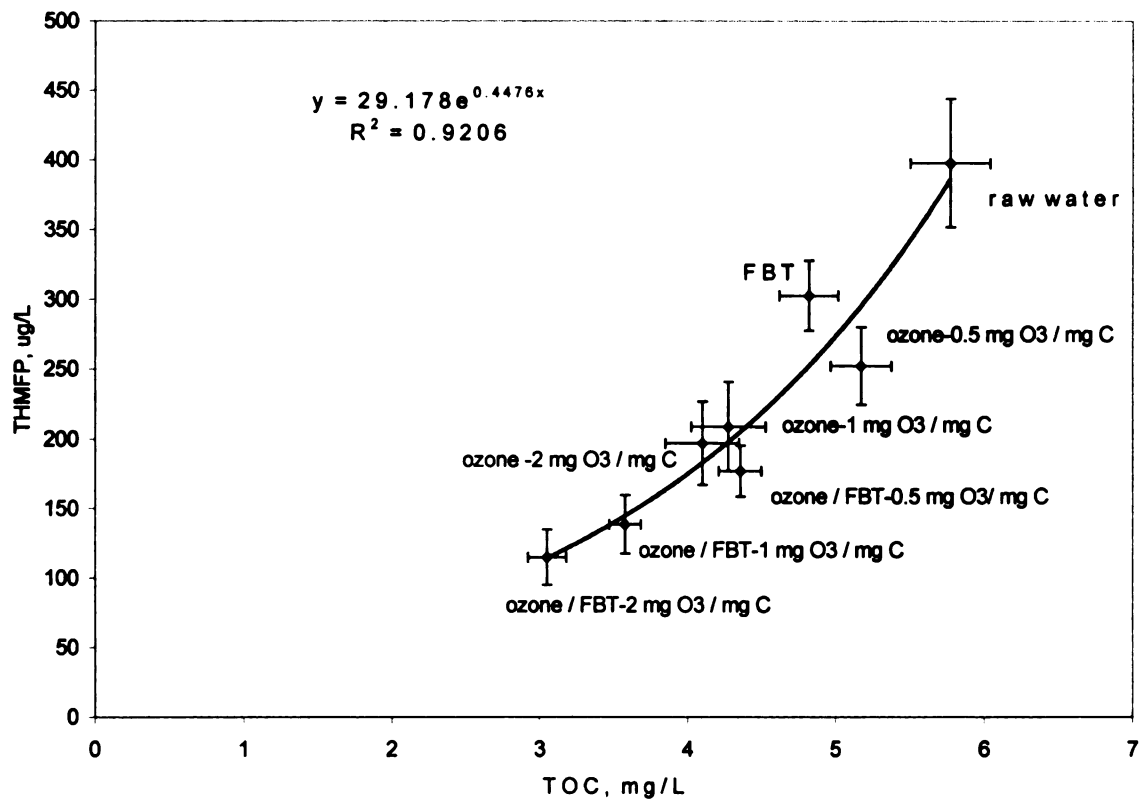


Figure 5.10. Correlation between average THMFP and TOC concentrations

5.5. THMFP AND UV-254

The ozone-dose-averaging approach was used to establish correlations between THMFP and UV-254. As can be seen in Figure 5.13, there exist excellent correlations between THMFP and UV-254 for ozonated water and water after ozonated and FBT, despite high standard deviations for THMFP. The relationships between THMFP and UV-254 are, however, different for different treatment stages, and, therefore, their use could be limited to a specific treatment train.

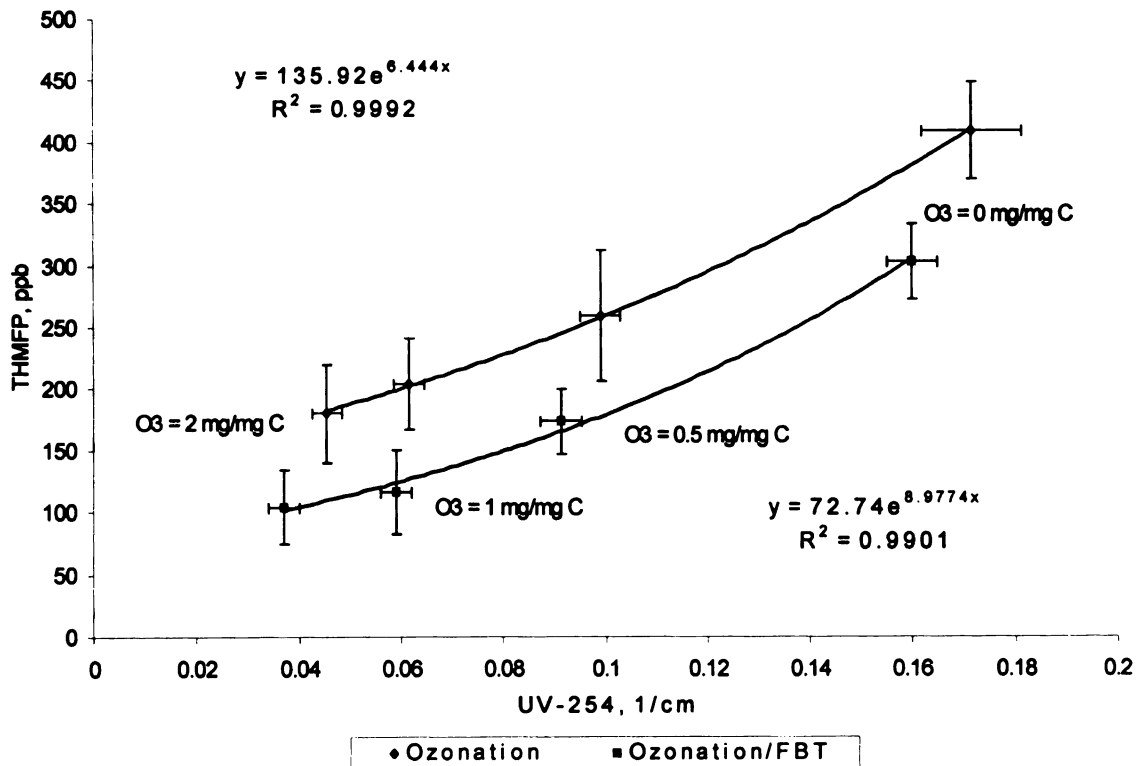


Figure 5.11. Correlation between average THMFP and UV-254
(ozone dose – 0-2 mg/mg C, EBCT = 180 min)

5.6. SUMMARY

The study presented in this chapter confirmed the hypothesis that there exists a correlation between UV-254 and TOC and between UV-254 and THMFP. However, these relationships were different for waters at different treatment stages. For this reason, neither of these parameters could be substituted for the other one when evaluating the ozonation and biodegradation processes.

This study showed that there exists a good linear correlation between HS and UV-254 and between TOC and THMFP, which did not appear to be different for waters at different treatment stages. When investigating ozonation and FBT processes, UV-254 and TOC could be used as surrogates for humic substances and THMFP, respectively.

In addition, the averaging approach was proposed. According to this approach the relationships between average data for each ozone dose were established. It was shown that the relationships so established were useful for the evaluation of the effect of ozone doses on the selected surrogate parameters.

6. OZONATION OF NOM

6.1. INTRODUCTION

This chapter presents the results of the bench-scale study that investigated the ozonation of NOM in Huron River water in more detail. The objectives of the study presented in this chapter were:

- To determine if the removal of organic carbon and UV-absorbing compounds during ozonation is affected by gas flow rate for the same ozone dose;
- To assess the effect of hydraulic retention time on TOC and UV-254 removal;
- To test the hypothesis that, when ozonation is conducted under conditions that do not result in the oxidation of organic carbon, BDOC concentration increases with ozone dose;
- To determine if UV-254 absorbance can be used to measure the specific ozone consumption rate;
- To determine if the specific ozone consumption rate can be used for the evaluation of the efficacy of the ozonation of NOM;
- To determine if humic and nonhumic fractions of NOM can be used to model the kinetics of ozone reactions with NOM; and if so to develop a mathematical model that describes the transformation of humic and nonhumic fractions during ozonation;
- To test the hypothesis that the rate constant of the ozone reaction with humic substances is a function of both temperature and the concentration of humic

substances and can be expressed in two independent terms: a temperature-dependent term and a concentration-dependent term;

- To test the hypothesis that the rate constant of the ozone reaction with nonhumic substances is a function of temperature and the concentration of nonhumic substances and can be expressed in two independent terms: a temperature-dependent term and a concentration-dependent term;
- To determine the kinetic parameters of the ozone reactions with humic and nonhumic substances, including stoichiometric coefficients and activation energies;
- To validate the developed model over a wide range of operational parameters, including ozone dose, temperature, and hydraulic retention time.

It should be noted that since pH and alkalinity did not change significantly during ozonation of Huron River water, the effect of these parameters was not investigated in this study. The study was conducted using the bench-scale ozonation system described in section 3.2.1. The operational parameters that were investigated included gas flow rate, ozone dose, hydraulic retention time, and temperature. The major parameters that were monitored in this study included TOC, UV-254, humic and nonhumic fractions, and BDOC. Biotreated water was obtained from the biofiltration system that was described in Section 3.2.5.

Section 6.2 investigates the effect of operational parameters, including ozone dose, gas flow rate, hydraulic retention and temperature, on the transformation of NOM during ozonation. The kinetic study of the ozone reactions with NOM is presented in Section 6.3. The summary of results is given in Section 6.4.

6.2. EFFECT OF OPERATIONAL PARAMETERS

6.2.1. Effect of Gas Flow Rate on the Oxidation of NOM by Ozone

The goal of these experiments was to determine the appropriate gas flow rate for subsequent ozonation experiments. The experiments were conducted with gas flow rates of 15, 25, and 36 mL/min. The liquid flow rate was 18 mL/min, which corresponded to a hydraulic retention time of 20 min. The ozone dose was varied from 0 to 5 mg/mg C. All experiments were conducted at room temperature.

Figure 6.1 shows the influent gas ozone concentrations that were required to achieve a certain level of ozone dose for given gas flow rates. As expected, the influent gas ozone concentration requirements decreased with an increase in gas flow rate. For example, in order to achieve an ozone dose of 1 mg/mg C, the ozone concentration in the influent gas was approximately 6 mg/L at a gas flow rate of 36 mL/min. To achieve the same ozone dose at a flow rate of 15 mL/min, an influent gas ozone concentration of approximately 14 mg/L was required. Similarly, an ozone dose of 2 mg/mg C required influent gas ozone concentrations of approximately 17 and 31 mg/L at gas flow rates of 36 and 15 mL/min, respectively.

No dissolved ozone was detected at ozone doses less than 0.6 mg/mg C (see Figure 6.2). An increase in ozone dose (by increasing the concentration of ozone in the influent gas) resulted in an increased dissolved ozone concentration. The gas flow rate, however, did not affect the dissolved ozone concentration.

Figure 6.3 shows that no TOC removal occurred at ozone doses less than 0.5 mg/mg C. Further increase in ozone dose did result in partial TOC removal. It did not

appear, however, that the gas flow rate affected TOC removal. This was expected considering the fact that, as was shown earlier, the gas flow rate did not affect dissolved ozone concentration.

Unlike TOC, UV-absorbing compounds were effectively removed at low ozone doses (less than 1 mg/mg C). At ozone doses greater than 2 mg/mg C, no significant removal of UV-254 was observed. The same effect was observed earlier in the pilot-scale studies that were described in Section 4.3. The gas flow rate did not effect the removal of UV-254, because, as was discussed earlier, the gas flow rate did not affect dissolved ozone concentration (see Fig 6.2).

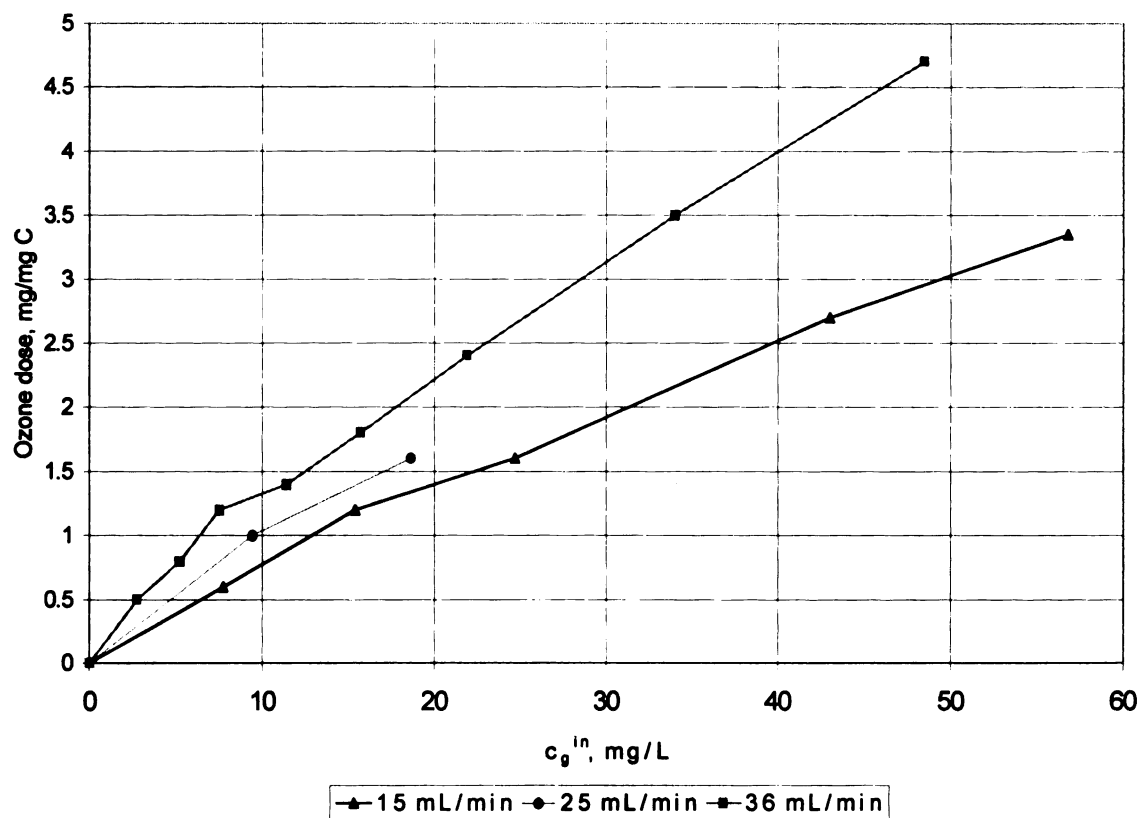


Figure 6.1. c_g^{in} requirements for various gas flow rates
(room temperature, RT = 20 minutes).

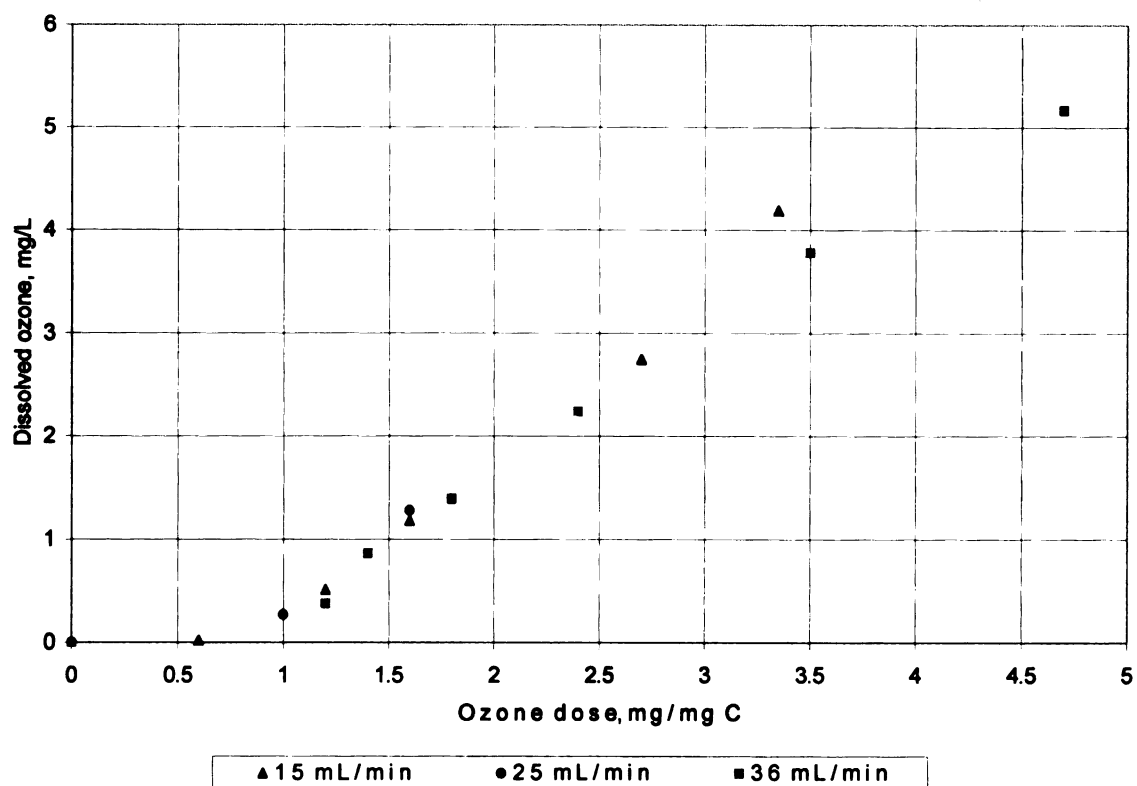


Figure 6.2. Dissolved ozone concentrations for various gas flow rates
(room temperature, RT = 20 minutes).

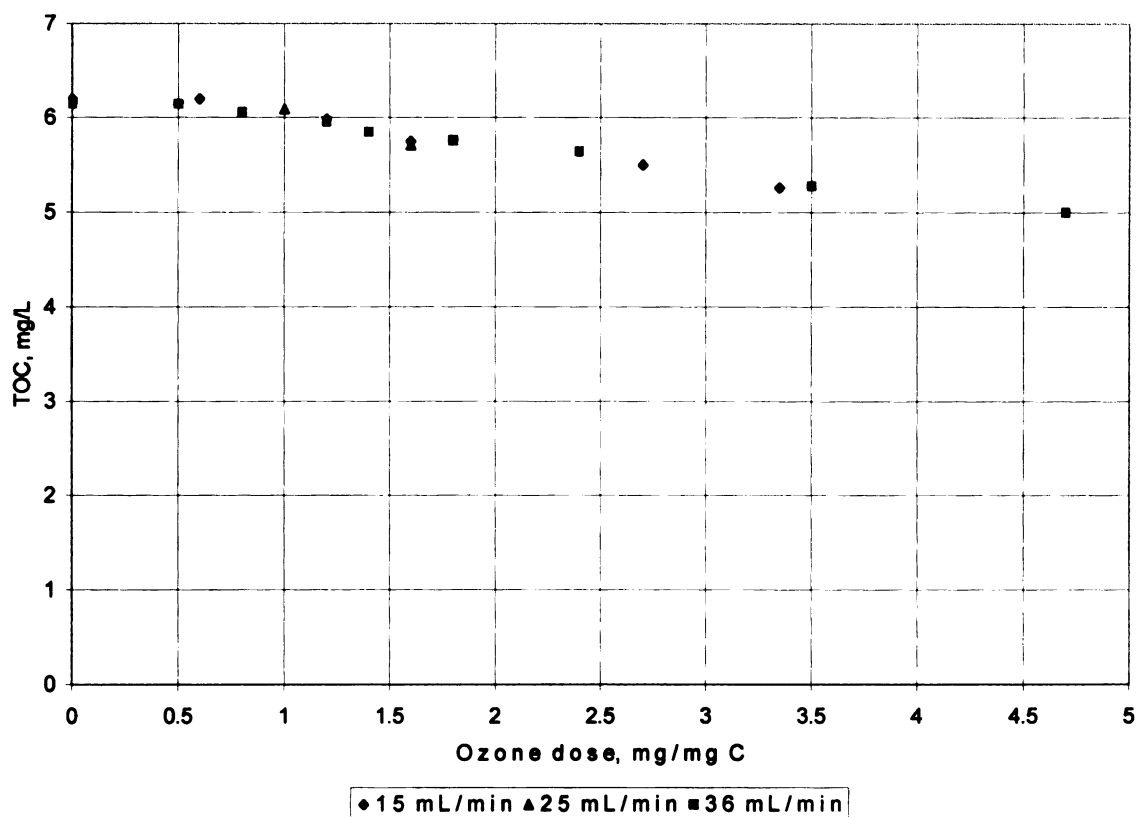


Figure 6.3. Effect of ozone dose on TOC concentration for various gas flow rates (room temperature, RT = 20 minutes).

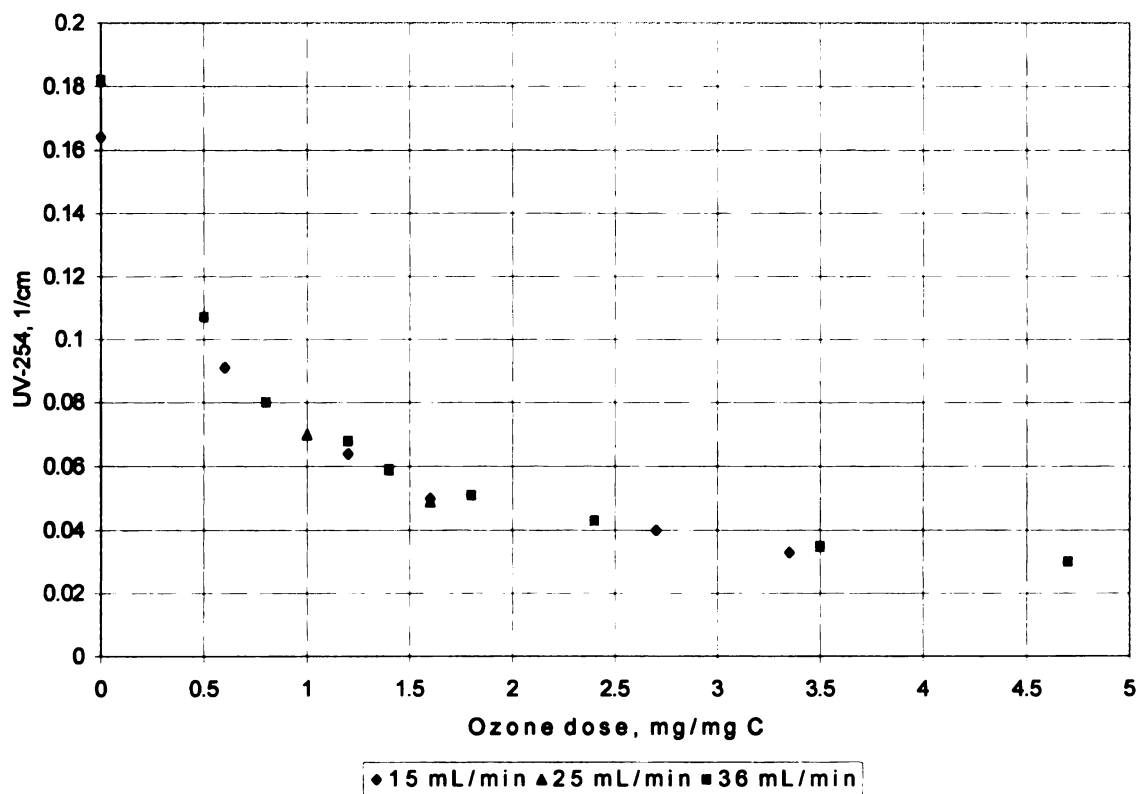


Figure 6.4. Effect of ozone dose on UV-254 absorbance for various gas flow rates (room temperature, RT = 20 minutes).

6.2.2. Effect of Hydraulic Retention Time

The goal of these experiments was to determine the effect of hydraulic retention time (HRT) on TOC and UV-254 during ozonation. The study was conducted using raw water. The HRT was varied from 10 to 60 min. The gas flow rate was 36 mL/min. This high flow rate was selected in order to minimize the retention time of the effluent gas in the reactor headspace. The ozone dose was varied from 0 to 6 mg/mg C. All experiments were conducted at room temperature.

Figure 6.5 shows the effect of HRT and ozone dose on the removal of TOC. At an HRT of 10 minutes and ozone doses less than 0.5 mg/mg C, no TOC removal was observed. With an increase in ozone dose from 0.5 to 3 mg/mg C, the removal of TOC steadily increased. At HRTs of 20, 40 and 60 minutes, the TOC removal was observed at ozone doses less than 0.5 mg/mg C and steadily increased with an increase in ozone dose. As can be seen in Figure 6.5, the removal of TOC increased with HRT. For example, at an ozone dose of 1 mg/mg C and an HRT of 10 minutes, the removal of TOC was not significant at 95% confidence interval. At the same ozone dose and HRTs of 40 and 60 minutes, TOC concentration decreased from 6.2 mg/L for raw water to approximately 5.8 and 5.4 mg/L after ozonation, respectively.

Figure 6.6 once again showed (see also Figure 6.4) that UV-absorbing compounds were effectively removed at low ozone doses (less than 1 mg/mg C). At ozone doses greater than 2 mg/mg C, little removal of UV-254 was observed. The removal of UV-absorbing compounds was not affected by HRT.

An attempt to explain the effect of HRT on the removal of TOC and UV-254 was made. Figure 6.7 shows that the influent gas ozone concentration required to achieve a given ozone dose decreased with an increase in HRT. As a result, the concentration of dissolved ozone for a given ozone dose also decreased with an increase in HRT (see Figure 6.8). The following hypothesis, therefore, could be formulated:

- 1) The removal of TOC decreases with a decrease in the concentration of dissolved ozone; the HRT has, however, a greater effect on TOC removal than does dissolved ozone concentration (as a result, for a given ozone dose, TOC removal increases with an increase in HRT, even though the dissolved ozone concentration decreases).
- 2) The removal of UV-254 is independent of HRT and dissolved ozone concentration.

To verify these hypotheses, the efficacy of ozonation in the bench-scale system was compared to that in the pilot-scale system. The operational conditions of the experiments are shown in Table 6.1. In order to achieve similar HRT in both system, the contact volume in the pilot-scale ozone contactor was reduced by half.

Table 6.1. Experimental conditions of bench- and pilot-scale ozonation systems

Parameter	Bench-scale system	Pilot-scale system
Water flow rate, mL/min	18	20
Gas flow rate, mL/min	15	15
Retention time, min	20	ca. 25
Ozone dose, mg/mg C	0 - 2.7	0 - 2.3
Temperature, °C	20	20

The major difference in the performance of bench-scale and pilot-scale ozone contactors (which actually made it possible to verify the hypothesis stated above) was in the efficiency of ozone utilization, ϵ , that was defined as

$$\epsilon = \frac{c_g^{\text{in}} - c_g^{\text{out}}}{c_g^{\text{in}}} \cdot 100\%$$

where c_g^{in} and c_g^{out} are the concentrations of ozone in influent and effluent gas, mg/L.

Figure 6.9 shows the ozone utilization efficiency in the bench-scale system. The efficiency was approximately 60 percent at an ozone dose of 0.5 mg/mg C and decreased with an increase in ozone dose. Only trace amounts of ozone were detected in the effluent gas from the pilot-scale ozone contactor. So, it was assumed that the efficiency of ozone utilization in the pilot-scale system was 100 percent.

Figure 6.10 shows the influent gas ozone concentrations in the bench- and pilot-scale systems, which were required to achieve a given ozone dose. In order to achieve the same ozone dose, the pilot system required lower ozone concentration in the effluent gas

than did the bench-scale system. As a result, under similar experimental conditions the dissolved ozone concentration was lower in the pilot ozonation system than that in the bench-scale ozonation system, as demonstrated in Figure 6.11.

As can be seen in Figure 6.12, the removal of TOC during ozonation was essentially the same in both systems at ozone doses less than 0.6 mg/mg C. The TOC concentration in the pilot system appears to level off at an ozone dose of 1 mg/mg C, whereas the TOC concentration in the bench system continued to decrease with an increase in ozone dose (the difference in TOC concentrations for raw water and after ozonation at a dose of 1 mg/mg C was statistically significant at 5 percent level). Since the dissolved ozone concentration in the bench-scale system was several times greater than that in the pilot-scale system and all other conditions were essentially the same for both systems, it appears that the removal of TOC increases with dissolved ozone concentration. This also suggests that HRT has greater effect on the removal of TOC than does the concentration of dissolved ozone. This is because the removal of TOC increased with HRT even though dissolved ozone concentration decreased.

Figure 6.13 shows that, for a given ozone dose, the removal of UV254-absorbing substances was essentially the same in the bench- and pilot-scale systems. Since the dissolved ozone concentration in the bench system was several times greater than that in the pilot-scale system, it appears that the removal of UV254-absorbing compounds is independent of ozone concentration. This also confirmed the hypothesis that the removal of UV-254 is independent of HRT for the range of HRTs studied.

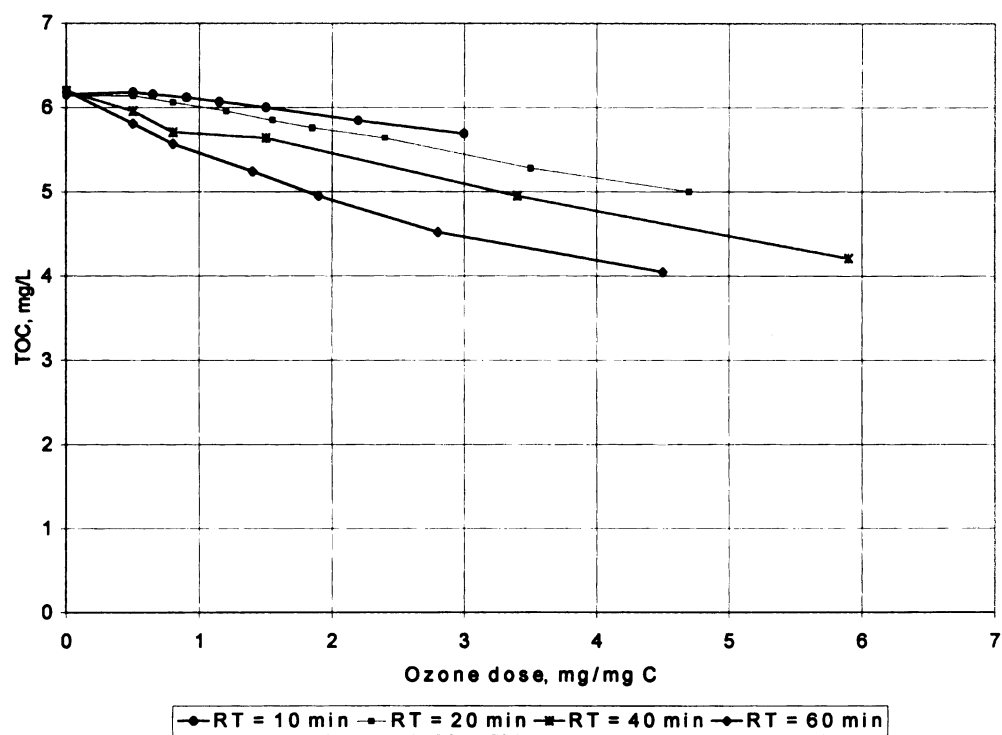


Figure 6.5. Effect of ozone dose on TOC concentration for various HRTs.

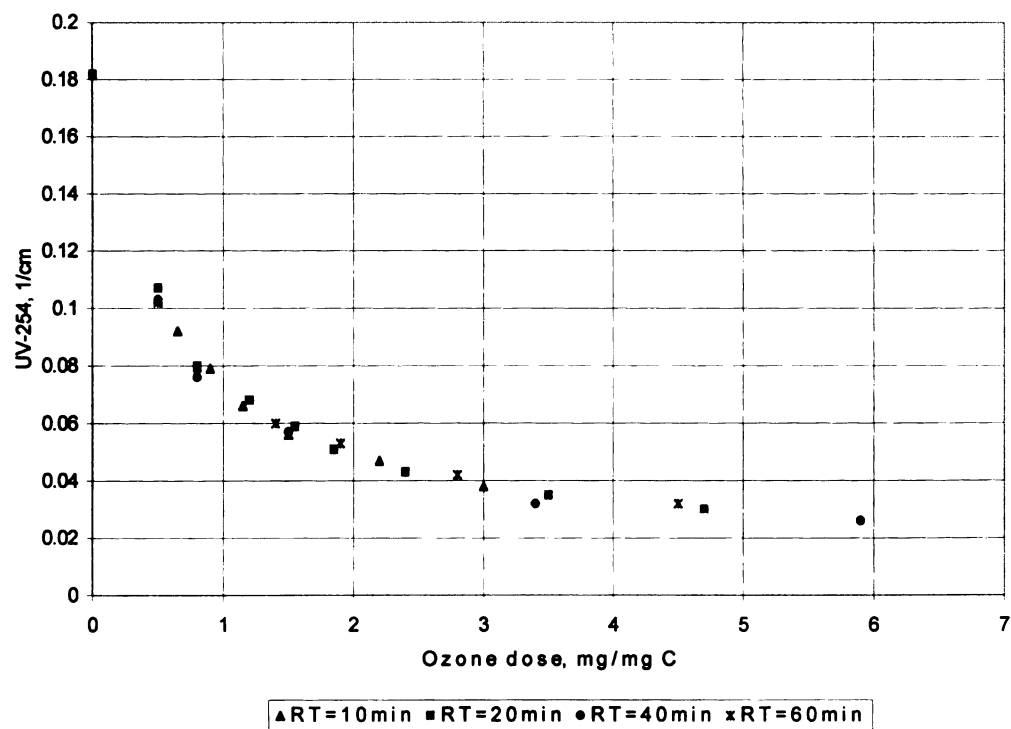


Figure 6.6. Effect of ozone dose on UV-254 absorbance for various HRTs.

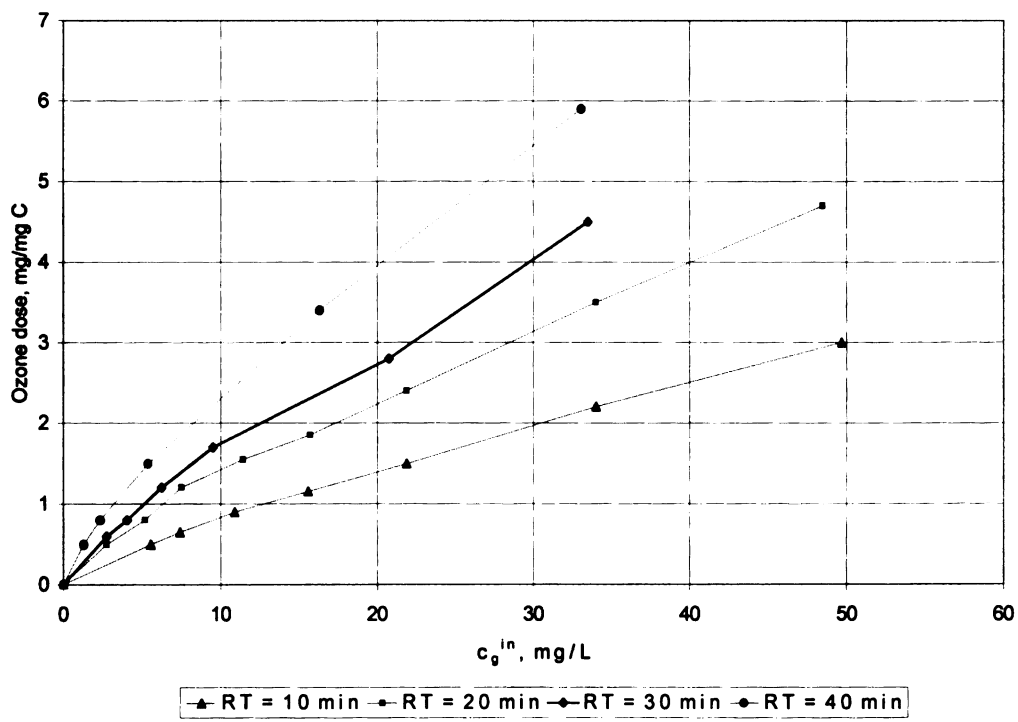


Figure 6.7. c_g^{in} requirements for various HRTs.

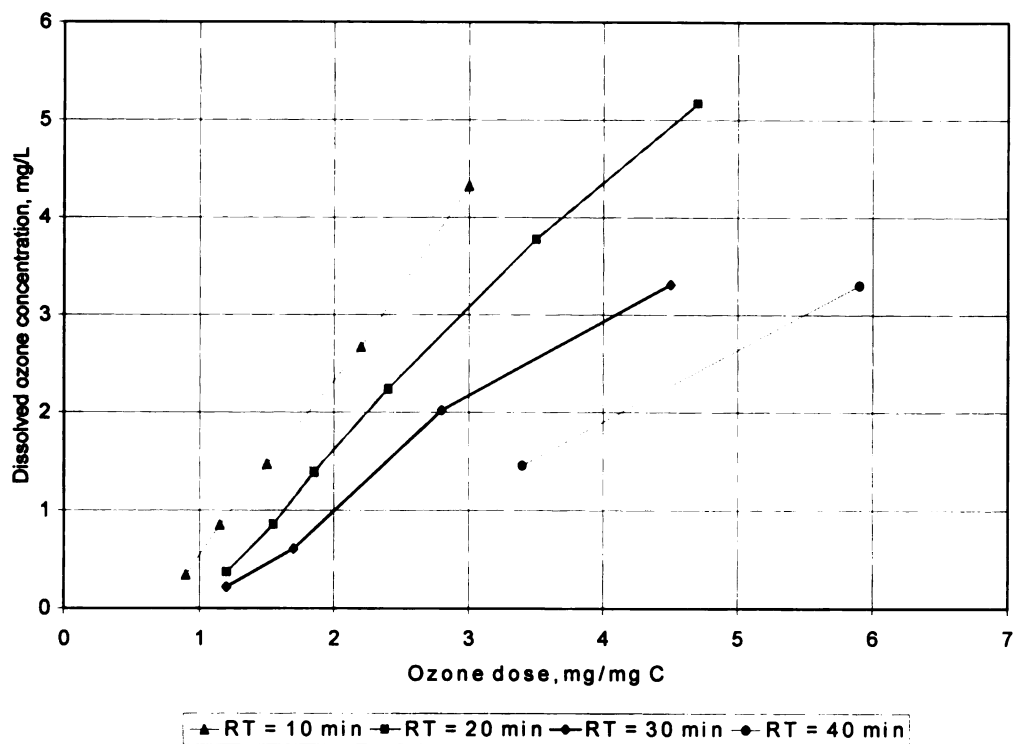


Figure 6.8. Dissolved ozone concentration for various HRTs

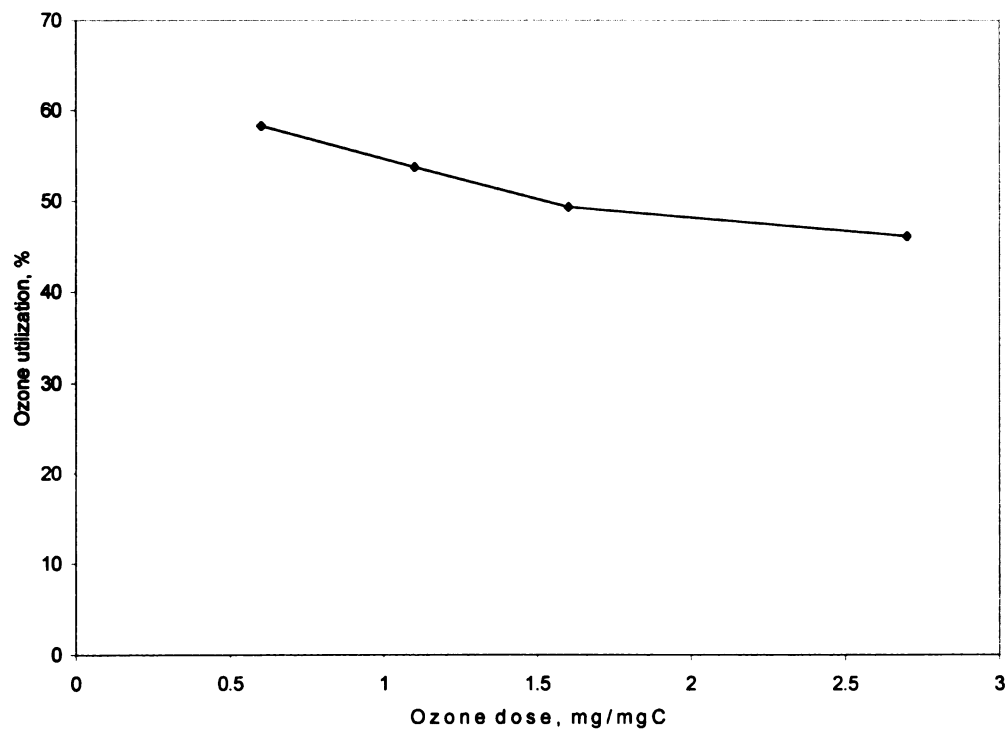


Figure 6.9. Efficiency of ozone utilization in the bench-scale ozone contactor
(HRT – 20 minutes)

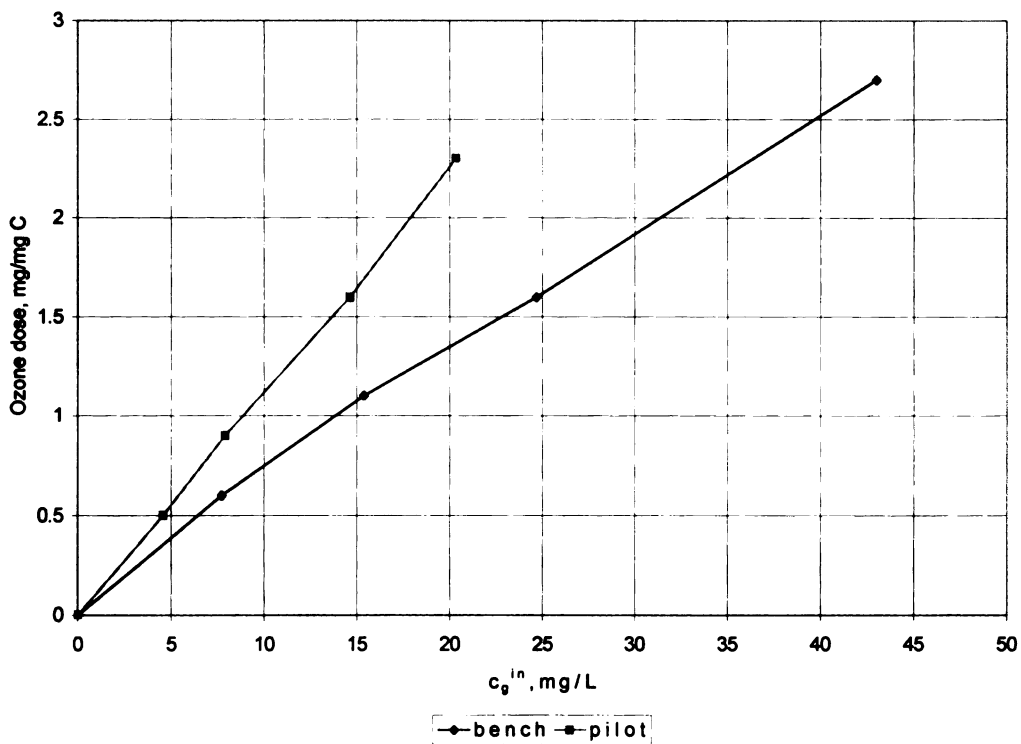


Figure 6.10. Influent gas ozone concentration requirements for bench- and pilot-scale systems (see Table 6.1 for experimental conditions)

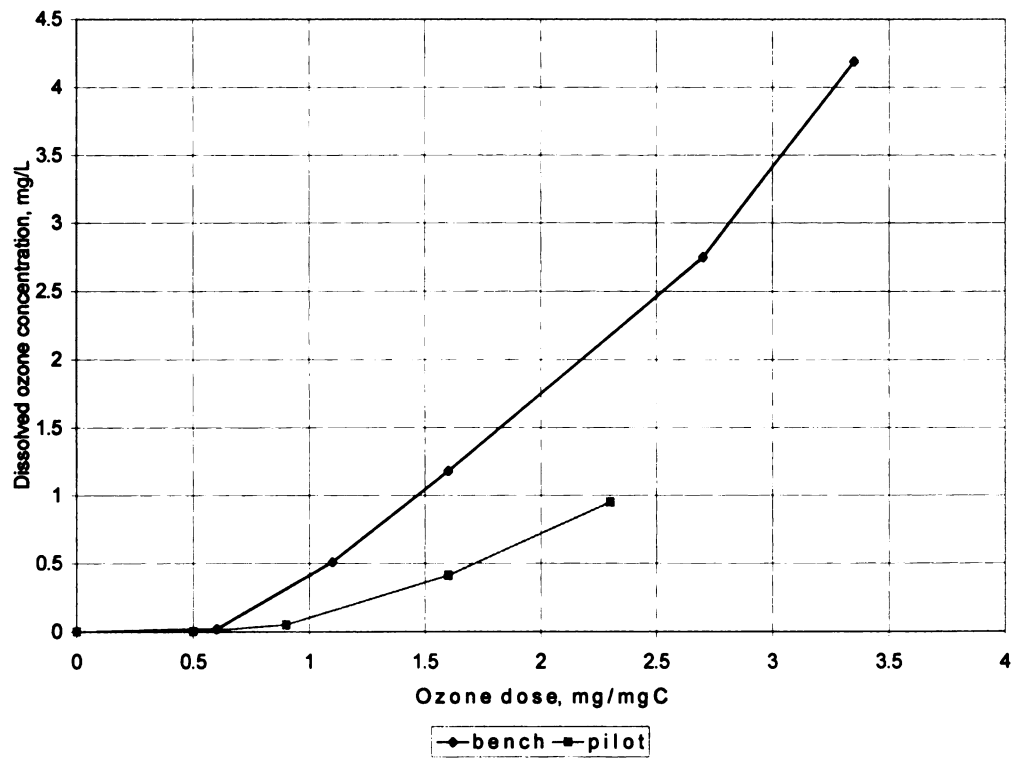


Figure 6.11. Dissolved ozone concentration for bench- and pilot-scale systems

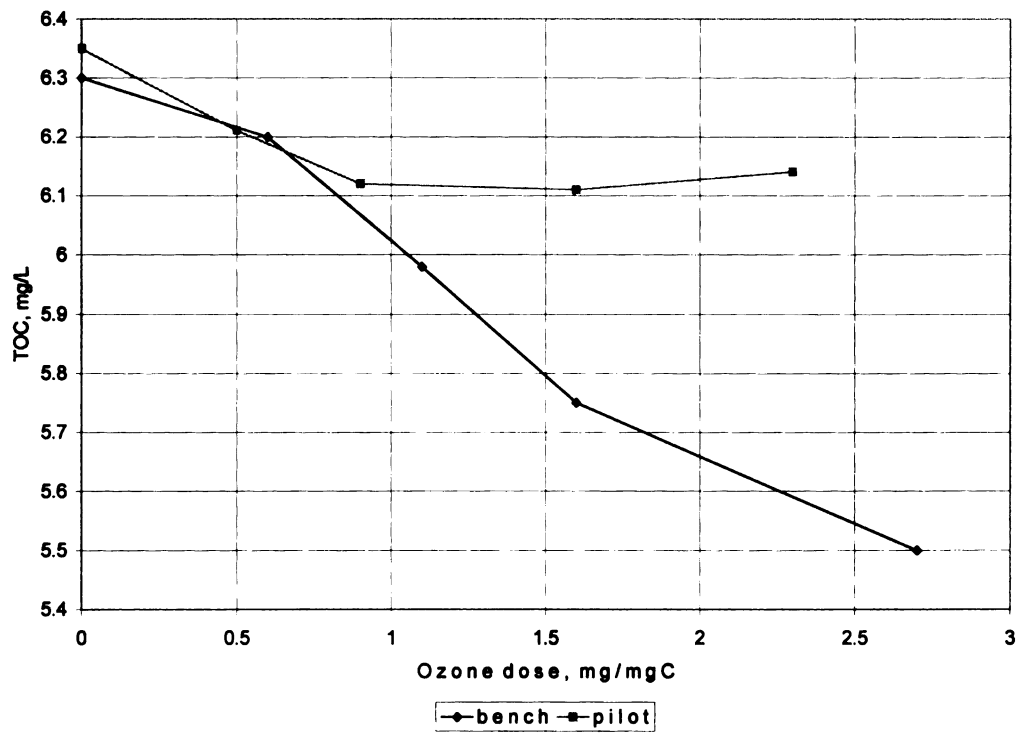


Figure 6.12. Removal of TOC during ozonation in the bench- and pilot-scale systems (experimental conditions are given in Table 6.1)

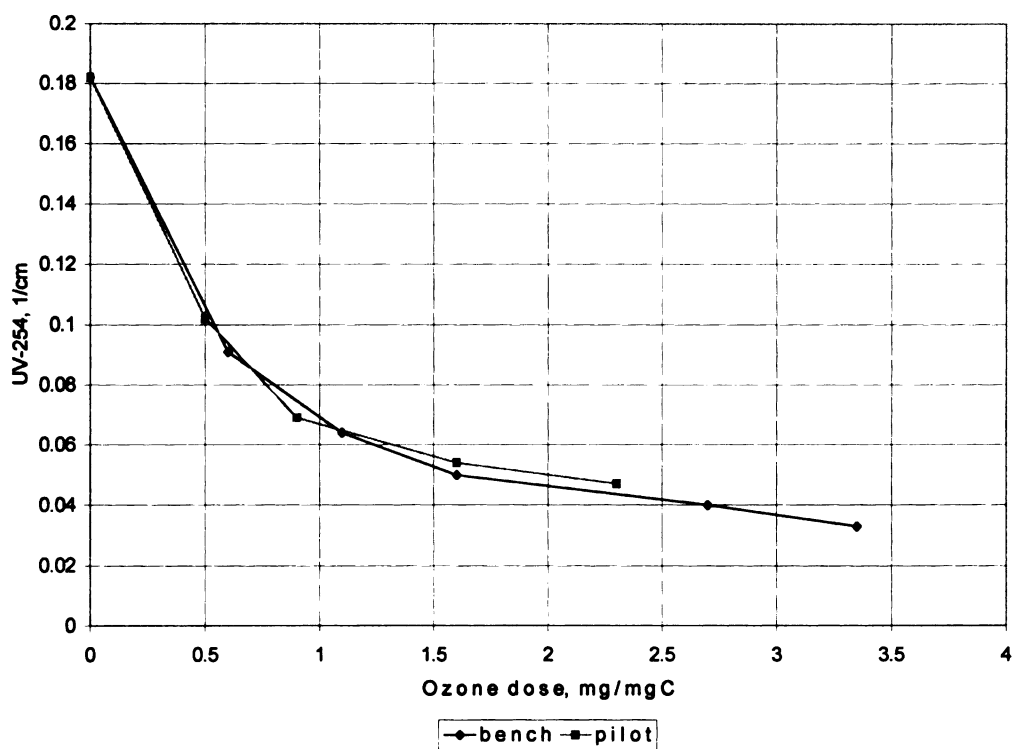


Figure 6.13. Removal of UV-254 during ozonation in the bench- and pilot-scale systems (experimental conditions are given in Table 6.1)

6.2.3. Effect of Ozone Dose on BDOC

The results of the pilot-scale study described in Chapter 4 showed that an increase in ozone dose from 0 to 1 mg/mg C resulted in an increased removal of TOC. The concentration of biodegradable organic matter appeared to decrease at the same time (see Figures 4.13). The removal of TOC leveled off with further increase in ozone dose. This was accompanied by an increase in the concentration of biodegradable organic matter. The hypothesis formulated based on this finding was that when ozonation is conducted under conditions that do not result in the oxidation of organic carbon, BDOC concentration increases with an increase in ozone dose. To verify this hypothesis bench-scale ozonation experiments were conducted. The ozonation effluents were analyzed for UV-254, TOC and BDOC. The BDOC was measured using the recirculating biofiltration system that was described in Section 3.2.5. Ozone dose was varied from 0 to 1 mg/mg C. The results of the experiments described in the previous section showed that for this range of ozone doses and a HRT of 10 minutes, the removal of TOC was not significant at 95% confidence interval. However, to ensure that no TOC was removed during ozonation, the experiments described in this section were conducted at a lower HRT of 7 minutes. As can be seen in Figure 6.14, the removal of UV-254 was the same at HRTs of 7 and 10 minutes.

Figure 6.15 shows the effect of ozone dose on BDOC concentration. As expected, the removal of TOC after ozonation was not significant at 95% confidence interval. BDOC concentration steadily increased with ozone dose and reached a concentration of

2.8 mg/L at an ozone dose of 1 mg/mg C compared to a BDOC concentration of 1.1 mg/L in raw water.

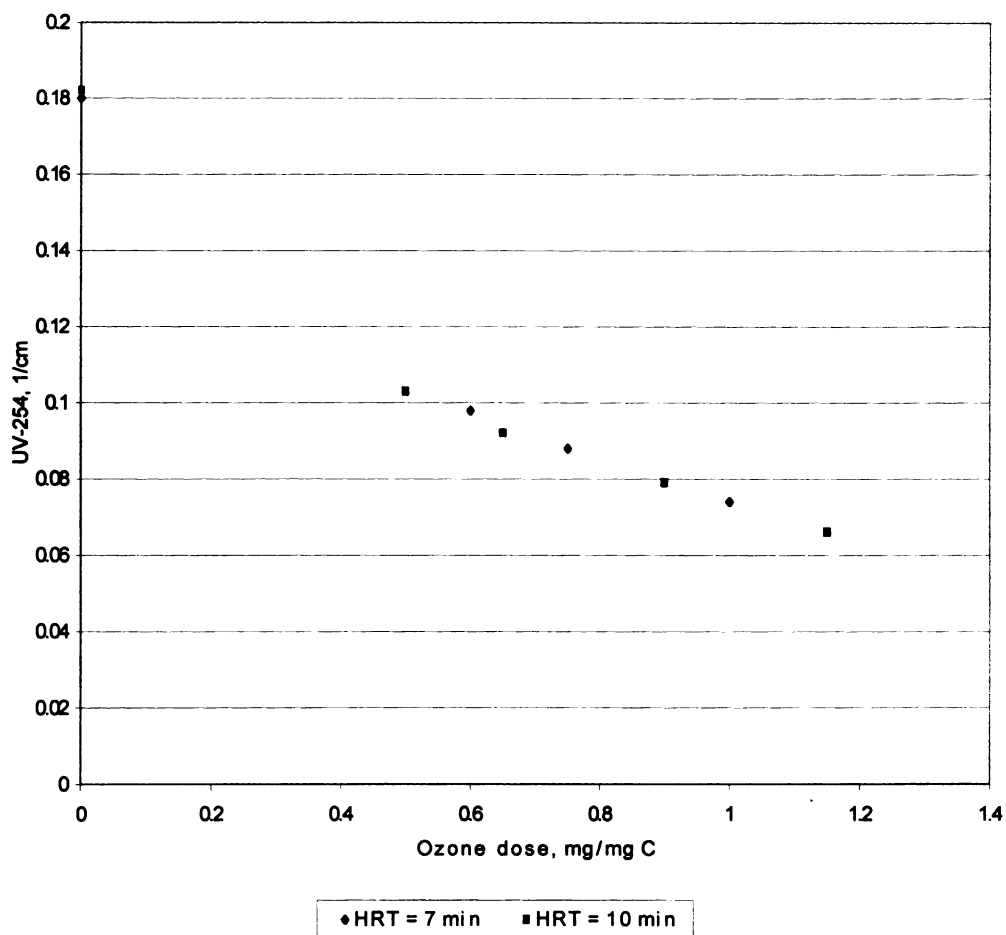


Figure 6.14. Removal of UV-254 during ozonation at low HRTs

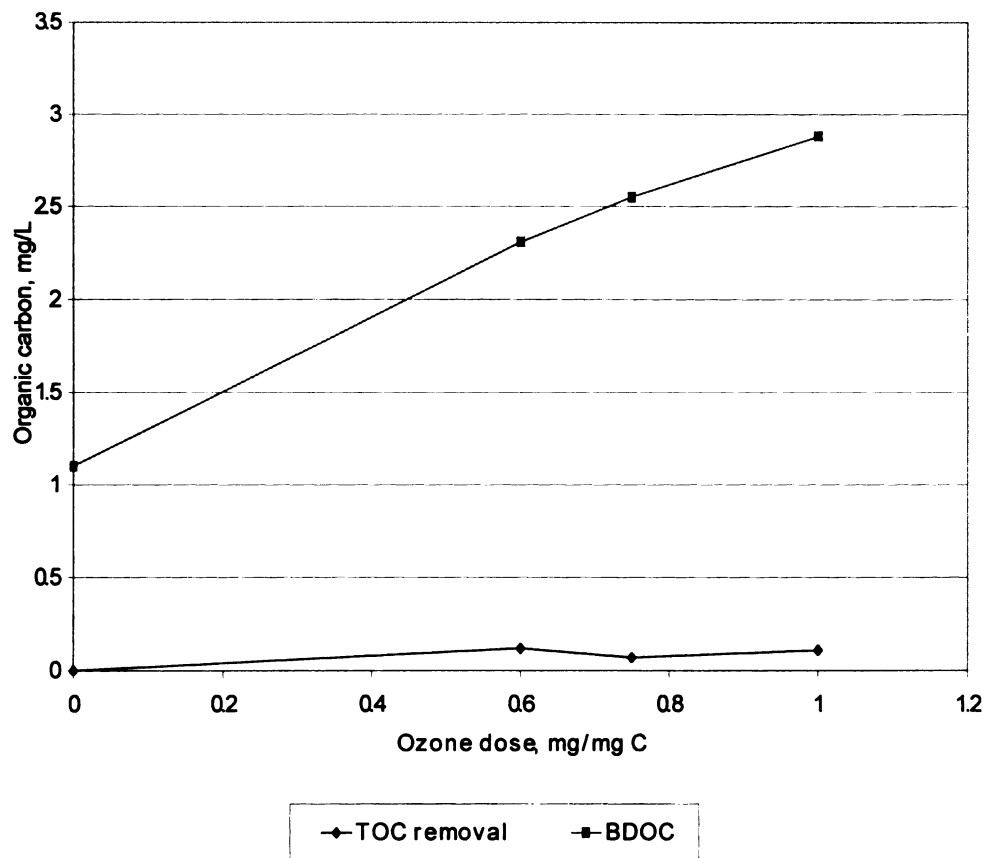


Figure 6.15. Effect of ozone dose on BDOC concentration
(HRT = 7 minutes)

6.3. OZONATION KINETICS

6.3.1. Introduction

This section describes the study of the kinetics of ozone reactions with NOM. The kinetics of the ozonation reactions in natural waters can be described in terms of two key process parameters: (1) specific ozone consumption rate of water, as proposed by Staehelin and Hoigné (1985), and (2) apparent oxidation rate constant of water, proposed by Yurteri and Gurol (1988). Although the Staehelin and Hoigné and Yurteri and Gurol approaches are similar in nature, there is a difference in terms of the interpretation of kinetic data. In natural waters, the specific rate of ozone consumption can be described as an overall expression, which is first-order with respect to ozone concentration (Staehelin and Hoigné, 1985):

$$\frac{d[O_3]}{dt} = -k_{O_3}[O_3] \quad (6.1)$$

where $[O_3]$ is the concentration of dissolved ozone and k_{O_3} is the specific ozone consumption rate.

According to Yurteri and Gurol (1988), the specific rate of ozone consumption can be expressed as

$$k_{O_3} = \sum_i k_i M_i \quad (6.2)$$

where M_i is the concentration of substrate i in water and k_i is the apparent reaction rate constant for M_i .

The apparent reaction rate constant, k_i , consists of two terms, which reflect direct and radical reactions of ozone with organic matter, as follows (Yurteri and Gurol, 1988):

$$k_i = (k_{di} + k_{ri} \psi_i) M_i \quad (6.3)$$

where k_{di} and k_{ri} are the rate constants for direct and radical reactions, respectively, and ψ_i is the factor, which accounts for initiation and scavenging of radical reactions and can be expressed as (Yurteri and Gurol, 1988):

$$\psi_i = \frac{2k_{1i}[\text{OH}^-] + k_{2i}M_i}{\sum_j k_{sj}[S_j]} \quad (6.4)$$

where k_{1i} and k_{2i} are the rate constants of the initiation step in the decomposition of ozone by OH^- and the substrate $[M_i]$, respectively; and S_i and k_{si} are the concentration and rate constants of scavengers, respectively.

Thus, it is mechanistically possible to obtain explicit relationships for the reactions of ozone with NOM. These relationships, however, have limited practical use because it is virtually impossible to account for all substrates and scavengers that participate in the reactions with ozone. A simpler approach must, therefore, be identified, which describes the reaction of ozone with NOM.

In this study, the kinetics of ozone reactions was expressed in terms of bulk characterization of NOM, as follows:

$$\frac{d[S]}{dt} = -k_T [O_3][S] \quad (6.5)$$

where, k_T is the total apparent rate constant of substrate [S]; and [S] is the bulk characteristics of NOM.

It should be noted that the total apparent rate constant, k_T , represents both direct and radical reactions and is dependent on the aqueous matrix, including such factors as alkalinity. It is important to realize that k_T is the function of the concentration of the solute [S], which is evident from the previous discussion, and, therefore, changes as the ozone reaction proceeds.

The use of bulk characterization of NOM to describe ozone reactions in water is not new (Bablon et al., 1991a). The major challenge, however, was to select appropriate bulk parameters, which would adequately describe the transformation of NOM in a particular treatment train, e.g. ozonation and biotreatment.

The use of specific rate of ozone consumption (see Equation 6.1) is an example of the bulk characterization approach. This parameter describes the extent of ozone reactions in water and may be useful in evaluating the effect of operational parameters on the ozonation of NOM.

This study also proposed the use of bulk characterization in terms of two parameters, HS and nonHS. These parameters were selected for the following reasons:

- HS and nonHS are representative of all NOM in water;
- HS and nonHS are separate and distinct fractions of NOM;

- HS and nonHS are categories of NOM, which are distinguished by its biodegradability: HS are essentially nonbiodegradable, whereas nonHS is a potentially biodegradable portion of NOM; and, finally,

- HS and nonHS can be quantified.

The particular objectives of this study were:

- To test the hypothesis that the specific rate of ozone consumption can be used to evaluate the efficacy of the ozonation of NOM;
- To demonstrate the use of HS and nonHS to describe the kinetics of ozone reactions in water;
- To test the hypothesis that the ozonation of NOM follows the following pathways:
 1. Ozone converts HS into nonHS
 2. Oxidation of organic carbon occurs through the reaction of ozone with nonHS
 3. Both reactions may proceed simultaneously.
- To verify the first order kinetics with respect to HS and nonHS;
- To determine the stoichiometric coefficients for the reactions of ozone with HS and nonHS;
- To determine the reaction rate coefficients and activation energies for the reaction of ozone with HS and nonHS; and
- To develop and validate a kinetic model that describes the transformation of NOM during ozonation.

6.3.2. Model Development

Two models describing the ozone reactions in water were developed. The models were based on the bulk characterization of NOM expressed either in terms of the specific rate of ozone consumption (Model I) or in terms of HS and nonHS (Model II).

6.3.2.1. Model Based on the Specific Ozone Consumption Rate

According to the theory of absorption with reaction (Anselmi et al. 1985; Dankwerts, 1970) and assuming that bench-scale ozone contactor could be considered as a completely mixed reactor for both liquid and gas phase and that the resistance to transport of ozone from gas phase to the interface was insignificant (Astarita, 1967), the mass balance for ozone could be described by the following system of ordinary differential equations:

$$V \frac{dc_L}{dt} = k_L a (\alpha c_g^{(i)} - c_L) V - k_{O_3} c_L V - Q c_L \quad (6.6)$$

$$H_g \frac{dc_g^{(i)}}{dt} = G(c_g^{(0)} - c_g^{(i)}) - k_L a (\alpha c_g^{(i)} - c_L) V \quad (6.7)$$

where V is the volume of the reactor, mL; Q and G are the liquid and gas flow rates, respectively, mL/min; c_L is the concentration of ozone in water, mg/L; c_g^0 is the concentration of ozone in the influent gas, mg/L; $c_g^{(i)}$ is the interfacial concentration of

ozone in the gas phase, mg/L; $k_L a$ is the mass transfer coefficient, 1/min; α is the ozone-water equilibrium constant; H_g is the gas hold-up.

For low ozone concentration, we could assume the validity of Henry's law, which could be written as (Roth and Sullivan, 1981):

$$Y = \frac{H}{P} X^* \quad (6.8)$$

where Y is the ozone mole fraction in gas phase; X^* is ozone mole fraction in equilibrium with the bulk mole fraction in the gas phase; H is the Henry's law constant, atm/mole fraction; P is the gas pressure, atm.

Since the ozone concentration in water is low, X^* could be expressed as (Sheffer and Esterson, 1982):

$$X^* = \frac{c_L^*}{10^3 \rho_{H_2O}} \frac{M_{H_2O}}{M_{O_3}} = \frac{18}{48 \cdot 10^6} c_L^* = 3.75 \cdot 10^{-7} c_L^* \quad (6.9)$$

where c_L^* is the ozone concentration in the equilibrium with the bulk concentration in gas phase, mg/L; M_{H_2O} and M_{O_3} are the molecular weight of water and ozone, respectively, mg/L; ρ_{H_2O} is the density of water, g/L.

Similarly,

$$Y = \frac{c_g}{10^3 \rho_{O_2}} \frac{M_{O_2}}{M_{O_3}} = \frac{32}{48 \cdot 1.43 \cdot 10^3} c_g = 4.66 \cdot 10^{-4} c_g \quad (6.10)$$

where c_g is the ozone concentration in gas phase, mg/L; M_{O_2} is the molecular weight of oxygen, respectively, mg/L; ρ_{O_2} is the density of water, g/L.

Assuming that gas pressure in the reactor is 1 atm, combining the Equations (6.8)-(6.10) gave

$$c_L^* = \frac{1243}{H} c_g \quad (6.11)$$

which gave the relationship between α and H for ozone-water systems:

$$\alpha = \frac{1243}{H} \quad (6.12)$$

The Henry's law constant was found to be satisfactorily modeled as a function of pH and temperature over the range of conditions used in water treatment, as follows (Roth and Sullivan, 1981):

$$H = 3.84 \cdot 10^7 [\text{OH}^-]^{0.035} e^{-\frac{2428}{T}} \quad (6.13)$$

where, $[\text{OH}^-]$ is the concentration of hydroxide ions, g-mol/L; T is temperature, K.

6.3.2.2. Model Based on HS and nonHS.

By taking into account the hypotheses regarding the transformation of HS and nonHS during ozonation and adding all the previous assumptions, the oxidation of NOM by ozone could be described by the following system of ordinary differential equations:

$$V \frac{dc_L}{dt} = (k_L a(\alpha c_g^{(i)} - c_L) - \nu_{HS} k_{HS} c_{HS} c_L - \nu_{nonHS} k_{nonHS} c_{nonHS} c_L) V - Q c_L \quad (6.14)$$

$$V \frac{dc_{HS}}{dt} = Q(c_{HS}^0 - c_{HS}) - k_{HS} c_{HS} c_L V \quad (6.15)$$

$$V \frac{dc_{nonHS}}{dt} = Q(c_{nonHS}^0 - c_{nonHS}) - k_{nonHS} c_{nonHS} c_L V + k_{HS} c_{HS} c_L V \quad (6.16)$$

$$H_g \frac{dc_g^{(i)}}{dt} = G(c_g^{(0)} - c_g^{(i)}) - k_L a(\alpha c_g^{(i)} - c_L) V \quad (6.17)$$

where k_{HS} and k_{nonHS} are the reaction rate coefficients for HS and nonHS, respectively, L/(mg min); ν_{HS} and ν_{nonHS} are stoichiometric coefficients for HS and nonHS, respectively; c_{HS}^0 and c_{nonHS}^0 are the initial concentrations of HS and nonHS, respectively, mg/L.

6.3.3. Rate of Ozone Consumption

Two methods for measuring the specific ozone consumption rate were investigated in this study: (1) the method, based on measuring UV-254 reduction in

samples after ozonation, and (2) the method based on the model described by Equations (6.6)-(6.7). The goal of the experiments presented in this section were:

- To test the hypothesis that UV-254 absorbance can be used to measure the concentration of dissolved ozone and the specific ozone consumption rate;
- To determine if the model described by Equations (6.6)-(6.7) can be used to determine the specific ozone consumption rate and to compare this method proposed with the spectroscopic method;
- To verify the first-order kinetics for ozone consumption; and
- To demonstrate the use of the specific rate of ozone consumption for the evaluation of the ozonation of NOM.

6.3.3.1. Spectroscopic Method

The major difficulty in using UV-254 absorbance to measure the rate of ozone depletion is that both ozone and NOM absorb UV light at a wavelength of 254 nm. Preliminary experiments were conducted to determine the effect of residual ozone on the UV-254 absorbance of NOM after ozonation. This was done by comparing (1) the UV-254 of the ozone contactor effluent after allowing the residual ozone to react with NOM with (2) the UV-254 of the effluent from the quenching tank (see Fig. 3.1) in which the reaction was quenched by purging all residual ozone with helium. The quenching procedure was described in Section 3.2.1. In addition, the samples were analyzed for TOC in order to determine if the removal of organic carbon occurred through the oxidation by ozone or through volatilization. The results are shown in Table 6.2.

Table 6.2 Effect of quenching on UV-254 and TOC after ozonation

Ozone dose, mg/mg C	UV-254 absorbance, 1/cm		TOC, mg/L	
	w/ quenching	w/o quenching	w/ quenching	w/o quenching
0.8	0.102	0.101	6.4	6.37
1.5	0.068	0.068	5.91	5.87
3.4	0.051	0.050	5.53	5.58

As can be seen in Table 6.2, the residual ozone did not appear to affect either UV-254 or TOC in ozonated samples. This suggested that the removal of TOC was due to the oxidation reactions rather than volatilization. This also suggested that the base line correction could be used to separate the UV absorbance of dissolved ozone from the UV absorbance of NOM. To prove this hypothesis, the values of ozone concentration measured using UV-254, as described below, were compared with those measured by the Indigo method.

The UV-254 measurements of ozonated samples were done by diverting the effluent to a head-space free 1-cm capped UV cell and measuring the reduction in UV-254 over time. The measurements were usually started 30 seconds after sample collection and, depending on the rate of UV-254 reduction, were taken every 15 to 60 seconds afterwards. A typical kinetic curve for UV-254 in ozonated samples is shown in Figure 6.16.

The UV-254 decreased with time and reached a plateau after several minutes. The UV-254 value at which the curve leveled off corresponded to the UV-254 absorbance of ozone-free sample. The curve, shown in Figure 6.17, was obtained by subtracting the UV-254 of ozone-free water from the actual values of UV-254. This curve described the kinetics of ozone depletion expressed in terms of UV-254. The tail of the curve was cut off as the accuracy of measurements decreased when the values approached zero. Figure 6.17 shows that the data were fitted very well by the exponential line:

$$UV254 = UV254_0 e^{-k_{UV}\tau} \quad (6.18)$$

where $UV254_0$ is the concentration of the dissolved ozone in the ozone contactor expressed in terms of UV absorbance, cm^{-1} ; k_{UV} is the specific rate of UV254 depletion.

The dissolved ozone concentration in the ozone contactor was calculated using the following equation:

$$c_L = \frac{M_{O_3} \cdot 1000}{\epsilon \cdot b} UV254_0 \quad (6.19)$$

where c_L is the concentration of dissolved ozone in the ozone contactor, mg/L; ϵ is the extinction coefficient ($\epsilon = 3000 \text{ L mole}^{-1}$ at 254 nm) (Masten, 1991); b is the cell width ($b = 1 \text{ cm}$).

The ozone concentrations that were determined using the spectroscopic method were compared with those measured using the Indigo method over a wide range of operational conditions, including:

- ozone dose - 0 to 5 mg/mg C
- gas flow rate - 15 to 36 mL/min
- retention time - 7 to 40 minutes
- temperature – 10 to 30°C.

For each ozonated sample, a kinetic curve of UV-254 depletion, similar to that shown in Figure 6.17, was obtained and the ozone concentration was determined using Equations (6.18) and (6.19). The correlation coefficient for the exponential regression lines so obtained ranged from 0.992 to 1, with an average of 0.997. Figure 6.18 shows that there exists a good agreement between the spectroscopic and Indigo methods (the slope of the regression line was 0.9925). Thus, the study showed that the rate of ozone consumption followed the first order kinetics and the specific ozone consumption rate could be determined from the UV depletion curve as

$$k_{O_3} = k_{UV} \quad (6.20)$$

The spectroscopic method for measuring the specific rate of ozone consumption is simple and requires only the measurements of UV254 absorbance. It also allows for the measurements of the dissolved ozone concentration. The limitations of the method are the following:

- the method cannot be used for high ozone consumption rate when the residual ozone is depleted quickly (for less than a minute); and
- the method should be validated for each water source under investigation.

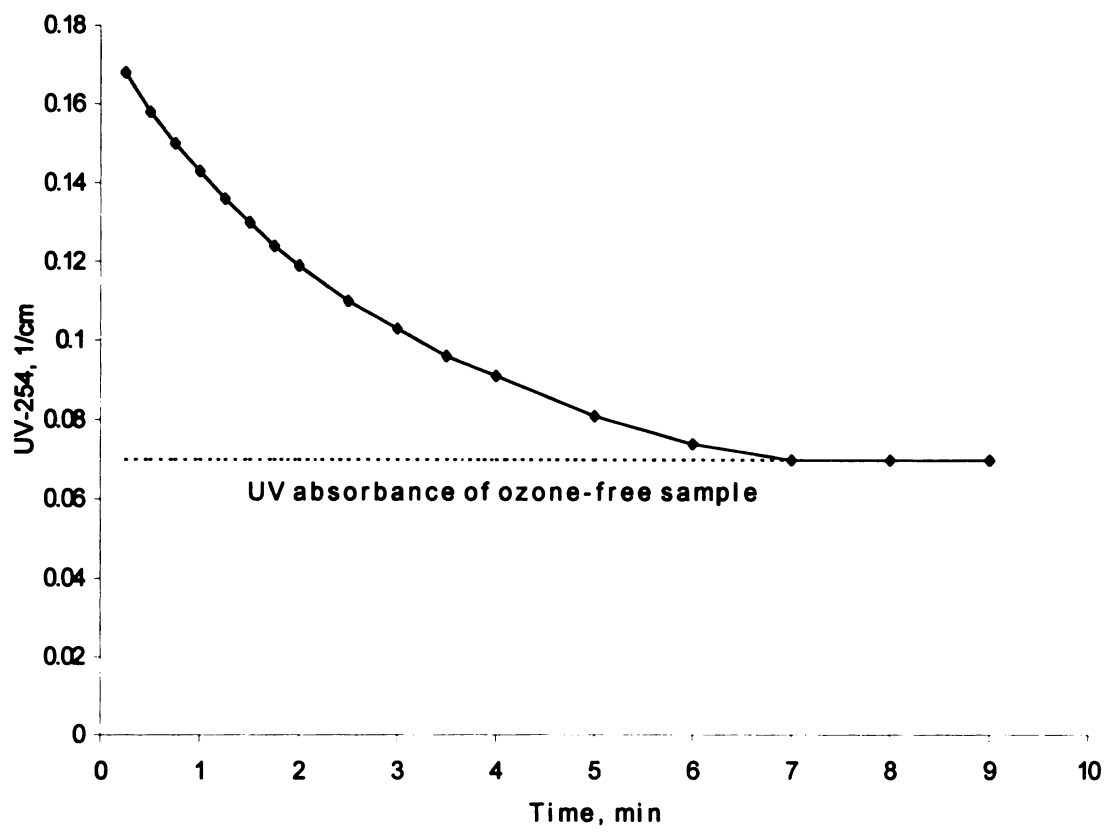


Figure 6.16. Kinetic curve of ozone depletion in water based on UV-254

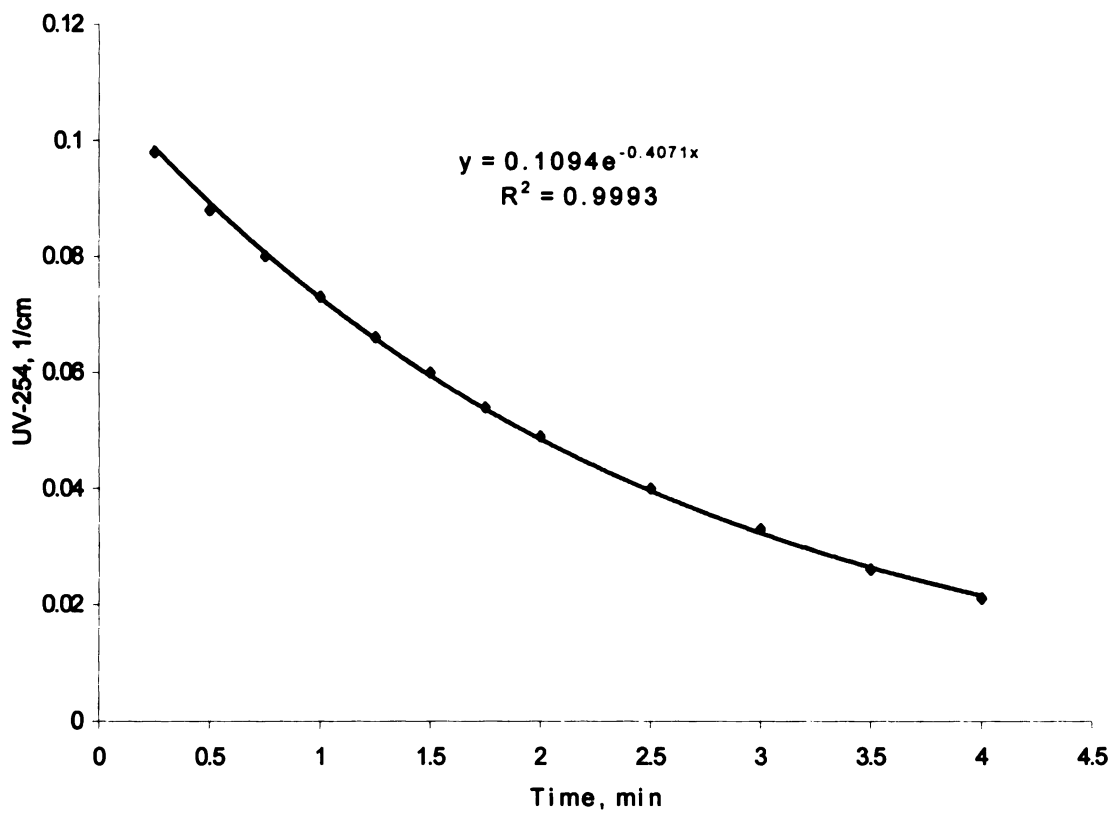


Figure 6.17. Kinetic curve of ozone depletion based on UV-254 using baseline correction

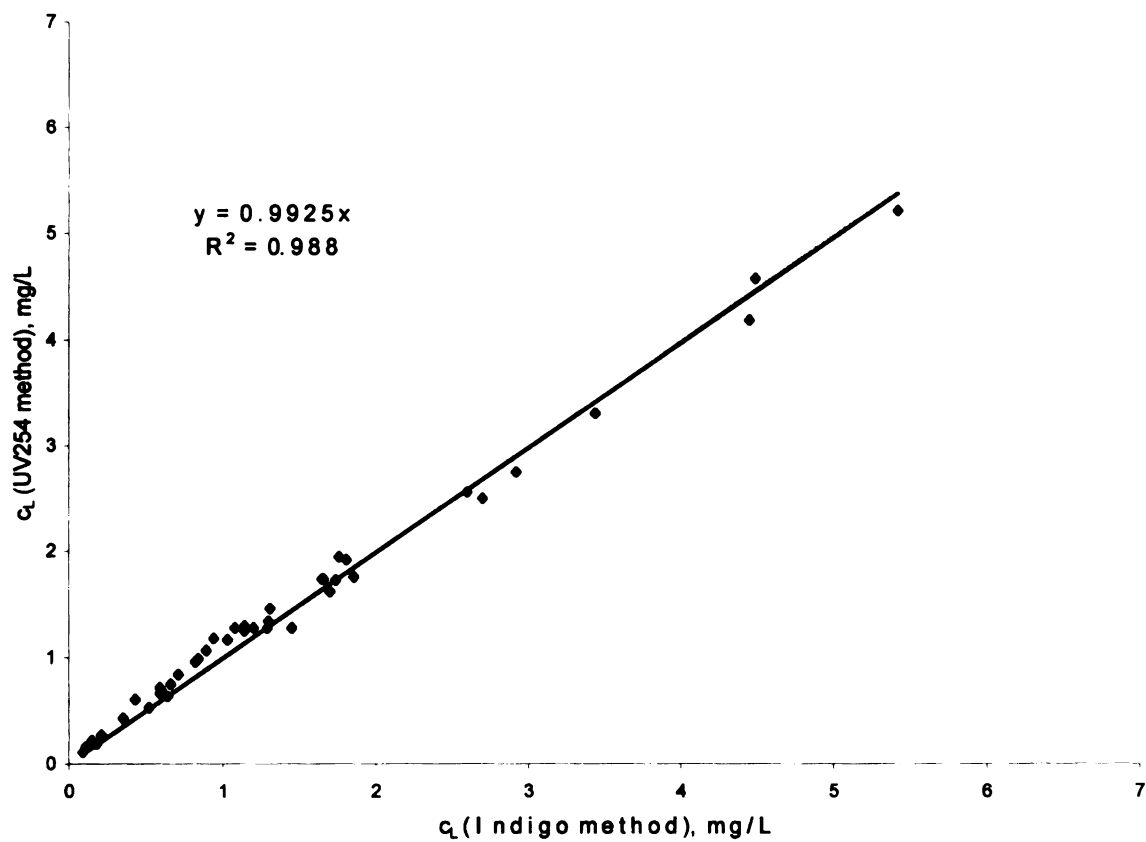


Figure 6.18. Correlation between dissolved ozone concentrations measured spectrophotometrically and by Indigo method

6.3.3.2. Method Based on Ozone Consumption Model

The second method for measuring the specific ozone consumption rate proposed in this study was based on the application of the ozone consumption model described by Equations (6.6) and (6.7). For steady state, Equations (6.6) and (6.7) became:

$$0 = k_L a (\alpha c_g^{(i)} - c_L) V - k_{O_3} c_L V - Q c_L \quad (6.21)$$

$$0 = G(c_g^{(0)} - c_g^{(i)}) - k_L a (\alpha c_g^{(i)} - c_L) V \quad (6.22)$$

Because the resistance to transport of ozone from gas phase to the interface is insignificant (Astarita, 1967), it was assumed that the interfacial concentration of ozone in gas phase was equal to the bulk gas phase ozone concentration. Then, the mass transfer coefficient, $k_L a$, could be calculated using Equation (6.22):

$$k_L a = \frac{G(c_g^0 - c_g^{out})}{V(\alpha c_g^{out} - c_L)} \quad (6.23)$$

and the specific rate of ozone consumption, k_{O_3} , could be calculated using Equation (6.21):

$$k_{O_3} = \frac{k_L a(\alpha c_g^{\text{out}} - c_L)V - Qc_L}{c_L V} \quad (6.24)$$

where c_g^{out} is the concentration of ozone in the effluent gas, mg/L.

In order to calculate the specific rate of ozone consumption, k_{O_3} , the dissolved ozone concentration and the concentration of ozone in the influent and effluent gas were measured. The ozone-water equilibrium coefficient, α , was determined using Equations (6.12) and (6.13). Since the ozone-water equilibrium coefficient is a function of pH and temperature, these parameters were measured in each experiment. The calculations were conducted for the same range of operational parameters that were described in the previous section. The values of the specific rate of ozone consumption so obtained were compared with those determined using the spectroscopic method. The results are shown in Figure 6.19. There exists a good agreement between the values obtained by two methods. The dispersion of the data was, however, greater than those for the dissolved ozone concentration (see Fig. 6.18). This could be attributed to the fact that the specific ozone consumption rate that was determined using the ozone consumption model (see Equation 6.6) involved the measurements of several parameters (dissolved ozone concentration, the concentration of ozone in the influent and effluent gas, pH, and temperature), each of which had an experimental error and could contribute to the total error (see Equation 6.23).

The method based on the ozone consumption model allows for the determination of both high and low specific rates of ozone consumption. The method, however, appears to be less accurate than the spectroscopic method.

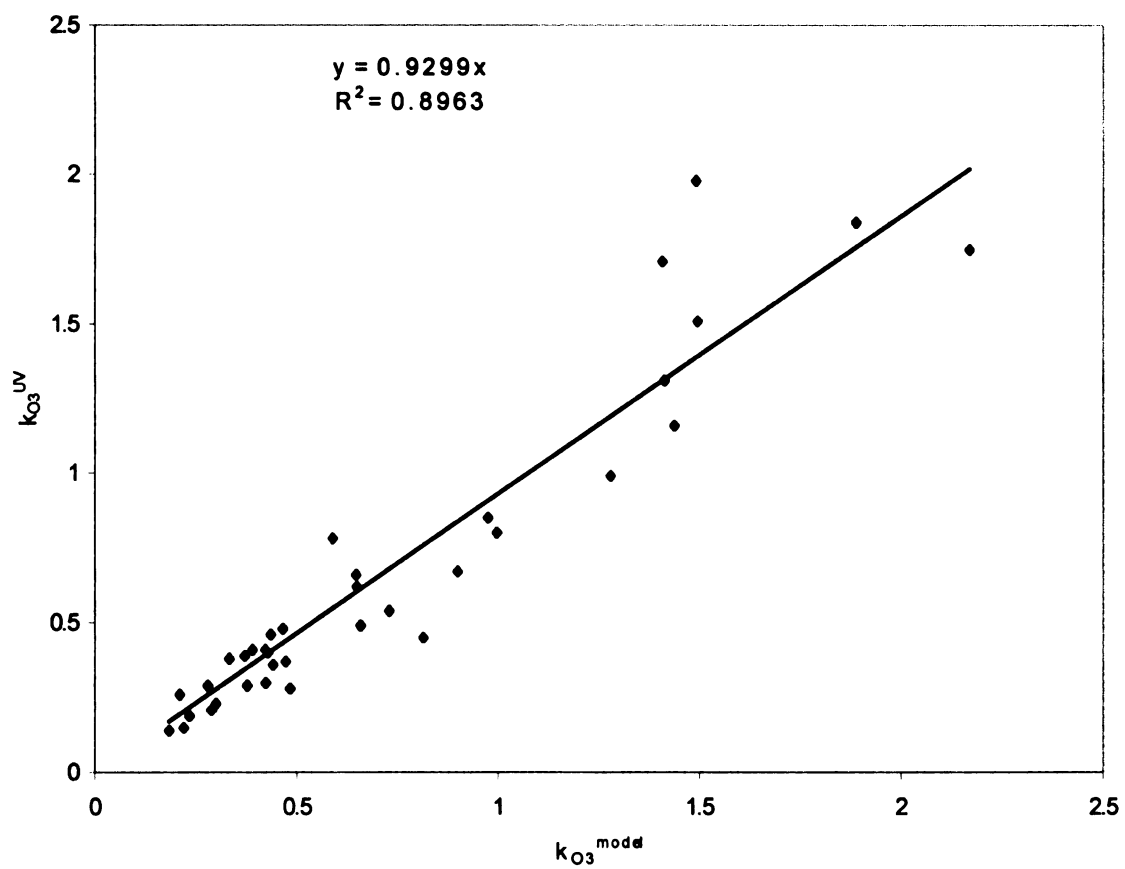


Fig 6.19. Correlation between the specific rates of ozone consumption determined by two methods

6.3.3.3. The Use of Ozone Consumption Rate to Evaluate the Efficacy of Ozonation

Hoigné (1994) identified the rate of ozone consumption as one of the parameters necessary for the quantification of physical and chemical properties of water with respect to ozone reactions. The goal of the study presented in this section was to determine if the specific ozone consumption rate could be used to evaluate the efficacy of ozone reactions in water. Particular objectives were to test the hypotheses that:

- the specific ozone consumption rate would decrease with the removal of NOM during ozonation;
- gas flow rate would not affect the specific ozone consumption rate;
- the specific ozone consumption rate would increase with retention time.

The experimental design was the same as described in Chapter 6.2. The specific rate of ozone consumption was determined using the spectroscopic method (see Section 6.3.3).

Figures 6.20-6.22 show results of the experiments conducted at room temperature and a retention time of 20 minutes. Ozone dose was varied from 1 to 5 mg/mg C. The gas flow rate was 15, 25, and 36 mL/min.

The k_{O_3} decreased with an increase in ozone dose (see Figure 6.20). Two regions could be identified. The first region, which corresponded to ozone doses of approximately 1.5 mg/mg C and less, was characterized by a sharp decrease in k_{O_3} when ozone dose increased. In the second region, which corresponded to ozone doses of approximately 1.5 mg/mg C and greater, a slow decrease in k_{O_3} with an increase in ozone dose was observed. This correlated well with UV-254 data that exhibited a similar

behavior during ozonation (see Figure 6.4). The flow rate did not appear to affect k_{O_3} . This is thought to be because neither UV-254 nor TOC removals were affected by gas flow rate (see Section 6.2).

The k_{O_3} decreased exponentially with a decrease in the concentration of UV-absorbing compounds during ozonation (see Fig. 6.21). The k_{O_3} dropped from 1.6 to 0.4 min^{-1} while TOC concentration did not change significantly (see Fig. 6.22). This decrease could be attributed to the removal of UV254-absorbing compounds. Further ozonation resulted in a decrease in TOC concentration from 5.8 to 5 mg/L, which was accompanied by a decrease in k_{O_3} from 0.4 to 0.1 1/min. It was difficult, however, to determine if this decrease was due to the removal of TOC or UV-absorbing compounds or both. It did not appear that gas flow rate affected the correlations between TOC and k_{O_3} or UV-254 and k_{O_3} .

Figures 6.23-6.25 show the plots of k_{O_3} versus ozone dose, UV-254 and TOC for various retention times. The gas flow rate was 36 mL/min in all experiments. Figure 6.23 shows that k_{O_3} decreased with an increase in ozone dose. It appears that the values of k_{O_3} were higher for higher retention times. Similar phenomenon was observed for the relationships between TOC and k_{O_3} or UV-254 and k_{O_3} (see Figures 6.24 and 6.25, respectively). This affect could not be attributed to the removal UV-254 absorbing compounds, since this removal during ozonation was not affected by retention time (see Section 6.2). The extent of the reaction of ozone with TOC increased with retention time (see Section 6.2), which could possibly be a contributing factor to higher k_{O_3} values at higher retention times.

The findings presented in this section suggest that the use k_{O_3} for the evaluation of ozonation may be limited. This is because, without having additional information, it would be difficult to attribute the k_{O_3} changes to either the reaction of ozone with UV-254-absorbing compounds or TOC or both.

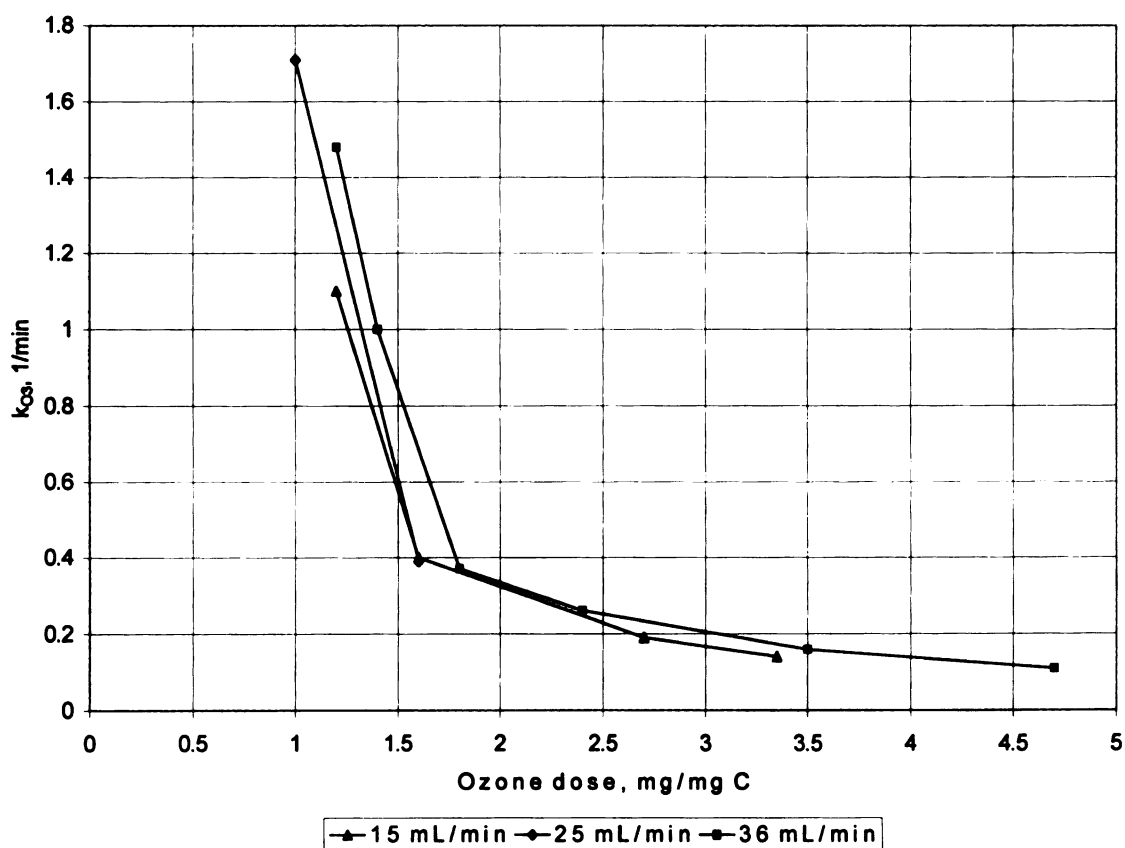


Figure 6.20. Effect of ozone dose on k_{O_3} for various gas flow rates
(HRT = 20 minutes)

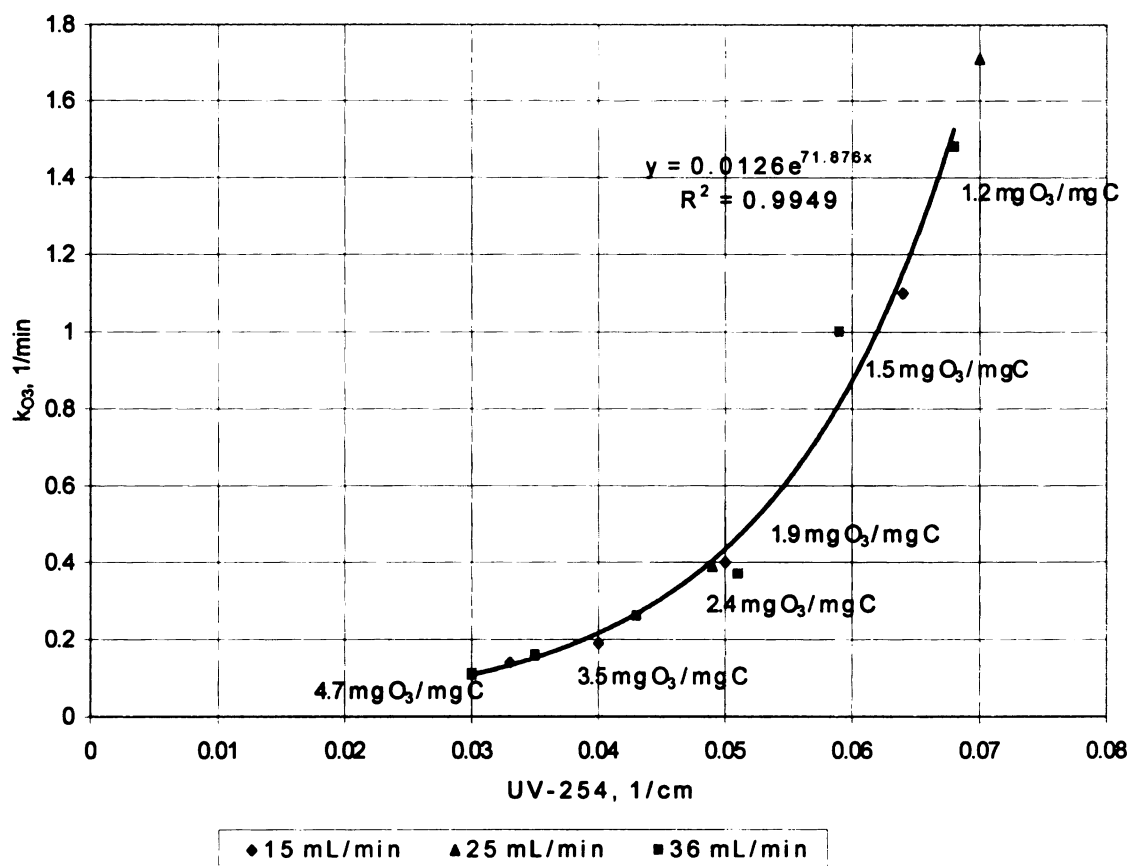


Figure 6.21. Correlation between UV-254 and k_{O_3} for various gas flow rates
(HRT = 20 minutes)

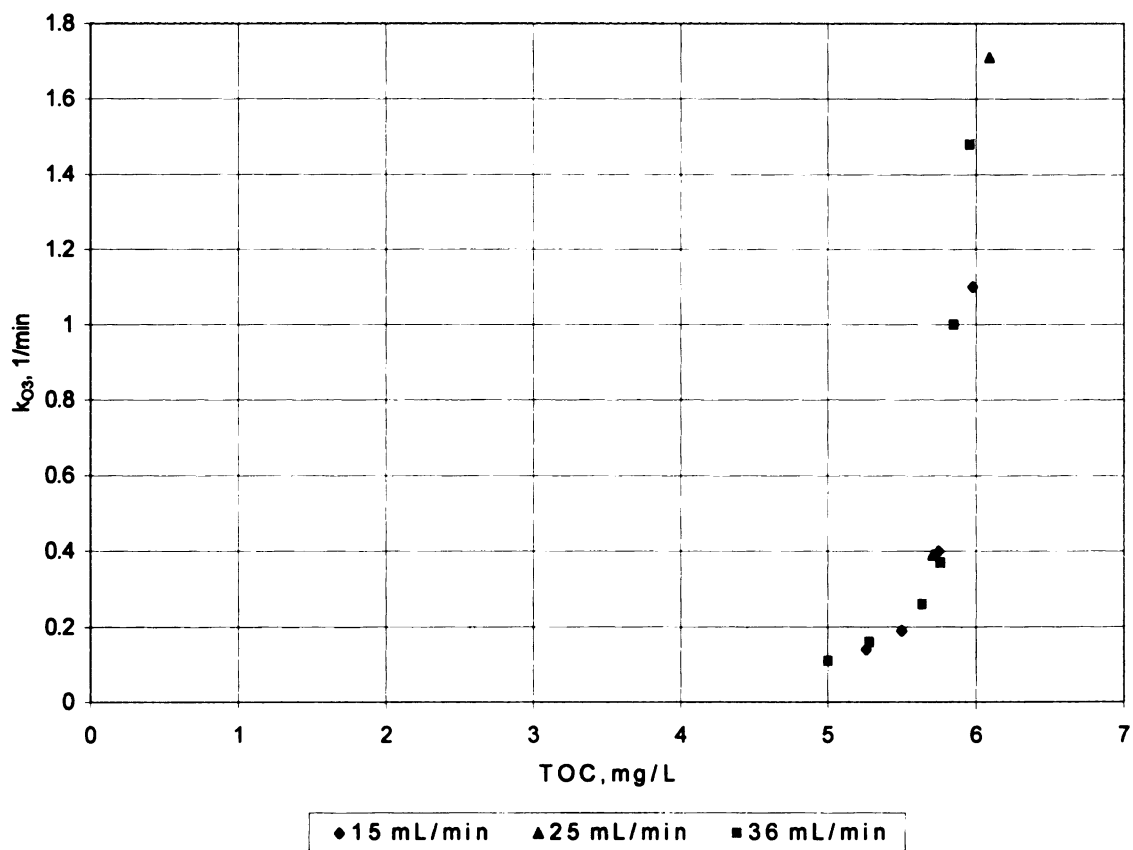


Figure 6.22 Correlation between TOC and k_{O_3} for various gas flow rates
(HRT = 20 minutes)

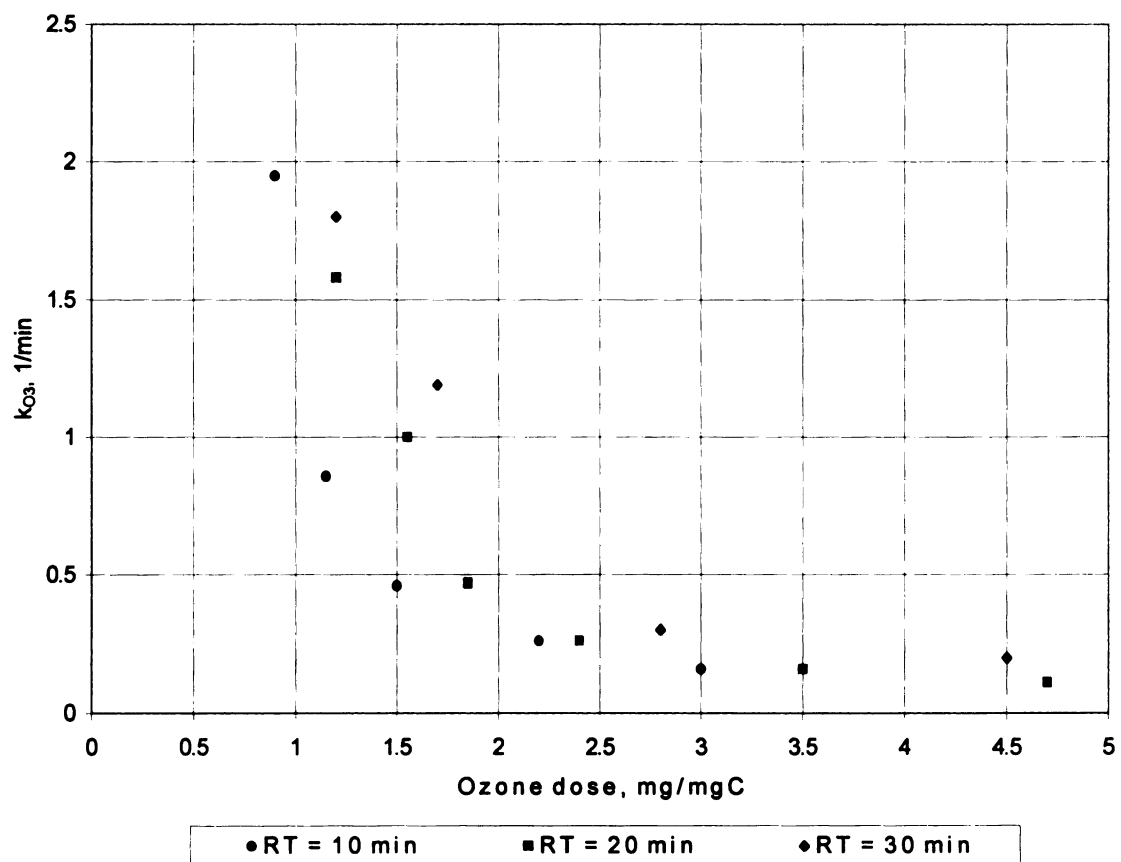


Figure 6.23 Effect of ozone dose on k_{O_3} for various retention times

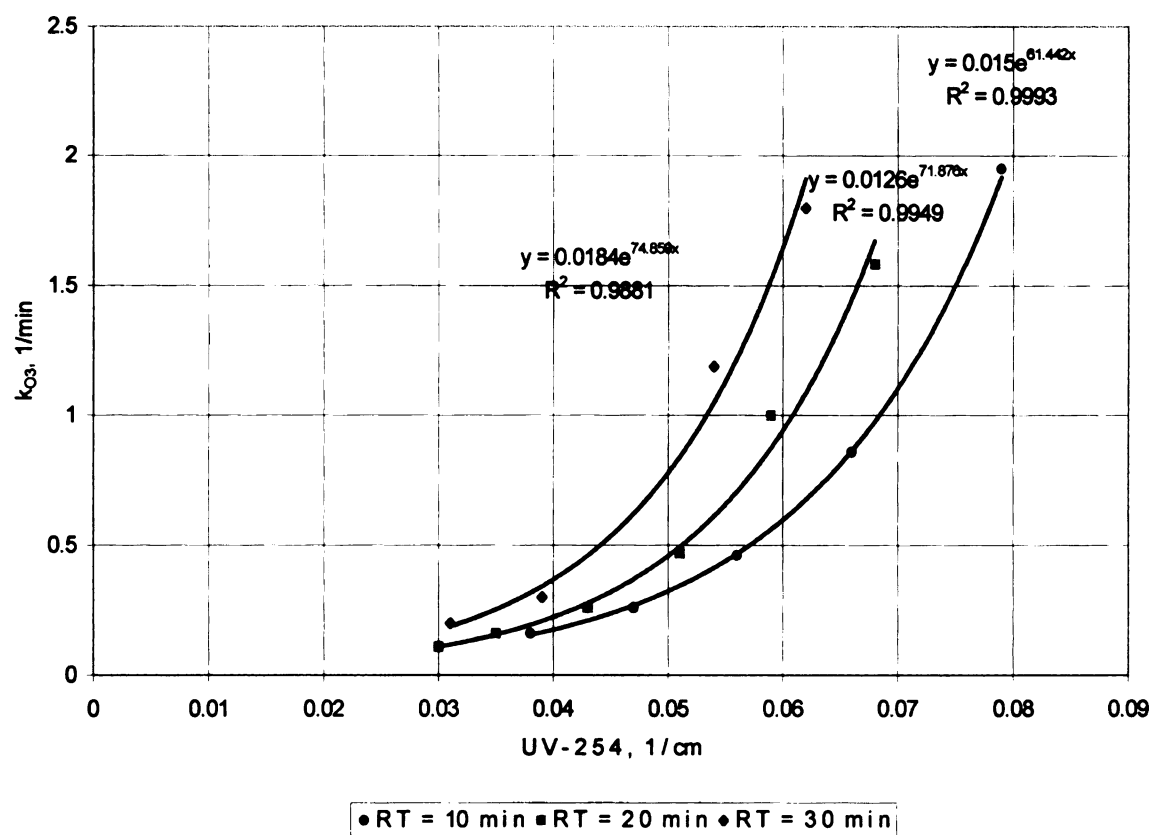


Figure 6.24 Relationship between UV-254 and k_{O_3} for various retention times

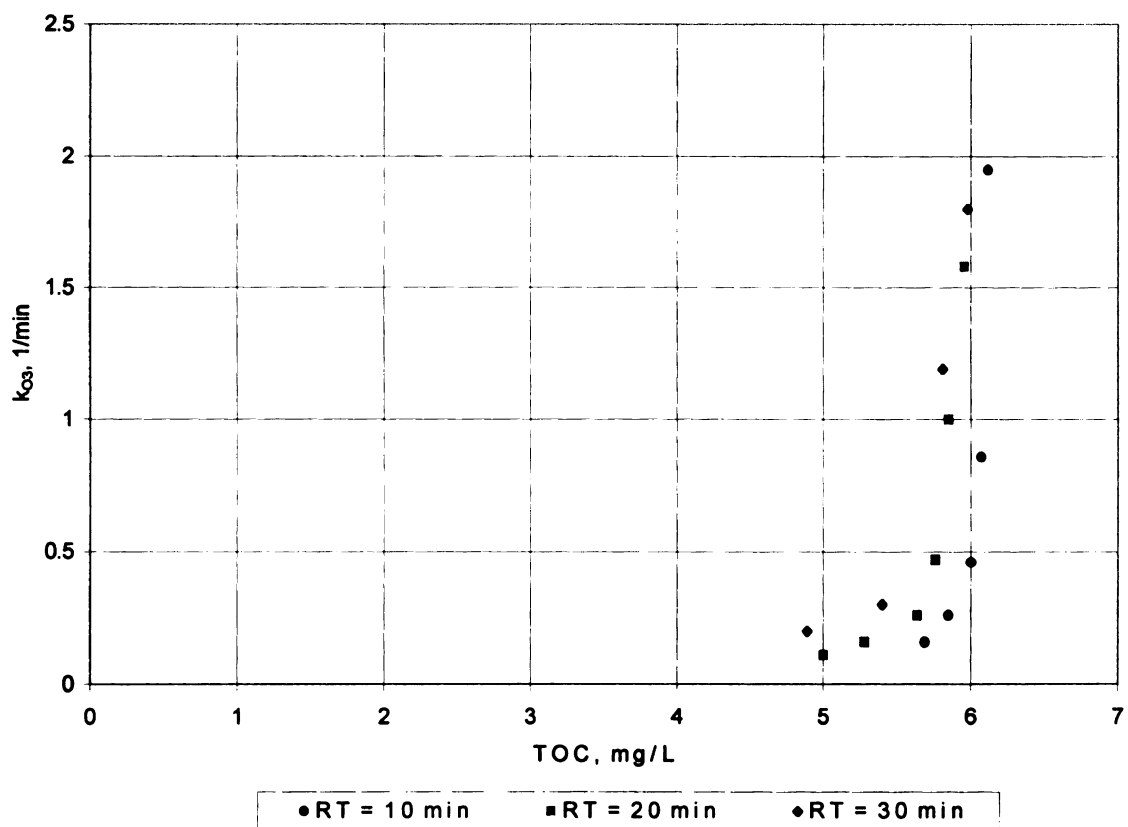


Figure 6.25. Relationship between TOC and k_{O_3} for various retention times

6.3.4. Reaction of Ozone with Humic Substances

This section presents the kinetic study of the ozone reaction with HS. The objectives of the study were:

- to test the hypothesis that, at an HRT of less than 10 minutes and ozone dose of 1 mg/mg C and less, ozone is directed solely for the oxidation of humic substances, which are converted into nonhumic materials;
- to determine the stoichiometric coefficient for the reaction of ozone with humic substances;
- to test the hypothesis that the rate constant of the ozone reaction with humic substances is a function of both temperature and the concentration of humic substances and can be expressed in two independent terms: a temperature-dependent term and a concentration-dependent term;
- to determine the kinetic parameters of the ozone reaction with humic substances.

6.3.4.1. Stoichiometric Coefficient

The results of the study presented in Section 6.2 showed that the removal of TOC was not significant at 95% confidence interval at an HRT of 10 minutes and ozone doses of 1 mg/mg C or less. It was also shown that the removal of UV-254-absorbing compounds increased with ozone dose and was independent of HRT (see Section 6.2) Taking into consideration that there exists a good correlation between HS and UV-254

(see Section 5.3), it was expected that at an HRT of less than 10 minutes and ozone doses of 1 mg/mg C or less, ozone would oxidize only humic substances, which would result in an increase in the concentration of nonhumic materials. Nonhumic substances were not expected to be oxidized under such conditions.

Figure 6.26 shows the experimental results for ozonation conducted at room temperature and a retention time of 7 minutes. The ozone dose was varied from 0 to 1 mg/mgC. It should be noted that on the plot in Figure 6.26, ozone dose was expressed in mg/L, instead of mg/mg C. This was done in order to be able to calculate the stoichiometric coefficient. The TOC removal was essentially at 95 percent confidence interval. The removal of humic substances followed the linear equation:

$$HS = -0.1931 \cdot [\text{ozone dose}] + 3.4167 \quad (6.25)$$

with $R^2 = 0.9947$.

An increase in the concentration of nonhumic substances followed the linear equation:

$$\text{nonHS} = 0.1925 \cdot [\text{ozone dose}] + 2.395 \quad (6.26)$$

with $R^2 = 0.8991$.

As can be seen in Figure 6.26 and from Equations (6.25) and (6.26), ozone oxidized humic substances, which were converted into nonhumic materials. The absolute values of slopes of lines described by Eqs. (6.25) and (6.26) indicates that no oxidation of nonhumic materials occurred.

The stoichiometric coefficient for the ozone reaction with humic substances was calculated from Equation (9.25) and was equal 5.17 mg O₃/mg HS.

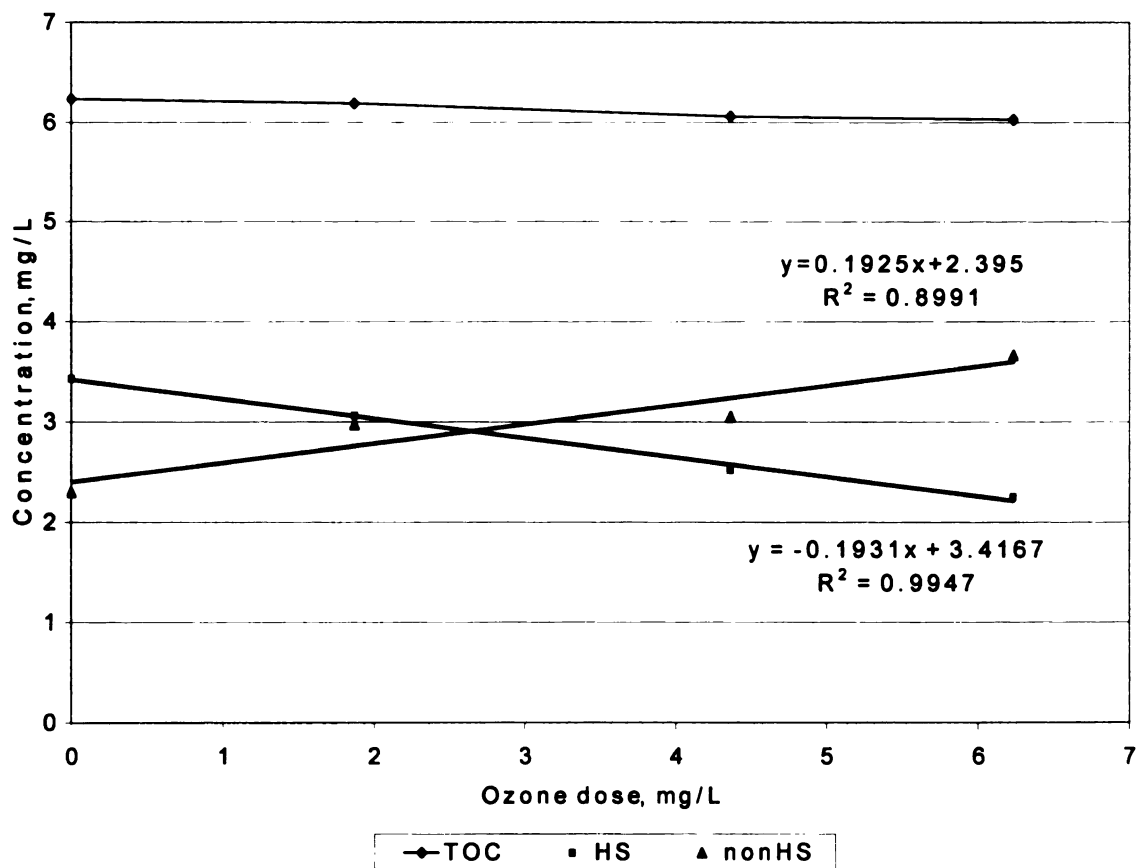


Figure 6.26. Transformation of organic matter during ozonation
(HRT = 7 minutes)

6.3.4.2. Reaction Rate Coefficient

The study presented in Section 6.2.3 and the evidence from the literature (Bablon et al., 1991b) showed that the rate coefficient of the ozone reactions in water depends on the concentration of NOM. It was thought that the rate coefficient of the reaction of ozone with humic substances is a function of temperature and the concentration of humic substances and can be expressed in two independent terms, as follows:

$$k_{HS} = k_{HS}(t) \cdot k_{HS}(c_{HS}) \quad (6.27)$$

where k_{HS} is the reaction rate coefficient; $k_{HS}(t)$ is the temperature-dependent term of the reaction rate coefficient; $k_{HS}(c_{HS})$ is the concentration-dependent term of the reaction rate coefficient.

The goals of the study presented in this section were to validate Equation (6.27) and to determine the rate coefficients for the ozone reaction with humic substances. The experiments were conducted at ozone doses ranging from 0 to 5 mg/mg C and at temperatures ranging from 10 to 30°C. The water flow rate was 18 mL/min, which corresponded to an HRT of 20 minutes. The reaction rate coefficient, k_{HS} , was determined using Equation (6.15), which for steady state gave:

$$k_{HS} = \frac{Q}{V} \frac{(c_{HS}^0 - c_{HS})}{c_{HS}c_L} \quad (6.28)$$

Figure 6.27 shows the effect of temperature and the concentration of humic substances on k_{HS} . The k_{HS} decreased exponentially with the removal of humic substances, as follows:

$$k_{HS} = ae^{bc_{HS}} \quad (6.29)$$

As can be seen in Figure 6.27, the exponential factor appears to be independent of temperature, whereas the preexponential factor increased with temperature. Thus, Equation 6.29 can be rewritten as

$$k_{HS} = k_{HS}^t e^{E_{HS}^c c_{HS}} \quad (6.30)$$

where E_{HS}^c is the exponential factor of the concentration-dependent term; k_{HS}^t is the temperature-dependent term.

The k_{HS}^t value was expected to vary with temperature by Arrhenius' Law:

$$k_{HS}^t = k_{HS}^0 e^{-\frac{E_{HS}^T}{RT}} \quad (6.31)$$

where k_{HS}^0 is the frequency factor; E_T is the activation energy; R is the universal gas constant; T is temperature, °K.

As can be seen in Figure 6.28, a plot of $\ln k_{HS}^t$ versus $1/T$ yielded a straight line, where the slope was $-E_{HS}^T/R$ and the intercept was $\ln k_{HS}^0$.

Combining Equations (6.30) and (6.31), the rate coefficient of the ozone reaction with humic substances could be expressed in two independent terms, as follows:

$$k_{HS} = k_{HS}^0 e^{-\frac{E_{HS}^T}{RT}} e^{E_{HS}^c c_{HS}} \quad (6.32)$$

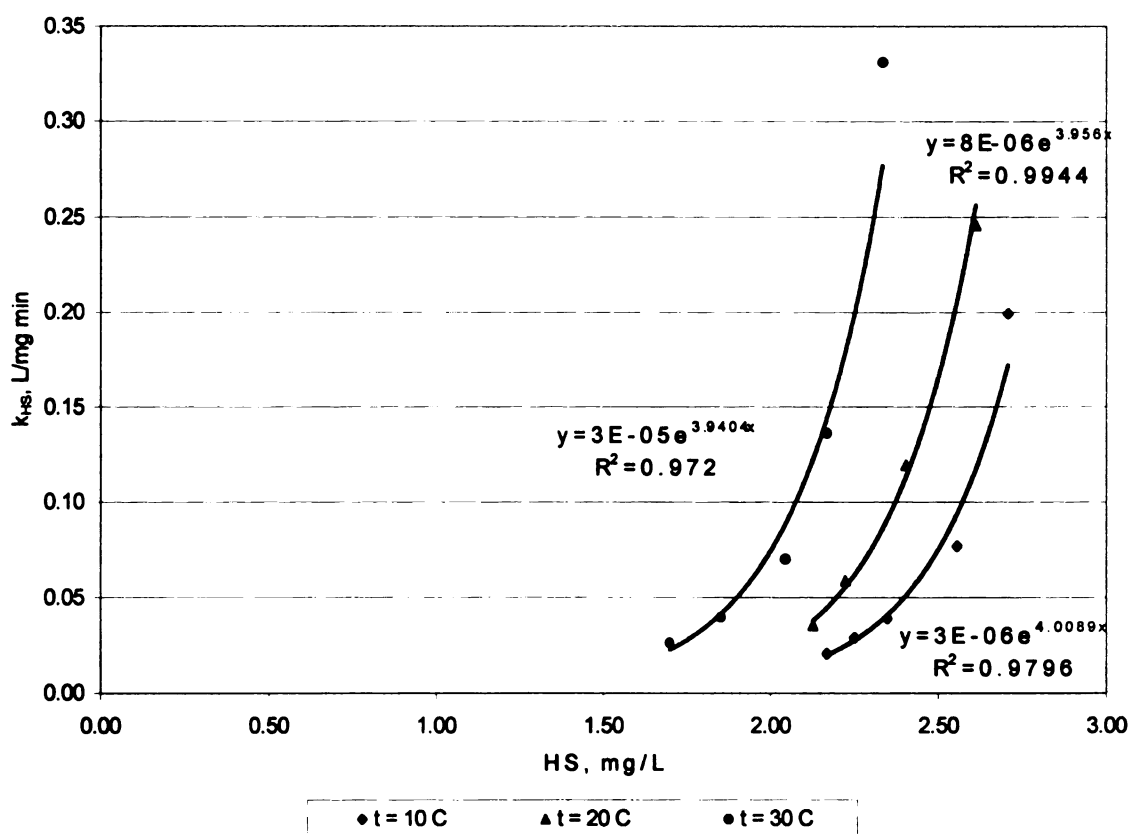


Figure 6.27. Relationship between HS and k_{HS} for various temperatures
(the data for 15°C are not included for ease of readability)

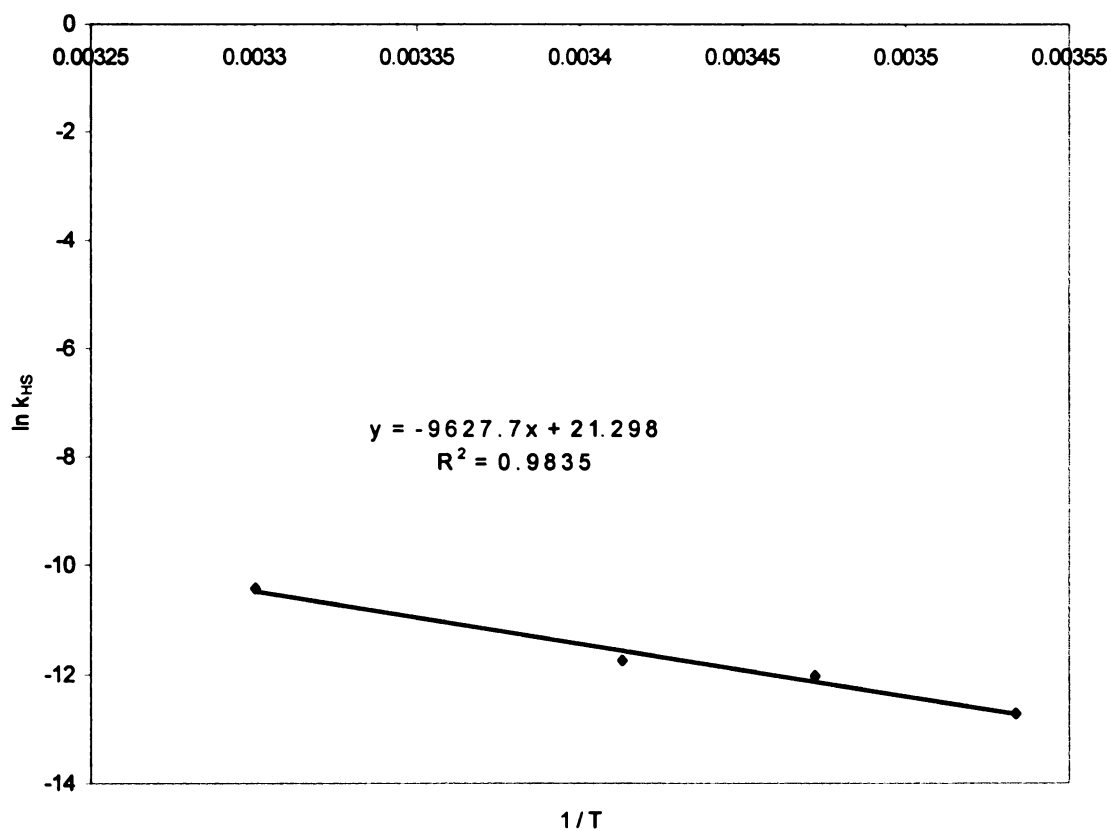


Figure 6.28. The plot of Arrhenius' equation for the reaction of ozone with humic substances

6.3.5. Reaction of Ozone with Nonhumic Substances

This section presents the kinetic study of the ozone reaction with nonhumic substances. The objectives of the study were:

- to determine the stoichiometric coefficient for the reaction of ozone with nonhumic substances;
- to test the hypothesis that the rate constant of the ozone reaction with nonhumic substances is a function of both temperature and the concentration of nonhumic substances and can be expressed in two independent terms: a temperature-dependent term and a concentration-dependent term;
- to determine the kinetic parameters of the ozone reaction with nonhumic substances.

6.3.5.1. Stoichiometric Coefficient

The stoichiometric coefficient for the ozone reaction with nonhumic substances was determined using the following equation:

$$v_{\text{nonHS}} = \frac{\left(\frac{G}{Q}(c_g^{\text{in}} - c_g^{\text{out}}) - v_{\text{HS}}(c_{\text{HS}}^0 - c_{\text{HS}})\right)}{(c_{\text{nonHS}}^0 - c_{\text{nonHS}} + c_{\text{HS}}^0 - c_{\text{HS}})} \quad (6.33)$$

where G and Q are the gas and water flow rates, respectively, mL/min; c_g^{in} and c_g^{out} are the concentration of ozone in influent and effluent, respectively, mg/L; c_{HS}^0 and c_{nonHS}^0 are the concentration of HS and nonHS in raw water, respectively, mg/L; c_{HS} and c_{nonHS} are the concentration of HS and nonHS in the effluent, respectively, mg/L.

The experimental design was the same as described in the previous section with the exception that ozone dose was varied from 1 to 5 mg/mg C. The gas and water flow rates were 36 and 18 mL/min, respectively. The results of the experiments are presented in Table 6.3.

Table 6.3. Experimental data for v_{nonHS}

Parameter	Raw water	Ozonated samples		
c_g^{in} , mg/L		6.98	16.22	27.04
c_g^{out} , mg/L		3.45	9.89	18.38
HS, mg/L	3.40	2.40	1.98	1.75
nonHS, mg/L	2.68	3.50	3.57	3.58
v_{nonHS} , mg O_3 /mg nonHS		10.1	10.0	11.7

The value of v_{nonHS} that was used in subsequent analysis was calculated as an average of the values determined in these experiments and was equal 10.6 mg O_3 /mg nonHS.

6.3.5.2. Reaction rate coefficient

The reaction rate coefficient, k_{nonHS} , was determined by combining Equations (6.15) and (6.16), which for steady state gave:

$$k_{\text{nonHS}} = \frac{Q (c_{\text{nonHS}}^0 - c_{\text{nonHS}} + c_{\text{HS}}^0 - c_{\text{HS}})}{V c_{\text{nonHS}} c_L} \quad (6.34)$$

The k_{nonHS} was determined using the data from the same series of experiments, which were used to determine k_{HS} with the exception that only data for an ozone dose of 1 mg/mg C and greater were used.

The values of k_{nonHS} for various ozone doses and temperatures are presented in Table 6.4. As expected, k_{nonHS} increased with temperature, but did not appear to be dependent of ozone dose. This is thought to be because the concentration of nonhumic substances remained at the same level during ozonation (see Table 6.3). For the range of operational conditions studied, the k_{nonHS} was assumed to independent of ozone dose and had, therefore, only a temperature-dependent term and could be expressed as:

$$k_{\text{nonHS}} = k_{\text{nonHS}}^0 e^{-\frac{E_{\text{nonHS}}^T}{RT}} \quad (6.35)$$

A plot of $\ln k_{\text{nonHS}}$ versus $1/T$, shown in Figure 6.29, yielded a straight line, where the slope was $-E_{\text{nonHS}}^T/R$ and the intercept was $\ln k_{\text{nonHS}}^0$.

Table 6.4 Values of k_{nonHS}

Ozone dose, mg/mg C	k_{nonHS} , L/mg min			
	Temperature, °C			
	10	15	20	30
1	0.001			
1.1		0.003		
1.2	0.001			
1.3			0.003	
1.4	0.002	0.002		
1.5			0.004	
1.7		0.002		
1.9				0.013
2.0		0.002		
3				0.009
5				0.009

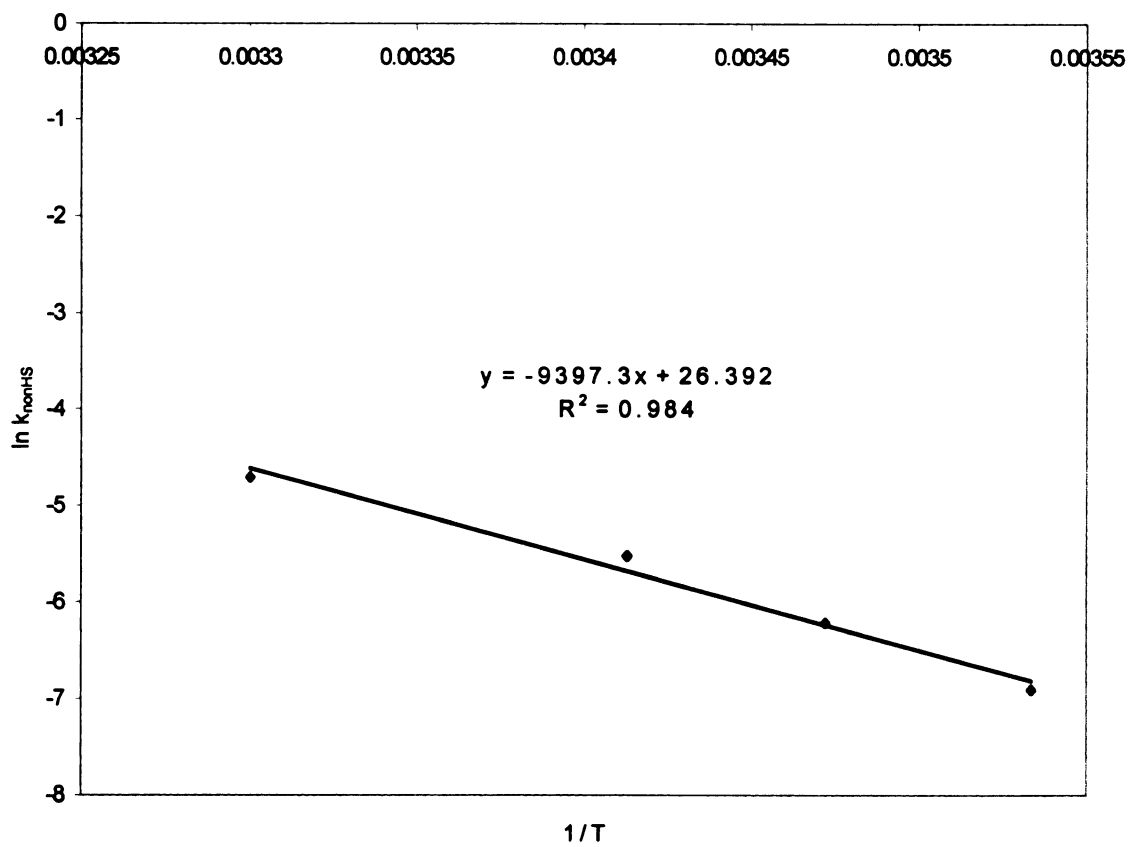


Figure 6.29. The plot of Arrhenius' equation for the reaction of ozone with nonhumic substances

6.3.6. Mass Transfer Coefficient

The mass transfer coefficient, k_La , was determined using Equations (6.23) and the data from the same series of experiments, which were used to determine k_{HS} and k_{nonHS} . The values of k_La for various ozone doses and temperatures are presented in Table 6.5. The k_La did not appear to be affected by either ozone dose or temperature for the range of operational conditions studied. The k_La used in the subsequent analysis was calculated as an average of the data presented in Table 6.5.

Table 6.5. Values of k_La

Ozone dose, mg/mg C	k_La , 1/min			
	Temperature, °C			
	10	15	20	30
1	0.73		0.60	
1.1		0.64		
1.2	0.71			
1.3			0.62	
1.4	0.89	0.68		0.67
1.5			0.83	
1.7		0.70		
1.9				0.80
2.0		0.79		
3				0.89
5				0.7

6.3.7. Ozonation Model

Resulting model, which described the ozonation kinetics of NOM, was obtained by combining Equations (6.14)-(6.17), (6.32) and (6.35), as follows (with the kinetic parameters are listed in Table 6.6):

$$V \frac{dc_L}{dt} = (k_L a(\alpha c_g^{(i)} - c_L) - v_{HS} k_{HS}^0 e^{-\frac{E_{HS}^T}{RT}} e^{E_{HS}^c c_{HS}} c_{HS} c_L - v_{nonHS} k_{nonHS}^0 e^{-\frac{E_{nonHS}^T}{RT}} c_{nonHS} c_L) V - Q c_L \quad (6.36)$$

$$V \frac{dc_{HS}}{dt} = Q(c_{HS}^0 - c_{HS}) - k_{HS}^0 e^{-\frac{E_{HS}^T}{RT}} e^{E_{HS}^c c_{HS}} c_{HS} c_L V \quad (6.37)$$

$$V \frac{dc_{nonHS}}{dt} = Q(c_{nonHS}^0 - c_{nonHS}) - k_{nonHS}^0 e^{-\frac{E_{nonHS}^T}{RT}} c_{nonHS} c_L V + k_{HS}^0 e^{-\frac{E_{HS}^T}{RT}} e^{E_{HS}^c c_{HS}} c_{HS} c_L V \quad (6.38)$$

$$H_g \frac{dc_g^{(i)}}{dt} = G(c_g^{(0)} - c_g^{(i)}) - k_L a(\alpha c_g^{(i)} - c_L) V \quad (6.39)$$

Table 6.6. Kinetic parameters for ozonation model

Parameter	Dimension	Value
v_{HS}	mg O ₃ /mg HS	5.17
v_{nonHS}	mg O ₃ /mg nonHS	10.6±0.04
k_{HS}^o	L/mg min	9628
E_{HS}^c	L/mg	3.97±0.02
$E_{HS/R}^I$	°K	1.78E+09
k_{nonHS}^o	L/mg min	9397
$E_{nonHS/R}^I$	°K	2.89E+11
k_{La}	1/min	0.7±0.1

6.3.8. Model Validation

The numerical calculations were performed using the ModelMaker computer simulation program (Cherwel Scientific, Oxford, United Kingdom). The ozonation model described by Equations (6.36)-(6.39) was validated for the following range of experimental conditions:

- Ozone dose – 0 to 4 mg/mg C
- Temperature – 10 to 25°C
- Retention time – 7 and 20 minutes.

First, the specific rates of ozone consumption could be determined independently using the spectroscopic method (see Section 6.3.3) and using the ozonation model described by Equations 6.14, in which the specific rate of ozone consumption could be described as follows:

$$k_{o_3}^m = v_{HS} k_{HS} c_{HS} + v_{nonHS} k_{nonHS} c_{HS} \quad (6.40)$$

The values of the specific ozone utilization rate determined using the spectroscopic method (k_{O_3}) were compared with those obtained using Equation (6.40) over a range of operational parameters described above. Figure 6.30 shows that there exists a good agreement between these parameters.

Figures 6.31-6.34 present the comparison of experimental and calculated data for the ozonation of raw water conducted at room temperature and a retention time of 7

minutes. There was a good agreement between measured and calculated ozone concentrations in the effluent gas (see Figure 6.31). The calculated dissolved ozone concentrations were, however, lower than the experimental values (see Figure 6.32). The model described very well the removal of HS and nonHS during ozonation (see Figures 6.33-6.34).

Figures 6.35-6.38 present the comparison of experimental and calculated data for ozonation of raw water conducted at room temperature and a retention time of 20 minutes. As can be seen there was a good agreement between the model and experimental data for all parameters.

Table 6.7 presents experimental and calculated data for ozonation at an ozone dose of 1 mg/mg C and a retention time of 7 minutes and temperatures ranging from 10 to 25°C. The calculated values of the influent gas ozone concentration were slightly lower than the experimental ones. The difference, however, did not exceed 15 percent. A good agreement between the calculated and experimental data was observed for the dissolved ozone concentration except for the values obtained at 10°C. The difference between calculated and experimental values for HS and nonHS did not exceed 5 percent.

Table 6.8 presents experimental and calculated data for ozonation at an ozone dose of 1 mg/mg C and a retention time of 20 minutes and temperatures ranging from 10 to 20°C. Very good agreement between calculated and experimental data was observed for all parameters except for dissolved ozone concentration, for which the calculated values were approximately 30 percent lower than the experimental data.

Thus, the model and experiments produced agreeable results for all parameters except for dissolved ozone concentration for which calculated values were lower than the

experimental values in two out of four series of experiments. Further studies are needed to reconcile this discrepancy. The model adequately described the transformation of humic and nonhumic substances. The relative difference between the experimental and calculated values did not exceed 10 percent with an average of 6 percent.

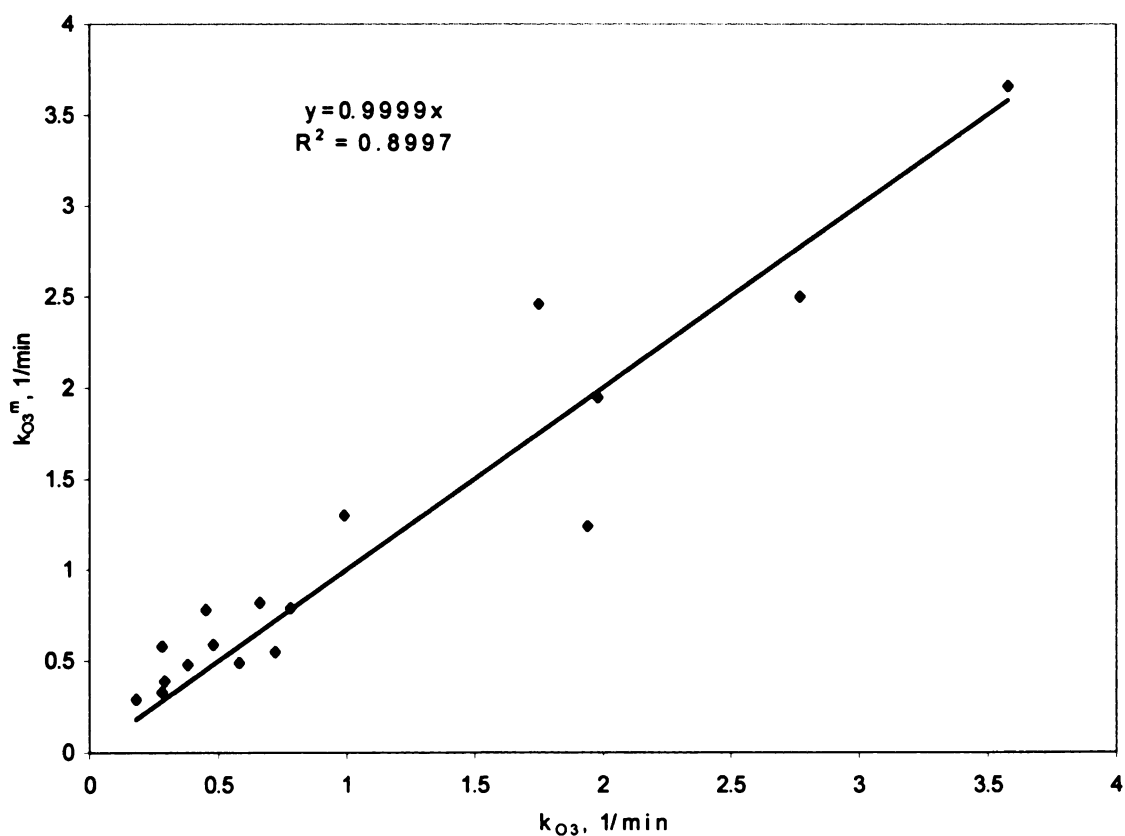


Figure 6.30. Specific ozone utilization rate determined spectrophotometrically and using Equation (6.40).

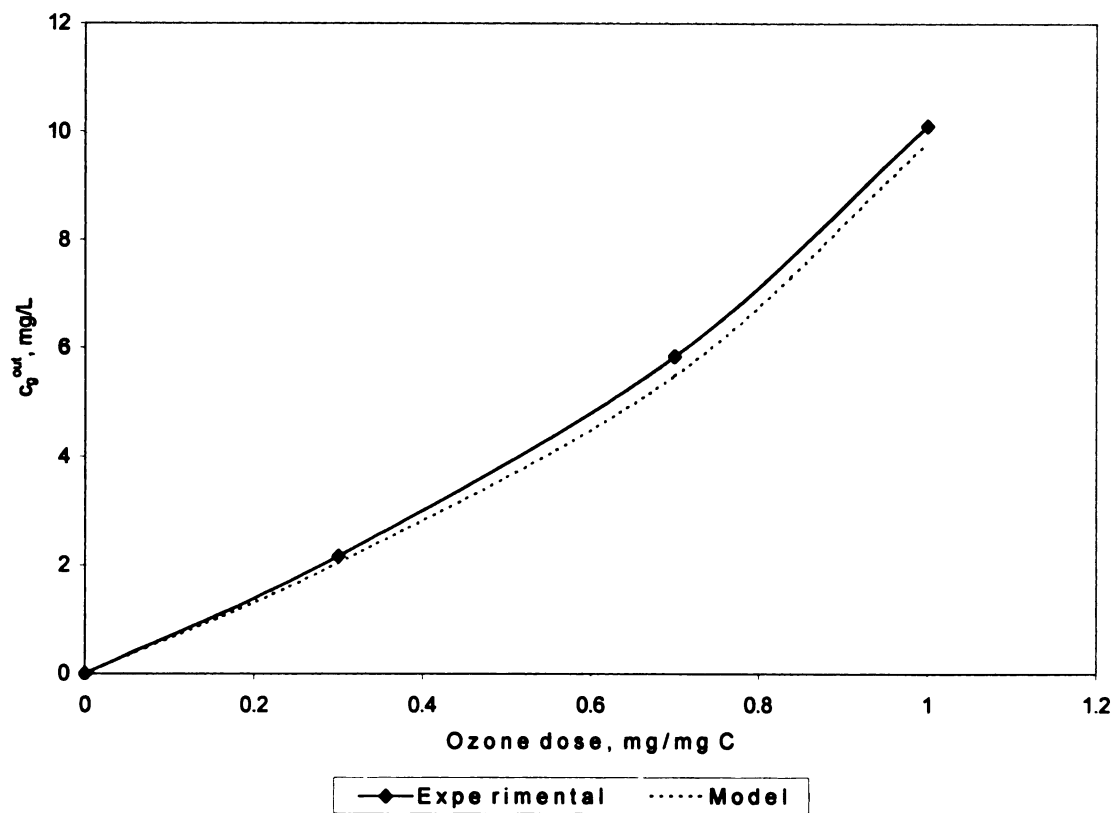


Figure 6.31. Experimental and calculated data for c_g^{out}
($t=20^{\circ}\text{C}$, $\text{RT}=7$ min)

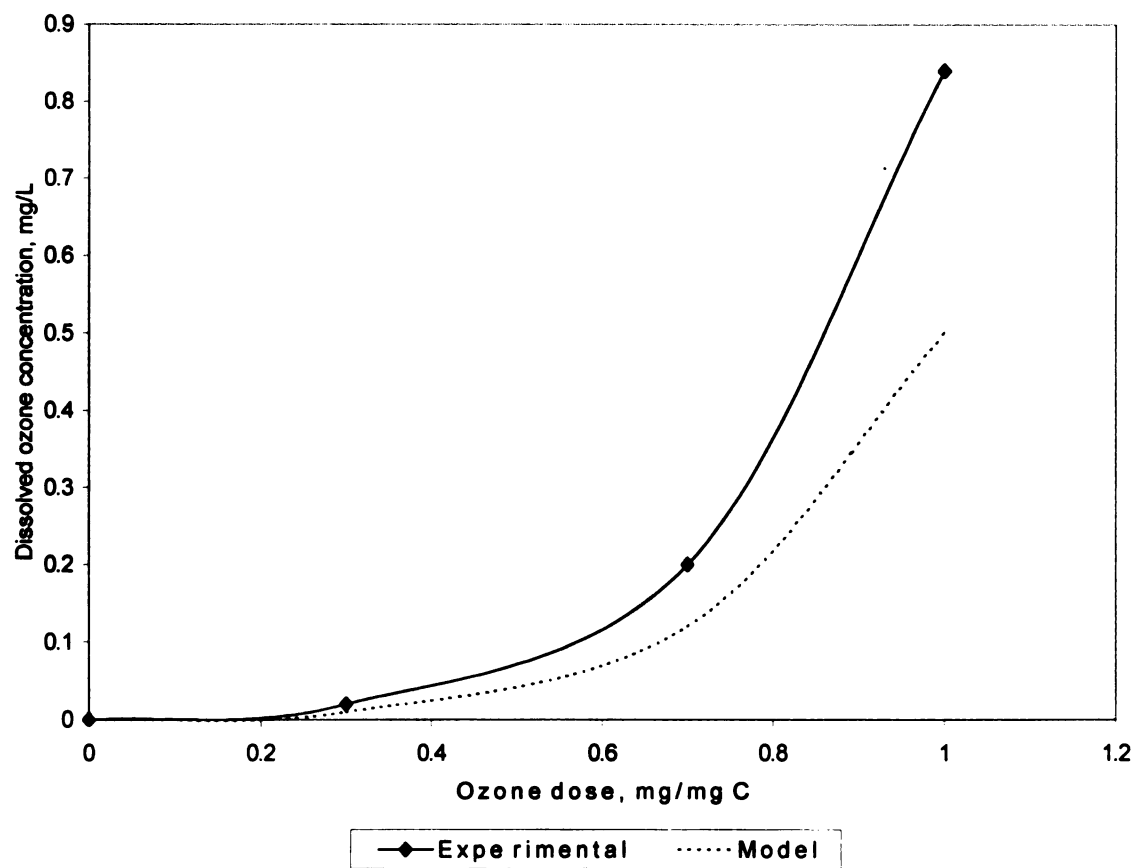


Figure 6.32. Experimental and calculated data for c_L
($t=20^{\circ}\text{C}$, $\text{RT}=7$ min)

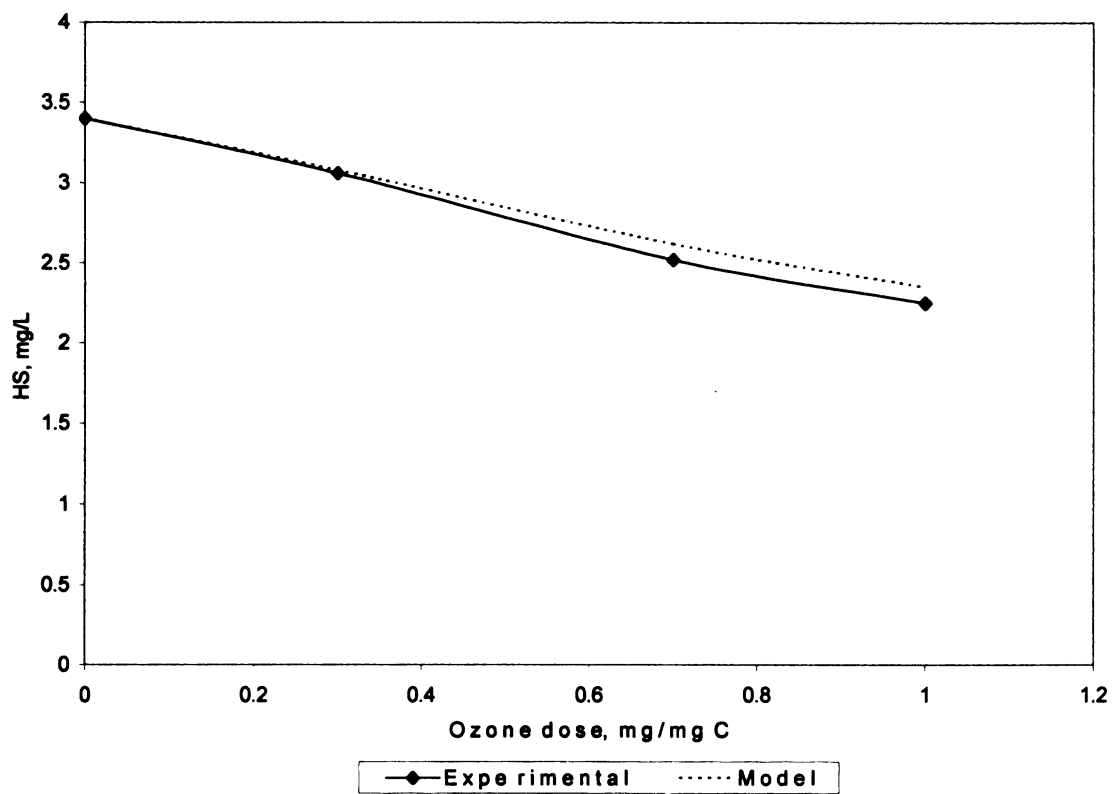


Figure 6.33. Experimental and calculated data for HS
($t=20^{\circ}\text{C}$, $\text{RT}=7$ min)

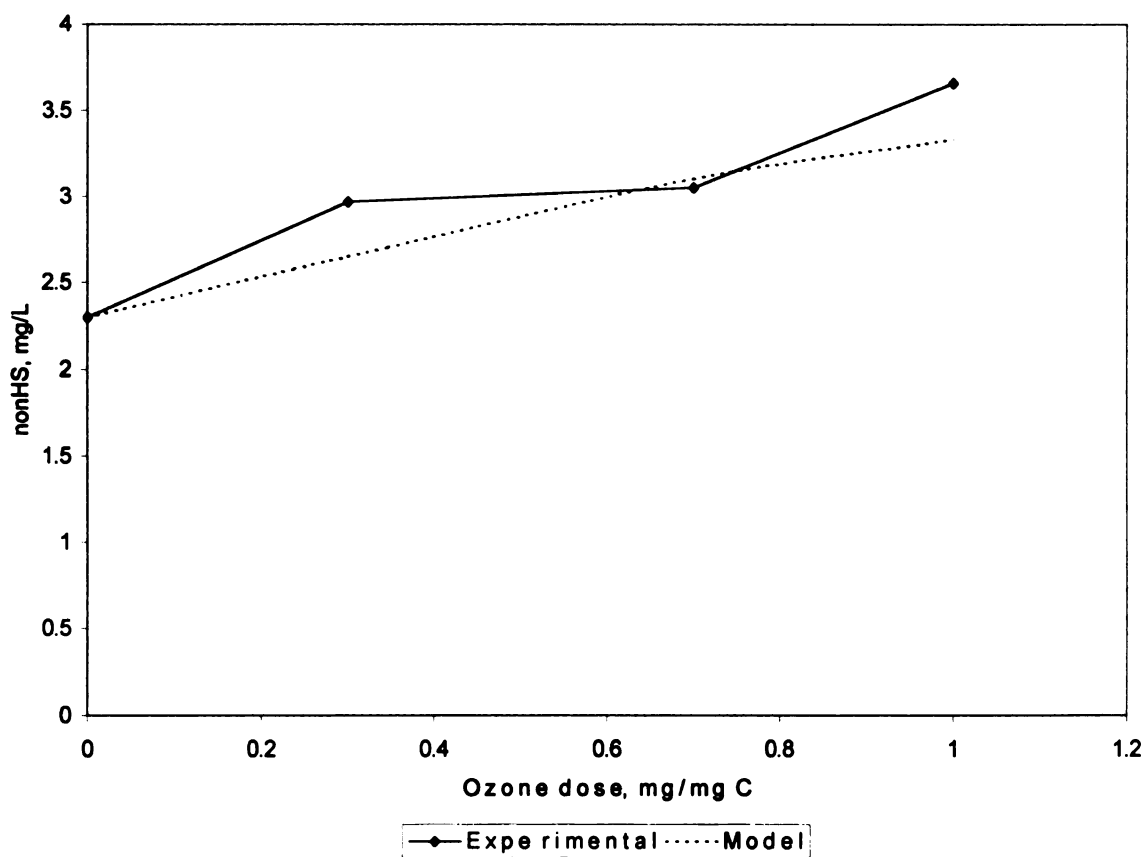


Figure 6.34. Experimental and calculated data for nonHS
($t=20^{\circ}\text{C}$, $\text{RT}=7$ min)

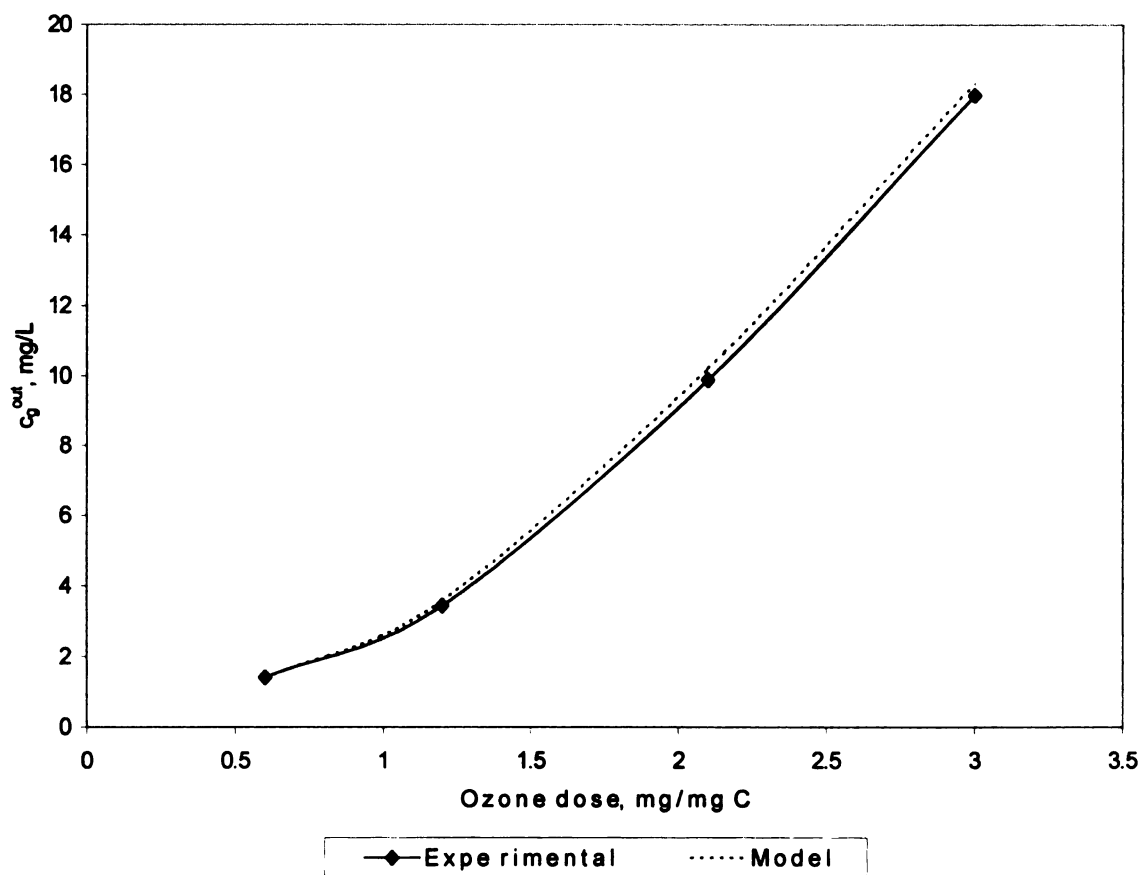


Figure 6.35. Experimental and calculated data for c_g
($t=20^\circ\text{C}$, $RT=20$ min)

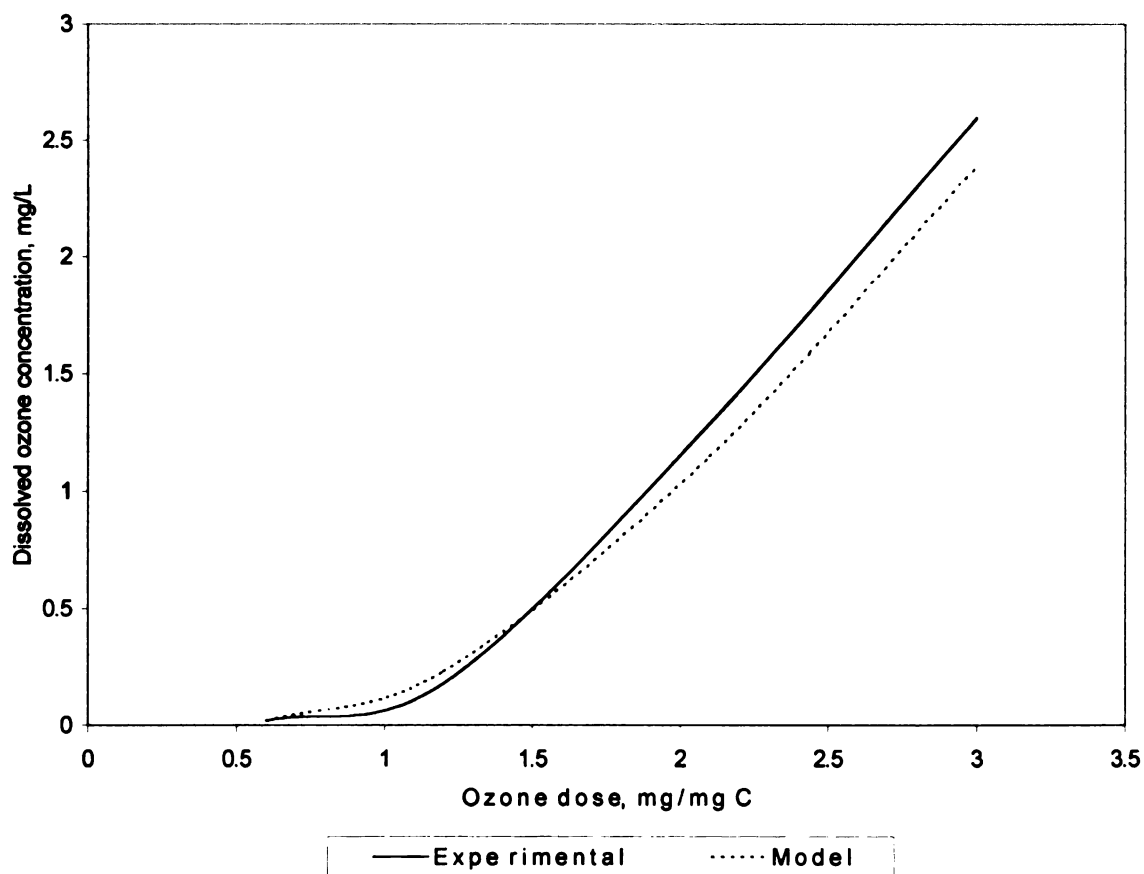


Figure 6.36. Experimental and calculated data for c_L
($t=20^{\circ}\text{C}$, $\text{RT}=20\text{ min}$)

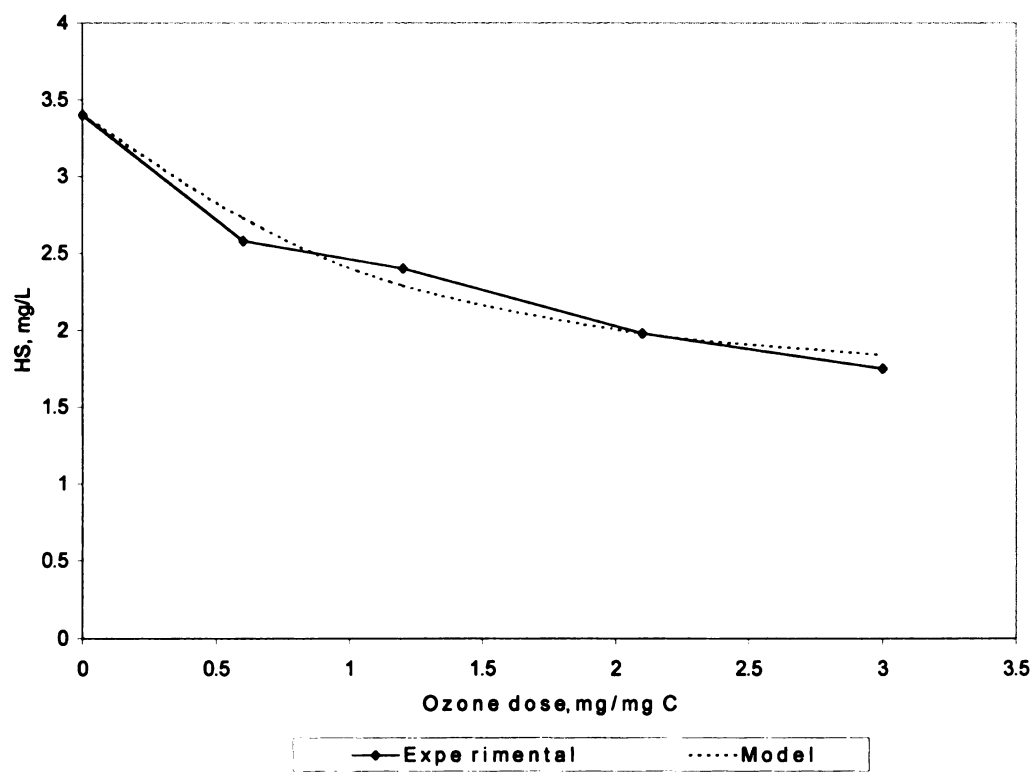


Figure 6.37. Experimental and calculated data for HS

($t=20^{\circ}\text{C}$, $\text{RT}=20\text{ min}$)

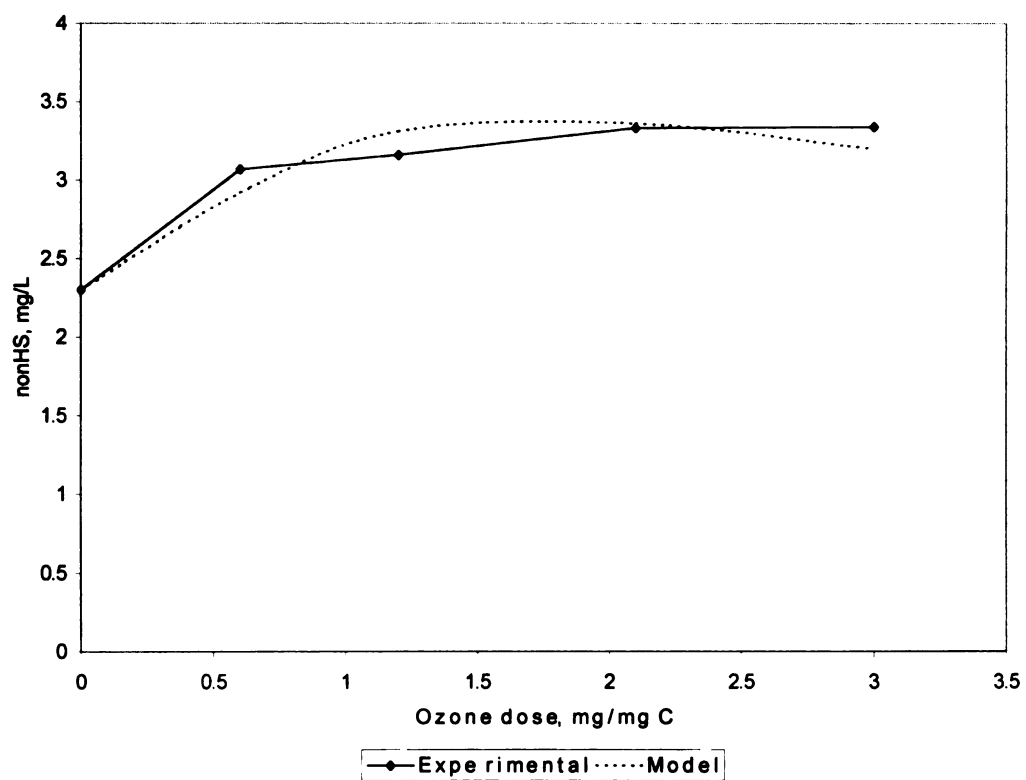


Figure 6.38. Experimental and calculated data for nonHS
($t=20^{\circ}\text{C}$, $\text{RT}=20\text{ min}$)

Table 6.7. Experimental and calculated data for ozonation of raw water
(ozone dose=1 mg/mg C, HRT=7 minutes)

t, °C	c _g , mg/L			c _L , mg/L		
	Experim	Model	Rel. differ, %	Experim	Model	Rel. differ, %
10	10.11	9.64	4.6	1.65	1.25	24.0
15	9.89	9.64	2.5	1.08	0.90	16.6
20	10.04	9.55	5.4	0.89	0.88	1.1
25	10.26	8.72	15.0	0.59	0.62	-5.0

t, °C	c _{HS} , mg/L*			c _{nonHS} , mg/L**		
	Experim	Model	Rel. differ, %	Experim	Model	Rel. differ, %
10	2.34	2.43	-3.8	3.15	3.24	-2.8
15	2.39	2.38	0.4	3.15	3.28	-4.1
20	2.45	2.39	2.4	3.13	3.28	-4.6
25	2.42	2.35	2.9	3.36	3.31	1.4

* - HS concentration in raw water was 3.36 mg/L

** - nonHS concentration in raw water was 2.2 mg/L

Table 6.8. Experimental and calculated data for ozonation of raw water
(ozone dose=1 mg/mg C, HRT=20 minutes)

t, °C	c _g , mg/L			c _L , mg/L		
	Experim	Model	Rel. differ, %	Experim	Model	Rel. differ, %
10	4.17	4.14	0.7	0.98	0.69	29.6
15	4.1	4.04	1.4	0.67	0.49	26.8
20	3.95	3.97	-0.5	0.5	0.33	34.0

t, °C	c _{HS} , mg/L*			c _{nonHS} , mg/L**		
	Experim	Model	Rel. differ, %	Experim	Model	Rel. differ, %
10	2.21	2.33	-5.4	3.13	3.15	-0.6
15	2.07	2.28	-10.1	3.37	3.19	5.3
20	2.05	2.25	-9.8	3.22	3.21	0.3

* - HS concentration in raw water was 3.4 mg/L

** - nonHS concentration in raw water was 2.3 mg/L

6.4. SUMMARY

The study presented in this Chapter investigated the effect of operational parameters, including ozone dose and HRT on the transformation of NOM during ozonation. Most of the UV-254-absorbing compounds in water were efficiently removed during ozonation at doses less than 1.5 mg/mg C. The HRT in the range from 10 to 60 minutes did not affect the removal of UV-254-absorbing compounds during ozonation. It appears that the removal of UV-254 was independent of the concentration of dissolved ozone. The removal of organic carbon increased with HRT and dissolved ozone concentration. Under the experimental conditions studied, gas flow rate did not affect the removal of either organic carbon or UV-254-absorbing compounds. This study confirmed the hypothesis that when ozonation was conducted at an HRT of less than 10 minutes and ozone doses of less than 1 mg/mg C, the concentration of BDOC increased with ozone dose.

This chapter presented the results of the kinetic study of the ozonation of NOM. Two models were developed. The first model was based on the specific ozone consumption rate and the second model described the changes in the concentration of humic and nonhumic substances during ozonation.

The specific rate of ozone consumption was measured using the spectroscopic method, which was developed in this study, and the methods based on the ozone consumption model described by Equations (6.6)-(6.7). It was shown that both methods gave agreeable results. The spectroscopic method, however, appeared to be more accurate than the method based on the ozone consumption model. The spectroscopic method was

also used to determine the concentration of dissolved ozone. It was shown that there existed a very good correlation between the dissolved ozone concentrations determined using the spectroscopic method and the Indigo method. The results of the experiments confirmed the first-order kinetics with respect to the specific ozone consumption rate. This study showed that the usefulness of the specific ozone consumption rate for the evaluation of ozonation efficacy was limited. This is because it was difficult to separate the effect of ozonation on UV-254-absorbing compounds and TOC based solely on the specific ozone consumption rate without additional information.

This study showed that humic and nonhumic fractions were good surrogate parameters for modeling the kinetics of ozone reaction in water. The results of the experiments confirmed the hypothesis that ozone converts humic substances into nonhumic materials and the removal of organic carbon appears to occur through the oxidation of nonhumic substances. It was shown that both reactions could proceed simultaneously. This study confirmed the hypothesis that the rate constant of the ozone reaction with humic substances was a function of temperature and the concentration of humic substances. This reaction rate constant could be represented as a product of two independent terms: a temperature-dependent terms and a concentration-dependent term. Under the operational conditions studied, the rate constant of the ozone reaction with nonhumic substances appeared to be independent of the concentration of nonhumic substances. The stoichiometric coefficients for the reactions of ozone with humic and nonhumic substances were 5.2 and 10.6 milligram of ozone per milligram of humic and nonhumic substances, respectively. This suggested that the amount of ozone required for the oxidation of nonhumic materials was approximately two times greater than that

required for the oxidation of humic substances. As was stated earlier, a mathematical model was developed that described the transformation of humic and nonhumic substances during ozonation. The kinetic parameters were determined and the model was verified over a wide range of ozone doses, temperatures, and HRTs. It was shown that the model adequately described the transformation of humic and nonhumic substances. The relative difference between the experimental and calculated data did not exceed 10 percent with an average of 6 percent.

7. BIODEGRADATION OF NOM

7.1. INTRODUCTION

Microorganisms can metabolize low molecular weight fractions of NOM and high molecular weight polymers can be hydrolyzed through the action of extracellular enzymes, which appears to be a key process controlling the overall rate of the degradation of NOM (Rittmann and Wooschlager, 1996). Klevens and Collins (1996) referred to these fractions as “fast” and “slow” BDOC. Monod kinetics adequately describes the utilization of “fast” BDOC (Rittmann and Wooschlager, 1996). However, in order to determine the kinetic biodegradation parameters, measurements of biomass concentration in the reactor are required. Considering low organic loading and low concentration of biomass attached to the support medium in the FBT column, accurate measurements of biomass concentration in the reactor were not possible. For this reason, a different approach to describe the biodegradation of NOM was proposed was proposed in this study, which is described in Section 7.2. The Monod kinetics was used only to determine the minimum concentration of substrate that required to maintain a steady-state biofilm (see Section 8.6)

The objective of the study presented in this section were:

- Using the concept of “fast” and “slow” BDOC, to determine biodegradation characteristics that quantify the efficacy of the biodegradation of NOM;
- To compare the biodegradation efficiency of FBT to that of biofiltration;
- To determine the effect of temperature on the efficiency of FBT;

- To test the hypothesis that when ozonation is conducted at an HRT of less than 10 minutes and ozone doses of 1 mg/mg C or less, the biodegradation efficiency increases with ozone dose.

The study was conducted using the FBT system, the biofiltration system, and the bench-scale ozonation system, which were described in Chapter 3. The experiments were conducted using raw and ozonated Huron River water. The operational parameters that were investigated included EBCT, ozone dose, and temperature. The parameters that were monitored in this study included TOC and UV-254 as they were shown to be good indicators of HS concentration and THMFP (see Chapter 5).

7.2. APPROACH

A typical curve of the removal of organic carbon in the biofiltration column or FBT column is shown in Figure 7.1. The tangent line to the curve changed from a sharp decrease after depletion of “fast” BDOC to a more graduate decrease during the assimilation of slowly biodegradable compounds. Nonbiodegradable organic carbon was estimated at the point where the curve leveled off. Klevens et al. (1996) operationally defined the distinction between “fast” and “slow” BDOC by bisecting the extreme tangent lines of the organic curve, as shown in 7.1. This definition provides, however, only graphical determination of “fast” and “slow” BDOC, but not the mathematical description.

Several operationally defined parameters were introduced in this study. As outlined in Figure 7.1, the abscissa of the intersection of two extreme tangent lines

operationally defined $EBCT_{min}$, which represented the EBCT that at least required to remove “fast” BDOC. The ordinate of the intersection less the concentration of nonbiodegradable organic carbon operationally defined $BDOC_{slow}$, which represented the amount of BDOC that at least remained after biodegradation at $EBCT_{min}$. The maximum rate of the biodegradation of fast BDOC, R_{max} , was determined by the slope of the tangent line to the curve at $EBCT = 0$. This tangent line was mathematically defined as the line that connected two adjacent points at the beginning of biodegradation, as shown in Figure 7.1. The second extreme tangent line was mathematically defined as the line that connected two adjacent points at the end of biodegradation.

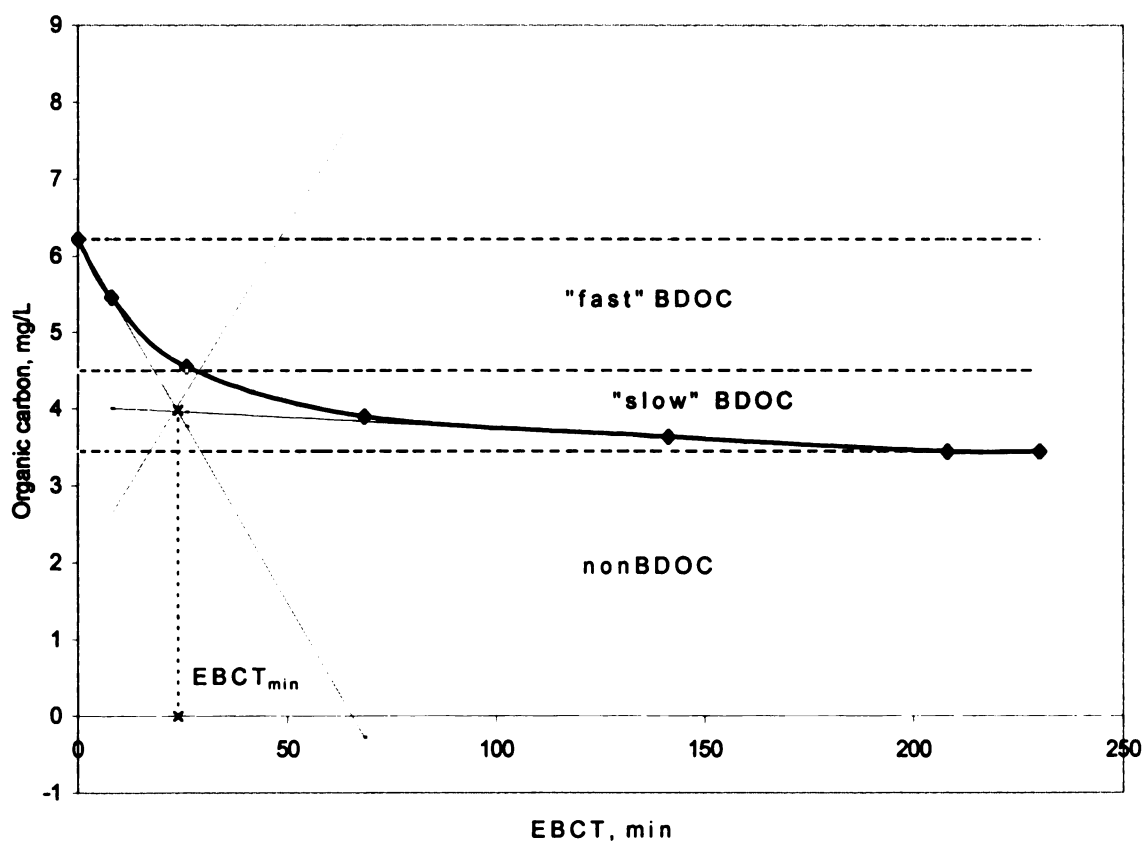


Figure 7.1. Biodegradable and nonbiodegradable fractions of NOM

7.3. FBT VS. BIOFILTRATION

The goal of the experiments presented in this section was to compare the efficiency of FBT to that of biofiltration with respect to the removal of NOM from raw water. It was expected that the biodegradation efficiency in the FBT column would be greater than that in the biofiltration system. This is because the available surface area of the fluidized bed is greater than that of the biofilter.

The study was conducted using the FBT column and the biofiltration column, which were described in Chapter 3. The flow rate to the FBT column was varied from 2 to 60 mL/min, which corresponded to EBCTs of 10 to 300 min. The flow rate to the biofiltration column was varied from 0.4 to 20 mL/min, which corresponded to EBCTs of 5 to 250 minutes. All experiments were conducted at room temperature. Most experiments were conducted in summer 1997. Additional data were collected in November 1997 to account for seasonal variations in the quality of Huron River water.

Changes in UV-254 of the raw water are shown in Figure 7.2. The removal of UV-254 increased with EBCT and leveled off at an EBCT of approximately 160-200 minutes reaching a level of 16 percent. The difference in the removal of UV-254-absorbing compounds by FBT and biofiltration was not significant at 5 percent level.

Figure 7.3 shows the removal of TOC by FBT and biofiltration. For both systems, the removal of TOC increased with EBCT and appeared to level off at an EBCT of approximately 150-200 minutes. It appears, however, that the FBT efficiency towards the removal of TOC was greater than that of biofiltration.

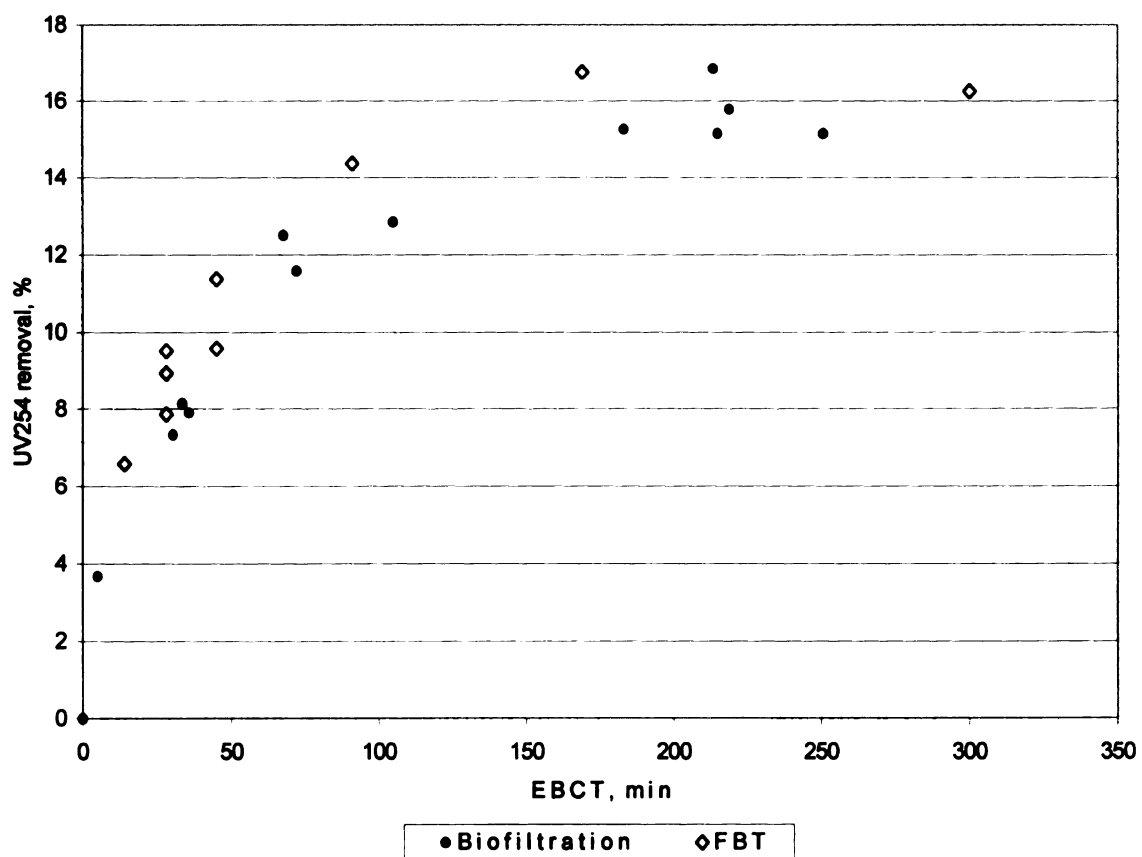


Figure 7.2. Removal of UV-254 from Huron River water by FBT and biofiltration

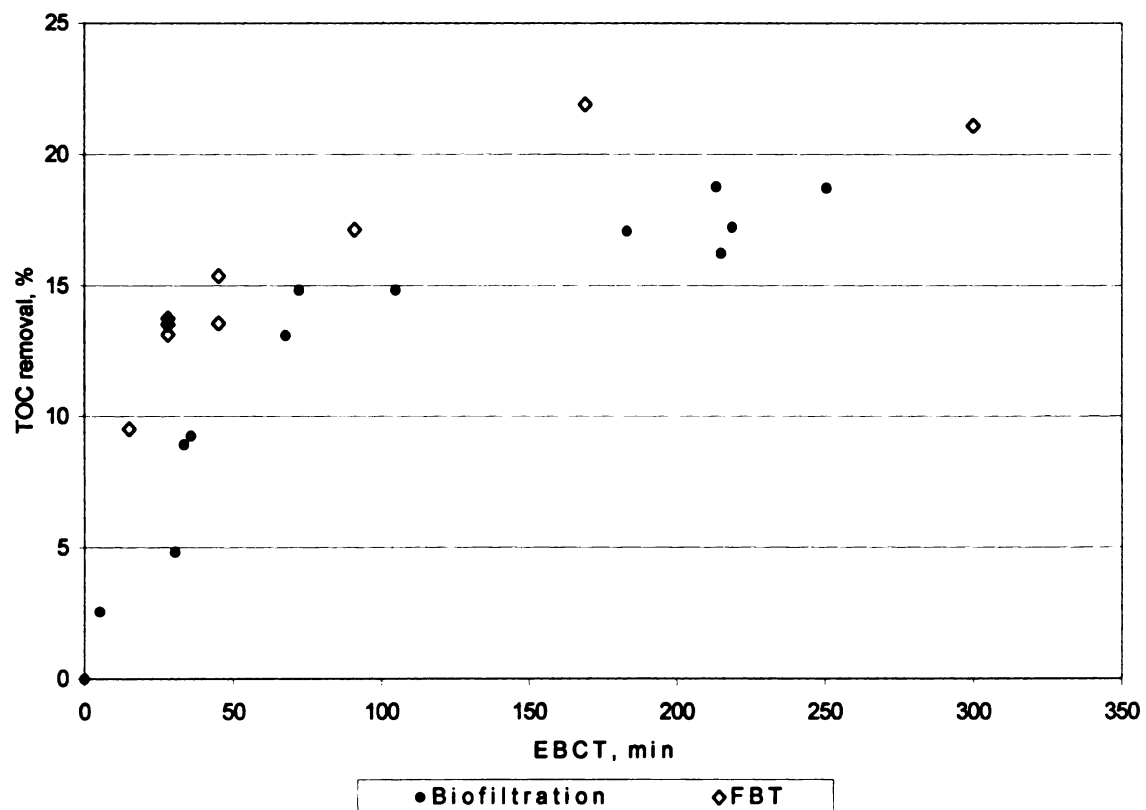


Figure 7.3. Removal of TOC from Huron River water by FBT and biofiltration

Using the approach, described in the previous section, an attempt was made to quantify the biodegradation efficiency of FBT and biofiltration. Figure 7.4 shows typical curves of the removal of BDOC by FBT and biofiltration. For both systems, two kinetic regions could be identified, which characterized the removal of “fast” and “slow” BDOC. The removal rate of “fast” BDOC in the FBT column was greater than that in the biofiltration column. Table 7.1 presents operationally defined biodegradation parameters for FBT and biofiltration. The $R_{\max}$ in the FBT system was two times greater than that in the biofiltration system. Consequently, $EBCT_{\min}$ was almost two times greater in the biofiltration system than that in the FBT system. The difference in $BDOC_{\text{slow}}$ for two systems was not significant at 5 percent level.

The results of the experiments showed that biodegradation efficiency in the FBT system was greater than that in the biofiltration system. It should be noted, however, that the systems were operated under different hydrodynamic conditions. In order to achieve the same EBCT, the flow rate to the FBT system was in the range from 2 to 60 mL/min, whereas the flow rate to the biofiltration was in the range from 0.4 to 20 mL/min. The biofiltration system was operated under plug-flow conditions, whereas the FBT system was operated as a CSTR. Considering that a commercial FBT system will be operated under conditions close to plug-flow conditions, the FBT efficiency is expected to be greater than that obtained in this study.

Table 7.1. Operationally defined biodegradation parameters for FBT and biofiltration

Treatment	Parameter			
	BDOC ₀ mg/L	R _{max} mg/L min	EBCT _{min} min	BDOC _{slow} mg/L
FBT ¹	1.2 ± 0.03	0.034 ± 0.003	26 ± 2	0.35 ± 0.06
Biofiltration ²	1.15 ± 0.07	0.017 ± 0.002	48 ± 3	0.38 ± 0.07

¹ two experiments

² four experiments

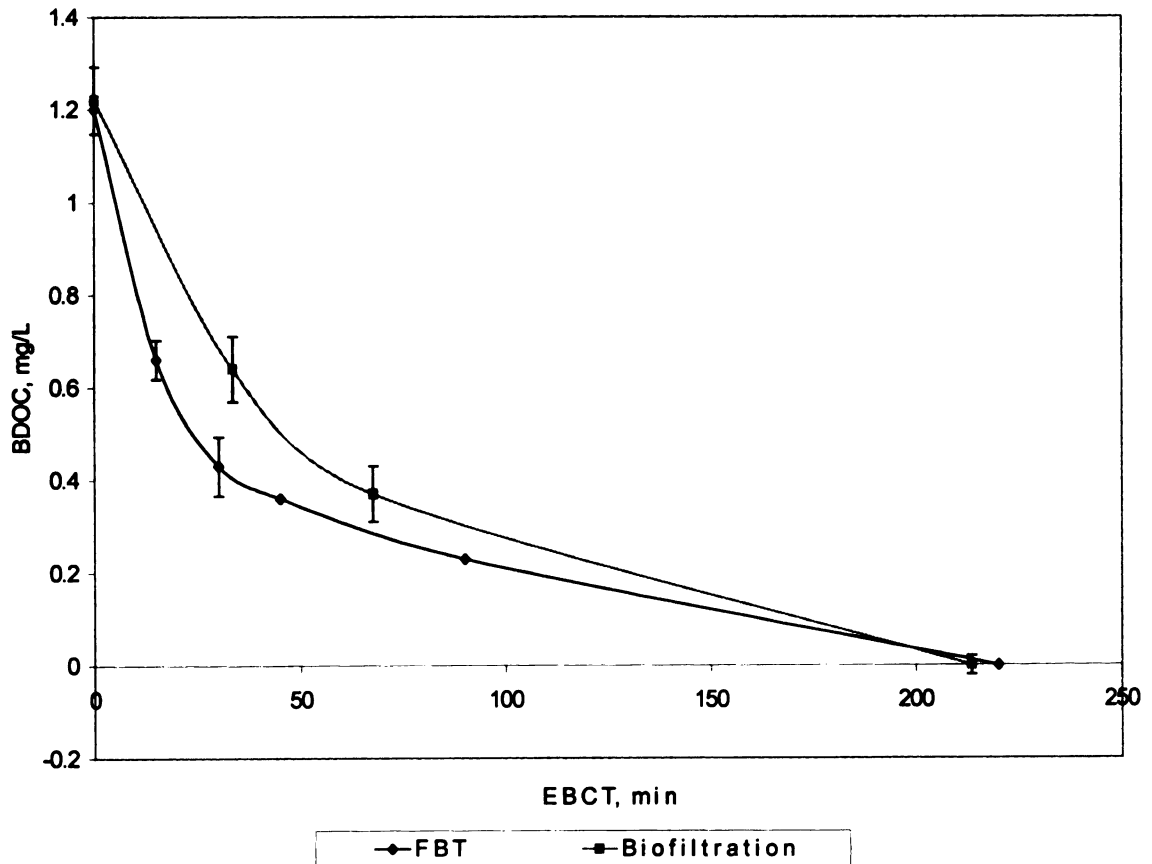


Figure 7.4. BDOC removal from Huron River water by FBT and biofiltration

7.4. EFFECT OF TEMPERATURE

The goal of the experiments presented in this section was to test the hypothesis that the FBT efficiency would increase with temperature. The experiments were conducted with raw water using the FBT system described in Section 3.4. Temperature was varied from 10 to 25°C. The EBCT was varied from 15 to 120 minutes.

Figures 7.5 and 7.6 show the effect of EBCT and temperature on the removal of TOC and UV-254 absorbance, respectively. The removal of organic carbon and UV-254 absorbing compounds increased with EBCT and appeared to be greater for higher temperatures. Figure 7.7 shows the removal of BDOC for various temperatures. For all temperatures studied, two kinetic regions could be identified, which characterized the removal of “fast” and “slow” BDOC. The removal rate of “fast” BDOC in the FBT column was greater for higher temperatures. Table 7.2 shows biodegradation characteristics for various temperatures. The $R_{\max}$ increased and $EBCT_{\min}$ decreased with an increase in temperature. The difference in $BDOC_{\text{slow}}$ does not appear to be significant at 5 percent level.

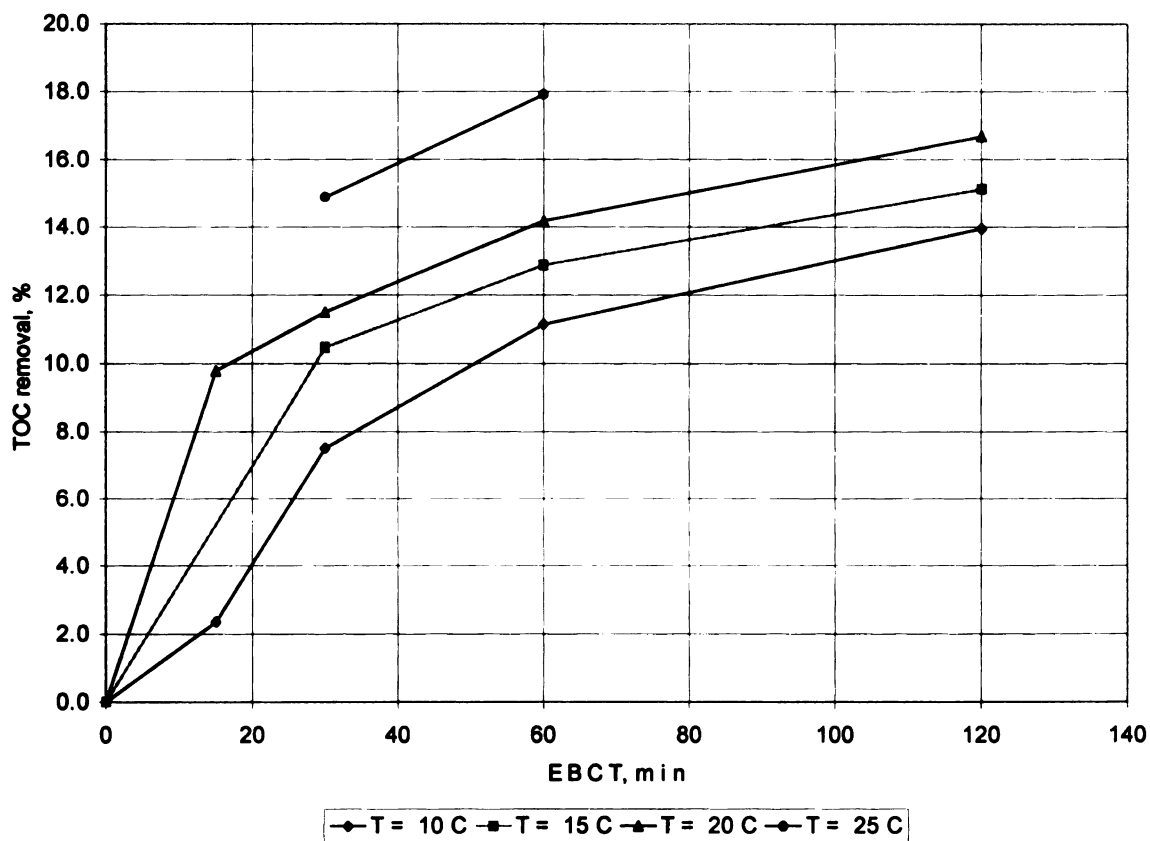


Figure 7.5. Removal of TOC from Huron River water by FBT for various temperatures

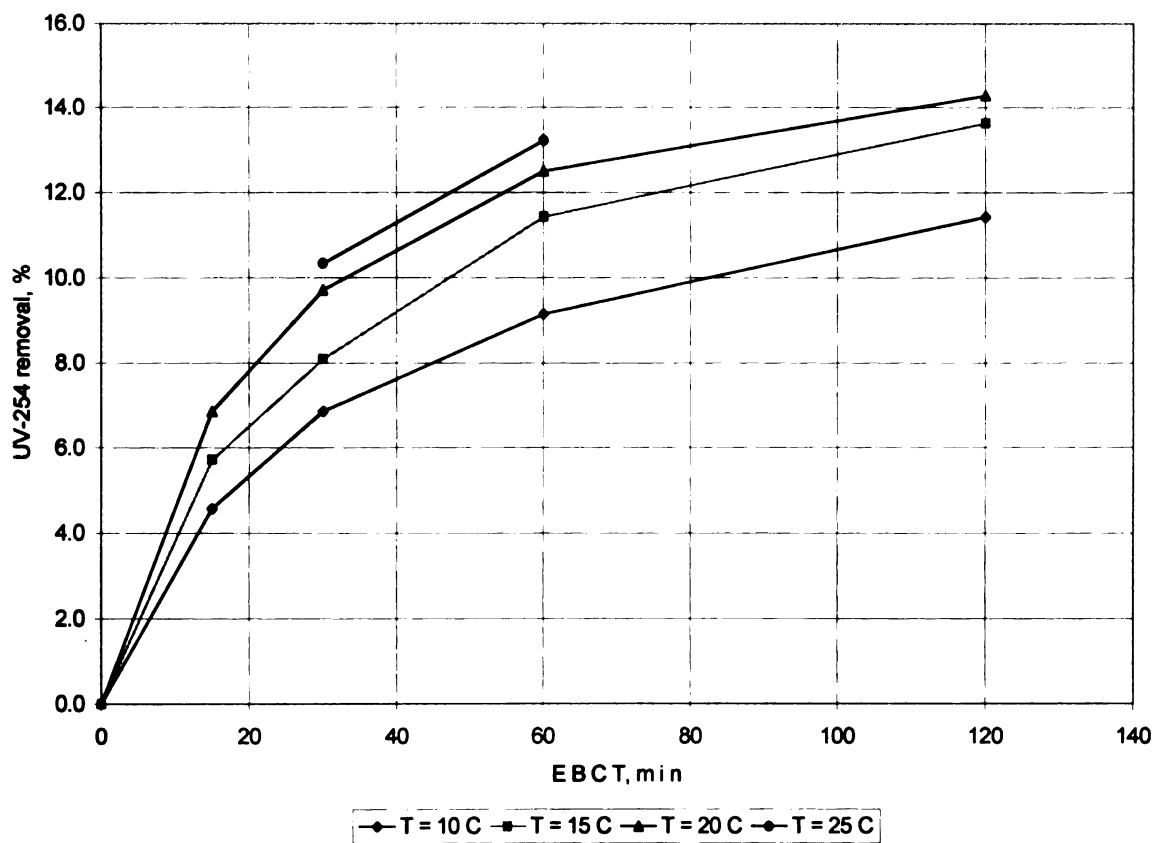


Figure 7.6. Removal of UV-254 from Huron River water by FBT for various temperatures

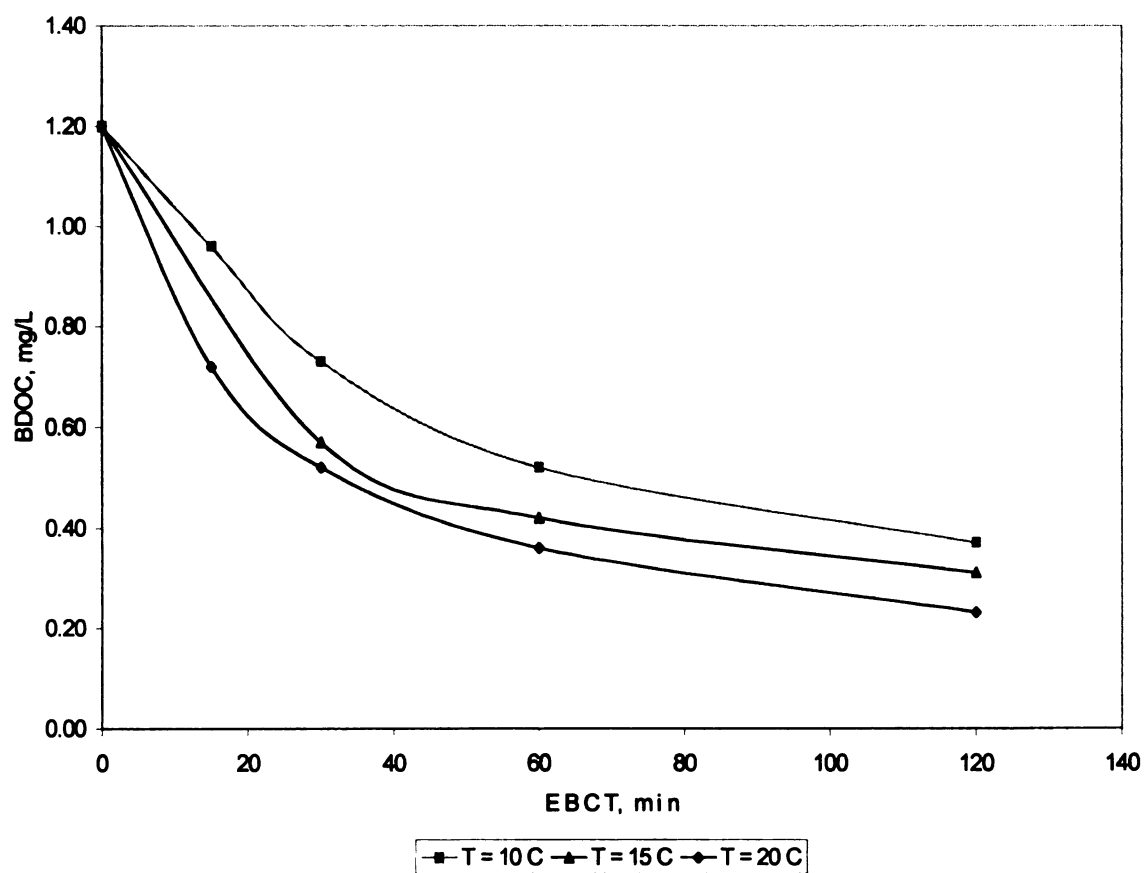


Figure 7.7. Removal of BDOC by FBT for various temperatures

Table 7.2. Effect of temperature on the biodegradation parameters

Temperature °C	Parameter			
	BDOC ₀ mg/L	R _{max} mg/L min	EBCT _{min} min	BDOC _{slow} mg/L
10 ¹	1.2	0.016	39	0.47
15 ¹	1.2	0.021	33	0.4
20 ²	1.2	0.034 ± 0.003	26 ± 2	0.35 ± 0.06

¹ one experiment

² two experiments

7.5. BIODEGRADATION OF OZONATED WATER

The results of the experiments presented in Section 6.2.3 showed that during ozonation at an HRT of 7 minutes and ozone doses ranging from 0 to 1 mg/mg C, BDOC concentration increased with ozone dose. This section presents the analysis of the effect of ozonation on the biodegradation characteristics of raw water, which were defined in Section 7.2. It was expected that under experimental conditions stated above, the biodegradation efficiency would increase with ozone dose.

The experimental design was described in Section 6.3.2. Briefly, ozonation was conducted in the bench-scale ozone contactor followed by biodegradation in the biofiltration column. Experiments were conducted at room temperature. The HRT in the ozone contactor was 7 minutes in all runs. Ozone dose was varied from 0 to 1 mg/L. No TOC removal was observed during ozonation under these conditions (see Section 6.3.2).

Figure 7.8 shows the removal of BDOC during biofiltration of samples ozonated at various ozone doses. As in previous cases, two kinetic regions could be identified in all samples, which characterized the removal of “fast” and “slow” BDOC. From visual observation of the graphs, ozonation resulted in an increase in the concentration of “fast” BDOC. Table 7.3 presents biodegradation characteristics of water after ozonation. For an ozone doses of 0.6, 0.75 and 1 mg/mg C, the $R_{\max}$ was from 0.09 to 0.11 mg/(L min) compared to 0.017 mg/(L min) for raw water. This corresponded to an approximately five-fold increase in $R_{\max}$ after ozonation. The $EBCT_{\min}$ decreased from 48 minutes for raw water to 17 minutes for the ozonated water. Considering that the BDOC concentration in the ozonated sample was only two times greater than that in the raw water and assuming that the BDOC removal follows the first-order kinetics (Klevens and Collins, 1996; Huck, Zhang, and Price, 1994), the result suggests that ozonation resulted in an approximately two-fold increase in biodegradation efficiency. The $BDOC_{\text{slow}}$, however, increased after ozonation. This finding suggests that along with “fast” BDOC ozonation also resulted in an increase in “slow” BDOC.

Table 7.3. Effect of ozonation on the biodegradation parameters

Ozone dose mg/mg C	Parameter			
	$BDOC_0$ mg/L	$R_{\max}$ mg/L min	$EBCT_{\min}$ min	$BDOC_{\text{slow}}$ mg/L
0 ¹	1.15 ± 0.07	0.017 ± 0.002	48 ± 3	0.38 ± 0.07
0.6 ²	2.31	0.09	17	0.84
0.75 ²	2.55	0.09	20	0.81
1 ²	2.78	0.11	24	0.79

¹ four experiments

² one experiment

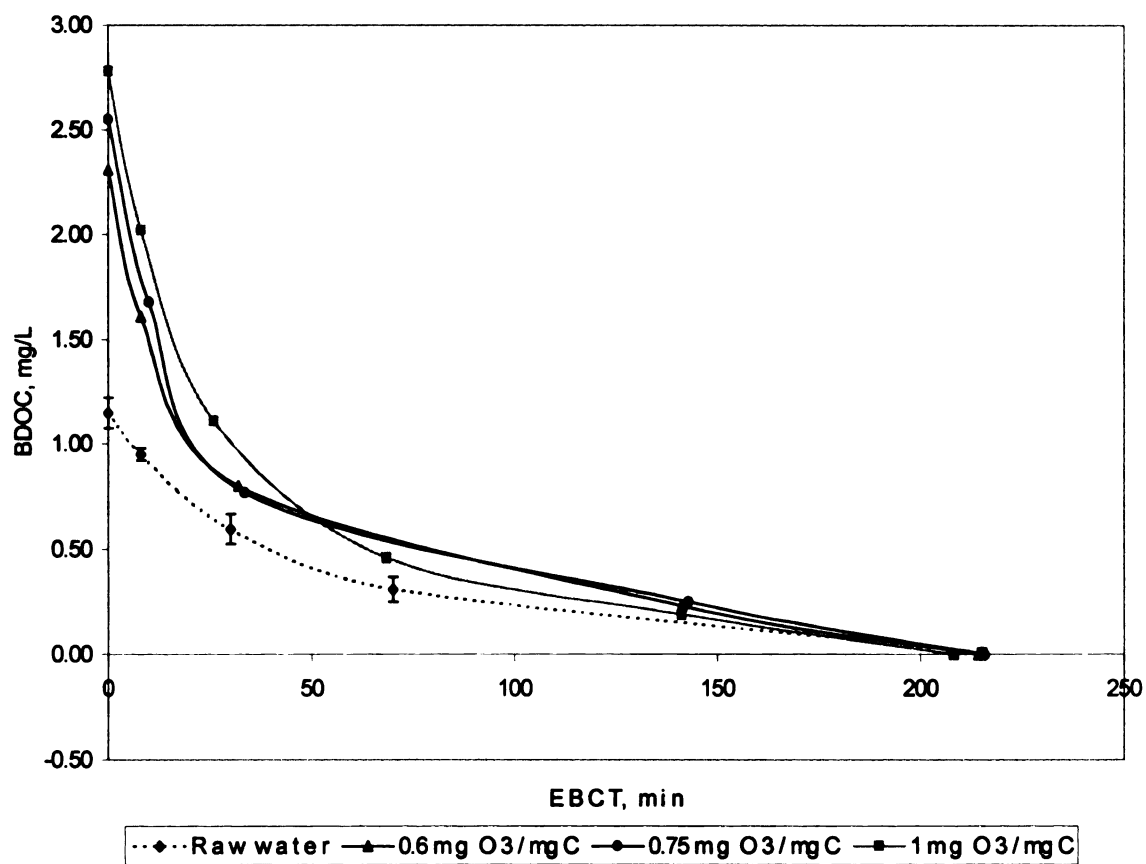


Figure 7.8. Biodegradation of ozonated samples
(ozonation effluent at an HRT of 7 minutes)

7.6. SUMMARY

Several biodegradation parameters were introduced in an attempt to quantify the efficacy of the biodegradation of NOM. These parameters included (1) the maximum rate of the biodegradation of “fast” BDOC ($R_{\max}$); (2) the minimum EBCT that required to eliminate “fast” BDOC ($EBCT_{\min}$); and (3) the minimum BDOC concentration that remained after biodegradation at $EBCT_{\min}$ ($BDOC_{\text{slow}}$). These biodegradation parameters were used to quantitatively describe the effect of temperature and ozone doses on the biodegradation of NOM and also to compare the efficiency of FBT to that of biofiltration.

This study showed that the removal of BDOC in the FBT system was greater than that in the biofiltration system. The $R_{\max}$ in the FBT column was two times greater than that in the biofiltration column.

The results of the experiments showed that the removal of TOC and UV-254 increased with temperature. An increase in temperature resulted in an increase in $R_{\max}$ and in a decrease in $EBCT_{\min}$. The removal of slowly biodegrading organic matter did not appear to be affected by temperature.

This study showed that ozonation at an HRT of 7 minutes and ozone doses of 0.6 to 1 mg/mg C significantly increased the efficiency of biodegradation of NOM compared to that of raw water. It also resulted in an increased the concentration of “fast” BDOC. The $BDOC_{\text{slow}}$ increased after ozonation, which suggested that along with “fast” BDOC concentration, ozonation also resulted in an increase in “slow” BDOC concentration.

8. EVALUATION OF COMBINED OZONATION AND FBT PROCESS

8.1. INTRODUCTION

The results of the experiments presented in Chapter 4 demonstrated a good potential of the ozonation/FBT system to control THM precursors. The study presented in Chapter 4, however, showed that along with breaking down high molecular weight compounds ozone also oxidized lower molecular weight compounds (less than 1000 daltons) that could, otherwise, be degraded biologically. It was also shown that a portion of ozone was consumed to mineralize organic carbon, which resulted in a decreased production of biodegradable organic matter.

The subsequent studies presented in Chapters 6 and 7 attempted to explain these findings. The bench-scale ozonation experiments described in Chapter 6 showed that the mineralization of organic carbon during ozonation increased with an increase in HRT. Since the ozone contactor in the ozonation/FBT system was operated at an HRT of approximately 100 minutes, ozonation resulted in a mineralization of up to 25 percent of organic carbon. From the bench-scale study (see Chapter 6), very little removal of organic carbon was observed after ozonation at an HRT of less than 10 minutes and ozone doses of up to 1 mg/mg C. Under these conditions, the concentration of BDOC and, hence the biodegradation efficiency, increased with ozone dose. The use of low HRT may, however, be limited by considerations of mass transfer efficiency and/or the CT requirements under SDWA D/DBP Rule if ozone is also used for disinfection. Another problem may arise from the fact that biodegradable organic matter in Huron River water

consisted of rapidly and slowly biodegrading fractions (“fast” and “slow” BDOC) (see Chapter 7). The “slow” BDOC accounted for nearly 30 percent of biodegradable organic matter in raw water. The results of the experiments demonstrated that along with an increase in “fast” BDOC concentration, ozonation also resulted in an increase in the concentration of “slow” BDOC. The slowly biodegradable organic materials may pose bacterial growth problems in the distribution system, if they are not removed in the treatment system. Thus, the optimization of the combined ozonation and FBT process should be directed towards:

- 1) increasing the removal of NOM;
- 2) reducing the ozone consumption by using ozone solely for the production of BDOC rather than for the mineralization of organic carbon;
- 3) reducing the biodegradation time by converting “slow” BDOC into “fast” BDOC.

The objectives of the study presented in this chapter was:

- to use the biodegradation characteristics developed in Section 7.2 for the evaluation of process efficiency;
- to test the hypothesis that using FBT prior to ozonation increases the production of low molecular weight compounds and biodegradable organic matter;
- to test the hypothesis that using biofiltration after FBT/ozonation results in a greater removal of NOM than does the ozonation/FBT process;
- to determine if the recycle of a portion of the ozonation effluent back to the FBT column increases the efficiency of the FBT/ozonation process combined with biofiltration;

- to test the hypothesis that adding an easily biodegradable carbon source to the FBT column increases the efficiency of the FBT/ozonation process combined with biofiltration (the FBT/ozonation process using an additional carbon source will be referred to as the stimulated FBT/ozonation process);
- to test the hypothesis that a recycle of a portion of the ozonation effluent back to the FBT column reduces the biodegradation time of the stimulated FBT/ozonation process combined with.

It should be noted that the use of biofiltration in combination with FBT/ozonation process does not represent a departure from the originally proposed ozonation/FBT process. This is because the process design of either the ozonation/FBT or FBT/ozonation process will require some sort of filtration as the final stage, which will be used to remove turbidity remaining in the system effluent and as a safeguard if any malfunctions of FBT operation occur. Besides, most existing water treatment plants currently use sand or GAC filtration as the final stage of the process. Therefore, if the proposed process is used for retrofitting of an existing facility, biofiltration will not require additional capital investments. The optimization of the combined ozonation and FBT process should be directed towards the minimization of biofiltration time in the biofilter rather than towards the elimination of the biofiltration step.

It should also be noted that the goal of the study presented in this chapter was not to determine the optimal conditions for the combined ozonation and FBT process, but to evaluate approaches that were expected to increase the efficiency of the process. This is because the FBT column in the existing pilot-scale system was operated as a CSTR (see Section 3.2.2). Commercial systems or a larger pilot-scale system (expected to be

installed in the near future) will be operated close to plug-flow conditions, in which the biodegradation efficiency is expected to be different from that in the existing system. Section 8.2 presents the results of the study of the single-pass FBT/ozonation process. The effect of the recycle on the performance of the FBT/ozonation is investigated in Section 8.3. The study of single-pass stimulated FBT/ozonation and stimulated FBT/ozonation with recycle are described in Sections 8.4 and 8.5, respectively. Section 8.6 provides additional information on the biodegradation kinetics in an attempt to explain the findings obtained in previous sections. Section 8.7 presents the summary of the results.

8.2. SINGLE PASS FBT/OZONATION PROCESS

As was stated earlier, the ozonation of Huron River water resulted in the oxidation of low molecular weight compounds and potentially biodegradable organic matter (see Chapter 4). The results of the experiments, presented in Chapters 7.3, showed that FBT could potentially remove up to 20 percent of TOC from Huron River water. The rapidly biodegradable fraction (“fast” BDOC) accounted for approximately 70 percent of the biodegradable organic matter in the raw water, which would be eliminated if the FBT is used prior to ozonation. In this case, ozone was expected to be used for the oxidation of slowly biodegradable or refractory organic matter. The objectives of the study presented in this section were:

- to compare the effect of ozone dose on the removal of TOC and UV-254 from the FBT effluent to that from raw water;

- to test the hypothesis that ozonation of the FBT effluent results in an increase in the concentration of low molecular weight compounds;
- to evaluate the efficiency of biofiltration for the removal of biodegradable organic matter produced from the FBT/ozonation effluent
- to determine biodegradation characteristics of the FBT/ozonation effluent using the approach developed in Section 7.2.

The study was conducted using the pilot-scale FBT/ozonation system described in Section 3.2.3. As was shown in Section 7.3, the EBCT in the FBT column that required to eliminate “fast” BDOC from raw water was approximately 30 minutes. As such, the EBCT in the FBT column was reduced from 180 minutes to 30 minutes as described in Section 3.2.3. The flow rate of raw water entering the system was 20 mL/min, which corresponded to an EBCT in the FBT column of 30 minutes and a retention time in the ozone contactor of approximately 60 minutes. The experiments were conducted at room temperature. Ozone dose was varied from 0 to 2 mg/mg C. The parameters that were monitored in this study included TOC concentration, UV-254 absorbance, and AMW distribution. The biodegradation characteristics, defined in Section 7.2, were also determined. A simplified schematic of the treatment train with sampling locations is shown in Figure 8.1.

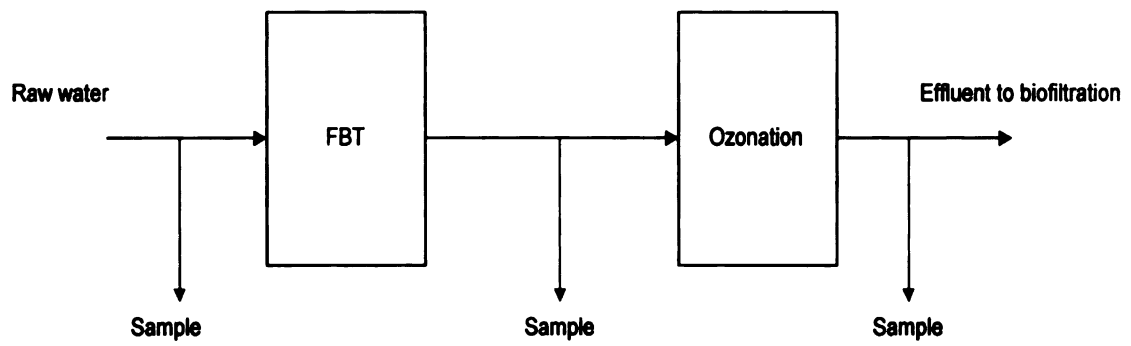


Figure 8.1. Simplified schematic of the FBT/ozonation process

Figures 8.2 and 8.3 show the effect of ozone doses on the removal of UV-254-absorbing compounds and TOC from raw water and from the FBT effluent. The use of FBT prior to ozonation resulted in a slight increase in the removal of UV-absorbing compounds compared to that removed by ozonation alone. This was consistent with the data obtained in Chapter 4 that showed that the removal of UV-254 absorbing compounds occurred mostly through ozonation rather than biodegradation. The TOC data were more remarkable. As expected, the removal of TOC after ozonation of raw water increased with ozone dose and reached a level of approximately 23 percent at a dose of 2 mg/mg C. This was consistent with the results obtained in Chapter 4. The FBT resulted in the removal of approximately 12 percent of organic carbon from raw water, which accounted for approximately 60-65 percent of biodegradable organic matter in raw water. The TOC removal during ozonation of the FBT effluent increased with ozone dose and reached a plateau at a dose of approximately 0.4 mg/mg C.

The study presented in Chapter 4 showed that when the removal of TOC during ozonation leveled off, the concentration of low molecular weight compounds and biodegradable organic matter increased with ozone dose. As such, ozonation of the FBT effluent at ozone doses greater than 0.4 mg/mg C was expected to result in an increased production of low-molecular weight compounds and biodegradable organic matter. Figure 8.4 shows the AMW distribution of organic matter in raw water, in the FBT effluent and in water after FBT and ozonation at ozone doses of 0.5 and 1 mg/mg C. The FBT resulted in a partial removal of low-molecular weight compounds (less than 500 daltons). The FBT also broke down higher molecular weight compounds into smaller constituents. This agreed with the previous findings (see Chapter 4). As expected, for

both ozone doses, ozonation of the FBT effluent resulted in a decrease in the concentration of high-molecular weight compounds and a simultaneous increase in the concentration of organic carbon in low molecular weight fractions (less than 1000 daltons). This increase was not observed during the ozonation of raw water conducted under similar conditions (see Section 4.3). This is thought to be because the removal of organic carbon during ozonation of raw water in the pilot-scale system increased with an increase in ozone dose of up to 1 mg/mg C, whereas the removal of organic carbon during ozonation of the FBT effluent leveled off at a dose of approximately 0.4 mg/mg C. The results of the experiments once again confirmed the hypothesis (see Chapter 4) that when ozonation does not result in the removal of organic carbon, the concentration of low molecular weight compounds increases with ozone dose.

The removal of biodegradable organic matter produced from the ozonation of FBT effluent was accomplished by biofiltration. The removal of organic carbon by the FBT/ozonation process followed by biofiltration was compared to that by the ozonation/FBT process described in Chapter 4. The results are presented Table 8.1. The ozonation/FBT process could potentially remove approximately 40 percent of organic carbon, which was achieved at an EBCT of 180 minutes. The FBT/ozonation process followed by biofiltration resulted in the same removal at a total EBCT of only 60 minutes. The process could potentially remove additional 7 percent of TOC, which indicated that the removal efficiency of the FBT/ozonation process followed by biofiltration was greater than that of the ozonation/FBT process. The removal of this remaining biodegradable organic matter by biofiltration was, however, slow.

Figure 8.5 shows the kinetic biodegradation curve for the FBT/ozonation effluent obtained at an EBCT in the FBT column of 30 minutes and an ozone dose of 1 mg/mg C. This curve was used to determine biodegradation characteristics of the FBT/ozonation effluent, which are presented in Table 8.2. As can be seen in Figure 8.5 and Table 8.2, the FBT/ozonation effluent contained at least 0.5 mg/L of “slow” BDOC. As a result, prolonged biofiltration was required to completely remove all biodegradable organic matter from the FBT/ozonation effluent, which agrees with the results presented in Table 8.1.

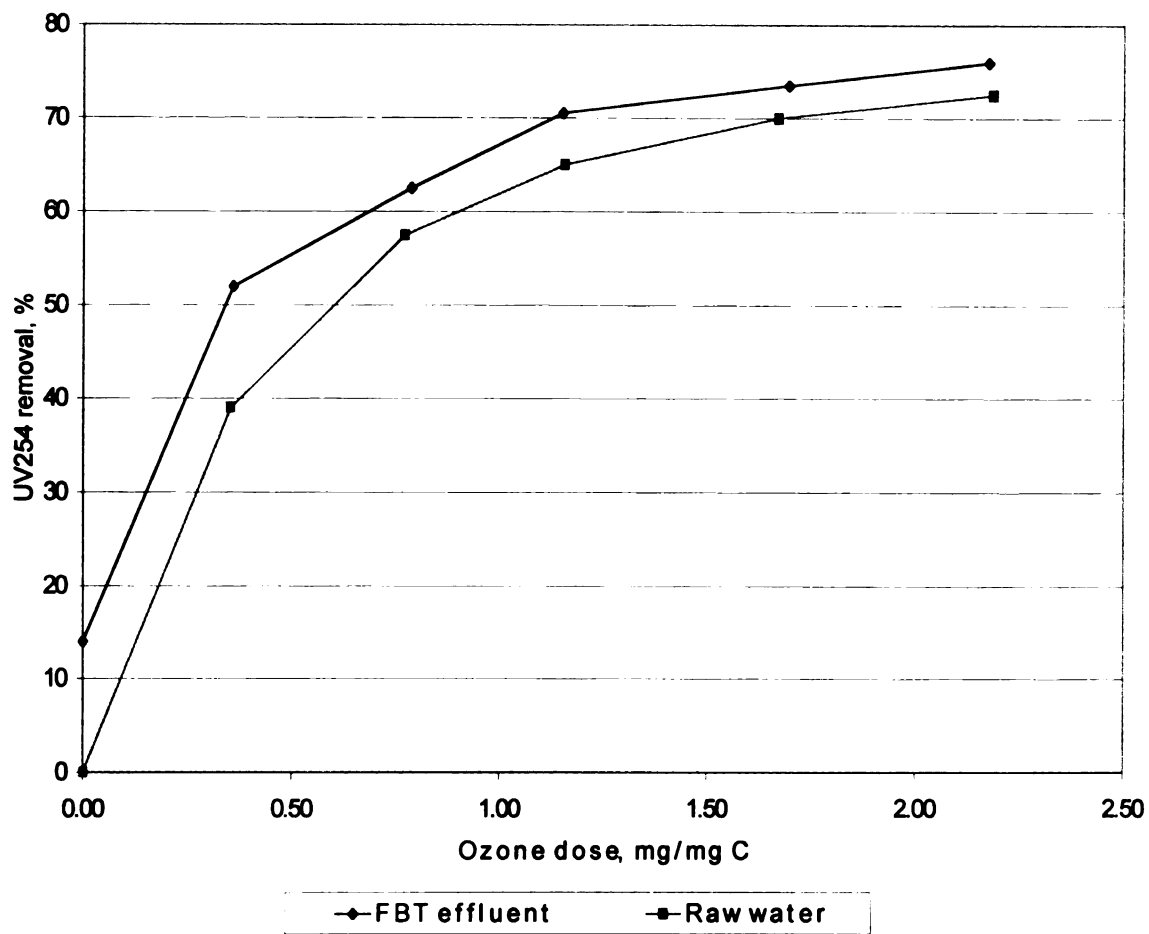


Figure 8.2. Removal of UV-254 during ozonation of raw water and FBT effluent
(FBT EBCT –30 minutes)

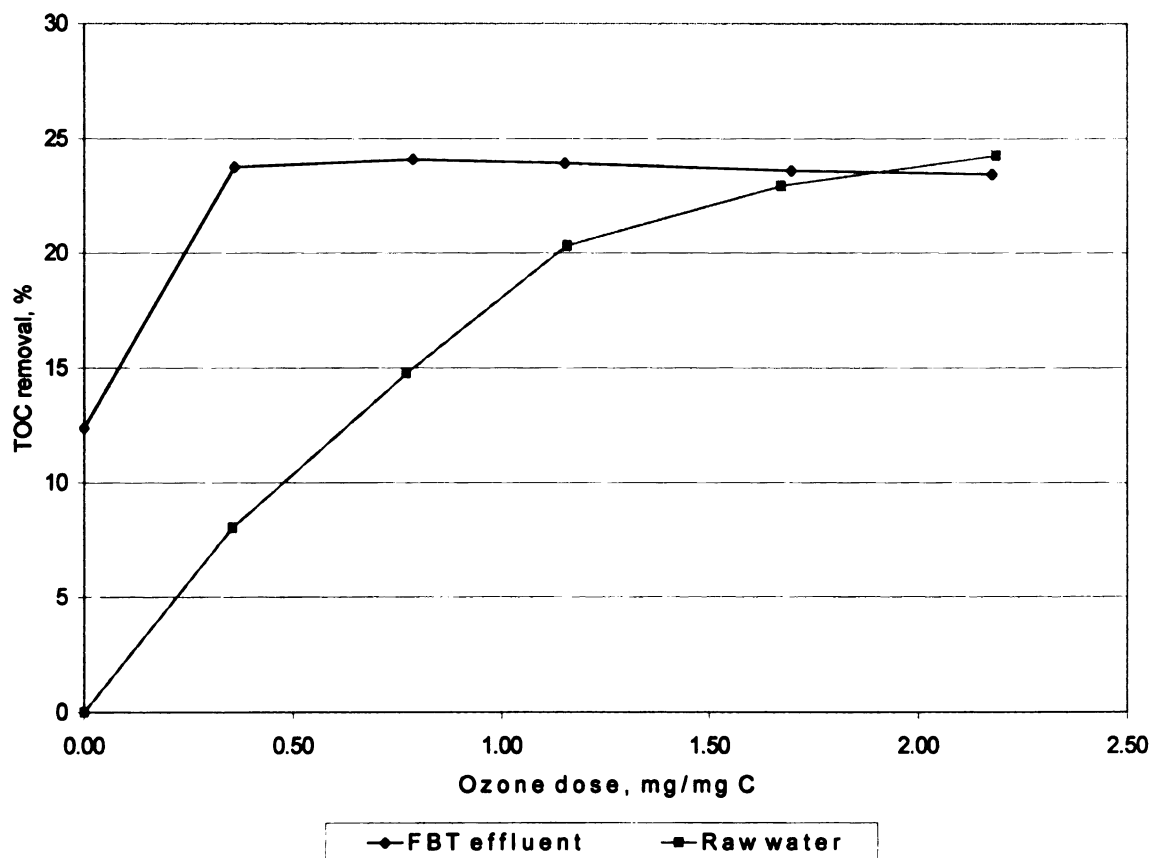


Figure 8.3. Removal of TOC during ozonation of raw water and FBT effluent
(FBT EBCT – 30 minutes)

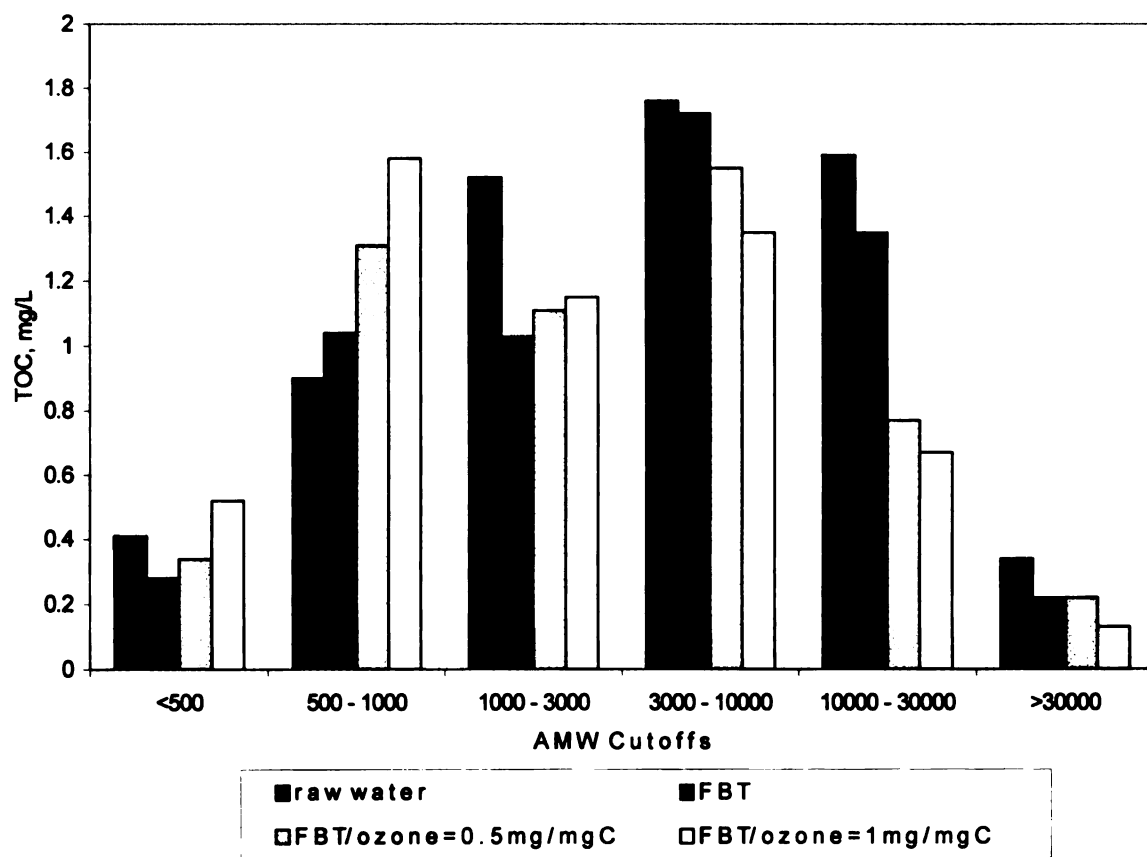


Figure 8.4. AMW of NOM after FBT and ozonation

Table 8.1. Efficiency of FBT/ozonation/biofiltration and ozonation/FBT

Parameter	FBT/ozonation/biofiltration			Ozonation/ FBT ¹
	1	2	3	
Ozone dose, mg/mg C	1.0	1.0	1.0	1.0
EBCT for FBT, min	30	30	30	180
Biofiltration EBCT, min	30	70	150	n/a
Total EBCT, min	60	100	180	180
TOC removal, %	39.4±1.1	42.5±1.1	46.5±0.2	39.7±2.1

¹see Chapter 4

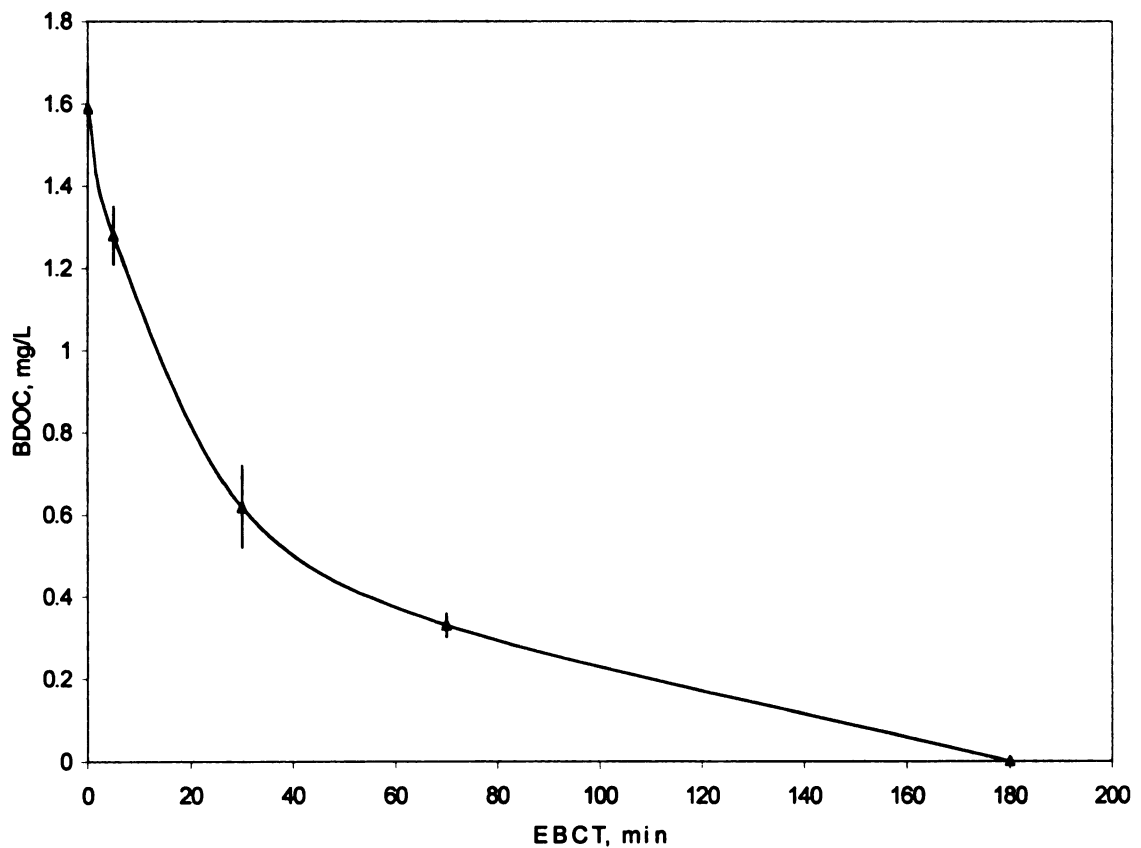


Figure 8.5. Biodegradation kinetics of the FBT/ozonation effluent

Table 8.2. Biodegradation characteristics of the FBT/ozonation effluent

Parameter	Value
BDOC₀, mg/L	1.59 ± 0.1
R_{max}, mg/L min	0.06 ± 0.02
EBCT_{min}, min	18.2 ± 0.6
BDOC_{slow}, mg/L	0.46 ± 0.16

8.3. FBT/OZONATION PROCESS WITH RECYCLE

The results of the study presented in the previous section showed that, under similar experimental conditions, FBT/ozonation followed by biofiltration resulted in a greater removal of organic matter and lower biodegradation time than did the ozonation/FBT process. It was, however, shown that the FBT/ozonation effluent contained at least 0.5 mg/L of slowly biodegradable organic matter, which was difficult to remove by subsequent biofiltration. The goal of the study presented in this section was to test the hypothesis that recycle of a portion of the ozonation effluent back to the FBT column would result in an increase in the removal of organic matter by subsequent biofiltration and in a decrease in biodegradation time. The effect of recycle on UV-254 and TOC concentration was also investigated.

The experimental design was the same as described in the previous section with the exception that a portion of the ozonation effluent was recycled back to the FBT column. The recycle flow was varied from 10 to 40 mL/min, which corresponded to

recycle ratios (recycle flow to influent flow) of 0.5 to 2. A simplified schematic of the process with sampling locations is shown in Figure 8.6.

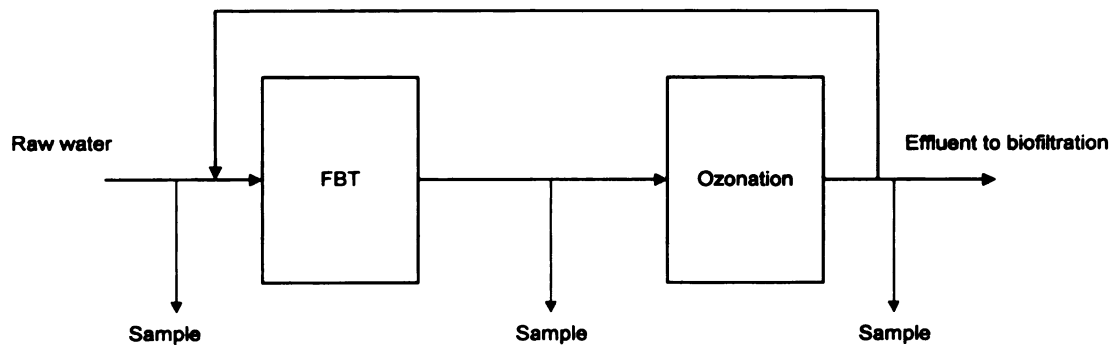


Figure 8.6. Simplified schematic of the FBT/ozonation process with recycle

Figure 8.7 shows the effect of recycle ratio on the removal of TOC after the FBT and ozonation stages at an ozone dose of 1 mg/mg C. With no recycle, FBT resulted in the removal of approximately 12 percent of organic carbon and the following ozonation eliminated approximately 9 percent of organic carbon. An increase in recycle ratio resulted in a decrease in the removal of organic carbon by ozonation. This is thought to be because of an increase in single-pass flow rate through the ozone contactor and, hence, a decrease in single-pass retention time. The removal of TOC after FBT and FBT/ozonation increased with recycle ratio. At recycle ratios of 1 and greater, no TOC removal during ozonation occurred and, as a result, the removal of TOC after FBT/ozonation leveled off. As can be seen in Figure 8.8, for other ozone doses (up to 2 mg/mg C) and a recycle ratio of 1, TOC removal during ozonation was not observed either.

Figure 8.9 shows that recycle did not affect the removal of UV-254 after FBT/ozonation. The UV-254 in the FBT effluent decreased with an increase in recycle ratio. However, this decrease could probably be attributed to a dilution of system influent with the recycle flow.

Figure 8.10 shows TOC removal during biofiltration of effluent obtained from the FBT/ozonation system at an ozone dose of 1 mg/mg C and a recycle ratio of 1. The results of biofiltration experiments using the effluent obtained from the single-pass FBT/ozonation system at an ozone dose of 1 mg/mg C are given for comparison. The data points at EBCT = 0 represented the removal of organic carbon by FBT/ozonation. It appears that using the recycle resulted in a slight increase in the removal of organic matter by FBT/ozonation followed by biofiltration. Although this increase was

statistically significant the effect was less than expected. As can be seen in Figure 8.10, the biodegradation rate of “fast” BDOC in the effluent from the recirculating FBT/ozonation system was lower than that from the single-pass FBT/ozonation system. This is thought to be because, in the recirculating FBT/ozonation system, FBT resulted in the removal of most easily biodegrading organic matter leaving slower biodegradable materials in the system effluent. As a result, a decrease in EBCT in the biofiltration system was not observed.

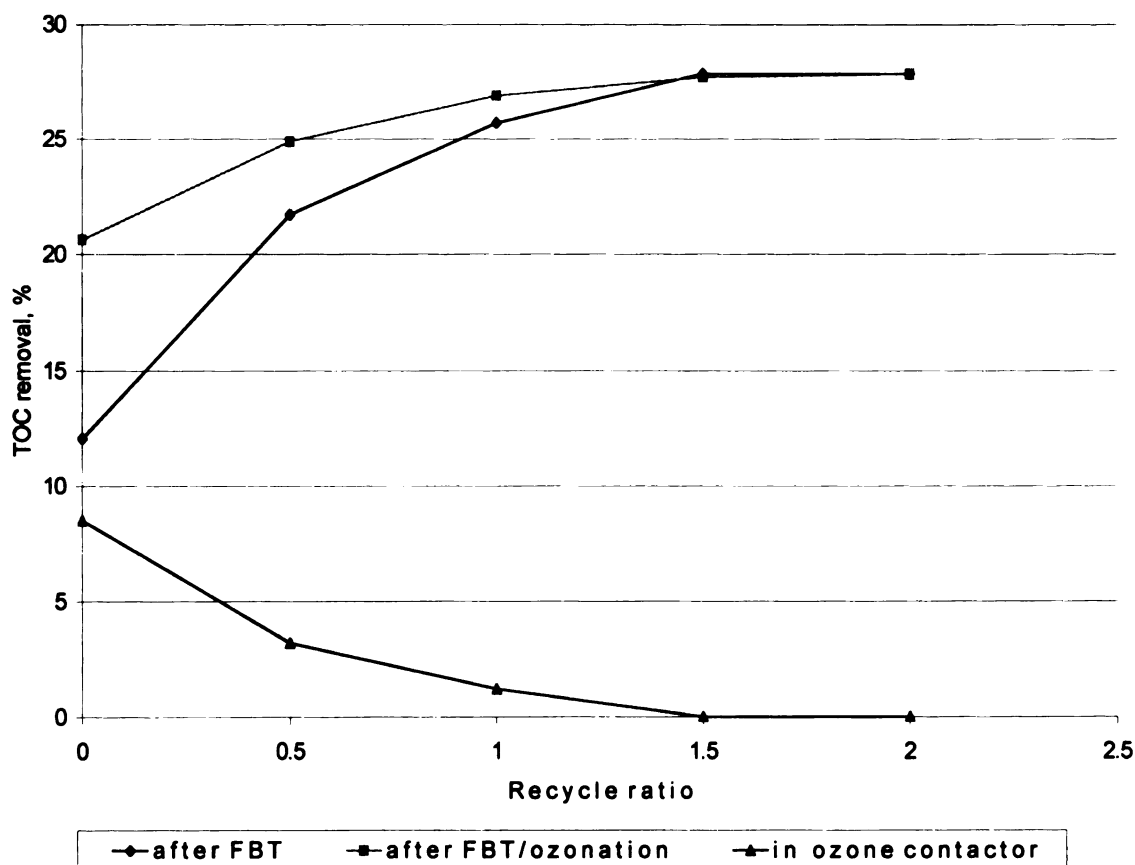


Figure 8.7. Effect of recycle on the removal of TOC by FBT/ozonation
(EBCT = 30 minutes, ozone dose = 1 mg/mg C)

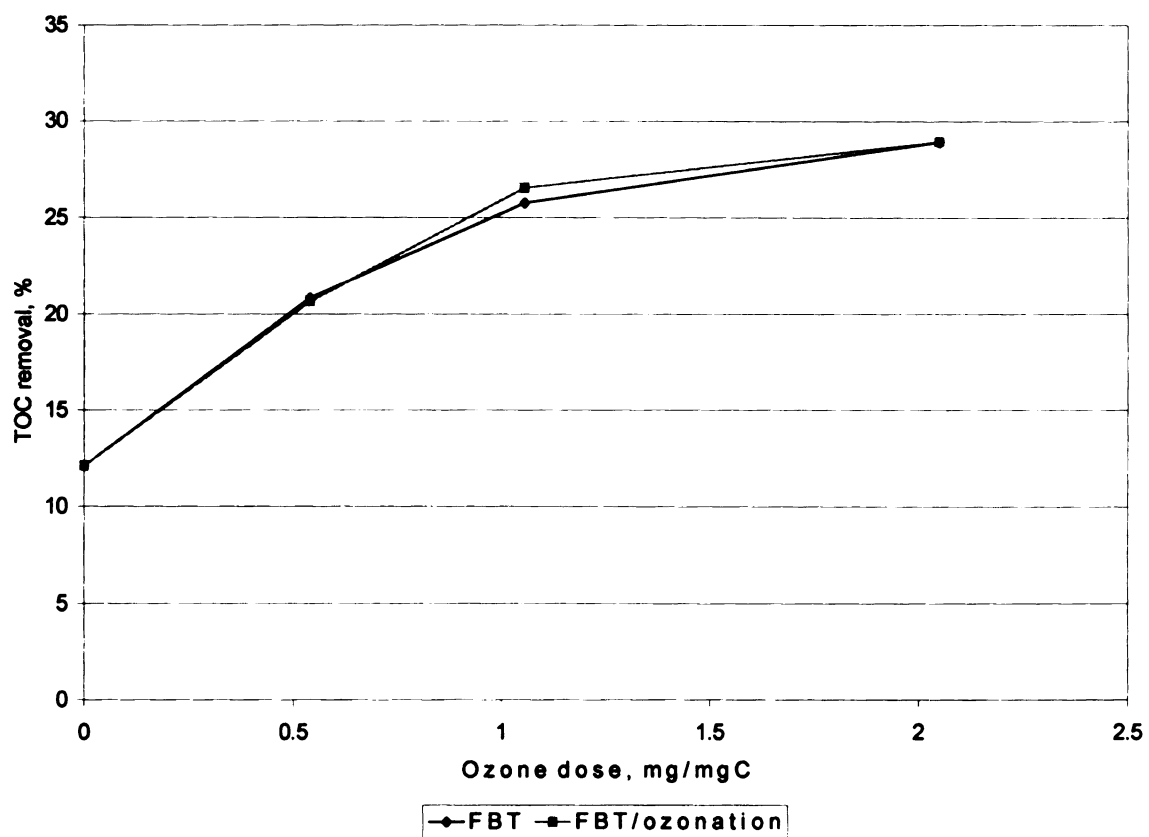


Figure 8.8. Effect of ozone dose on the removal of TOC by FBT/ozonation with recycle
(EBCT =30 minutes, recycle ratio = 1)

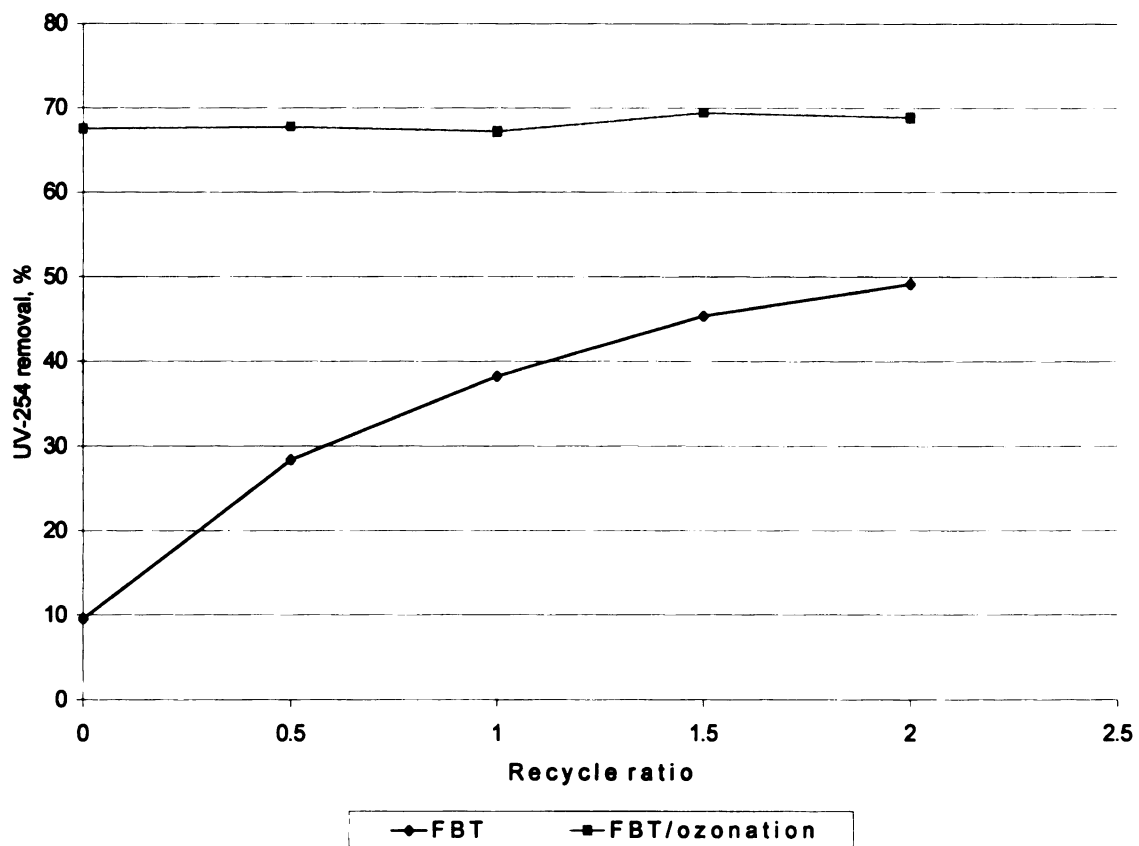


Figure 8.9. Effect of recycle on the removal of UV-254 by FBT/ozonation
(EBCT =30 minutes, ozone dose = 1 mg/mg C)

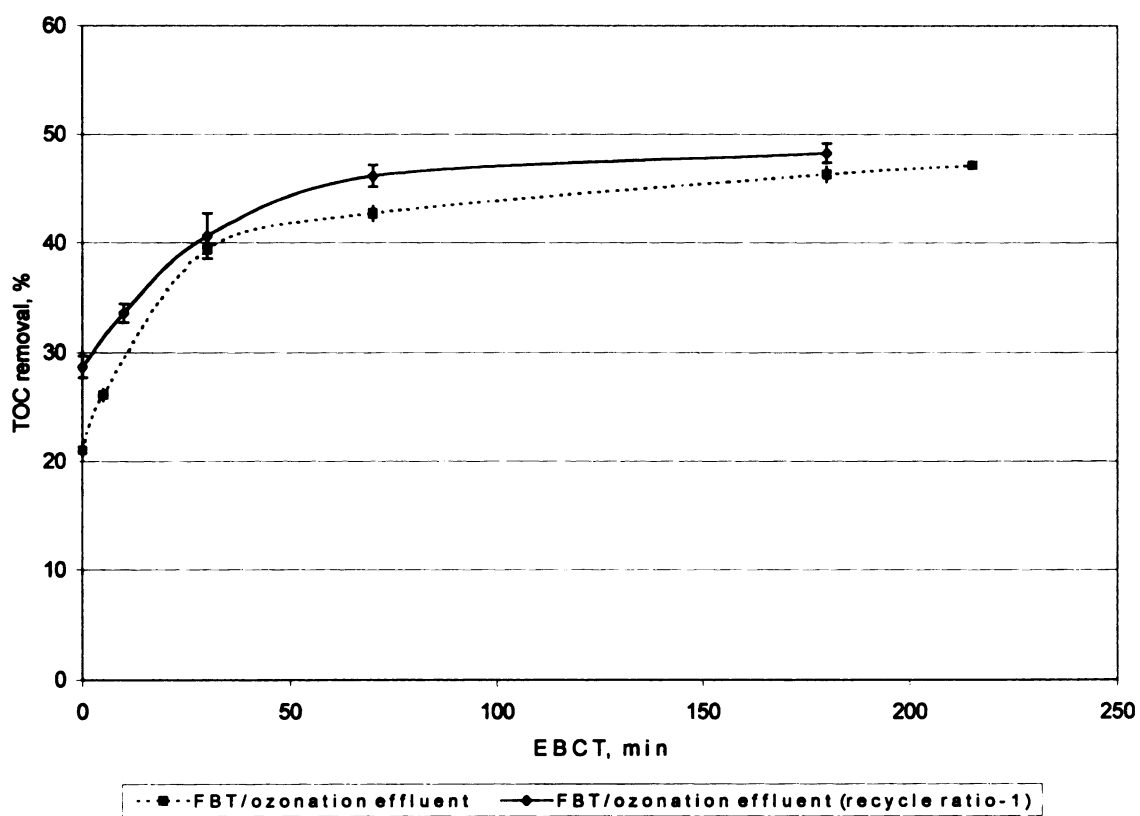


Figure 8.10. Biofiltration of the FBT/ozonation effluent

(FBT/ozonation: EBCT =30 minutes, ozone dose = 1 mg/mg C; recycle ratio = 1)

8.4. STIMULATED FBT/OZONATION PROCESS

The study presented in the previous section did not confirm the hypothesis that that recycle of a portion of the ozonation effluent back to the FBT column would result in an increased biofiltration efficiency. This was thought to be because FBT was able to remove only most easily biodegrading organic matter and slower biodegradable materials were remained in the FBT/ozonation effluent.

This section describes the experiments in which the possibility of adding an easily biodegradable carbon source in order to enhance the biodegradation of NOM was explored. It was expected that adding an easily biodegradable material would result in an increased growth of microorganisms that would be able to metabolize slow biodegradable organic matter. Of course, there was a possibility that microorganisms would utilize only easily biodegradable organic matter and leave slowly degrading materials.

The experimental design was the same as described in Section 8.2 with the exception that an easily biodegradable carbon source was used in these experiments. A solution of 500 mg/L of acetic acid in Milli-Q water was pumped into the bottom of the FBT column at rates of 0.1 and 0.2 mL/min, which corresponded to acetate dose of 2.5 and 5 mg/L. Ozone dose was 1 mg/mg C in all experiments.

Figure 8.11 shows the effect of acetate dose on the removal of TOC from raw water after FBT (no ozonation). The TOC removal appears to increase with the addition of acetate. However, the difference was statistically significant only for data points obtained at acetate doses of 0 and 5 mg/L. It was really surprising, however, that, when acetate was added, no TOC removal was observed during ozonation of the FBT effluent.

The effect of biofiltration on the removal of organic matter from the stimulated FBT/ozonation effluent is shown in Figure 8.12. The acetate dose was 2.5 mg/mg C. The results of biofiltration of the effluent from the FBT/ozonation system (no acetate) are given for comparison. The data points at EBCT = 0 represented the removal of organic carbon by FBT/ozonation. As can be seen, the rate at which “fast” BDOC was removed from the stimulated FBT/ozonation effluent was greater than that from the FBT/ozonation (no acetate) effluent. The potential removal of organic carbon by the stimulated FBT/ozonation process followed by biofiltration was also greater than that by the FBT/ozonation process (no acetate) followed by biofiltration.

Figure 8.13 shows the biodegradation kinetic curve for the stimulated FBT/ozonation effluent obtained at an EBCT in the FBT column of 30 minutes, an ozone dose of 1 mg/mg C, and an acetate dose of 2.5 mg/L. Table 8.3 presents biodegradation characteristics of this effluent. As can be seen in Figure 8.13 and Table 8.3, the stimulated FBT/ozonation effluent had high concentration of “fast” BDOC, which was rapidly removed by biofiltration. However, at least 0.5 mg/L of “slow” BDOC remained in the effluent after stimulated FBT/ozonation.

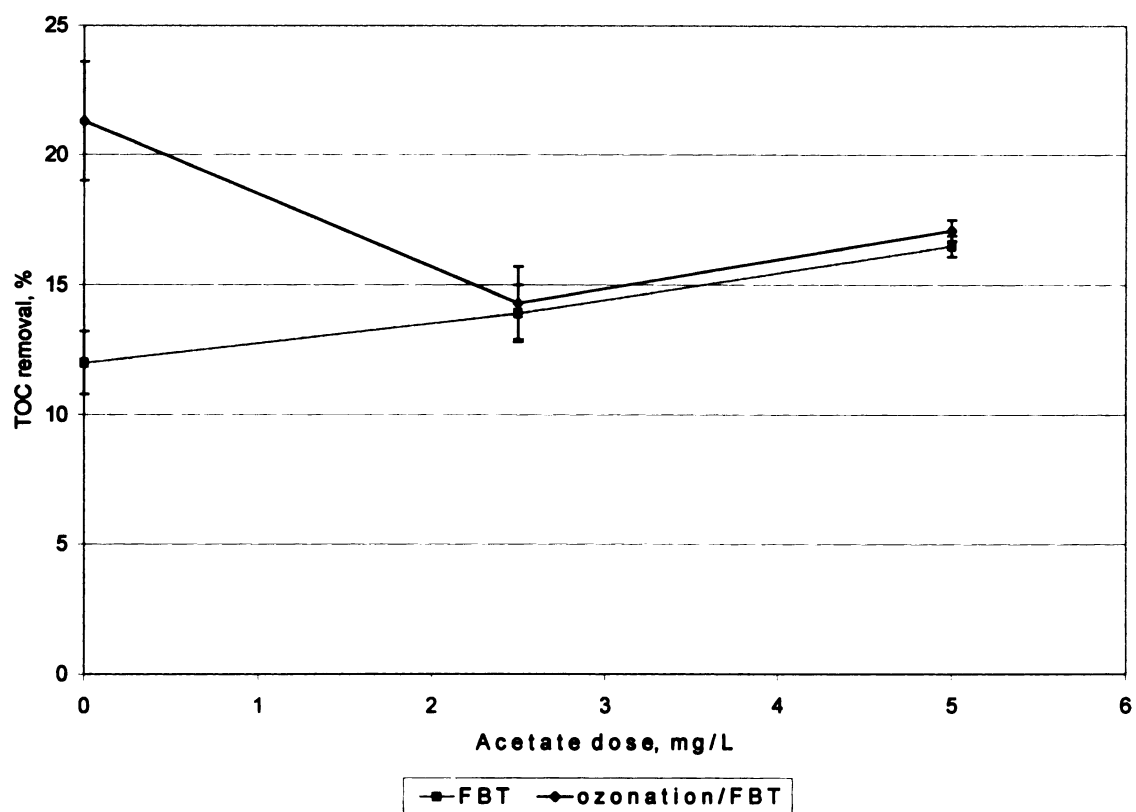


Figure 8.11. Effect of acetate dose on the removal of TOC by FBT and FBT/ozonation
(ozone dose – 1 mg/mg C, FBT EBCT – 30 minutes)

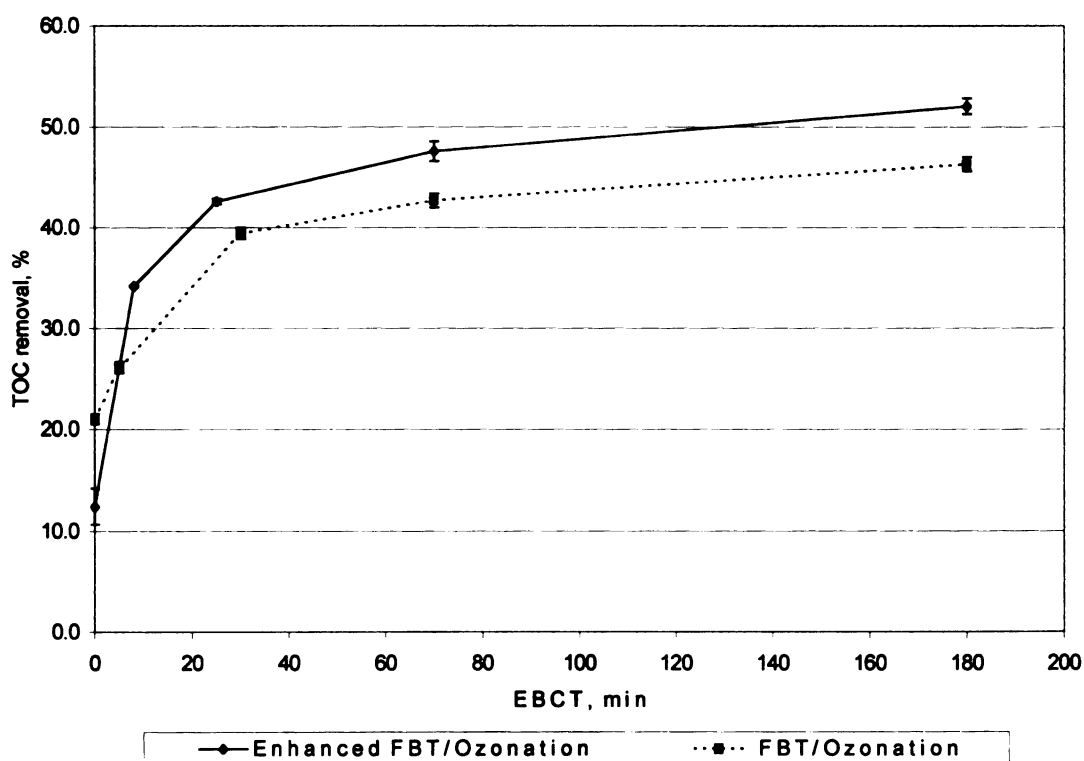


Figure 8.12. Biofiltration of effluents from FBT/ozonation and stimulated FBT/ozonation
(FBT EBCT - 30 minutes, ozone dose – 1 mg/mg C, acetate dose 2.5 mg/L)

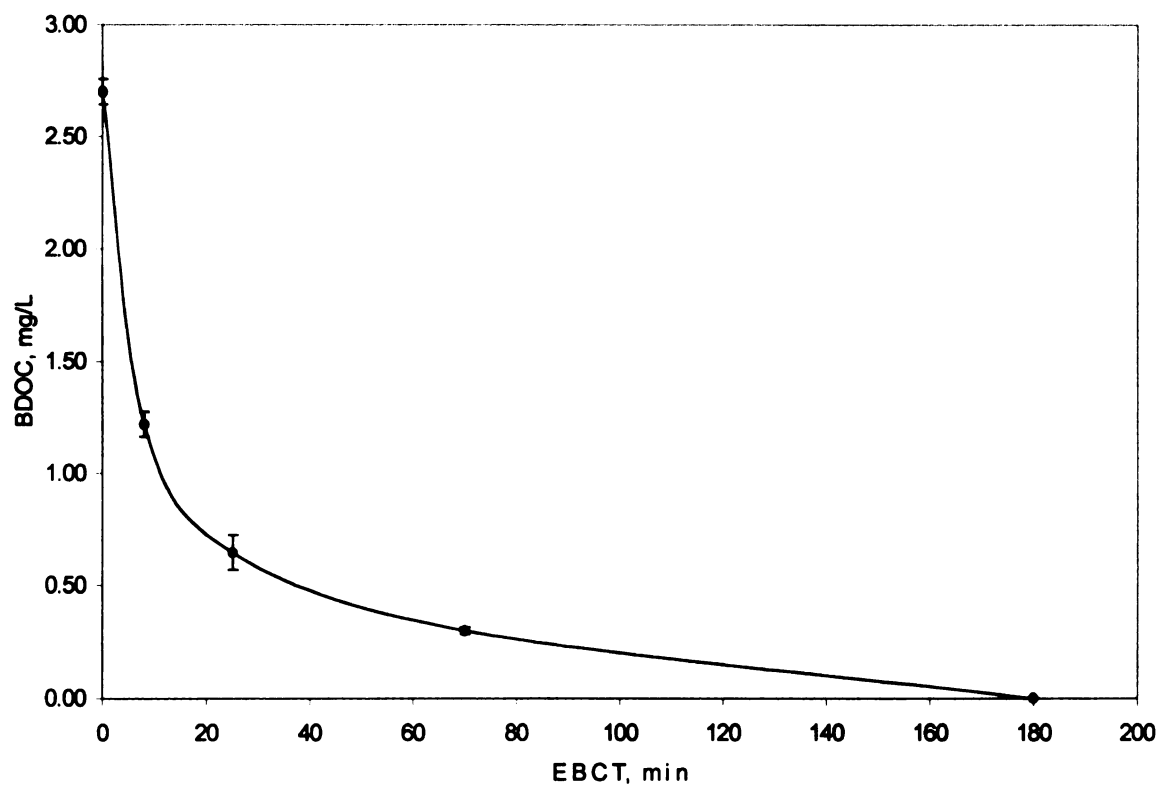


Figure 8.13. Biodegradation kinetics of stimulated FBT/ozonation effluent
(ozone dose – 1 mg/mg C, FBT EBCT – 30 minutes, acetate dose – 2.5 mg/L)

Table 8.3. Biodegradation characteristics of stimulated FBT/ozonation effluent

Parameter	Value
BDOC ₀ , mg/L	2.7 ± 0.06
R _{max} , mg/L min	0.19 ± 0.01
EBCT _{min} , min	12.3 ± 0.8
BDOC _{slow} , mg/L	0.47 ± 0.02

8.5. STIMULATED FBT/OZONATION PROCESS WITH RECYCLE

The results of the study presented in the previous section showed that stimulated FBT/ozonation followed by biofiltration resulted in an increased removal of organic matter. However, the stimulated FBT/ozonation effluent contained at least 0.5 mg/mg C of slowly biodegrading organic carbon, which was difficult to remove by biofiltration.

The goal of the study presented in this section was to investigate the efficiency of the stimulated FBT/ozonation process with recycle. Without adding an easily biodegradable carbon source, the recycle operation was shown to be ineffective (see Section 8.3). The result of experiments presented in Section 8.4 showed that adding 2.5 mg/L of acetate to the FBT column resulted in an increased production of “fast” BDOC after FBT/ozonation, which was rapidly removed by biofiltration. This suggested that stimulated FBT/ozonation was able to convert slowly biodegrading organic materials into “fast” BDOC. It was, therefore, expected that using recycle in this case would result in increased process efficiency.

The experimental design was the same as described in the previous section with the exception that a portion of the ozonation effluent was recycled back to the FBT column at recycle ratios of 0.5 and 1. Higher recycle ratios were not tested in this study.

Figure 8.14 shows the removal of organic carbon during biofiltration of the effluent from the recirculating stimulated FBT/ozonation system with recycle ratios varying from 0 to 1. The data points at $EBCT = 0$ represented the removal of TOC after stimulated FBT/ozonation with recycle ratios of 0, 0.5 and 1. As can be seen, the recycle did not result in an increase in the maximum removal of organic carbon after stimulated FBT/ozonation followed by biofiltration. However, biofiltration time appears to decrease with an increase in recycle ratio. Figure 8.15 shows biofiltration kinetics for the effluents from the stimulated FBT/ozonation for various recycle ratios and Table 8.4 presents biodegradation characteristics of these effluents. As expected, BDOC concentration in the FBT/ozonation effluent ($BDOC_0$) decreased with an increase in recycle ratio because of an increased removal of organic carbon in the FBT/ozonation system (see data points at $EBCT = 0$ in Figure 8.14). It appears that R_{max} decreased proportionally to $BDOC_0$. The effluents were characterized by low $EBCT_{min}$. The difference in $EBCT_{min}$ for various recycle ratios does not, however, appear to be statistically significant. Finally, the concentration of slowly biodegradable organic matter in the FBT/ozonation effluent decreased with an increase in recycle ratio.

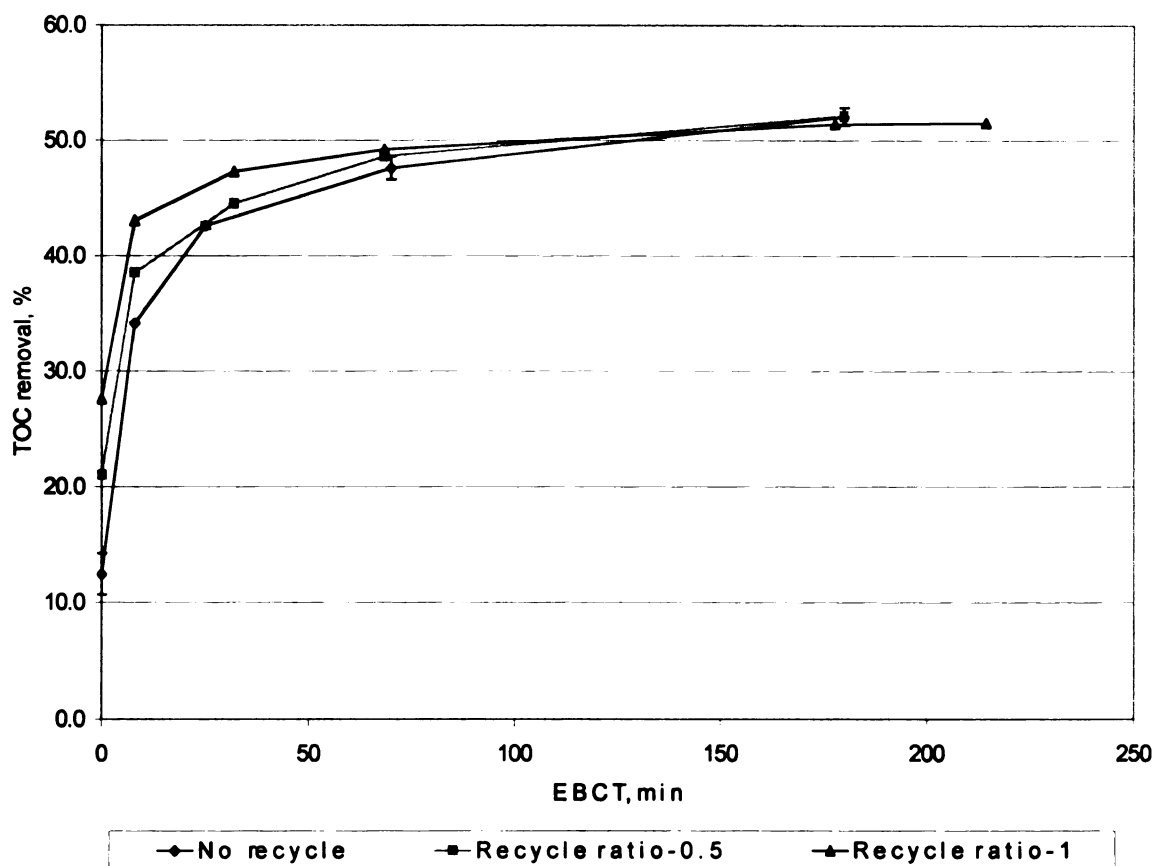


Figure 8.14. Biofiltration of effluents from stimulated FBT/ozonation with recycle (FBT EBCT - 30 minutes, ozone dose – 1 mg/mg C, acetate dose - 2.5 mg/L)

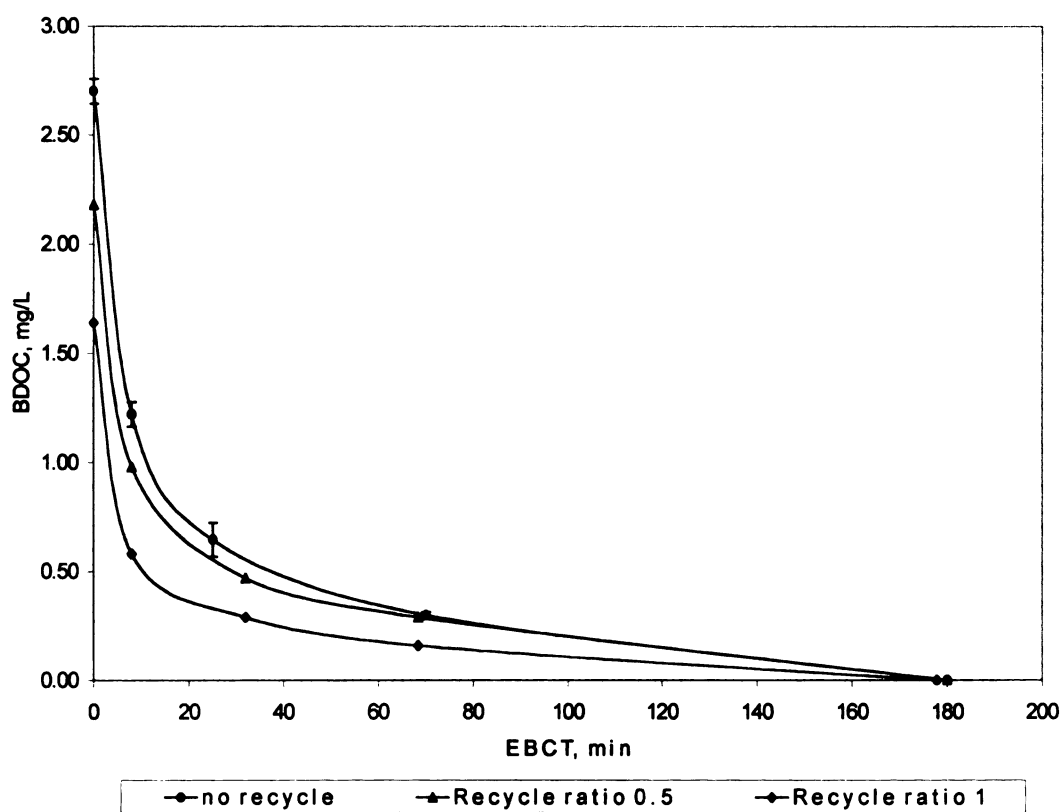


Figure 8.15. Biodegradation kinetics of effluents from stimulated FBT/ozonation with recycle

(FBT EBCT - 30 minutes, ozone dose - 1 mg/mg C, acetate dose - 2.5 mg/L)

Table 8.3. Biodegradation characteristics of recirculating stimulated FBT/ozonation effluents

Parameter	Recycle ratio		
	0	0.5	1
BDOC ₀ , mg/L	2.7 ± 0.06	2.18	1.64
R _{max} , mg/L min	0.19 ± 0.01	0.15	0.13
EBCT _{min} , min	12.3 ± 0.8	11.9	10.5
BDOC _{slow} , mg/L	0.47 ± 0.02	0.4	0.24

8.6. BIODEGRADATION KINETICS

Models describing the kinetics of substrate utilization by biofilms generally include terms for the mass transfer of the substrate from the bulk solution to the biofilm surface, as well as simultaneous diffusion and biotransformation within the biofilm (Criddle, Alvarez, and McCarthy, 1991). While the models are complex even for some idealized situations (Rittmann and McCarty, 1980), the models describing the biodegradation in a recirculating FBT column for the treatment of drinking water could be significantly simplified. First, a recirculating FBT column could be considered as a completely mixed reactor, since the recirculation rate was much greater than the rate of substrate influx. Secondly, since the liquid rate through the bed was high, the resistance to mass transfer in the diffusion layer between the bulk liquid and the biofilm could be neglected.

For a CSTR, the rate of substrate utilization can be written as follows:

$$\frac{dS_e}{dt} = \frac{1}{\tau}(S_0 - S_e) - aJ \quad (8.1)$$

where S_0 and S_e are the substrate concentrations in the influent and effluent, respectively; J is the flux of the substrate into the biofilm; a is the area of biofilm per unit volume of reactor; τ is the hydraulic retention time.

At steady state, $dS_e/dt = 0$, and

$$\frac{1}{\tau}(S_0 - S_e) = aJ \quad (8.2)$$

The flux J is influenced by molecular diffusion of the substrate in the biofilm and by the rate of substrate utilization within the biofilm. With low substrate concentrations, the feed rate to the biofilm is sufficiently low, so the active population of bacteria is relatively low, and the biofilm can be considered as fully penetrated (Criddle, Alvarez, and MacCarthy, 1991). For the fully-penetrated biofilm, the flux is influenced only by bioreaction kinetics. The kinetics of these reactions follows a Monod relationship (Rittmann and McCarty, 1981):

$$J = \frac{k_m L_f X_f S_f}{S_f + K_s} \quad (8.3)$$

where S_f is the substrate concentration within the biofilm; k_m is the maximum specific rate of substrate utilization, time^{-1} ; K_s is the half-velocity coefficient; X_f is the density of the biofilm; L_f is the biofilm thickness.

Under CSTR conditions, for fully penetrated biofilms and for low substrate concentration, $S_f = S_e$ and $S \ll K_s$ (Criddle, Alvarez, and MacCarthy, 1991). Thus, Equation (8.3) could be reduced to a first-order relationship with respect to substrate concentration, which agrees with the findings of Huck, Zhang, and Price (1994):

$$\frac{1}{\tau}(S_0 - S_e) = k'XS_e \quad (8.4)$$

where $X = aL_fX_f$ is the concentration of biomass in the reactor, $k' = k_m/K_s$.

To verify the first-order biodegradation kinetics with respect to substrate concentration, the values of $R_{\max}$ for all samples obtained as described in the previous sections were plotted versus the concentration of BDOC. The plot in Figure 8.16 shows that there existed a linear correlation between $R_{\max}$ and BDOC concentration. The results agree with the findings by Huck, Zhang, and Price (1994), who obtained similar relationships.

It should be noted that, considering the low organic load, the development of the biofilm on the support media was important. There exists a minimum substrate concentration $S_{\min}$ below which a steady-state biofilm cannot exist and the biofilm will be constantly losing its mass (Criddle, Alvarez, and MacCarthy, 1991). Huck, Zhang, and Price (1994) identified $S_{\min}$ as the abscissa of the intersection of the regression line with the abscissa line. From Figure 8.16, $S_{\min}$ was approximately 1 mg/L. This finding may

suggest that the existence of “slow” BDOC could not simply be attributed to the fact that the concentration of BDOC was below S_{min} . Additional studies, however, are needed to explain the efficient biodegradation of organic matter in the effluents from the stimulated recirculating FBT/ozonation process at BDOC concentrations significantly lower than S_{min} .

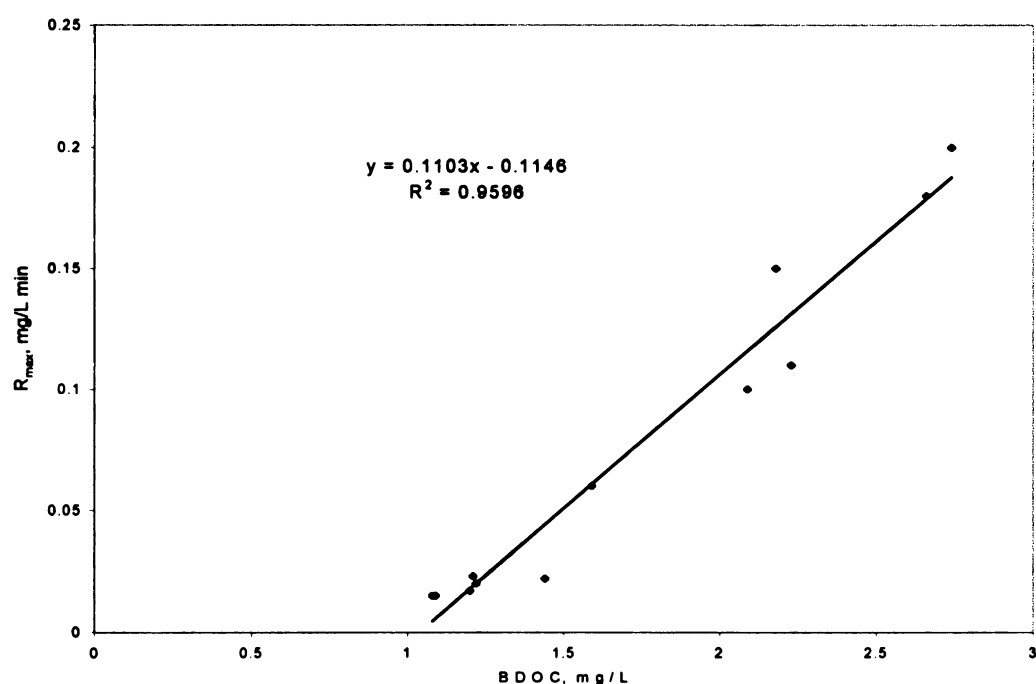


Figure 8.16. Relationship between BDOC concentration and biodegradation rate

8.7. SUMMARY

The study presented in this section showed that using FBT prior to ozonation resulted in an increased production of low molecular weight compounds and biodegradable organic matter. This was not observed in the ozonation/FBT process conducted under similar conditions. The biodegradable organic matter produced from the FBT/ozonation process was removed by biofiltration. It was shown that the FBT/ozonation process followed by biofiltration was more efficient than the ozonation/FBT process in terms of the removal of organic matter and biodegradation time. However, the effluent from the FBT/ozonation process contained at least 0.5 mg/L of slowly biodegrading organic carbon, which was difficult to remove by biofiltration. The hypothesis that the recycle of a portion of ozonation effluent back to the FBT column would increase the efficiency of the process was not confirmed. This is thought to be because of slow biodegradation of NOM. As a result, FBT resulted in the removal of fastest biodegrading fractions of organic matter leaving slower biodegradable materials in the system effluent. These materials were difficult to remove by following biofiltration.

The results of experiments confirmed the hypothesis that adding an easily biodegrading carbon source to the FBT column resulted in an increased removal of organic matter. In addition, the stimulated FBT/ozonation process resulted in an increased production of “fast” BDOC that was efficiently removed by biofiltration. However, the effluent from stimulated FBT/ozonation still contained at least 0.5 mg/L of slowly biodegrading carbon, which was difficult to remove by biofiltration. The recycle mode of operation resulted in a decrease in the concentration of “slow” BDOC in the

effluent from the stimulated FBT/ozonation and, consequently, in low biofiltration time required to remove remaining biodegradable organic matter. Thus, the study showed that adding an easily biodegrading organic carbon in combination with the recycle mode operation resulted in an increased process efficiency in terms of the removal of organic matter and biodegradation time.

The study also showed that the effluent from the stimulated FBT/ozonation was efficiently biodegraded even at the substrate concentration below $S_{\min}$. Further studies are needed to explain this phenomenon and to better understand the transformation of NOM during stimulated biodegradation and to determine optimal operational parameters (dose of a carbon source, recycle flow, EBCT etc.). The measurements of assimilable organic carbon (AOC) will also be needed to evaluate the regrowth potential of treated water.

9. ECONOMIC ANALYSIS

In this chapter, the cost of the proposed combined ozonation and FBT process was compared with the cost of conventional flocculation-sedimentation-filtration processes with and without ozonation and granular activated adsorption for a design capacity of 1 MGD.

A simplified schematic of the combined ozonation and FBT process is shown in Figure 9.1. The treatment train includes pumping water into an FBT column, from where it flows by gravity into an ozonation tank followed by sand filtration and chlorination. A portion of the ozonation effluent is recycled back to the FBT column. Values for design and operating parameters used to estimate the cost of the facility are summarized in Table 9.1.

The annual cost analysis method was used to consolidate capital and operating cost into a single estimate. The capital recovery factor was calculated using the amortization period and interest rate given in Table 9.1. The salvage value cost was not included in cost analysis. The conventional treatment costs were presented in Wiesner et al. (1994) and were based on the “typical” values observed in practice rather than values taken from specific operating facilities. Since these values were based on 1992-1993 prices, these costs were increased by 10 percent to reflect an increase in price for the last 5 years. This modest increase was assumed to yield a more cautious estimate of the cost-effectiveness of the proposed process.

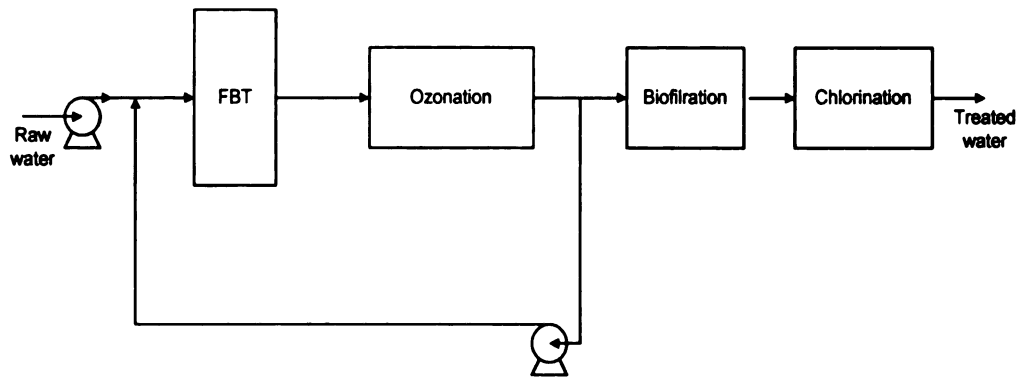


Figure 9.1. Simplified schematic of the combined ozonation and FBT process

Table 9.1 Values for major cost, design and operating parameters

Parameter	Value
Cost parameters	
Amortization period, years	20
Annual interest rate, percent	10
Land cost, \$/acres	not included
Labor, \$/hr	30
Electricity, \$/kW·hr	0.07
Acetic acid, \$/drum	465.60
Design and operating parameters	
FBT media	activated carbon
FBT EBCT, min	30
Acetic acid dose, mg/L	2.5
Filter media	sand
Biofilter EBCT, min	10
Filtration rate, gpm/sq ft	3
Ozone dose, mg/L	6 ¹
HRT in ozone contactor, min	10
Design recycle ratio	2
Operating recycle ratio	1

¹Based on TOC concentration in raw water of 6 mg/mg C and ozone dose of 1 mg/mg C

Compared to “typical” values observed in practice (Weisner et al. 1994), the cost of ozonation treatment in the proposed process was increased by 60 percent. This was done to reflect a greater anticipated consumption of ozone in the proposed process compared to that in conventional ozonation facilities. (Typical ozone doses used in conventional treatment are in the range from 3 to 5 mg/L (Scadsen, 1998; Bellamy et al. 1990).) Since the chlorination cost was not significant compared to other costs, this cost was roughly estimated using the six-tenths rule based on the cost of 50 MGD chlorination facility (Water Treatment Plant Design, 1998).

The equipment and operating cost data for FBT were provided by EFX Systems, Inc. (Rajan, 1998). Installation, piping, instrumentation and control, electrical, building, and engineering and supervision costs were determined using designated percentage factors to the equipment cost (Water Treatment Plant Design, 1998; Peters and Timmerhaus, 1991). Considering that FBT systems are preengineered systems, the cost factors for installation, piping, and engineering were reduced to 20, 20 and 10 percent, respectively. The operating cost was calculated based on using activated carbon as an FBT medium, rather than a significantly cheaper inert material (e.g., sand), which was used in pilot testing. This was done to yield a more cautious estimate of the cost-effectiveness of the proposed process and to ensure the feasibility of future studies using activated carbon.

The biofilter was sized based on a filtration rate of 3 gpm/sq ft (Water Treatment Plant Design, 1998). It was assumed that a standby FBT pump would be used for filter backwashing. The pumps were sized using the data presented in Robinson (1996) and in

Crane (1978). The equipment cost for the pump station and biofiltration were found in Process Plant Construction Estimating Standards (1998). Installation, piping, instrumentation and control, electrical, building, and engineering and supervision costs were determined using designated percentage factors to the equipment cost (Water Treatment Plant Design, 1998; Peters and Timmerhaus, 1991).

The calculations of the capital and operating cost of the proposed process are presented in Appendix B. The data are summarized in Table 9.2. The most significant costs were associated with FBT and ozonation, which suggests that these are the areas in which optimization efforts should be directed. The economical feasibility of increasing recycle ratio is presented in Figure 9.2. The cost of treatment by conventional GAC is given for comparison. When the recycle ratio increased from 2 to 3.5, the total cost of treatment by the proposed process was estimated to increase by approximately 10 percent. At recycle ratios less than 7, the cost of treatment by FBT was estimated to be lower than that by GAC. At recycle ratios greater than 6, GAC appears to be economically more feasible.

Table 9.3 presents the cost of treatment by the combined ozonation and FBT process (recycle ratio 2) and by conventional processes. The cost of treatment by the ozonation and FBT process was estimated to be approximately 20 percent greater than conventional flocculation/sedimentation processes and 40 percent less than flocculation/sedimentation processes with ozonation and GAC. However, conventional flocculation/sedimentation processes are not technically feasible for the treatment of waters having quality similar to that of Huron River water (Scadsen, 1998). The ozonation and FBT process appears to be technically and economically feasible and

should be considered seriously when evaluating the construction of new or retrofitting existing facilities, especially for small systems.

Table 9.2 Cost breakdown for the combined ozonation and FBT process

Unit operation	Total cost, \$/1,000 gal
Pump station	0.13
FBT	1.11
Ozonation ¹	0.72
Biofiltration	0.06
Chlorination	0.05
Total cost	2.07

¹Wiesner, 1994

Table 9.3. Cost of selected treatment systems

Treatment system	Total cost, \$/1,000 gal
Flocculation/sedimentation + filtration ¹	1.68
Flocculation/sedimentation + ozonation + GAC ¹	3.55
FBT + ozonation + biofiltration	2.07

¹Wiesner, 1994

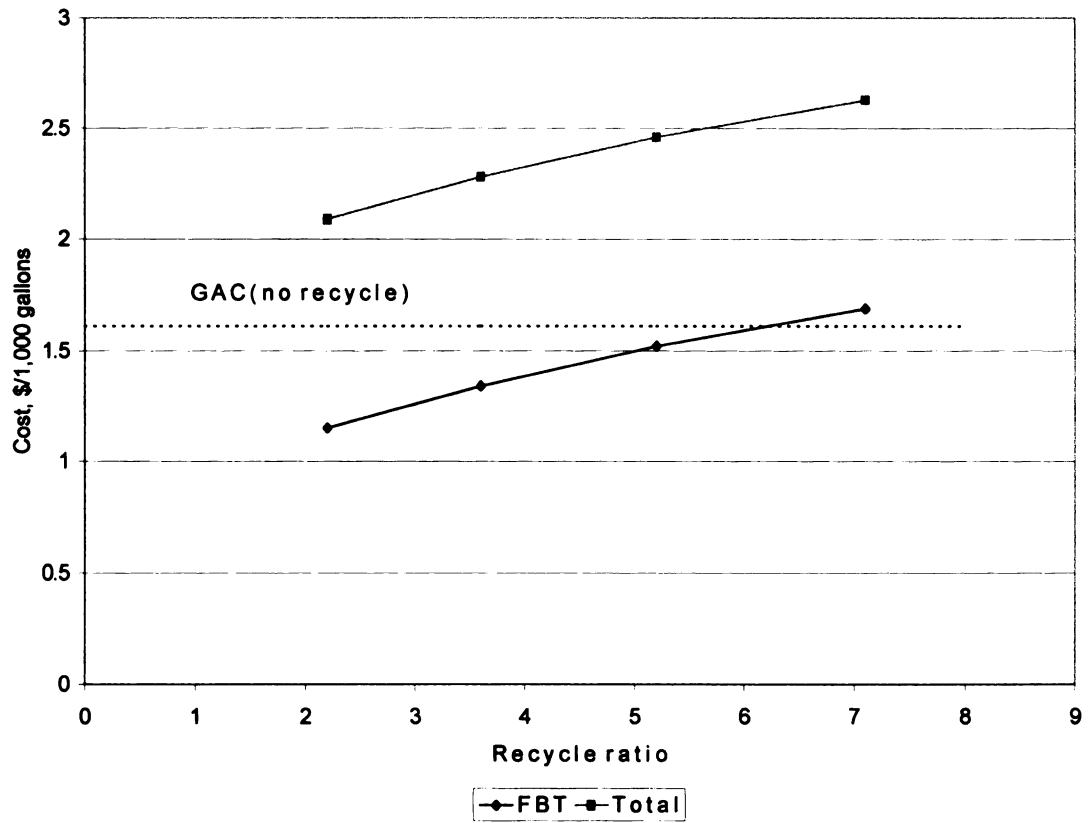


Figure 9.2. Effect of recycle on the cost of treatment by combined FBT/ozonation.

10. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

Section 10.1 presents summary of the significant results and conclusions from the experimental results and data analysis. Recommendations for future research are given in Section 10.2.

10.1. CONCLUSIONS

10.1.1. General Conclusions

The following conclusions highlight the major results of the study presented in this thesis (particular results are discussed in subsequent sections):

1. A combination of factors affected the removal of organic carbon during ozonation of Huron River water. These included ozone dose, hydraulic retention time (HRT), and dissolved ozone concentration.
2. If ozonation is to be incorporated into an ozonation/biodegradation treatment train, the ozonation should be conducted under conditions that do not result in the destruction of organic carbon. In this way, ozonation is directed for the production of biodegradable organic matter, which is removed by biotreatment.
3. An ozone-dose averaging approach for developing the correlations between water quality surrogate parameters was proposed and shown to be useful in evaluating the efficiency of ozonation and FBT processes.

4. The UV-254 absorbance of ozonated Huron River water could be used to determine the dissolved ozone concentration and the specific ozone consumption rate.
5. Several biodegradation characteristics were developed and used to quantify the efficiency of the biodegradation of NOM.
6. Combined ozonation and FBT treatment for the control THM precursors in drinking water was shown to be technically and economically feasible.
7. Adding acetate to the FBT column in combination with the recycle mode of operation provided a synergetic effect that resulted in an increase in the efficiency of the combined ozonation and FBT process in terms of the ozone consumption and biodegradation time.

10.1.2. Surrogate Characterization of NOM

The goal of the surrogate characterization study was to establish the relationships between TOC, UV-254, HS, and THMFP and to determine if any of these parameters could be used as surrogates for the others during the investigation of the combined ozonation and FBT process. The following conclusions can be made upon the results of this study:

1. There existed good correlations between TOC and UV-254 for raw water and ozonated and biotreated waters. The relationships between these parameters were, however, different for waters at different treatment stages. For this reason, these

parameters could not be substituted for each other when evaluating various treatment alternatives.

2. There existed a good correlation between UV-254 and humic substance concentrations, which did not change for waters at different treatment stages. As such, the UV-254 could be used as a surrogate for humic substances.
3. There existed a good correlation between TOC concentration and THMFP, which did not change for waters at different treatment stages. As such, the TOC concentration could be used as a surrogate for THMFP.
4. There existed a good correlation between UV-254 and THMFP, which, however, was different for waters at different treatment stages. For this reason, the UV-254 could not be used as a surrogate for THMFP when evaluating various treatment alternatives.

10.1.3. Ozonation Studies

The following conclusions can be made upon the results of ozonation studies using Huron River water:

1. Generally, the removal of organic carbon increased with ozone dose, hydraulic retention time (HRT), and dissolved ozone concentration. At low HRT (less than 10 minutes), ozonation at doses of up to 1 mg/mg C resulted in very little destruction of TOC. At a concentration of dissolved ozone of less than 1 mg/L (normally maintained in commercial ozonation systems) and HRTs greater than 10 minutes, the removal of organic carbon increased with ozone dose and leveled off at an ozone dose of approximately 1-1.5 mg/mg C.

2. For the range of experimental conditions studied, the removal of UV-254-absorbing compound increased with an increase in ozone dose (up to 5 mg/mg C) and was not affected by HRT (ranging from 7 to 60 minutes).
3. Ozonation, conducted under conditions that resulted in the destruction of organic carbon, did not result in an increased production of low-molecular weight compounds (less than 1000 daltons) or biodegradable organic matter. When little removal of organic carbon during ozonation was observed, the concentrations of low molecular weight compounds and BDOC increased with an increase in ozone dose.
4. The ozonation of NOM follows the following pathways: (1) ozone converts humic substances into nonhumic materials; (2) the destruction of organic carbon occurs through the reaction of ozone with nonhumic substances; (3) both reactions can proceed simultaneously.
5. The reaction rate constant of the ozone reactions with humic substances was a function of temperature and the concentration of humic substances and was represented as the product of two independent terms: temperature- and concentration-dependent terms (see Equation 6.32). The reaction rate constant of the ozone reactions with nonhumic substances was a function of temperature only.
6. The amount of ozone required for the destruction of nonhumic substances was approximately two times greater than that required for the oxidation of humic substances. This suggested that ozonation should be directed towards the oxidation of essentially nonbiodegradable humic substances rather than potentially biodegradable nonhumic materials.

7. A mathematical model that described the transformation of NOM in terms of the concentration of humic and nonhumic substances was developed. The kinetic parameters, including stoichiometric coefficients and activation energies were determined. The model adequately described the transformation of humic and nonhumic fractions during ozonation. The relative difference between experimental and calculated data did not exceed 10 percent with an average of ± 6 percent.
8. The second model that was tested in this study was based on the specific ozone consumption rate. Using the specific rate of ozone utilization for the evaluation of the ozonation efficiency was, however, prone to possible misinterpretations. This is because, using only the specific ozone consumption rate, it was difficult to separate the effect of ozonation on the removal of organic carbon from that on the removal of UV-254-absorbing compounds. For this reason, the model based on the specific rate of ozone utilization was less useful than the model based on the concentrations of humic and nonhumic substances.

10.1.4. Biodegradation Studies

The following conclusions can be made upon the biodegradation studies of raw and ozonated waters:

1. The biodegradable organic matter in Huron River water consisted of two fractions: fast and slowly biodegrading fractions ("fast" and "slow" BDOC). Several operationally defined biodegradation parameters were introduced in an attempt to quantify the efficacy of the biodegradation of NOM. These parameters included (1)

- the maximum rate of the biodegradation of “fast” BDOC ($R_{\max}$); (2) the minimum EBCT that required to eliminate “fast” BDOC ($EBCT_{\min}$); and (3) the BDOC concentration that at least remained after biodegradation at $EBCT_{\min}$ ($BDOC_{\text{slow}}$).
2. The removal of “fast” BDOC in the FBT system was greater than that in the biofiltration system. The $R_{\max}$ in the FBT column was two times greater than that in the biofiltration column. The removal efficiency of “slow” BDOC was essentially the same for both systems.
 3. Increasing temperature resulted in an increase in $R_{\max}$ and in a decrease in $EBCT_{\min}$. The removal of slowly biodegrading organic matter did not appear to be affected by temperature.
 4. Biodegradability of NOM in water increased after ozonation (under conditions when little destruction of organic carbon occurred). However, ozonated water contained at least 0.5 mg/L of slowly biodegradable organic carbon, which was difficult to remove by biotreatment. These slowly biodegrading organic materials can pose the bacterial regrowth problem in the distribution system if they are not removed in the treatment system. (The approaches of reducing $BDOC_{\text{slow}}$ are summarized in Section 10.1.5.)

10.1.5. Pilot-Scale Study of the Combined Ozonation and FBT Process

The following conclusions are from the pilot-scale study of the combined ozonation and FBT process:

1. At an EBCT of up to 180 minutes and ozone dose of up 2 mg/mg C, the ozonation/FBT process was able to remove up to 50 percent of TOC and humic

substances, up to 80 percent of UV-254, up to 70 percent of THMFP, and up to 80 percent of turbidity. The removal of organic matter was comparable to that achieved at Ann Arbor Water Treatment plant, which included softening, flocculation/sedimentation, ozonation, and activated carbon adsorption.

2. The use of recycle of a portion of the system effluent back to the ozone contactor in order to increase the removal efficiency relative to ozone consumption was investigated. Recycling at a recycle ratio of 1 resulted in an increase in the removal of organic matter by 3 percent. Although the difference was statistically significant, the effect was less than expected.
3. Using FBT prior to ozonation resulted in an increased production of low molecular weight compounds and biodegradable organic matter, which was removed by biofiltration. The FBT/ozonation process followed by biofiltration was more efficient than the ozonation/FBT process in terms of the removal of organic matter and biodegradation time. The effluent from the FBT/ozonation system contained at least 0.5 mg/L of “slow” BDOC, which was difficult to remove by biofiltration. Recycle of a portion of the FBT/ozonation effluent back to the FBT column did not result in significant increase in the reduction of BDOC_{slow} and total biodegradation time.
4. Adding an easily biodegradable carbon source (acetate) to the FBT column resulted in an increase in the removal of organic carbon by FBT. The stimulated FBT/ozonation process resulted in an increased production of “fast” BDOC, which was efficiently removed by biofiltration. The efficiency of the stimulated FBT/ozonation process followed by biofiltration was greater than that of the FBT/ozonation process (no acetate) followed by biofiltration in terms of the removal of organic matter relative to

ozone consumption. However, the stimulated FBT/ozonation effluent still contained at least 0.5 mg/L of slowly biodegrading organic carbon, which was difficult to remove by biofiltration.

5. The recycle mode of operation resulted in a decrease in the concentration of “slow” BDOC in the effluent from the stimulated FBT/ozonation process and, consequently, in a decrease in biofiltration time.
6. For a design capacity of 1 MGD, the cost of treatment by the stimulated recirculating FBT/ozonation process followed by biofiltration was estimated to be 40 percent less than that by a flocculation/sedimentation process with ozonation and GAC.

10.2. RECOMMENDATIONS FOR FUTURE RESEARCH

1. The study presented herein included one source water. The applicability of the results to different sources of water supplies needs to be demonstrated.
2. The Huron River water contained low bromide concentration. As bromide may affect the kinetics of ozone reaction in water and DBP speciation (Krasner et al., 1996, von Gunten and Hoigné, 1996), the applicability of the results for water containing high concentration of bromide needs to be demonstrated.
3. The pilot-scale FBT system was operated as a CSTR. The plug-flow systems should be investigated. It is expected that the efficiency of the efficiency of FBT would increase when operated under plug-flow conditions.
4. Detail study needs to be conducted to better understand the transformation of NOM during stimulated biodegradation.

5. This study used acetic acid as an easily biodegradable carbon source. Other sources of easily biodegradable organic carbon need to be investigated for their applicability in the ozonation and FBT systems. The effect of nutrients on the efficiency of stimulated FBT should also be addressed.
6. The results of the studies 3 – 6 should serve as basis for optimizing the operational parameters including the dose of carbon source and recycle ratio.
7. In this study, the FBT system used an inert material as a support medium. It needs to be demonstrated if using activated carbon can increase process efficiency.
8. The analysis of assimilable organic carbon as an indicator of the effluent regrowth potential should be included in future studies. The water also needs to be analyzed for haloacetic acid formation potential, as haloacetic acids are regulated by US EPA (Oxenford, 1996).
9. The mathematical ozonation model and kinetic ozonation parameters, that were developed in this study, needs to be verified for its applicability to biodegradation effluents.
10. Studies are needed to determine if there exists a correlation between BDOC and the concentration of nonhumic substances. If such correlation is established, a model that describes the transformation of NOM during ozonation and FBT (including recirculating and stimulated modes of operation) can be developed.

APPENDICES

Appendix A. List of formulas

Ozone dose (expressed as milligram of ozone per liter (mg/L)):

$$\text{Ozone dose} = \frac{G(c_g^{\text{in}} - c_g^{\text{out}})}{Q}$$

where, G and Q are gas and water flow rates, respectively, mL/min; c_g^{in} and c_g^{out} are the concentration of ozone in the influent and effluent gas, respectively, mg/L.

Ozone dose (expressed as milligram of ozone per milligram of TOC (mg/mg C)):

$$\text{Ozone dose} = \frac{G(c_g^{\text{in}} - c_g^{\text{out}})}{Q \cdot \text{TOC}}$$

where, TOC is the concentration of total organic carbon in the influent, mg/L.

Gaseous ozone concentration using the spectroscopic method:

$$c_g = 48,000 \frac{A}{\epsilon \cdot b} \frac{p_{\text{atm}}}{p_{\text{atm}} + p_{\text{gauge}}}$$

where, c_g is ozone concentration in gas phase, mg/L; A is absorbance; ϵ is the extinction coefficient, L/mole cm; b is UV pathlength, cm; P_{atm} is atmospheric pressure, psi; P_{gauge} is pressure in the UV cell, psig.

EBCT in the FBT system (min):

$$EBCT = \frac{\pi d^2 H}{4Q}$$

where d is the column diameter, cm.; H is the bed height, cm; Q water flow rate, mL/min.

Biofilter EBCT (min):

$$EBCT = \text{elapsed time} \frac{\text{bed volume}}{\text{sample volume}}$$

Appendix B. Annual cost analysis

Table B.1. Pump station

Amortization period	20
Annual interest rate	0.1
Capital recovery factor	0.1175

Design capacity	1 MGD
Capital cost	\$ 102,044.00
Operating cost	\$ 33,435.79
Annualized capital cost	\$ 11,986.05
Annualized operating cost	\$ 33,435.79
Total annual cost	\$ 45,421.84
Cost per 1000 gallons	\$ 0.12

<u>Capital cost</u>	% of equip	Quantity	Cost		
Pumps		2	\$ 19,400.00	\$	38,800.00
Installation	40			\$	15,520.00
Piping	30			\$	11,640.00
Instrument and control	20			\$	7,760.00
Electrical	10			\$	3,880.00
Buildings	20			\$	7,760.00
Engineering and Superv	10			\$	3,880.00
Contingency	15			\$	12,804.00
Total capital				\$	102,044.00

Operating cost

Electricity				\$	27,435.79
		Hr/yr	Labor/hr		
Labor		200	\$ 30.00	\$	6,000.00
Total operating				\$	33,435.79

Pumps	Centrifugal				
Pump specific speed		1800 rpm			
Pump efficiency		0.8			
Motor efficiency		0.80			
Capacity		1 MGD			
		694 GPM		Q	
Pressure head		200 ft		H	
Electricity	\$	0.07 kW hr			
Work horsepower		35.11			
BHP		43.89		WH/(pump efficiency)	
Motor HP		55		(Q*H*SG)/3956	
Motor size		60		BHP/(motor efficiency)	
Kilowatts		44.742		0.745*motor HP	
Energy cost per year	\$	27,435.79			

References:

Robinson R.N. Chemical Engineering Reference Manual, Profess. Publ., Belmont, Ca, 1996
 Crane, Flow of Fluids, Crane Co. 1978

Table B.2. Biofiltration

Amortization period	20
Annual interest rate	0.1
Capital recovery factor	0.1175

Design capacity	1 MGD
Capital cost	\$ 74,250.00
Operating cost	\$ 15,000.00
Annualized capital cost	\$ 8,721.38
Annualized operating cost	\$ 15,000.00
Total annual cost	\$ 23,721.38
Cost per 1000 gallons	\$ 0.06

<u>Capital cost</u>	% of equip	Quantity	Cost	
Equipment (2 biofilters)		2	\$ 16,500.00	\$ 33,000.00
Installation	40			\$ 13,200.00
Piping	20			\$ 6,600.00
Instrument and control	20			\$ 6,600.00
Electrical	10			\$ 3,300.00
Buildings	20			\$ 6,600.00
Contingency	15			\$ 4,950.00
Total capital				\$ 74,250.00

<u>Operating cost</u>	Hr/yr	Labor/hr	
Labor	500	\$ 30.00	\$ 15,000.00
Total operating			\$ 15,000.00

Note: one of the FBR pumps can be used for backwashing

Sizing

Capacity	1 MGD
	694 GPM
EBCT	10 minutes
Filtration rate	3 gpm/sq ft
Surface area required	231 sq ft
Filter bed volume	6944 gallons
	928.4 cu. ft
Filter media depth	4.01 ft
Filter diameter	9.69 sq ft.

References:

Water Treatment Plant Design. 3d edition. McGraw-Hills, NY, 1990
Process Plant Construction Estimating Standards, Richardson Engineering Services, Arizona, 1997.
Peters and Timmerhaus. Plant Design and Economics, McGraw Hills, 1991

Table B.3. Chlorine Basin

Amortization period	20
Annual interest rate	0.1
Capital recovery factor	0.1175

Design capacity	1 MGD
Capital cost	\$ 120,000.00
Operating cost	\$ 7,825.00
Annualized capital cost	\$ 14,095.15
Annualized operating cost	\$ 7,825.00
Total annual cost	\$ 21,920.15
Cost per 1000 gallons	\$ 0.06

<u>Capital cost</u>	% of equip	Quantity	Cost		
Chlorine basin		1	\$ 120,000.00	\$	120,000.00
Installation	n/a				
Piping	n/a				
Instrument and control	n/a				
Electrical	n/a				
Buildings	n/a				
Engineering and Supervis	n/a				
Contingency	n/a				
Total capital				\$	120,000.00

<u>Operating cost</u>	Cost/kg	Quant, kg/day		
Chlorine	0.25	20	\$	1,825.00
	Hr/yr	Labor/hr		
Labor	200	\$ 30.00	\$	6,000.00
Total operating			\$	7,825.00

References:

Water Treatment Plant Design. 3d edition. McGraw-Hills, NY, 1990

Peters and Timmerhaus. Plant Design and Economics, McGraw Hills, 1991

Table B.4. FBT (recycle ratio – 2)

Amortization period	20
Annual interest rate	0.1
Capital recovery factor	0.1175
Design capacity	1 MGD
Recycle ratio	2
Treatment train	dual
Biofilm support medium	activated carbon
Capital cost	\$ 2,947,650.00
Operating cost	\$ 57,622.84
Annualized capital cost	\$ 346,229.86
Annualized operating cost	\$ 57,622.84
Total annual cost	\$ 403,852.71
Cost per 1000 gallons	\$ 1.11
Capital cost	% of equip
Equipment	\$ 1,290,000.00
Installation	20 \$ 258,000.00
Piping	20 \$ 258,000.00
Instrumentation and control	20 \$ 258,000.00
Electrical	10 \$ 129,000.00
Buildings	20 \$ 258,000.00
Engineering and Supervision	10 \$ 129,000.00
Contingency	15 \$ 367,650.00
Total capital	\$ 2,947,650.00
Operating cost (no acetate)	\$ 50,000.00
Acetate cost	\$ 7,622.84
Total operating	\$ 57,622.84
Acetate	
Capacity	1 MGD
Dose	2.5 mg/L
Amount	9.45 kg/day
Cost per kg	\$ 2.21
Annual cost	\$ 7,622.84
Cost per 1000 gallons	0.02

References:

Rajan R.V. Equipment and Operating Cost for FBT Systems, 1998
 Water Treatment Plant Design. 3d edition. McGraw-Hills, NY, 1990
 Peters and Timmerhaus. Plant Design and Economics, McGraw Hills, 1991

Table B.5. FBT (recycle ratio – 3.5)

Amortization period		20
Annual interest rate		0.1
Capital recovery factor		0.1175
Design capacity		1 MGD
Recycle ratio		3.5
Treatment train	dual	
Biofilm support medium	activated carbon	
Capital cost	\$	3,427,500.00
Operating cost	\$	70,588.35
Annualized capital cost	\$	402,592.86
Annualized operating cost	\$	70,588.35
Total annual cost	\$	473,181.21
Cost per 1000 gallons	\$	1.30
Capital cost	% of equip	
Equipment		\$ 1,500,000.00
Installation	20	\$ 300,000.00
Piping	20	\$ 300,000.00
Instrumentation and control	20	\$ 300,000.00
Electrical	10	\$ 150,000.00
Buildings	20	\$ 300,000.00
Engineering and Supervision	10	\$ 150,000.00
Contingency	15	\$ 427,500.00
Total capital		\$ 3,427,500.00
Operating cost (no acetate)		\$ 63,000.00
Acetate cost		\$ 7,588.35
Total operating		\$ 70,588.35
Acetate		
Capacity		1 MGD
Dose		2.5 mg/L
Amount		9.45 kg/day
Cost per kg	\$	2.20
Annual cost	\$	7,588.35
Cost per 1000 gallons		0.02

References:

Rajan R.V. Equipment and Operating Cost for FBT Systems, 1998
 Water Treatment Plant Design. 3d edition. McGraw-Hills, NY, 1990
 Peters and Timmerhaus. Plant Design and Economics, McGraw Hills, 1991

Table B.6. FBT (recycle ratio – 5)

Amortization period	20
Annual interest rate	0.1
Capital recovery factor	0.1175
Design capacity	1 MGD
Recycle ratio	5
Treatment train	dual
Biofilm support medium	activated carbon
Capital cost	\$ 3,884,500.00
Operating cost	\$ 84,988.35
Annualized capital cost	\$ 456,271.91
Annualized operating cost	\$ 84,988.35
Total annual cost	\$ 541,260.26
Cost per 1000 gallons	\$ 1.48

<u>Capital cost</u>	% of equip	
Equipment		\$ 1,700,000.00
Installation	20	\$ 340,000.00
Piping	20	\$ 340,000.00
Instrumentation and control	20	\$ 340,000.00
Electrical	10	\$ 170,000.00
Buildings	20	\$ 340,000.00
Engineering and Supervision	10	\$ 170,000.00
Contingency	15	\$ 484,500.00
Total capital		\$ 3,884,500.00

Operating cost (no acetate)	\$ 77,400.00
Acetate cost	\$ 7,588.35
Total operating	\$ 84,988.35

<i>Acetate</i>	
Capacity	
Dose	1 MGD
Amount	2.5 mg/L
Cost per kg	9.45 kg/day
Annual cost	\$ 2.20
Cost per 1000 gallons	\$ 7,588.35
	0.02

References:

Rajan R.V. Equipment and Operating Cost for FBT Systems, 1998
 Water Treatment Plant Design. 3d edition. McGraw-Hills, NY, 1990
 Peters and Timmerhaus. Plant Design and Economics, McGraw Hills, 1991

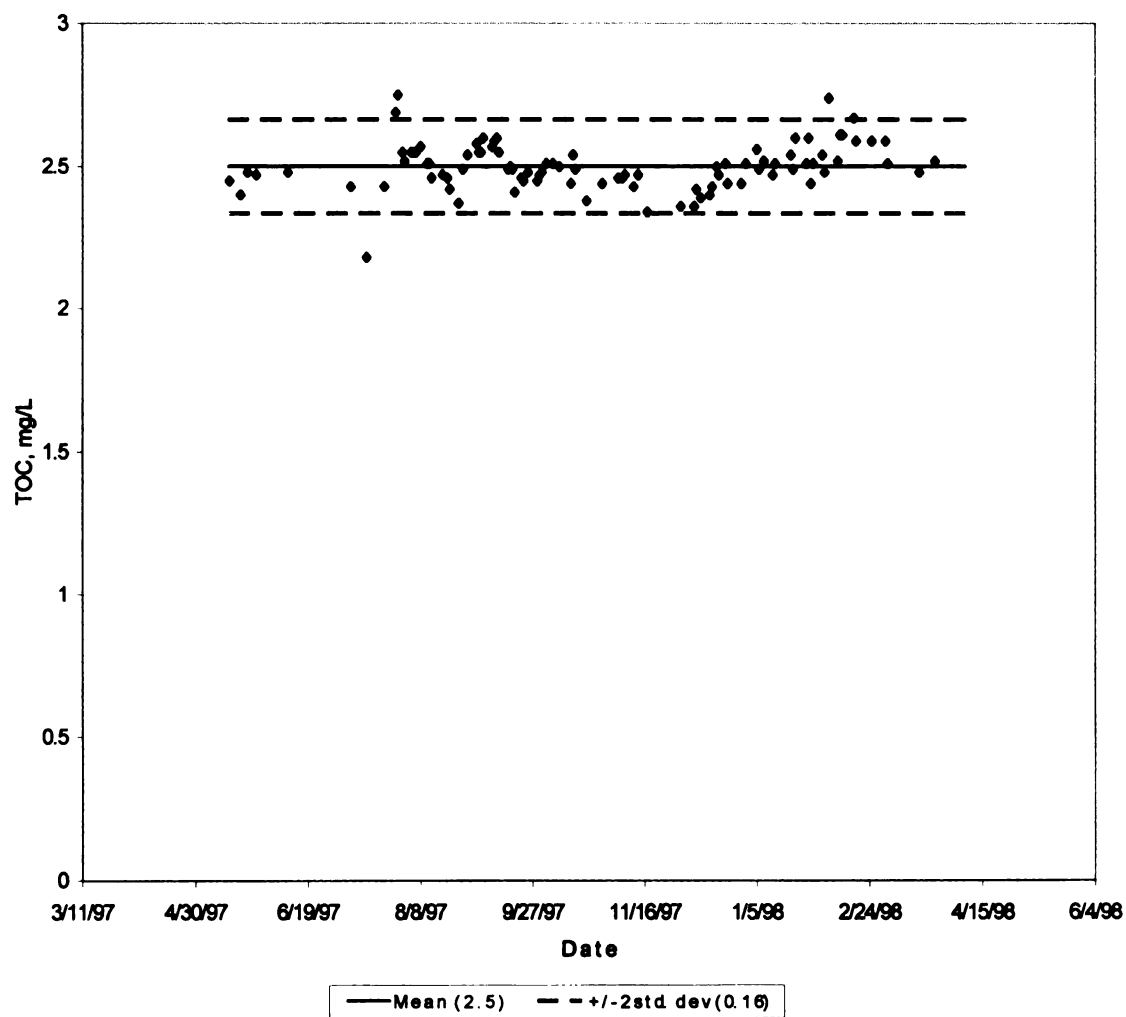
Table B.7. FBT (recycle ratio – 7)

Amortization period		20
Annual interest rate		0.1
Capital recovery factor		0.1175
Design capacity		1 MGD
Recycle ratio		7
Treatment train		dual
Biofilm support medium		activated carbon
Capital cost		\$ 4,272,950.00
Operating cost		\$ 100,338.35
Annualized capital cost		\$ 501,899.10
Annualized operating cost		\$ 100,338.35
Total annual cost		\$ 602,237.45
Cost per 1000 gallons		\$ 1.65
<u>Capital cost</u>	<u>% of equip</u>	
Equipment		\$ 1,870,000.00
Installation	20	\$ 374,000.00
Piping	20	\$ 374,000.00
Instrumentation and control	20	\$ 374,000.00
Electrical	10	\$ 187,000.00
Buildings	20	\$ 374,000.00
Engineering and Supervision	10	\$ 187,000.00
Contingency	15	\$ 532,950.00
Total capital		\$ 4,272,950.00
Operating cost (no acetate)		\$ 92,750.00
Acetate cost		\$ 7,588.35
Total operating		\$ 100,338.35
<u>Acetate</u>		
Capacity		
Dose		1 MGD
Amount		2.5 mg/L
Cost per kg		9.45 kg/day
Annual cost	\$	2.20
Cost per 1000 gallons	\$	7,588.35
		0.02

References:

Rajan R.V. Equipment and Operating Cost for FBT Systems, 1998
 Water Treatment Plant Design. 3d edition. McGraw-Hills, NY, 1990
 Peters and Timmerhaus. Plant Design and Economics, McGraw Hills, 1991

Appendix C. Control charts



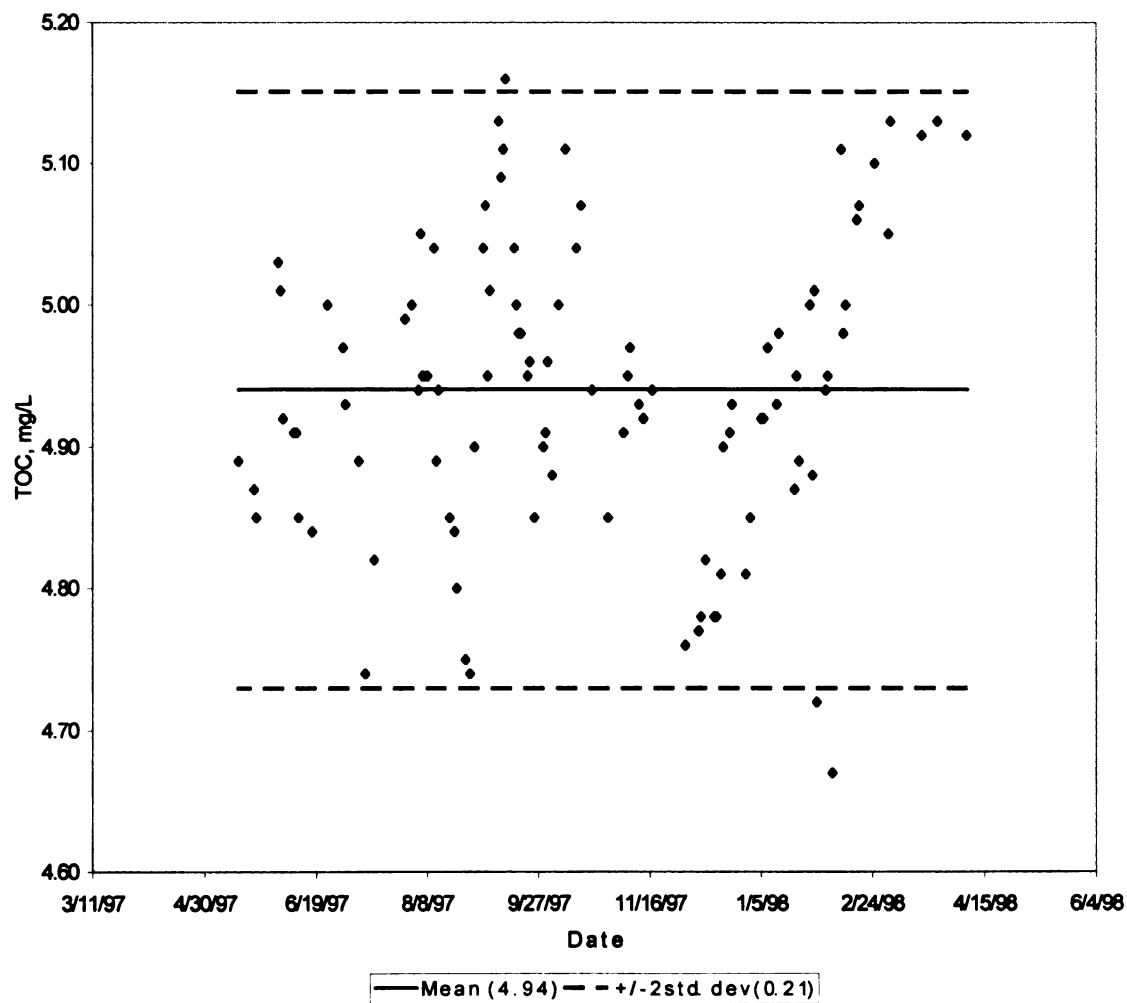
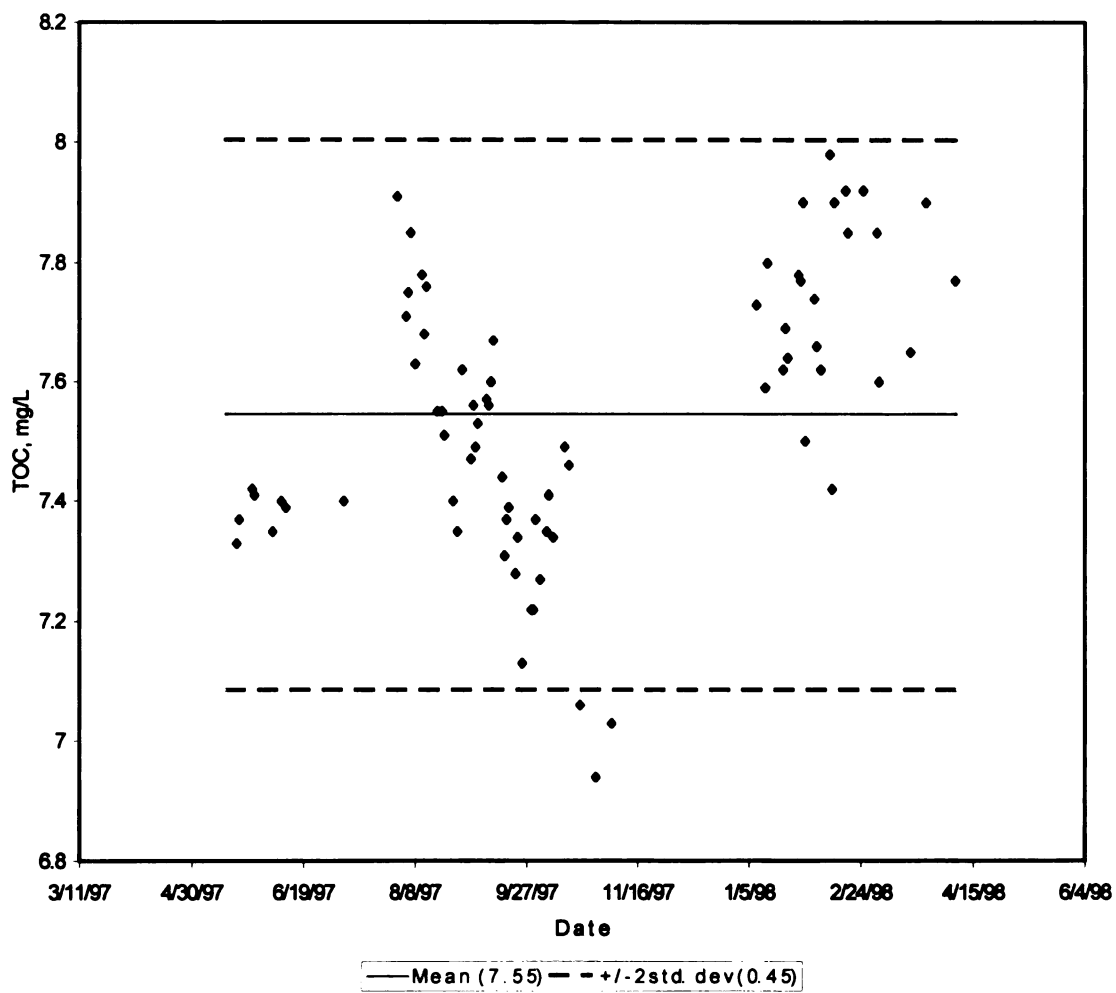


Figure C.3. TOC standard – 5.0 mg/L



Appendix D. Spreadsheet Formats

Table D.1. Spreadsheet format for pilot-scale system data entry

Water source

Huron River, Ann Arbor, MI

 DATE

 Date collected

Mode of operation

Sequence

 Recycle

 Biostimulant

Operating conditions

FBR bed height	<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td></tr></table> cm		Comments:
FBR diameter	<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td></tr></table> in		
Bed volume	<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td></tr></table> mL/min		
Water flow	<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td></tr></table> mL/min		
Gas flow	<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td></tr></table> mL/min		
Recycle	<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td></tr></table> mL/min		
Line pressure	<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td></tr></table> psig		
Temperature	<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td></tr></table> C		
Biostimulant flow	<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td></tr></table> mL/min		
Biostimulant dose	<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td></tr></table> mg/L		
Influent gas UV254	<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td></tr></table> 1/cm		
Influent gas O3	<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td></tr></table> mg/L		
RT dissolved O3	<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td></tr></table> mg/L		
(Influent TOC)	<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td></tr></table> mg/L		
Ozone dose	<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td></tr></table> mgO3/mgC		
EBCT	<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td></tr></table> min		

Water quality

Parameter	Influent	RT/FBR	Effluent	
pH				
Alk, mg/L as CaCO3				
Turbidity, NTU				
TOC, mg/L				
UV254, 1/cm				
HS, mg/L				
nonHS, mg/L				
MW500, mg/L				
Cl2 demand, mg/L				
THMFP, ug/L				
CHCl3, ug/L				
CHCl2Br, ug/L				
CHClBr2, ug/L				
CHBr3, ug/L				

Table D.2. Spreadsheet format for bench-scale system data entry

[illegible]

Table D.3. Spreadsheet format for HS data entry

Water ID				
Date processed				
Date analyzed				
System				
Treatment				
Ozonation				
Ret time, min				
Ozone dose, mg/L				
Temperature, C				
Biofiltration				
EBCT, min				
FBR				
EBCT, min				
Temperature, C				
Sample to XAD column				
TOC, mg/L				
UV-254, 1/cm				
Column				
TOC, mg/L				
NaOH				
Column NaOH				
DI water				
Column DI				
Column effluent				
Column eluent				
HS concentration, mg/L				
nonHS concentr, mg/L				
Sample TOC, mg/L				
HS + nonHS, mg/L				
(HS+nonHS)/sample TOC				
Comments				

Table D.4. Spreadsheet format for biodegradability data entry

Water source
Date collected

Start
Finish

Experimental setup

Column diameter	2.54	cm
Bed height	20	cm
Bed volume	101	cm ³
Filter media	"baker"	
Flow		
Mode of operation		
Sample volume		mL
Flow rate		mL/min
Single pass contact time		min

Sample description

System 1 effluent		
Mode:	Flow/recl	mL/min
Dose:	FBR EBCT	
Biostimulant	Dose:	mg/L
Influent TOC	UV-254:	
FBR effl	FBT removal	
Effluent TOC	Ozonation removal	
	Total removal	
Biodeg clmn	Addnl biodegradable	
	Potential removal	

Sample collection		Ellaps time hr	EBCT min	UV-254		TOC			Comments
Date	Time			1/cm	% removal	mg/L	Std.dev	% removal	
gradability, mgC/l									

Table D.5. Spreadsheet format for MWD data entry

Water source		Sample collected	
Date collected		Sample processed	
		Sample analyzed	
System			
Sequence			
Recycle			
Biostimulant			
<i>Operating conditions</i>		<i>Comments</i>	
Water flow		Samples: Sample 1: Sample 2: Sample 3:	
Gas flow			
Recycle			
Line pressure			
Biostimulant flow			
Biostimulant dose			
Influent gas UV254			
Influent gas O3			
RT dissolved O3			
(Influent TOC)			
Ozone dose			
EBCT			
<i>Cumulative distribution</i>			
Molecular weight cutoff			
<500			
1000			
3000			
10000			
30000			
Sample filtered			
Sample unfiltered			
<i>Fractions</i>			
MWCO			
<500			
500 - 1000			
1000 - 3000			
3000 - 10000			
10000 - 30000			
>30000			

Table D.6. Spreadsheet format for TOC data entry

ID	Sample	Collected	DATE	Comments
0	Standards			
1	TOC System1			
2	TOC System2			
3	TOC Bench system			
4	HS			
5	MWD: 5.1-effluent; 5.2-FBR; 5.3-Influent; 5.4-biodegr. column			
6	Biodegradability			

#	ID	Description	TOC, mg/L	Std.dev	Comments
1	0	Chk #1			
2	0	Chk#2			
3	0	Chk#3			
4	0	Chk#4			
5	0	Chk#5			
6					
7					
8					
9					
10					
11					
12					
13					
14					
15					
16					
17					
18					
19					
20					
21					
22					
23					
24					
25					
26					
27					
28					
29					
30					
31					
32					
33					
34					
35					
36					
37					
38					
39					
40					
41					
42					
43					
44					
45					
46					
47					
48					
49					
50					
51					
52					
53					

REFERENCES

- Ahmad, R. 1998. Biological Step Help Meets THM Regs. *World Water and Environ. Engineer.* 2:18.
- Amirtharajah, A. and O'Melia, C.R. 1990. Coagulation Processes: Destabilization, Mixing, and Flocculation. In *Water Quality and Treatment*. 4th edition. F.W. Pontius, ed. McGraw-Hill, Inc., New York, pp. 269-366
- Amy, G. L., Kuo, C., and Sierka, R. 1988. Ozonation of Humic Substances: Effect on Molecular Weight Distribution of Dissolved Organic Carbon and Trihalomethane Formation Potential. *Ozone Sci. and Engrnr*, 10:39-54.
- Amy, G.L., Collins, M.R., Kuo, C.J., and King, P.H. 1987. Comparing Gel Permeation Chromatography and Ultrafiltration for the Molecular Weight Characterization of Aquatic Organic Matter. *J. AWWA*, 79:1:43-49.
- Amy, G.L., Sierka, R.A., Bedessem, J., Price, D., and Tan, L. 1992. Molecular Size Distribution of Dissolved Organic Matter. *J. AWWA*, 84:6:67-75.
- Anderson, L.J., Johnson, J.D., and Christman, R.F. 1986. Extent of Ozone Reaction with Isolated Aquatic Fulvic Acid. *Environ. Sci. & Technol.*, 20:739-742
- Anselmi, G., Lignola, P.G., Raitano, C., and Volpicelli, G. 1985. Ozone Absorption with Reaction in Benzenesulfonic Acid Aqueous Solutions. *Chemical Engrg. Sci.* 40:7:1033-1040.
- Arora, H., LeChevallier, M.W., and Dixon, K.L. 1997. DBP Occurrence Survey. *J. AWWA*, 89:6:60-68.
- Astarita, G. 1967. Mass Transfer with Chemical Reactions. Elsevier Publishing Co., New York.
- Babcock, D. and Singer, P. 1979. Chlorination and Coagulation of Humic and Fulvic Acids. *J. AWWA*, 71:3:149-152.
- Bablon, G. et al. 1991a. Fundamental Aspects . In *Ozone in Water Treatment: Application and Engineering*. Ed. by B. Langlas, D.A. Reckhow and D.R. Brink. Lewis Publisher, Inc., Chelsea. pp. 11-132.
- Bablon, G. et al. 1991b. Practical Application of Ozone. In *Ozone in Water Treatment: Application and Engineering*. Ed. by B. Langlas, D.A. Reckhow and D.R. Brink. Lewis Publisher, Inc., Chelsea.

- Bellamy, W.D. et al. 1991. Economics of Ozone Systems. In *Ozone in Water Treatment: Application and Engineering*. Ed. by B. Langlas, D.A. Reckhow and D.R. Brink. Lewis Publisher, Inc., Chelsea.
- Botterro, J.Y. and Bersillon, J.L. 1989. Aluminum and Iron (III) Chemistry: Some Implications for Organic Substance Removal. In: *Aquatic Humic Substances. Influence on Fate and Treatment of Pollutants*. I.F. Suffet and P. MacCarthy, Eds. American Chemical Society, Washington, DC. pp. 425-442.
- Chadik, P.A. and Amy, G.L. 1983. Removing Trihalomethanes Precursors From Various Natural Waters by Metal Coagulants. *J. AWWA*, 75:10:532-535.
- Cipparone, L.A., Diehl, A.C., and Speitel, G.E. 1997. Ozonation and BDOC Removal: Effect on Water Quality. *J. AWWA*, 89:2:84-97.
- Cleasby, J. L. 1990. Filtration. In *Water Quality and Treatment*. 4th edition. F.W. Pontius, ed. McGraw-Hill, Inc., New York, pp. 455-560
- Cleasby, J.L. 1991. Source Water Quality and Pretreatment Options for Slow Sand Filters. In *Slow Sand Filtration*. Eds. G.S. Logdson. New York: American Society of Civil Engineers.
- Cleasby, J.L., Hilmoe, D.J., Dimitracopoulos, C.J. 1984. Slow Sand and Direct In-line Filtration of a Surface Water. *J. AWWA*, 76:12:44-54.
- 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. *Environ. Sci. Technol.*, 20:10:1028-1032
- Collins, M.R. and Vaughan, C.W. 1993. Assessing Biofilter Treatability of Natural Organic Matter. In *Proc. 1993 Ann. AWWA Conf.*, Miami, Florida, pp. 1249-1273.
- Crane, 1978. Flow of Fluids. Crane Co.
- Criddle, C.S, Alvarez, K., and MacCarthy, P.L. 1991. Microbial Processes in Porous Media. In *Transport Processes in Porous Media*. Eds. J. Bears and M.Y. Corapcioglu. NATO Advanced Studies Institute Series E: Applied Sciences, V. 202. Kluwer Academic Publishing Co., Dordrecht, The Netherland, pp. 641-691.
- Dankwerts, P.V. 1970. Gas-Liquid Reactions. McGraw-Hill, New York.
- Dempsey, B.A., Ganho, R.M., and O'Melia, C.R. 1984. The Coagulation of Humic Substances by Means of Alum Salts. *J. AWWA*, 76:4:141-150.

- Eaton, A. 1995. Measuring UV-absorbing Organics: a Standard Method. *J. AWWA*, 87:2:86-90
- Edzwald, J.K., Becker, W.C., and Wattier, K.L. 1985. Surrogate parameters for Monitoring Organic Matter and THM Precursors. *J. AWWA*, 76:4:120-132.
- Flogstad, H and Odergaard, H. 1985. Treatment of Humic Waters by Ozone. *Ozone Sci. Eng.*, 7:2:121-136.
- Fox, K.R., Miltner, G.S., Logsdon, G.S., Dicks, D.L., and Drolet, L.F. 1984. Pilot-Plant Studies of Slow-Rate Filtration. *J. AWWA*, 76:12:62-68.
- Freeman, D.H. and Cheung, L.S. 1981. A Gel Partition Model for Organic Desorption from a Pond Sediment. *Science (Washington, D.C)*, 214:790-792.
- Georgeson, D.L. and Karimi, A.A. 1988. Water Quality Improvements with the Use of Ozone at the Los Angeles Water Treatment Plant. *Ozone Sci. Engrg.*, 10:3:255-276.
- Glaze, W.H., Koga, M, and Cancilla, D. 1989. Ozonation By-Products. Improvement of an Aqueous-Phase Derivatization Method for the detection of Formaldehyde and Other Carbonyl Compounds Formed by the Ozonation of Drinking Water. *Environ. Sci. Technol.*, 23:7:838-847.
- Glazer, H.T. and Edzwald, J.K. 1979. Coagulation and Direct Filtration of Humic Substances with Polyethylenimine. *Environ. Sci. Technol.*, 13:3:299-307.
- Goel, S., Hozalski, R.M., and Bouwer, E.J. 1995. Biodegradation of NOM: Effect of NOM source and Ozone Dose. *J. AWWA*, 87:1:90-105.
- Heinzle, E., Geiger, F., Fahmy, M., and Kut, O.M. 1992. Integrated Ozonation-Biotreatment of Pulp Bleaching Effluents Containing Chlorinated Phenolic Compounds. *Biotechnol. Prog.*, 8:67-77.
- Hickey, R.F., Wagner, D. and Mazewski, G. 1991. Treating Contaminated Groundwater Using a Fluidized-Bed Reactor. *Remediation*, Autumn, 447-459.
- Hill, C.G. 1977. An Introduction to Chemical Engineering Kinetics and Reactor Design. New York: John Wiley and Sons, Inc. 1977 p. 36.
- Hoigné, J. Characterization of water Quality Criteria for Ozonation Processes. Part 1: Minimal Set of Analytical Data, 1994. *Ozone Sci Engrg.* 16:383-389.
- Huck, P. M. 1990. Measurements of Biodegradable Organic Carbon and Bacterial Growth Potential in Drinking Water. *J. AWWA*. 82:7:78-86.

- Huck, P.M., Zhang, S., and Price, M.L. 1994. BOM Removal During Biological Treatment: a First-order Model. *J. AWWA*, 83:12:69-71.
- Jackson, J.L., Hong, S., and Summers, R.S. 1993. The Use of Ultrafiltration to Characterize GAC Breakthrough of Organic Matter in Molecular Size Fractions. In *Proc. 1993 Ann. AWWA Conf.*, Miami, Florida, pp. 93-107.
- Joret, J.C. and Lévy, Y. 1988. Rapid Method for Estimating Bioeliminable Organic Carbon in Water. In *Proc. 1988 AWWA Ann Conf.*, Orlando, Florida.
- Kaastrup, E. and Halmo, T.M. 1989. Removal of Aquatic Humus by Ozonation and Activated-Carbon Adsorption. In *Aquatic Humic Substances. Influence on Fate and Treatment of Pollutants*. I.F. Suffet and P. MacCarthy, Ed. American Chemical Society, Washington, DC. pp. 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.
- Killops, S.D. 1986. Volatile Ozonation Products of Aqueous Humic Material. *Water Res.*, 20:2:153-165.
- Klevens, C.M. and Collins, M.R. 1996. Natural Organic Matter Characterization and Treatability by Biological Activated Carbon Filtration. In *Proc. 1996 ACS Symposium – Disinfection By-Products and NOM Precursors*. Washington, DC, pp. 211-246.
- Kolb, B., Auer, M. and Pospisil, P. 1983. Methods for Quantitative Analysis of Volatile Halocarbons from Aqueous Samples by Equilibrium Headspace Gas Chromatography with Capillary Columns. *J. Chromatography*. 279:341-349.
- Krasner, S.W., Croué, J-P., Buffle, J., and Perdue, E.M. 1996. Three Approaches for Characterizing NOM. *J. AWWA*. 88:6:66-79.
- Krasner, S.W., Scriminty, M.J., Chinn, R., Chowdhury, Z.K., and Owen, D.M. 1996. The Impact of TOC and Bromide on Chlorination By-product Formation. In *Disinfection By-products in Water Treatment*, Eds. R.A. Minear and G.L. Amy. Lewis Publisher, pp. 59-90.
- Krasner, S.W., Scriminti, M.J., and Coffey, B.M. 1993. Testing Biologically Active Filters for Removing Aldehydes During Ozonation. *J. AWWA*, 85:5:62-71.
- Kruithof, J.C., van der Gaag, M.A., and van der Kooy, D. 1989. Effect of Ozonation and Chlorination on Humic Substances in Water. In *Aquatic Humic Substances. Influence on Fate and Treatment of Pollutants*. I.F. Suffet and P. MacCarthy, Eds. American Chemical Society, Washington, DC. pp. 663-680.

- Larose, J., Grasmick, A., Blondeau, P., Elmaleh, S., and Legeron, J.P. 1982. Elimination of Humic Materials. *Ozone Sci. Eng.*, 4:2:79-89.
- Lawrence, J., Tosine, H, Onuska, F.I, and Comba, M.E. 1980. The Ozonation of Natural Waters: Product Identification. *Ozone Sci. Eng.*, 2:1:55-64.
- Lee M.C., Snoeyink, V.L., and Crittenden, J.C. 1981. Activated Carbon Adsorption of Humic Substances. *J. AWWA*, 73:8:440-446.
- Legube B., Croué, J.P., de Laat, J., and Doré, M. 1989. Ozonation of an Extracted Aquatic Fulvic Acid: Theoretical and Practical Aspects. *Ozone Sci. Eng.*, 11:1:69-92.
- Liao, W., Christman, R.F., Johnson, J.D., and Millington, D.S. 1982. Structural Characterization of Aquatic Humic Material. *Envir. Sci. Technol.*, 16:7:403-410.
- Lykins, B.W. and Clark, R.M. 1989. Trihalomethanes Precursor and Total Organic Carbon Removal by Conventional Treatment and Carbon. In *Aquatic Humic Substances. Influence on Fate and Treatment of Pollutants*. I.F. Suffet and P. MacCarthy, Eds. American Chemical Society, Washington, DC., pp. 597-622.
- MacCarthy, P. and Suffet, I.H. 1989. Introduction to *Aquatic Humic Substances. Influence on Fate and Treatment of Pollutants*. I.F. Suffet and P. MacCarthy, Eds.. American Chemical Society, Washington, DC. p. xvii-xxx.
- Malevalle, J.P., Anselme, C, and Marsigny, O. 1989. Effect of Humic Substances on Membrane Process. In *Aquatic Humic Substances. Influence on Fate and Treatment of Pollutants*. I.F. Suffet and P. MacCarthy, Eds. American Chemical Society, Washington, DC. pp. 749-768.
- Malley, J.P., Eighmy, T.T., Collins, M.R., Royce, J.A., and Morgan, D.F. 1993. The Performance and Microbiology of Ozone-Enhanced Biological Filtration. *J. AWWA*, 85:12:47-57.
- Manahan, S.E. 1991. Environmental Chemistry. Fifth Ed., Lewis Publisher, Chelsea, MI. pp. 83-92.
- Manahan, S.E. 1989. Interaction of Hazardous-Waste Chemicals with Humic Acids. In *Aquatic Humic Substances. Influence on Fate and Treatment of Pollutants*. I.F. Suffet and P. MacCarthy, Eds. American Chemical Society, Washington, DC, pp. 83-92.
- Masten, S.J. 1991. Ozonation of VOC's in the Presence of Humic Acid and Soils. *Ozone: Sci. Engrg.*, 13:3: 287-312.
- McCreary, J.J. and Snoeyink, V.L. 1980. Characterization and Activated Carbon Adsorption of Several Humic Substances. *Water Res.*, 14:151-160.

- Meijers, A.P. 1976. Quality Aspect of Ozonation. *Water Res.*, 10:647-656.
- Mellema, J. 1998. The use of AMWD for the Evaluation of Ozonation and Biotreatment Processes. M.S. Thesis. Michigan State University.
- Mogren, E.M., Scarpino, P., and Summers, R.S. 1990. Measurements of Biodegradable Dissolved Organic Carbon in Drinking Water In *Proc. 1990 AWWA Ann Conf.*, Cincinnati, Ohio.
- Moore, J.W. and Pearson, R.G. 1981. Kinetics and Mechanisms: A Study of Homogeneous Chemical Reactions, 3rd ed. New York: Wiley-Interscience, pp. 68-70.
- Morris, J.K. and Knocke, W.R. 1984. Temperature Effects on the Use of Metal Ion Coagulants for Water Treatment. *J. AWWA*, 76:3:74-79.
- Najm, I.N., Patania, N.L., Jacangelo, J.G., and Krasner, S.W. 1994. Evaluating Surrogates for Disinfection By-products. *Jour. AWWA*, 86:6:98-106.
- National Research Council, 1997. Safe Water from Every Tap. Improving Water Service to Small Communities. National Academy Press, Washington, DC.
- Oxenford, J. L. 1996. Disinfection By-products: Current Practice and Future Directions. In *Disinfection By-products in Water Treatment*, Eds. R.A. Minear and G.L. Amy. Lewis Publisher, pp. 3-16.
- Peters, M.S. and Timmerhaus, K.D. 1991. Plant Design and Economics for Chemical Engineers. McGraw-Hill. New York.
- Pirbazary, M., Ravindran, V., Wong, S-P., and Stevens, M.R. 1989. Adsorption of Micropollutants on Activated Carbon. In *Aquatic Humic Substances. Influence on Fate and Treatment of Pollutants*. I.F. Suffet and P. MacCarthy, Eds. American Chemical Society, Washington, DC. pp. 549-578.
- Pontius, W.F. 1995. An Update of the Federal Drinking Water Regs. *J. AWWA*, 87:2:48-58.
- Price, M.L., Bailey, R.W., Enos, A.K., Hook, M., and Hermanowicz, W. 1993. Evaluation of Ozonation/Biological Treatment for Disinfection Byproducts Control and Biologically Stable Water. *Ozone Sci. Engr.*, 15:95-130.
- Process Plant Construction Estimating Standards. 1998. Richardson Engineering Services, Mesa, Arizona.
- Rachwal, A.J., Foster, D.M., and Holmes, M. 1992. Combining Ozone/Advanced Oxidation and Biological Filtration Processes for Organics Removal from Water. In *Proc. 1992 AWWA Confer.*, Toronto, Ontario, 543-559.

- Rajan, R.V. 1998. Capital and Operating Costs of FBT Systems. EFX Systems, Inc.
- Reckhow, D.A. and Singer, P.C. 1990. Chlorination By-Products in Drinking Waters: From Formation Potentials to Finished Water Concentrations. *Jour. AWWA*, 82:4:173-180.
- Reckhow, D.A., Xie, Y., McEnroe, R., Byrnes, P., Tobiason, J.E., and Switzenbaum, M.S. 1993. The Use of Chemical Surrogates for Assimilable Organic Carbon. *Proc. AWWA Annual Conference*, Miami, Florida.
- Reckhow, D.A., Legube, B., and Singer, P.C. 1986. The Ozonation of Organic Halide Precursor: Effect of Bicarbonate. *Water Res.*, 20:8:987-998.
- Rittmann, B.E. and McCarthy, P.L. 1980. Model of Steady-State Biofilm Kinetics. *Biotech. and Bioengrg.*, 22:2343-2357.
- Rittmann, B.E. and J.E. Wooschlager, III, 1996. Fundamental Components for Modeling BOM and Regrowth. In *Proc. 4th International BOM Conference*, Waterloo, Canada. p. 66-72.
- Robinson, N.R. 1996. Chemical Engineering Reference Manual. Professional Publications. Belmont, CA.
- Roth, J.A. and Sullivan, D.E. 1981. Solubility of Ozone in Water. *Ind. Eng. Chem. Fundam.*, 20:2:140-144.
- Scadsen, J. 1997. 1996 Laboratory Report. *Environmental Health Laboratories*.
- Scadsen, J. 1998. Personal Communication.
- Schnitzer, M. and Khan, S.U. 1972. Humic Substances in the Environment, New York: Marcel Dekker, Inc.
- Semmens, M.J. and Field, T.K. 1980. Coagulation: Experience in Organic Removal. *J. AWWA*, 72:8:476-482.
- Servais, P., Billen, G., and Hascoet, M. 1987. Determination of Biodegradable Fraction of Dissolved Organic Matter in Waters. *Water Res.*, 21:4:445-450.
- Sheffer, S. and Esterson, G.L. 1982. Mass Transfer and reaction Kinetics in the Ozone/Tap Water System. *Water Res.*, 16:383-389.
- Shukairy, H.M. and Summers, R.S. 1992. The Impact of Preozonation and Biodegradation on Disinfection By-product Formation. *Water Res.*, 26:9:1217-1227.

- Shukairy, H.M. and Summers, R.S. 1996. DBP speciation and Kinetics as Affected by Ozonation and Biotreatment. In *Disinfection By-products in Water Treatment*, Eds. R.A. Minear and G.L. Amy. Lewis Publisher, pp. 311-338.
- Singer, P.C. 1989. Impact of Ozonation on the Removal of Particles, TOC, and THM Precursors. *AWWA Research Foundation Report*.
- Singer, P.C. and Chang, S.D. 1989. Correlation Between Trihalomethane and Total Organic Halides Formed During Water Treatment. *J. AWWA*, 81:61-69.
- Sontheimer, H. and Hubele, C. 1987. The Use of Ozone and Granular Activated Carbon in Drinking Water Treatment. In *Treatment of Drinking Water for Organic Contaminants*. Eds. P.M. Huck and P. Toft. Pergamon Press, New York, pp. 45-66.
- Speece, R.E., Madrid, M., and Needhan, K. Downflow Bubble Ozone Aeration. 1971. *J. Sanitary Engineering Division. Proc. Of the American Society of Civil Engineers*, V. 97, No. SA4, 433-441.
- Speitel, G.E., 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. *J. AWWA*, 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. *Environ. Sci. Technol.*, 19:12:1206-1213.
- Standard Methods for the Examination of Water and Wastewater. 18th ed. 1992. Greenberg, A.E., Clesceri, L.S., and Eaton, A.D., Eds., APHA, AWWA, WEF.
- Stevens, A.A., Moore, L.A., Slocum, C.J., Smith, B.L., Seeger, D.R. and Ireland, J.C. 1989. Chlorinated Humic Acid Mixtures: Criteria for Detection of Disinfection Byproducts in Drinking Water. In *Aquatic Humic Substances. Influence on Fate and Treatment of Pollutants*. I.F. Suffet and P. MacCarthy, Eds. American Chemical Society, Washington, DC. pp. 681-695.
- Thurman, E.M. 1985. Humic Substances in Groundwater. *Humic Substances in Soil, Sediment and Water*. G.R. Aiken, D.M. McKnight, R.B. Wershaw, and P. MacCarthy, Eds. New York: John Wiley and Sons. pp. 87-103.
- Thurman, E.M. and Malcolm, R.L. 1981. Preparative Isolation of Aquatic Humic Substances. *Envir. Sci. Technol.*, 15:4:463-466.
- Trussel, R.R. and Umphres, M.D. 1978. The formation of Trihalomethanes. *J. AWWA*. 70:11: 604-612.
- U.S. EPA Drinking Water Regulations. 1997. *Ozone News*, 25:4:10-19.

- U.S. EPA, 1993. Technical and Economic Capacity of States and Public Water Systems to Implement Drinking Water Regulations: Report to Congress. EPA 810/R-93/001, Sept. 1993.
- van der Kooij, D. 1992. Assimilable Organic Carbon as an Indicator of Bacterial Regrowth. *J. AWWA*, 84:2:57-65.
- van der Kooij, D., Visser, A. and Hijnen, W.A.M. 1982. Determining the Concentration of Easily Assimilable Organic Carbon in Drinking Water. *Jour. AWWA*, 74:10:540-545.
- Ventresque, C., Bablon, G., and Jadas-Hécart, A. 1990. Ozone: A Means of Stimulating Biological Activated Carbon Reactors. *Ozone Sci. Engnr.*, 13:91-107.
- Veenstra, J.N., Barber, J.B., and Khan, P.A. 1983. Ozonation: Its Effect on the Apparent Molecular Weight of Naturally Occurring Organics and Trihalomethane Production. *Ozone Sci. Eng.*, 5:4:225-244.
- Vik, E.A. and Eikebrokk, B. 1989. Coagulation Process for Removal of Humic Substances from Drinking Water. In *Aquatic Humic Substances. Influence on Fate and Treatment of Pollutants*. I.F. Suffet and P. MacCarthy, Eds. American Chemical Society, Washington, DC, pp. 385-408.
- Voice, T.C., Pak, D., Zhao, X., Shi, J., and Hickey, R.F. 1992. Biological Activated Carbon in Fluidized Bed Reactors for the Treatment of Groundwater Contaminated with Volatile Aromatic Hydrocarbons. *Water Res.*, 26:10:1389-1401.
- Volk, C., Roche, P., Renner, C., Paiullard, H., and Joret, J.C. 1993. Effects of Ozone-Hydrogen Peroxide Combination on the Formation of Biodegradable Organic Carbon. *Ozone Sci Engng.* 15:405-418.
- von Gunten, U. and Hoigné, J. 196. Ozonation of Bromide-Containing Waters: Bromate Formation through Ozone and Hydroxyl Radicals. In *Disinfection By-products in Water Treatment*, Eds. R.A. Minear and G.L. Amy. Lewis Publisher, pp. 187-206.
- Water Treatment Plant Design, 1990. McGraw-Hill. New York.
- Watts, C.D. 1985. Organic By-products of Ozonation of Humic and Fulvic Acid. *Proc. Intl. Conf., Role of Ozone in Water and Wastewater Treatment*. R. Perry and R.E. McIntyre, Eds. Selper Ltd., London, England.
- Weisner, M.R., Hackney, J., Sethi, S., Jacangelo, J.G., and Laine, J.-M., 1994. Cost Estimates for Membrane Filtration and Conventional Treatment. *J. AWWA*, 86:12:33-41.

Yurteri, C. and Gurol, M.D. 1988. Evaluation of Kinetic Parameters for the Ozonation of Organic Micropollutants. *Water Res.*, 22:465-476.

MICHIGAN STATE UNIV. LIBRARIES



31293017665153