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Disinfection and Self-Sensitized Degradation of Natural Organic Matter (NOM) by TiO₂ Photocatalysis with Visible light

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Disinfection and Self-Sensitized Degradation of Natural Organic Matter (NOM) by TiO_2
Photocatalysis with Visible light

by

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A THESIS

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Abstract

The reaction of natural organic matter (NOM) with chlorine results in formation of disinfection by products (DBPs), known carcinogens. Fulvic acid (FA), a key component of NOM is likely a precursor to DBPs. Photocatalytic advanced oxidation using TiO_2 is efficient under UV irradiation and known to degrade humics with reduction of DBPs. However, TiO_2 may be dye “sensitized” for visible light, where the dye excited state transfers an electron to TiO_2 conduction band. NOM adsorbs on the surface of TiO_2 and sensitizes (“self-sensitization”). NOM undergoes an initial oxidative step upon visible light absorption and transfers an electron to the TiO_2 conduction band. Oxygen captures the electron, forming superoxide which can aid in degradation of NOM. Model studies with Suwannee river fulvic acid are reported and then extended to “real water samples” from Southern Alberta. The humic model shows different degradation behavior from ‘real’ samples. In addition to reduction of NOM by “self-sensitization”, the active species also achieve reduction of Total coliform and *Escherichia coli*. The objective of this research is to treat NOM and simultaneously enhance disinfection.

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To Dad, Mom, Vikas, Uphar, Upkar and Anand

Table of Contents

Abstract.....	ii
Acknowledgements.....	iii
Dedication.....	v
Table of Contents.....	vi
List of Schemes and Tables.....	x
List of Figures.....	xi
List of Symbols, Abbreviations and Nomenclature.....	xiii
Chapter 1: Introduction.....	1
1.1 Natural Organic Matter	1
1.2 Aquatic DOC Origin, Structure and Composition.....	3
1.2.1 Fractionation and Isolation of DOC.....	8
1.2.2 Characterization of DOC.....	11
1.2.2.1 Structural Characterization.....	11
1.3 NOM as a Concern: Undesirable in Water and Wastewater Treatment Units...15	
1.3.1 The Direct Problems.....	15
1.3.2 The Indirect Problems: Chlorination and DBPs Formation.....	17
1.3.2.1 Role of Chlorine: Disinfection of Drinking Water.....	17
1.3.2.2 Formation of DBPs: A Potential Carcinogenic Agent.....	20

1.4 Control of DBPs: Different Methods to Reduce NOM (DBPs precursors)	
Concentration in Water Supplies.....	26
1.4.1 Conventional Drinking Water Treatment.....	27
1.4.2 Advanced Oxidation Technologies (AOT).....	28
1.5 Heterogeneous Photocatalysis: Photo-activated Catalytic Oxidation.....	30
1.5.1 TiO ₂ Photocatalysis.....	32
1.5.2 Self-Sensitization.....	36
1.5.2.1 Humic Substances as Natural Photosensitizers.....	38
1.5.2.2 Use of Humic substances as Sensitizers for Extending the Photoresponse of Semiconductor.....	42
1.5.2.3 Mechanism of Self-Sensitization: Extending Spectral Response of TiO ₂ to the Visible Region.....	44
1.6 Research Objectives.....	47
1.7 Thesis Organization.....	47

Chapter 2: Self-Sensitized Degradation of Natural Organic Matter (NOM) using

TiO₂ Photocatalysis with Visible Light.....	49
2.1 Abstract.....	49
2.2 Introduction.....	51
2.3 Materials and Methods.....	55
2.3.1 Materials.....	55
2.3.2 Reagents used.....	56
2.3.3 Preparation of Model Water.....	56

2.3.4 Irradiation Protocol.....	57
2.3.4.1 Dark Adsorption and Irradiation Experiments.....	57
2.3.5 Sample Chlorination.....	59
2.3.6 Analysis of the Sample.....	60
2.3.6.1 Determination of DOC.....	60
2.3.6.2 UV-VIS Absorption Spectrum.....	60
2.3.6.3 Fluorescence Measurements.....	61
2.3.6.4 Chloroform Analysis.....	61
2.4 Results and Discussion.....	63
2.4.1 DOC.....	63
2.4.2 UV-Visible Spectra.....	66
2.4.3 Fluorescence Spectrum.....	70
2.4.4 Chloroform (CHCl ₃) Concentration.....	77
2.5 Conclusions.....	79

Chapter 3: Coliform Inhibition by Natural Organic Matter (NOM) Sensitized

Photocatalysis under Visible light.....	81
3.1 Abstract.....	81
3.2 Introduction.....	82
3.3 Materials and Methods.....	83
3.3.1 Materials.....	83
3.3.2 Experimental Protocol.....	84
3.3.3 Recovery Experiment.....	85

3.3.4 Total Coliform and E.coli enumeration.....	86
3.4 Results.....	87
3.5 Discussion.....	93
3.6 Conclusions.....	95
Chapter 4: Conclusions and Future Research Directions.....	96
4.1 Self-sensitized Photocatalysis.....	96
4.2 Coliform Reduction.....	99
4.3 Future Research Directions.....	100
Supplementary materials.....	105
Supplementary material for chapter II.....	106
Appendix- 1A.....	110
Appendix- 1B.....	113
References.....	114

List of Schemes and Table

Scheme 1.1.	Operational classification of dissolved organic carbon.....	9
Scheme 1.2.	Formation of DBPs.....	22
Scheme 1.3.	TiO ₂ Photocatalysis (UV illumination).....	35
Scheme 1.4.	TiO ₂ Photocatalysis (Visible illumination) " <u>SELF-SENSITIZATION</u> ".....	46
Table 1.1.	Common properties of HA and FA.....	6

List of Figures

- Figure 2.1.** Change in the concentration of DOC in various water samples as a function of light dosage.....64
- Figure 2.2.** UV₂₅₄ absorbance spectra of various water samples containing NOM as a function of light dosage.....68
- Figure 2.3.** Fluorescence emission intensity of NOM/FA present in the “Model Water” water sample with excitation at 350nm over the extent of irradiation periods.....71
- Figure 2.4.** Fluorescence emission intensity of NOM present in the “Treated Waste Water” sample with excitation at 350nm over the extent of irradiation periods.....72
- Figure 2.5.** Fluorescence emission intensity of NOM present in the “Village of Gleichen” water sample with excitation at 350nm over the extent of irradiation periods73
- Figure 2.6.** Fluorescence emission intensity of NOM present in the “Town of Standard” water sample with excitation at 350nm over the extent of irradiation periods.....74
- Figure 2.7.** Trichloromethane formation in various water samples after moderate light doses.....77

Figure 3.1. Inactivation of Total coliform	88
Figure 3.2. Inactivation of E.coli.....	89
Figure 3.3. Changes in absorption spectra of 4-CP (33 ppm) upon irradiation with visible lamps in presence of FA (10 ppm) and Degussa P25 TiO ₂	92
Figure 2. S1. UV absorbance spectra of “Model water” sample containing NOM as a function of wavelength.....	106
Figure 2. S2. UV absorbance spectra of “Treated waste water” sample containing NOM as a function of wavelength.....	107
Figure 2. S3. UV absorbance spectra of “town of Standard water” sample containing NOM as a function of wavelength.....	108
Figure 2. S4. UV absorbance spectra of “village of Gleichen” water sample containing NOM as a function of wavelength.....	109
Figure A.1. UV absorbance spectra of “Model water” sample containing NOM (desorbed from the surface of TiO ₂) as a function of wavelength.....	111
Figure A.2. UV absorbance spectra of “Treated waste water” sample containing NOM (desorbed from the surface of TiO ₂) as a function of wavelength.....	112

List of Symbols, Abbreviations, Nomenclature

NOM	Natural organic matter
DBPs	Disinfection by-products
THM	Tri-halo methane
HAA	Halo acetic acid
FA	Fulvic acid
DOM	Dissolved organic matter
SRFA	Suwannee river fulvic acid
LFA	Laurentian fulvic acid
DOC	Dissolved organic carbon
HS	Humic substances
NHS	Non humic substances
ICT-MS	Ion Cyclotron Mass Spectroscopy
SEC	Size Exclusion Chromatography
NMR	Nuclear magnetic resonance
TOC	Total organic carbon
POC	Particulate organic carbon
μ	Micron or Micrometer
TiO ₂	Titanium di-oxide
AOT	Advanced Oxidation Technologies
λ	Wavelength
LUMO	Lowest unoccupied molecular orbital
HOMO	Highest occupied molecular orbital

SRFA ^{·+}	SRFA cationic radical
CB	Conduction Band
ROS	Reactive oxygen species
CHCl ₃	Chloroform or Trichloromethane
PVDF	Polyvinylidene fluoride
CW	Cool white
MΩ·cm	Megaohm- centimeter
ppm	Parts per million
J	Joule
GC- ECD	Gas chromatograph electron capture detector
kJ	Kilo Joule
FTIR	Fourier transform infrared spectroscopy
HA	Humic acid
O ₂ ^{·-}	Superoxide radical anion
UV-VIS	Ultraviolet Visible spectra
UV ₂₅₄	UV absorbance at 254 nm
IHSS	International Humic Substances Society
h	Hour
Irr.	Irradiation
TCM	Trichloro Methane
LED	Light emitting diode
E.coli	Escherichia coli
kWhr	Kilo Watt hour
mW	Milli Watt

MAC	Maximum acceptable concentration
MPN	Most probable number
DST [®]	Defined Substrate Technology [®]
ONPG	Ortho-Nitrophenyl- β -D-galactopyranoside
MUG	4-methyl-umbelliferyl- β -D-glucuronide
4-CP	4- chloro phenol
U.S. EPA	U.S Environmental protection agency
SOD	Superoxide dismutase
DNA	Deoxyribo-nucleic acid
H ₂ O ₂	Hydrogen peroxide
NSERC	Natural Sciences and Engineering Research Council
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
DC	Direct Current
meq/dry g	milli equivalent/dry gram

Chapter 1

Introduction

1.1 Natural Organic Matter

Naturally occurring organic matter (NOM) is a poorly characterized concoction of organic compounds, small molecules, oligomers and polymers which are ever present to varying degrees in dissolved and particulate forms in soil, sediments and water sources (surface and ground water). NOM (except marine) is mainly formed in soils and finally leaches into lacustrine, riverine and estuarine waters. All the biogeochemical processes taking place in the natural drainage basins come together in the rivers and hence rivers contain, natural organic matter being synthesized and degraded in both, the terrestrial and aquatic environments^{1,2}.

The concentration, composition and chemistry of NOM in different water types vary with the sources of organic matter (allochthonous or autochthonous) where the commonly larger fraction, allochthonous NOM, originates from terrestrial or pedogenic (soil origin) sources with limited biological activity, and autochthonous NOM originates from macrophytes, algae, bacteria or phytoplankton sources in water with a high level of biological activity. Further, ionic strength, pH, temperature, climate, local soil and

vegetation types also affect the concentration and chemistry of NOM in water. The presence of microbiological degradation mechanisms and light induced chemical reactions also impact the chemistry of NOM in water¹. Delpla et al.³ in a review reported that all the above mentioned factors play a significant role in the increased occurrence of NOM in various types of water sources. The quantitative and qualitative changes in NOM indeed presents a challenge to the existing drinking water treatment processes (for reasons discussed later in the introduction).

NOM in aquatic sources is quantitatively determined by a comprehensive measurement, i.e., total organic carbon (TOC), since approximately 50% of the weight of NOM consists of carbon. The term “total organic carbon” (TOC) includes all covalently bonded carbon species from methane with a molecular weight of 16 Dalton, to the large and complex mixture of organic compounds assemblies (500-100000 Dalton), in association with elements such as hydrogen, nitrogen, phosphorus, sulphur and oxygen^{1,4}. TOC in nature practically corresponds with NOM because xenobiotic organic contaminants in aquatic systems generally exhibit a minor fraction of carbon. Operationally, TOC in aquatic systems can be divided into “Dissolved organic carbon (DOC)” and “Particulate organic carbon (POC)” where POC is a fraction that is retained on a 0.45 µm filter membrane while DOC is a fraction that is presumably smaller than

0.45 μm in diameter. In most waters, DOC (~90%) forms the major fraction of TOC while POC forms a minor fraction (~10%)^{1,4}. The DOC concentrations range from 0.1 mg/L in ground water sources to 5-10 mg/L in surface water sources². TOC measures DOC and corresponds to the organic matter studied in the filtered samples of the present research.

1.2 Aquatic DOC Origin, Structure and Composition

Aquatic DOC which is commonly soil derived (allochthonous) in fresh water can be divided into humic substances (HS) and non-humic substances (NHS). The largest fraction is generally humic substances which make up approximately 50-70% of the dissolved organic carbon (DOC) in water. The remaining 30-50% of organic matter consists of low molar mass acids such as oxalic, citric, formic, and acetic acids (~25%), neutral compounds such as carbohydrate materials (~15%), and other species (~10%). HS have larger apparent molecular weights (over 500 g/mole) than NHS. NHS, a minor portion (carbohydrates, lipids, amino acids and various small molecular weight acids), are easily lost during biogeochemical degradation and much carbon integrates into the geopolymeric materials that make up the HS pool^{2,4}.

The term HS goes back to 1839, when Sprengel for the first time studied the origin

and chemical nature of soil organic matter. This was followed by the isolation of two light yellow colored samples from mineral water and slimy mud rich in iron oxides by the pioneer Swedish chemist, Berzelius in the same year⁵. Such observations rapidly led to the classification of soil organic matter as humic acids (soluble only in basic media), fulvic acids (soluble under all pH conditions) and humin (water insoluble). These operational categories remain fundamental today.

Aquatic HS are mainly polar, straw colored, organic acids that are derived from soil humus, terrestrial and aquatic plants⁶. HS primarily originate from diagenesis of plant sources and assemble into chemically heterogeneous organic compound mixtures. They can be considered as organic 'leftovers', formed from the combination of biogeochemical degradation and condensation of plant residual material. They are refractory, chemically functional with high content of carboxylate functionality and their colloidal aggregates exhibit apparently high molecular weight. HS is rich in aromatic carbon, carboxyl, phenolic, hydroxyl, ketone structures and conjugated double bonds (well established by infrared, ¹³C-NMR spectroscopy, and titrimetric methods)⁷. They represent a large mass of biomolecular detrital material, which modulates ecosystem function and elemental cycles in aquatic and terrestrial environments. The widely accepted basic characterization of HS for operational purposes is the fractionation

scheme based on the solubility under acidic or alkaline conditions mentioned above⁸.

The fractions are:

- 1) *Humic Acid (HA)*: It is the fraction of HS that is quantitatively precipitated from aqueous solutions when pH is decreased below 2.
- 2) *Fulvic Acid (FA)*: It is the fraction of HS that is soluble under all conditions of pH.
- 3) *Humin*: It is the fraction of HS that is not soluble in water at any pH value.

Each fraction consists of a very complicated and heterogeneous mixture of organic substances. Although the thousands of chemical structures of HA and FA are beyond summarizing, typical chemical and physical properties are mentioned in the table below adapted from Xing, Snoeyink and Jenkins^{9,10}.

Table 1.1. Common properties of HA and FA.

Property	HA	FA
Elemental composition (% by weight)		
Carbon	50-60	40-50
Hydrogen	4-6	4-6
Oxygen	30-35	44-50
Nitrogen	2-4	<1-3
Sulphur	1-2	0-2
Solubility in strong acid	Not soluble	soluble
Apparent Molecular weight range (Atomic mass units)	Few 100- several million	180-10,000
Functional group distribution (% of oxygen is indicated in functional groups)		
Carboxyl -COOH	14-45	58-65
Phenol -Ph	10-38	9-19
Alcohol -R-OH	13-15	11-16
Carbonyl -C=O	4-23	4-11
Methoxyl -O-CH₃	1-5	1-2

(adapted from Xing, Snoeyink and Jenkins^{9,10})

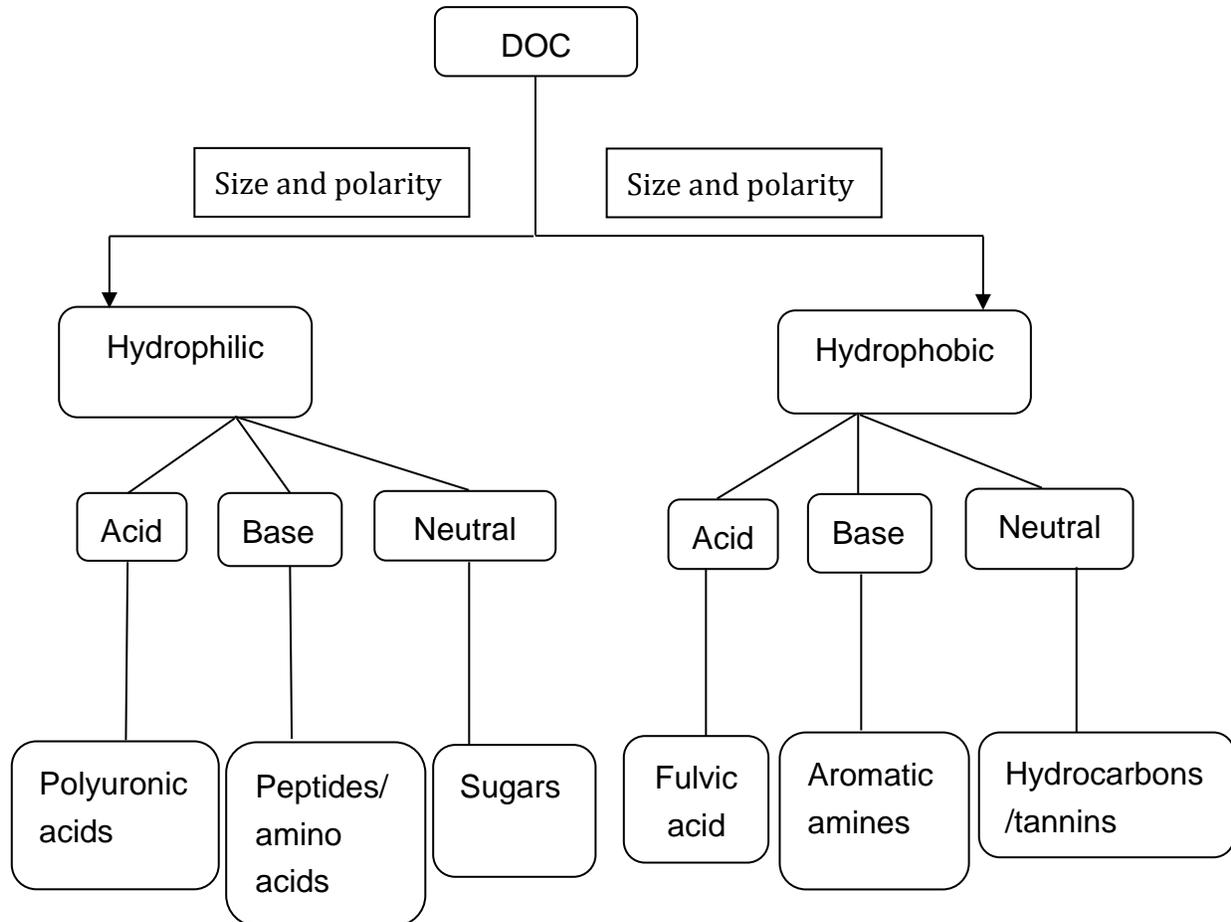
The aquatic (all surface and ground waters) FA has an apparent molecular weight range of 500- 2000 atomic mass units, and the aquatic HA has an apparent molecular weight in the range 1000-10000 atomic mass units and sometimes upto 100,000⁸. Since molecular weight is not well defined, concentration is commonly given in milliequivalents of carboxylic acids. Aquatic HA are larger and colloidal in nature as compared to aquatic FA. FA has usually more carboxylic functional groups and oxygen hence less carbon on a mass basis than HA. HA has more phenolic and other aromatic groups and less polarity than FA. FA is more soluble in water since it has more polar groups per unit mass than HA⁸. The total acidities of FA (6-12 meq/dry g) has been found to be considerably higher than the HA (4-8 meq/dry g)¹¹. FA acts as a polyelectrolyte due to the protonation and deprotonation of oxygenated functional groups^{2,12}. At pH values typical of natural waters (>4), FA mixtures carry a net negative charge¹³. Perdue and Ritchie¹⁴ stated that in different water types approximately 60% of aquatic DOC are HS, in which the ratio between FA and HA is generally 3:1. Generally, ground water concentration of humic substances is found to be lower than surface water.

1.2.1 Fractionation and Isolation of DOC

The chemically diverse nature of organic matter dissolved in various types of water make it hardly possible for researchers to characterize them in any single structural, chemical and functional category. For the characterization of DOC it is important to isolate and fractionate the DOC into separate molecular groups having similar key chemical or physical properties. Leenheer¹⁵ presented a classification of DOC based on the procedures of isolation and fractionation using proprietary non-ionic (Amberlite XAD-8 or DAX-8) and ionic resin adsorbents.

The Leenheer analytical procedure, called DOC fractionation analysis, separated DOC into fractions based on their size and polarity: hydrophobic organic matter (retained on DAX 8)/hydrophilic organic matter (passed through DAX 8). The hydrophobic materials were then eluted from the DAX 8 with either base to yield hydrophobic acids fraction or with acid to yield hydrophobic bases fraction. These fractions can then be sub fractionated into compound-class characteristics, specific compound characteristics and organic/inorganic complexes characteristics. The major DOC fractions operationally fractionated are thereby defined as hydrophobic base (HPOB), hydrophobic acid (HPOA), hydrophobic neutral (HPON), hydrophilic base (HPIB), hydrophilic acid (HPIA) and hydrophilic neutral (HPIN). The overall division is

reproduced from Leenheer and Croue¹ in the following chart.



Scheme 1.1. Operational classification of dissolved organic carbon (adapted from

Croue et al.¹ p5.)

In the resin column fractionation technique, the terms “hydrophobic and hydrophilic” are operationally defined by the separation procedures¹⁵. The hydrophobic fraction of DOC is humic substances (HS) and the hydrophilic fraction of DOC is non-humic substances (NHS). Hence, the different terminologies used are mainly based upon the operation or objective of the research study being carried out. For example the hydrophobic acid fraction (HPOA) of DOC which dissolves in both acid and base solutions is fulvic acid while the hydrophobic acid fraction (HPOA) of DOC which dissolves only in base solutions is called humic acid. These subfractions can further be used for selective study of DOC and helps in analyzing the nature and behavior of the organic matter in water samples from different water sources.

In addition, elemental analysis for carbon, hydrogen, oxygen, nitrogen, sulphur, phosphorous and the non oxidisable element content ash has also been used as an initial approach to characterize DOC. Conventional measures of molecular weight, molecular size, molecular shape, electrostatic charge characteristics; or some combination of these characteristics has also been used to characterize DOC¹⁶.

1.2.2 Characterization of DOC

The fractionation and isolation of DOC is based on simple functional characteristics and is operational, yet widely used in research, but it does not at any point indicate distinct types of organic molecules or overall molecular structure. Therefore this kind of characterization is somewhat unsatisfactory in terms of scientific concepts where there is a possibility of extracting a fraction from water sample that might not be a part of NOM/DOC but is organic in nature or vice-versa. Due to the ambiguity surrounding the structure and characterization of NOM/DOC, there is a high probability of differences in the study, amongst researchers, using the same source of NOM/DOC sample and the uncertainty becomes even higher when the NOM/DOC sample is from different sources of water.

1.2.2.1 Structural Characterization

As early as 1981 (Underdown, Langford)¹⁷ in a report stated that anomalous light scattering increases with concentration could be observed indicating a decrease in average particle size as overall aggregation increased. This was explained as many small particles aggregating to form particles larger than critical size for polydispersity.

Wershaw¹⁸ introduced the concept of aggregation or self-aggregation of smaller

molecules of different particle sizes into larger molecular associations, based on the application of particle size determination by small angle X-ray scattering techniques. HS formed molecular aggregates in solution which were pH dependent. Wershaw proposed that hydrogen bonds, pi-bonds, charge transfer complexes and multivalent metal ion bridging are the mechanisms responsible for the molecular aggregation of smaller humic molecules in solution. Wershaw also reported the presence of surface active properties (hydrophobic interior, hydrophilic exterior) of HS where intermolecular interactions between humic molecules and intramolecular interactions between molecule's functional groups change the chemical and physical properties of humic material in different aqueous environments. These interactions control the self-association and eventually the size, shape, and polarity of humic aggregates.

Piccolo¹⁹ published a detailed description of supramolecular structure of HS. They used gel permeation chromatography and high-pressure size exclusion chromatography to study structural changes in HS effective size as a function of solution conditions. They observed changes in retention time of HS, due to the decrease in the apparent size of humic materials, upon small addition of an organic acid like acetic acid. The addition of acetic acid lowered the pH of HS solution and allowed specific acetate interactions. The authors attributed the size change to the disaggregation of weakly

stabilized molecular associations of HS clusters and further proposed that “at neutral or alkaline pH conditions, small heterogeneous molecules assemble into supramolecular associations of high apparent molecular size materials by weak forces such as, hydrogen bonds, van der Waals forces, π - π , CH- π hydrophobic interactions”.

A nuclear magnetic resonance (NMR) study by Simpson²⁰ was also consistent with the aggregation/disaggregation view of HS. Field gradient NMR showed different functionalities diffuse at different rates. A detailed study was done by Cook et al.²¹ on Laurentian Fulvic Acid (LFA) using liquid state heteronuclear multidimensional NMR. Cook and Langford reported that high field (high resolution) ¹³C NMR resolved many sharp lines characteristic of the fast relaxation of small molecules. The authors supported mesostructural model and presence of carbohydrate based strong metal binding moieties that were previously proposed from solid-state ¹³C CP-MAS-NMR studies by the same authors²². The ultimate measurements have been made using high resolution mass spectra (MS). FT Ion Cyclotron Resonance MS with electrospray ionization of the reference Suwannee River Fulvic Acid revealed more than 4500 distinct molecular formulas in the sample at masses below 1000²³. Sutton and Sposito²⁴ have summarized and reviewed various concepts of molecular structures of humic substances and codified “The New View”.

Recently developed very precise methods that characterize NOM/HS are as follows⁷:

- 1) *Electro spray ionization-mass spectrometry (ESI-MS)*
- 2) *Pyrolysis gas chromatography- mass spectrometry (Py-GC-MS)*
- 3) *Liquid Chromatography-mass spectrometry (LC-MS)*
- 4) *Multidimensional NMR techniques*
- 5) *Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS)*

The applications of mass spectrometry bypass the need for fractionation or derivatisation and have become a very important tool for the characterization of HS by direct analysis.

Smejkalova et al.²⁵ among others, studied the diffusion ordered nuclear magnetic resonance spectroscopy (DOSY-NMR) on FA and HA of different origins. They observed lower diffusion coefficient in DOSY spectra at increasing concentrations of HS material, indicating an aggregation of smaller heterogeneous molecules into apparently supramolecular associations. The authors further observed an increase in the diffusivity on acidifying of HS solutions indicating decrease of aggregation and molecular size thereby confirming the supramolecular nature of HS. A study by Nebiosso and Piccolo²⁶ concludes that HS or NOM are composed by heterogeneous molecules that associate as a function of size, shape, chemical affinity and hydrophobicity, and the

characterization of the structural components of single molecules is restricted by the intermolecular interactions that stabilize their supramolecular associations.

None of these experiments exclude the possibility that some of the components are covalent smaller polymers. Thus, a contemporary summary would be that HS are dynamic assemblies of small molecules, oligomers and polymers aggregated by a large number of weak interactions. It is important to realize that functional behavior is not just a sum of the individual molecules, but a function of the nature of the aggregates.

1.3 NOM as a Concern: Undesirable in Water and Wastewater Treatment Units

The aesthetic (color, taste and odor) problems caused by the presence of certain NOM in drinking water systems are not the only major concerns in water supply. The presence of NOM in water sources also leads to the following problems in water and wastewater treatment units:

1.3.1 The Direct Problems

Organic micropollutants, toxic elements and hydrophobic organic chemicals can be stabilized in the water column by adsorption, ion exchange and complexation reactions with NOM and, as a result, are advectively transported downstream rather

than concentrating on sediment particles. Dilution of the contaminant concentrations downstream can favor the reversible dissociation from the NOM and make the contaminant available for accumulation far from the site of contamination⁸. Precipitation of NOM in the distribution system promotes bacterial regrowth resulting in deterioration of tap water quality and increasing the need for interior cleaning of the pipes. NOM competes with pollutant compounds for adsorption sites in granular activated carbon (GAC) adsorption, hence affecting the performance of unit processes.

Oxidation processes like ozonation can change the chemical structure of NOM leading to the formation of biodegradable organic compounds. These biodegradable organic compounds enhance regrowth of microorganisms within the water distribution systems. During coagulation, stabilization of dispersed and colloidal particles can occur through the adsorption of the higher molecular weight HS/NOM on the surface of the mineral particles. A strong interaction often has been observed between the dissolved HS/NOM and the flocculants. In most cases, higher HS/NOM concentrations mean larger flocculant dosages and therefore higher treatment costs and increased sludge volumes. The complex mixture of NOM results in the irreversible fouling of the membrane during water treatment method by membrane filtration⁸.

1.3.2 *The Indirect problems: Chlorination and DBPs Formation*

The indirect problem that is more challenging is the reaction of NOM with *chlorine* or other chloro disinfectants resulting in the formation of *disinfection by-products* (DBPs).

1.3.2.1 *Role of chlorine: Disinfection of Drinking water*

Water disinfection is without question one of the most important barriers to waterborne disease in most parts of the world. The microbiological quality is indicated by testing drinking water for *Escherichia coli*, a bacterium that is always present in the intestines of humans and other animals and whose presence in drinking water would indicate faecal matter, hence potentially pathogenic, contamination of the water. The maximum acceptable concentration (MAC) of *E.coli* in drinking water is **none** detectable per 100 ml²⁷.

Escherichia coli is a member of the total coliform group, part of the family Enterobacteriaceae, and is described as a facultative anaerobic, Gram-negative, non-spore-forming, rod-shaped bacterium that possesses the enzyme β -glucuronidase. *E.coli* can survive in the environment with or without air and is the only group that is found exclusively in the faeces of humans and other animals. Generally, greater than

10^6 *E. coli* cells are present in 1 g of colon material. Its presence in water indicates not only recent faecal contamination of the water but also the possible presence of intestinal disease-causing bacteria, viruses and protozoa. There are many strains (over 700 serotypes) of *E. coli*. Most of the *E. coli* are normal inhabitants of the small intestine and colon and do not cause diseases in the intestines (non-pathogenic) whereas a few other strains of *E. coli* (enterovirulent *E. coli* strains) also exist that can cause serious illness (pathogenic).

Chlorine (Cl_2) has been used widely for over a century now to disinfect municipal drinking water supplies and swimming pools freeing them from pathogenic microorganisms²⁸. Chlorine is a highly reactive and toxic element which has an ability to oxidize (high oxidizing potential of 1.36 volts) all proteins present in living organisms. Chlorine is fairly persistent, relatively cheap and easy to use. It is normally applied as a part of the water treatment process prior to pumping into the distribution system. The objectives of carrying chlorination into distribution are as follows:

1. Inactivate microorganisms in the distribution system,
2. Control biofilm growth.

Chlorine dosage, chlorine demand and chlorine residual are the terms commonly

used with chlorination. Chlorine dosage is the amount of chlorine added to the water and is expressed as (parts per million) ppm or mg/L. Chlorine demand is the amount of chlorine consumed by bacteria, algae, organic compounds and some inorganic substances like iron and manganese and is expressed as ppm or mg/L. Chlorine demand is time dependent since many of the reactions are not instantaneous and need time to be carried to completion. Chlorine residual is the amount of chlorine remaining in the water at the time of measurement and is expressed as ppm or mg/L.

Chlorine in gaseous form, solid form (bleaching powder) or chlorine-based bleach in liquid form is widely applied as a disinfectant on a large scale. Bleach consists of chlorine gas dissolved in an alkali-solution, such as sodium hydroxide (NaOH) to form sodium hypochlorite (NaOCl). When chlorine in any form dissolves in water, a mixture of hypochlorite (OCl⁻) and chloride (Cl⁻) is formed:



The disproportion and dissociation equations are in dynamic equilibrium and the amount of hypochlorous acid and hypochlorite ion formed is a function of pH and temperature. At pH 7.5, chlorine is equally divided between HOCl and OCl⁻. The hypochlorous acid is more active disinfectant than hypochlorite ion. Disinfection is more

effective at a pH between 7-7.5, since the amount of hypochlorous acid present at that pH is approximately 70-80%.

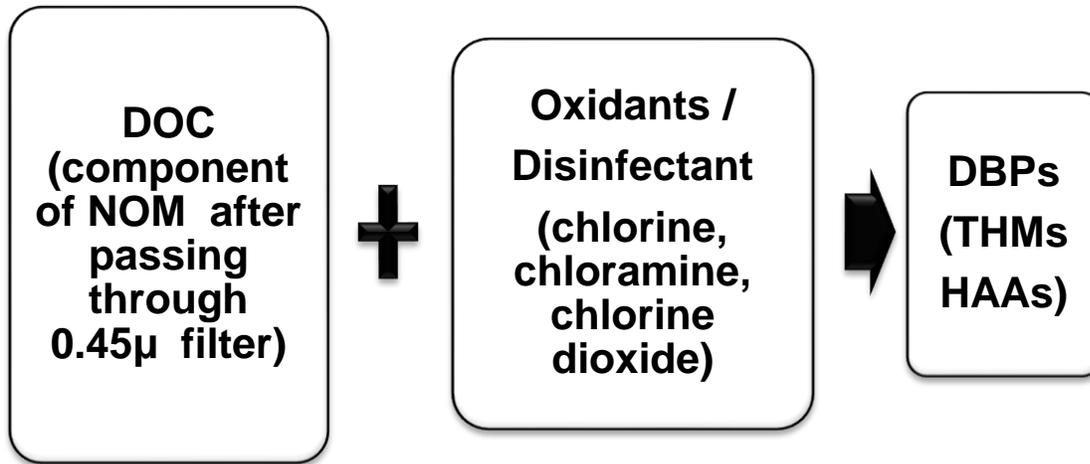
When chlorine in any form is fed into water, it first reacts with any iron, manganese, or hydrogen sulfide that may be in the water. If any residual (un-reacted) chlorine remains, it will next react with any organic material (including bacteria) present. Finished drinking water generally takes hours or days to reach its customers, especially in large distribution systems. In order to ensure that the water remains protected (disinfected) throughout the distribution system, an excess of chlorine is added. It is called free chlorine residual which can be in either form of HOCl or OCl⁻ and concentration ranging from 3-5 mg/L. Hence chlorine provides residual protection in water distribution systems. Any free residual chlorine will remain in drinking water. Approximately 90% of water supply systems in Canada use chlorine for disinfection^{29,30}.

1.3.2.2 Formation of DBPs: A Potential Carcinogenic Agent

DBPs are defined as a group of organic and inorganic compounds formed during water disinfection by the reactions between the primary disinfectant *Chlorine* and *NOM*.

The secondary disinfectants like ozone, chloramine and chlorine dioxide also produces their own suite of chemical DBPs during water disinfection. The hydrophobic and high molecular mass fraction of NOM is considered to be the more important source of DBP precursors than the hydrophilic fraction and low molecular mass compounds. As mentioned before, the FA fraction has been reported to contribute about 85-90% of DOC of all surface and ground water sources; it is considered likely to be the main precursor to DBPs³¹⁻³³.

It was 1974, when Dutch water chemist, J. J. Rook, reported that chloroform and other trihalomethanes (THMs) were formed at higher concentrations in chlorinated drinking water than in raw surface water samples. He attributed this formation to the reaction between chlorine and NOM³⁴.



Scheme 1.2. Formation of DBPs.

In Canada, more than 80% people are served by sophisticated urban drinking water systems (municipal water system). In contrast the remaining population, rural and first nations, is served by more than 80% of the water treatment systems. Most people are exposed to DBPs during their lifetime, which puts their health at risk. To ensure public health and safety, Health Canada²⁷ has established standards and regulations for four types of DBPs in drinking water covering large and small surface water and all ground public water systems:

1. *Trihalomethanes (THMs)* - A group of four chemicals, chloroform, bromodichloromethane, dibromochloromethane and bromoform forms THMs, when chlorine or other disinfectants react with NOM or inorganic matter in water. *Chloroform* is the most common THM present in chlorinated water. The maximum allowable annual average level for Total Trihalomethanes (TTHMs) is 100 (parts per billion) ppb or 0.1 mg/L.
2. *Haloacetic acid (HAAs)* - A group of five chemicals, monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, and dibromoacetic acid forms HAAs, when chlorine or other disinfectants react with NOM or inorganic matter in water. The maximum allowable annual average level for Total Haloaceticacid (HAA5) is 80 ppb or 0.08 mg/L.
3. *Bromate*- It is a chemical formed when ozone (as a disinfectant) reacts with naturally occurring bromide in source water. The maximum allowable annual average level for bromate is 10 ppb or 0.01 mg/L.
4. *Chlorite*- It is a chemical formed when chlorine dioxide (as a disinfectant) reacts with NOM or inorganic matter in water. The maximum allowable monthly average level for chlorite is 1 parts per million (ppm) or 1 mg/L.

United States Environmental Protection Agency (US-EPA) has also established standards and regulations under Stage 1 Disinfectants/Disinfection Byproducts rule, for same four types of DBPs in drinking water covering large and small surface water and all ground public water systems: namely THMs (80 ppb or 0.08 mg/L), HAAs (60 ppb or 0.06 mg/L), Bromate (10 ppb or 0.01 mg/L), Chlorite (1 ppm or 1 mg/L)³⁵.

There has always been a health concern surrounding the presence of DBPs in drinking water. A rich literature reporting adverse health effects through toxicological laboratory studies is available and has been reviewed^{36,37}. DBPs are potentially carcinogenic in nature. Many studies have linked DBPs presence to miscarriage, fetal malformations, and increased risk of still births, preterm delivery, low birth weight and cardiac anomalies. Not only they are ingested by drinking chlorinated water, but inhalation and dermal absorption (in swimming pools or during a hot shower or bath) are among many different ways by which DBPs can be introduced to the human body or any other living organism consuming chlorinated water^{36,37}.

Chowdhury et al.³⁸ have investigated occurrence of DBPs and their associated cancer risks, throughout the Canadian provinces. They have reported that approximately 703 cancer cases per year are caused by exposure to THMs in drinking water. The concentration of trihalomethane (THMs) was found to be highest in Manitoba

followed by Nova Scotia and Saskatchewan. The concentration of Haloacetic acid (HAAs) was found to be highest in Nova Scotia followed by Newfoundland and Labrador. They observed that ingestion of THMs was the leading cause of cancer risk in human beings followed by inhalation and dermal contacts, contributing approximately 40% of total cancer risks. Chloroform (CHCl_3) and bromodichloromethane formed 74-97% and 3-14% of THMs related to cancer risk respectively. They also observed a decrease in average THMs concentrations in ground water sourced systems. Epidemiological studies funded by Health Canada concluded that 14-16% of bladder cancers in Ontario may be attributable to drinking water containing relatively high levels of chlorination byproducts³⁰.

Other than above mentioned characterized DBPs, there is a continuous emergence of DBPs that are not yet regulated but are found to be more toxic than the regulated ones. They are haloacetonitriles, haloketones, nitrosamines, MX (3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone) and MX analogues, haloaldehydes, halomethanes, haloamides, tribromopyrrole, halonitromethanes, iodo-THMs, iodo-acids, haloacids, haloacetates, non-halogenated aldehydes and ketones, volatile organic compounds, oxyhalides, carboxylic acids and miscellaneous DBPs^{36,38}. The list does not end here, as, approximately 50% of the DBPs in drinking water are yet to be

identified. Hence, the exposure to more and more regulated and unregulated DBPs over the period of time, increases the risk of cancer, chronic and subchronic diseases in human beings. The occurrences of different DBPs and their possible effects on human beings essentially need a detailed study to regulate and evaluate the overall risk from DBPs in drinking water³⁸. Higher levels of THMs and HAAs in drinking water have been widely reported in Canadian provinces. Variations in their levels can be attributed to source water quality, type of treatment process, type of disinfectant and environmental conditions. A report on DBPs levels in Calgary's water treatment plant found them to be below the analytical method detection limit³⁹.

1.4 Control of DBPs: Different Methods to Reduce NOM (DBPs precursors)

Concentration in Water Supplies

NOM acts as DBPs precursor in water treatment units; thereby, increasing the NOM level affects DBPs formation in two ways. First, increasing the NOM level will increase the level of DBPs precursors, which increases DBPs formation. Second, increasing the NOM level will increase the chlorine demand of the water. A high chlorine demand in turn requires a high chlorine dosage to maintain the proper chlorine residual in distribution systems. This high chlorine dosage leads to a further increase in the

formation of DBPs⁴⁰. To control the formation of DBPs and meet the Health Canada regulations, drinking water treatment units use *following* processes to reduce the concentration of NOM and subsequently DBPs formation:

1.4.1 Conventional Drinking Water Treatment

Conventional drinking water treatment plants over the world use the basic processes of coagulation-flocculation-sedimentation, sand filtration that contribute to the reduction of NOM concentration, then chlorination for disinfection, supplying filtered water to the distribution channels. Coagulation, broadly defined as a treatment process that includes chemical addition, rapid mixing, and flocculation, can remove NOM⁴¹. For some contaminated waters or some systems, however, coagulation may not be sufficient for adequate NOM removal to meet the regulations, or is entirely absent as in some small systems. In such cases, additional or alternative treatment may be needed to meet DBPs regulation. Many other technologies are in use today, such as activated carbon filtration (GAC- granular activated carbon), membrane filtration techniques, and nanofiltration^{41,42}.

While each treatment process has its own pros and cons but the main drawback of all these technologies is that they merely transfer the pollutant to another phase, rather

than eliminate it. The contaminants are most often transferred to a solid (disposed off in landfills) or subjected to a treatment or regeneration process requiring high energy. It is practically impossible to remove or degrade all the NOM fractions present in a raw/source water by following one particular class of treatment process. Hence, we need economically feasible and environmentally sound integration of water treatment methods that will destroy the pollutant instead of merely relocating it.

1.4.2 *Advanced Oxidation Technologies (AOT)*

Oxidation to carbon dioxide is the only way to eliminate organic pollutants completely. It is an approach emerging from the research phase and in process of becoming a favourable technology for the degradation of established contaminants and also emerging pollutants in the water and waste water treatment industry.

In the past few decades, an effort has been made to introduce “advanced oxidation technologies” (AOT) as a treatment method to degrade (oxidize) recalcitrant (eg.NOM) pollutants to more biodegradable compounds or by mineralization to CO₂ and other inorganics. Glaze et al.⁴³ defined the concept of AOTs as systems that rely on in-situ generation of highly reactive oxygen species (e.g. OH·) in the presence of one or more primary oxidants (e.g. ozone, hydrogen peroxide, oxygen), energy sources (e.g.

ultraviolet light) and catalyst (TiO_2 , modified TiO_2 , ZnO). After fluorine, the hydroxyl radical is the second strongest common oxidant having an oxidation potential of 2.8 eV. Hydroxyl radicals, drive an unselective oxidative degradation of the pollutants in the water matrix, resulting in the complete mineralization of the organic pollutants/contaminants to carbon dioxide⁴⁴⁻⁴⁷. AOT'S like UV/Ozone, Ozone/ H_2O_2 , UV/ H_2O_2 , UV/Ozone/ H_2O_2 , vacuum ultraviolet radiation or ionizing radiation have been in use to treat contaminated water⁴⁴. It involves the use of light source and an oxidant to generate radicals, which attack the organic pollutants to initiate oxidation.

In addition to above mentioned AOT's, TiO_2 photocatalysis or semiconductor photocatalysis has also been studied by many researchers to degrade a majority of organic compounds found in the aquatic environment^{48,49}. The focus of the present study is semiconductor photocatalysis which involves a photochemical reaction at a solid surface of usually a semiconductor catalyst, which itself does not undergo change. The semiconductor catalyst is non-soluble in the reaction medium, hence is called heterogeneous photocatalyst and the process is also called heterogeneous photocatalysis. The photocatalytic reaction occurs in the adsorbed phase. Heterogeneous photocatalytic process commonly consists of utilizing near UV radiation to photo-excite a semiconductor catalyst in the presence of oxygen. Under these

circumstances, oxidizing species either bound hydroxyl radicals or surface 'holes', (more oxidizing than OH radicals) are generated⁴⁸. Using photocatalysis, most organic pollutants can be completely mineralized reacting with the oxidizing species to form CO₂, water and dilute concentration of simple mineral acids. The process is heterogeneous because there are two active phases, solid and liquid. Where this process can be carried out utilizing the near part of solar spectrum ($\lambda > 385$ nm) it transforms into a low cost option, but such applications require relatively long exposure.

1.5 Heterogeneous Photocatalysis: Photo-activated Catalytic Oxidation

During the last couple of decades, heterogeneous AOTs, i.e. the photo-activated catalytic oxidation or photocatalytic oxidation or photocatalysis have become the focus of much research work^{50,51}. The research work carried out in this thesis is in association with the RES'EAU-WaterNET (www.reseauwaternet.ca) which is Canada's first program (and the only NSERC Strategic Network) devoted exclusively to the "objective of developing innovative and affordable solutions for providing drinking water to small, rural and First Nations communities." The primary goals of this network are Characterizing Source Water Quality; Development of Innovative Treatment Solutions; Diffusion of Innovative Solutions. These goals limit the use of homogeneous AOTs in

small-scale water treatment plants, as it is difficult to ship and store complex chemicals or generate a chemical (ozone) in the small-scale water treatment plants. In addition to these hindrances, homogeneous AOTs often require lots of technical and operating skills and attention. Hence it is not attractive for small-scale water treatment plants. The RES'EAU waternet mandate requires operator friendly and relatively passive technology for small-scale water treatment plants, which can prevent DBPs formation and meet the regulations for quality drinking water as per Health Canada.

In that case, heterogeneous photocatalysis/TiO₂ photocatalysis is an effective alternative method for the complete degradation of majority of organic pollutants/contaminants found in an aquatic environment^{48,49}. The photocatalytic oxidation allows the oxidative degradation of the contaminants (NOM/DBP precursors) in water supplies upon irradiation with UV light (UV light photocatalysis) or visible light (Solar photocatalysis) in conjunction with a catalyst.

The term “photocatalysis” is a compound concept since photons are consumed during this process, where by definition, a catalyst accelerates a process/reaction without changing the position of the reaction equilibrium and must be recovered unchanged after the reaction. However, here the catalyst is not light, but the light absorbing material, an electronically excited particle which is indeed recovered

unchanged (but in its electronic ground state) after the reaction. Such a catalyst is active only in its excited state⁵². Photochemical reactions are processes during which energy required for their activation is provided by an electromagnetic radiation.

The principle that is primarily followed in photochemistry or photochemical reactions is Grotthuss-Draper law (1812, 1842) which states that *“Only the light which is absorbed by a molecule can be effective in producing photochemical change in the molecule”*. This idea can be extended once the particle (photon) character of light is introduced (Stark-Einstein Law or photo equivalence law, 1908-1913)⁵².

1.5.1 TiO_2 Photocatalysis

The best possible candidate for heterogeneous photocatalyst has been TiO_2 for its widespread environmental applications, due to the following properties^{50,51,53}:

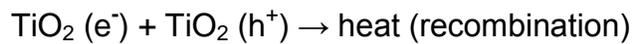
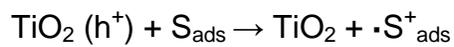
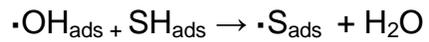
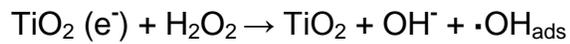
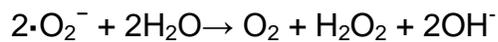
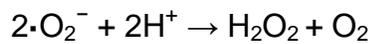
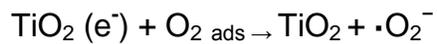
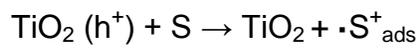
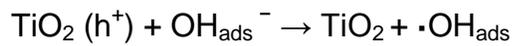
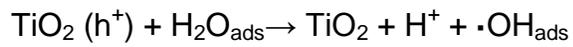
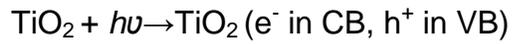
- Inexpensive, readily available, non-toxic, harmless.
- Biologically inert, chemically and physically stable.
- Exhibits tunable properties, which can be modified by size reduction, doping, sensitizers etc.
- Capable of extended use without substantial loss of photocatalytic activity.

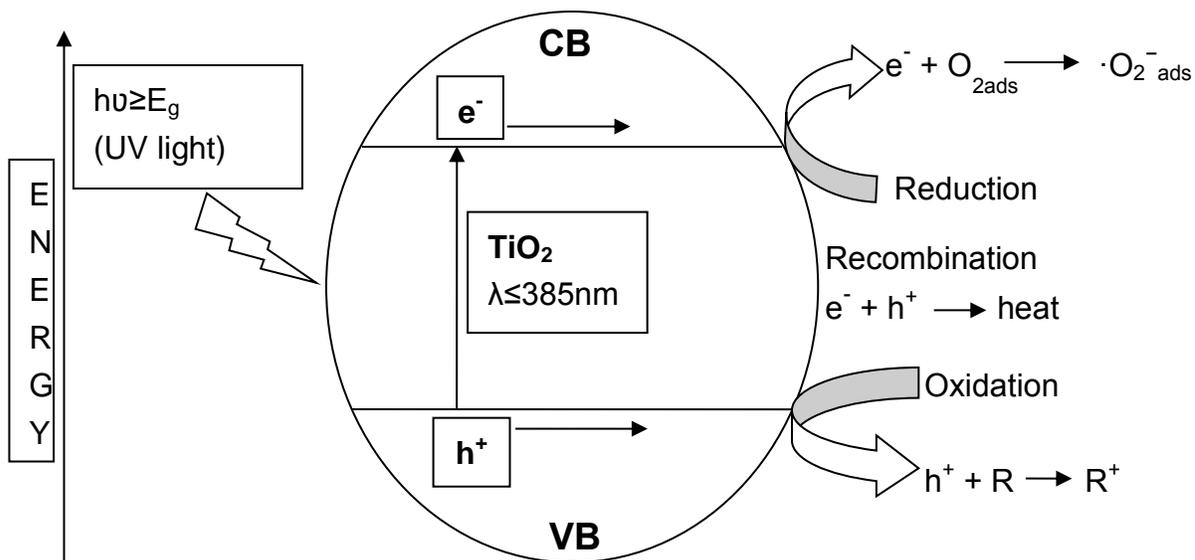
The commercially available TiO_2 , Degussa P25, has been so far the common

choice as a reference heterogeneous photocatalyst by researchers^{49-51,54}. It offers a unique combination of anatase (75%) and rutile (25%) forms of TiO₂. Its particle size is 22-30 nm (crystal) in 1000-3000 nm aggregates with density of 1.5 g/cm³ and specific surface area of 50±15 m²/g.

Due to its large band gap (Band gap energy (E_g) = 3.2 eV), TiO₂ photocatalyst absorbs only under UVA irradiation (λ ≤ 385 nm). TiO₂ photocatalysis initiates upon absorbing UVA light, photons with energy equal to or larger than the band gap energy of TiO₂ semiconductor (3.2 eV). As a result, an electron (e⁻) is excited from valence band (VB) to conduction band (CB), leaving a hole (h⁺) in the valence band. As noted above, valence band holes are powerful oxidants (3 V) and conduction band electrons are good reductants. The generated holes may directly attack and oxidize substrate (S) or pollutant molecules. Holes also oxidize hydroxyl groups into hydroxyl radicals (·OH). Conduction band electrons are trapped by the adsorbed molecular oxygen resulting in the formation of superoxide anion. Superoxide anion is a reactive oxygen species that may directly attacks organic molecules and intermediates adsorbed on the surface of the catalyst. Superoxide anion after protonation disproportionates to give hydroxyl radicals, hydrogen peroxide and oxygen. Oxygen is also important as an electron scavenger in that it reduces the recombination of CB electrons and VB holes during

photocatalysis. Following are the possible mechanistic steps during TiO_2 photocatalysis^{48-50,55,56}:





e^- : excited electrons in CB
 h^+ : holes in VB
 R : Reactants/contaminants

CB- Conduction band
 VB- Valence band

Scheme 1.3. TiO₂ Photocatalysis (UV illumination)

Kent et al.⁵⁷ fractionated the NOM content of the French river in Nova Scotia, Canada and studied the UV/TiO₂ photocatalytic oxidation of those fractions for the formation of DBPs. They observed 20-25% decrease in trihalomethane formation potential (THMFP) after treatment. Sitnichenko et al.⁵⁸ reported the photocatalytic efficiency of O₂/TiO₂/UV in degrading ≥90% of FA (in terms of DOC) in a wide range of pH.

1.5.2 SELF-SENSITIZATION

Although, UV irradiated TiO₂ photocatalysis is the most widely used process for the degradation of organics and pollutants, the relatively large band gap (~3.2 eV) of a TiO₂ semiconductor practically restricts its ability to absorb light of wavelength $\lambda > 385$ nm. The energy of the UV photons is higher than that of the photons of average solar irradiation. The sunlight UV intensity is only 3-5% of the total light intensity. Hence, in order to extend its absorbance range into the visible region, either TiO₂ can be modified structurally or TiO₂ can be dye sensitized. Sensitization of TiO₂ by various dyes has been studied extensively over the years. Looking back seven decades, Goodeve and Kitchener⁵⁹ studied photosensitization of titanium dioxide. They studied the bleaching action of a powder that was made by dyeing TiO₂ with Chlorazol sky blue, upon

exposure to full mercury arc.

There have been many studies done on the degradation of organic dyes using visible light and TiO_2 photocatalyst⁶⁰⁻⁶⁴. The photosensitization of TiO_2 by waste organic dyes is an interesting and useful phenomenon promoting selective removal of coloured/colourless pollutants⁶⁵⁻⁶⁸. The main advantage of using this heterogeneous photocatalytic treatment is that the spectral response of the inorganic semiconductor TiO_2 has been extended to the visible region; consequently there will be minimum dependence on UV light and a substantial number of solar photons can be harvested. Hence, this approach promises to be of significant economic importance. Dyes, alarmingly comprise a major part of the organic pollutants coming out of textile and photography industry. This category of pollutant is always on the radar of environmental protection agency's regulations and wastewater treatment industry. In particular, in the *Dye/TiO₂/Visible Light* photocatalytic system, the dye acts as both a sensitizer and/or a substrate whereas TiO_2 particles are a pre-requisite for the propagation of the reaction and visible light fuels the reaction^{66,67,69}.

An analogous blueprint can be adapted to *HS/TiO₂/Visible light* in treating NOM/HS in water supplies thereby reducing the formation of DBPs in drinking water and promising a way to meet the Health Canada or USEPA drinking water regulations⁷⁰.

1.5.2.1 Humic substances as Natural Photosensitizers

Humic substances act as natural electron acceptors and electron donors in the environment⁷¹. Beyond photocatalysis, the photosensitizing capacity of humic substances as natural photosensitizers in homogeneous and heterogeneous solutions has been extensively studied by many researchers^{72,73}. Cooper et al.⁸ reported that sunlight induces photochemical reactions in humic substances present in natural water and initiates chains of redox chemistry forming primary and secondary products/species. NOM either dissolved or particulate is a major absorber of light in water sources. The chromophores in fulvic acid beyond the characteristic UV band of an aromatic ring are associated to a large extent with aromatic moieties, notably quinone systems.

This aromaticity of fulvic acids is therefore significant in an ecological context because light absorbance by fulvic acids can control photic zone depth and attenuation of ultraviolet and visible light. NOM absorbs most of the solar energy entering water between 300-500 nm⁸. The energy absorbed by a molecule therefore lies in between 95 and 58 kcal/mol, which is sufficient to produce excited states that may sensitize a number of different photochemical processes, either directly or by sensitizing singlet oxygen (22.5 kcal/mol)⁷⁴, leading to structural changes and decomposition of non-

absorbing molecules. Reactive species that may include singlet oxygen, RO_2^* , hydroxyl radicals, superoxide, and hydrogen peroxide generated during photochemical processes can, over the period of time, oxidize various pollutants in natural waters to complete degradation. These reactive species and the primary and secondary decomposition products are reported to be quite reactive to other species, which do not absorb solar energy^{8,12,72,73,75-77}.

Zepp et al.⁷⁸ demonstrated the rapid photochemical generation of singlet molecular oxygen in water from highly colored rivers of North Florida and Okafenokee swamp in United States. A very high concentration of organics, mostly FA, is found in these rivers. They observed that generation of singlet oxygen upon exposure of water sources to sun light was rapid enough to contribute significantly to oxidative processes in natural waters. The possible mechanism for HS sensitization in the aquatic environment was suggested to primarily involve the absorption of light energy by the sensitizer/HS resulting in the formation of triplet excited states of the sensitizer/HS. This was followed by the transfer of energy from the triplet excited states of sensitizer/HS to the ground state oxygen which resulted in the generation of singlet molecular oxygen 1O_2 . The singlet molecular oxygen is an excited form of oxygen that is more powerful oxidant than triplet oxygen. It reacts rapidly with unsaturated acceptors in natural waters

eventually may lead to their degradation.

In an another set of experiment, Zepp et al.⁷⁹ used 2, 5-dimethylfuran to chemically trap singlet oxygen formed in water samples exposed to sunlight confirming the generation of singlet oxygen in natural waters. The authors concluded that singlet oxygen is an important intermediate in the transformation or oxygenation of certain pollutants and biologically important substances in lakes and rivers. Also, it is possible that peroxides which form in singlet oxygen reactions may initiate the free radical oxidation of aquatic pollutants. In a separate study they observed noticeable fading of the Okefenokee Swamp water upon exposure to sunlight whereas, no fading was observed when oxygen was removed from the water by degassing before sunlight exposure. In a like manner, they suggested the role of singlet oxygen in the well-known fading of colour that gives fulvic (i.e. yellow) acid its name.

Zepp et al.⁷⁹ studied the role of humic substances as a photosensitizer in natural waters which can lead to photosensitized reactions. Experimentally, the photoisomerization of 1,3-pentadiene and photooxygenation of 2,5- dimethylfuran were used to explore the nature and concentration of the excited species of HS involved in the rate determining steps of the sensitization processes in natural waters. It was proposed that a photosensitizer molecule (HS) was promoted to first excited singlet

state ($^1\text{HS}^*$) upon exposure to sunlight. Singlet excited state being short lived (10 ns) decayed in part by undergoing intersystem crossing to excited triplet states of HS ($^3\text{HS}^*$). The authors observed that humus sensitized photoreactions are mediated by energy transfer from the longer lived triplet excited states of the humic substances to oxygen resulting in the formation of singlet molecular oxygen. In the photic zone of natural waters, the concentration of oxygen is considerably higher (as it is close to air saturated zone) than that of xenobiotic pollutants which may be triplet energy acceptors. With this fact, they demonstrated that most of the electronic energy is transferred from excited triplet states of HS to oxygen with formation of singlet molecular oxygen. The kinetic studies also showed that most of the triplet state energies of humic substances are high enough to transfer to oxygen producing singlet oxygen. The quantum efficiencies were in the range of 0.4-1.5% for the formation of triplets in the UVA region. Based on action spectra, they reported that solar ultraviolet radiation plays a significant role in inducing reactions of organic contaminants. They concluded that certain commercial humic substances show the same photosensitizing behavior as shown by humic substances in fresh waters.

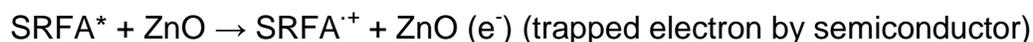
Chen et al.⁸⁰ in a photosensitization study observed that fulvic acid was a more efficient sensitizer than humic acid throughout the reactions. Although sunlight and

oxygen decrease the intensities of color and fluorescence in natural waters, influence on the total amounts of dissolved organic carbon (DOC) are negligible on the time scale of the study in the following, hence removal of the humic substances prior to the chlorination of potable waters require specific interventions.

1.5.2.2 Use of Humic substances as Sensitizers for Extending the Photoresponse of Semiconductor

Extending the absorption range of a large band gap semiconductor like TiO_2 and ZnO by using humic substances as sensitizers was suggested by Langford and Carey⁸¹. Vinodgopal et al.⁸² demonstrated a direct charge transfer interaction between ZnO colloids as a large band gap semiconductor and Suwanee River Fulvic Acid (SRFA) as a sensitizer, by using fluorescence emission of SRFA and picosecond laser flash photolysis. They observed that SRFA has a broad excitation emission fluorescence spectrum with maximum at 475 nm, with 0.011 yield and a featureless absorption spectrum with no maximum or minimum. Upon subsequent addition of ZnO to SRFA they observed a decrease in the fluorescence quantum yield of SRFA (to 0.003), attributing it to the quenching of the excited singlet state of SRFA by ZnO . The experiment suggested an electron injection from excited singlet state of SRFA to ZnO

semiconductor, which was confirmed by a broad transient similar to the blue colour of TiO₂ that forms on UV irradiation and hence corresponding to an electron in the conduction band. They reported a large value for an apparent adsorption equilibrium constant ($K_{ad} = 12000 \pm 500 \text{ M}^{-1}$) indicating a strong adsorption of SRFA on ZnO semiconductor, resulting in an efficient quenching of the excited singlet state of SRFA by ZnO. Their reports suggested that association between a sensitizer and a semiconductor is a prerequisite for the heterogeneous charge transfer process at the semiconductor sensitizer interface. An upper limit for the sensitization efficiency was reported to be 73%. Furthermore, they were also able to characterize all the products [SRFA*, SRFA^{•+}, ZnO (e⁻)] by Laser flash photolysis measurements.



Since the Vinodgopal et al. work, many groups have worked on HS (HA or FA) sensitized photoreactions on semiconductor particles (ZnO or TiO₂)^{83,84}. Ljubas⁸⁵ studied the application of photocatalysis and sunlight/H₂O₂ in degrading NOM content in natural lake water and was successful in degrading the NOM content but the technique was not economically feasible. Cho et al.⁷⁰ investigated the photosensitized degradation

of commercial HA on TiO₂ under visible light ($\lambda > 420$ nm). They observed a decrease in UV absorbance and fluorescence emission of HA upon irradiation. The DOC concentration remained unchanged during humus-mediated sensitization reactions in their experiments.

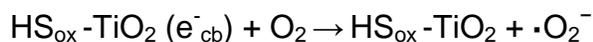
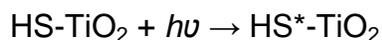
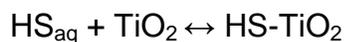
1.5.2.3 Mechanism of Self-sensitization: Extending Spectral Response of TiO₂ to the Visible Region

In self-sensitization photocatalysis, a sensitizer HS is anchored on to the surface of semiconductor TiO₂ particles by following possible mechanisms⁸⁶:

- Covalent bonding
- Ion-pair type association
- Physisorption
- Hydrophobic interactions

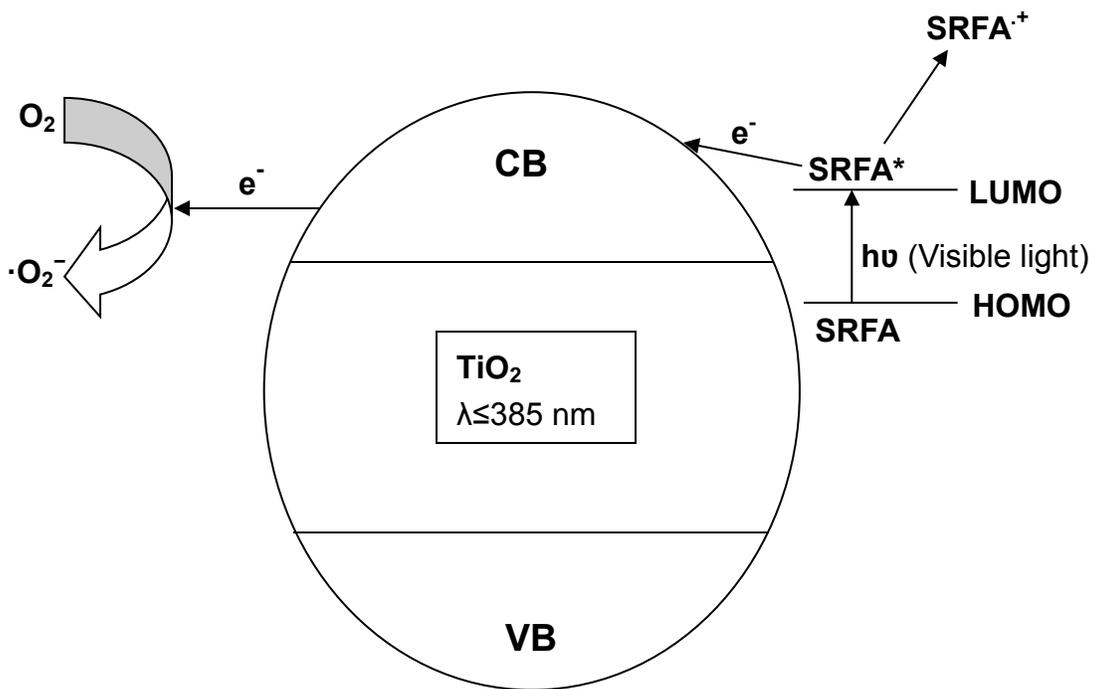
HS upon irradiation with sunlight / visible light excites an electron from its highest occupied molecular orbital (HOMO) state to the lowest unoccupied molecular orbital (LUMO) state. As already discussed above, the excited state may either undergo relaxation process by non-radiative and fluorescence paths or undergoes subsequent sensitization reactions. In the present case where TiO₂ semiconductor is being used as

a catalyst, HS after visible light induced excitation subsequently sensitizes a semiconductor oxide surface by the electron transfer. If the energy of the excited state of HS is higher than the conduction band of TiO₂, an electron is injected from the excited- state HS into the TiO₂ conduction band (CB). As a result, HS is converted to a cationic radical (HS^{•+}), and the injected electron in the TiO₂ conduction band can reduce the surface-sorbed oxygen O₂ producing $\cdot\text{O}_2^-$ or $\cdot\text{OOH}$ as a reactive species that can also disproportionate to give $\cdot\text{OH}$. At the same time there is a competition from recombination of cationic radical and electron, forming HS. The reactive species attack pollutants (in this case NOM) and may degrade them to complete mineralization. The HS cationic radical (HS^{•+}) might also react with some NOM components and oxygen species eventually leading to mineralization.





→ degraded or mineralized products



SRFA an acceptor too.

SRFA = Suwanee River reference Fulvic Acid (IHSS) as a model compound for HS.

Scheme 1.4. TiO₂ Photocatalysis (Visible illumination) “SELF-SENSITIZATION”

1.6 Research Objectives

A promising approach to decrease the concentration of DBPs in drinking water is to eliminate the reaction between organic molecules (NOM) and disinfectant (primarily chlorine) by removing NOM, mainly FA, prior to disinfection and simultaneously enhance disinfection. Since disinfection should never be compromised as DBPs have chronic side effects but disinfection will have short term effects on human beings. We aim at removal of DBP precursors without compromise to the disinfection efficiency.

1.7 Thesis Organization

This thesis is arranged into *four* chapters, one appendix and supplementary information. The chapters II and III are provided in a paper format.

Chapter 1 provides background information on the main topic of the thesis. With the introduction to natural organic matter and issues related to it, this chapter lays down foundation for the whole thesis.

Chapter 2 illustrates self-sensitized degradation of NOM using TiO₂ photocatalyst with visible light. One 'lab based' sample and three 'real water' samples have been analyzed for the degradation of NOM and subsequent reduction of DBPs, after photocatalytic treatment. (*The paper has been submitted to "Water Research" journal*).

Chapter 3 deals with coliform inactivation using TiO_2 photocatalyst and NOM as a sensitizer with visible light. Inactivation of Total coliform and E.coli in the wastewater obtained from Bonnybrook wastewater treatment plant has been studied. (*The paper has been submitted to "Water Research" journal*).

Chapter 4 provides overall outcomes of the research work that was carried out in order to compose this thesis. Future research work has also been illustrated in this chapter.

Appendix -1A provides some information about the preliminary experiments performed to analyze the role of desorbed species from the surface of TiO_2 . The species adsorbed on the surface of TiO_2 were extracted using 0.1M sodium bicarbonate to give some understanding of materials adsorbed on the surface of TiO_2 .

Appendix -1B provides information about the role of contributors to chapter 2 and chapter 3.

Supplementary materials contain some extra information related to *Chapter 2*.

Chapter 2

Self-Sensitized Degradation of Natural Organic Matter (NOM) using TiO₂

Photocatalysis with Visible Light¹

2.1 Abstract

This study is aimed at degradation of natural organic matter (NOM) using TiO₂ catalyzed photo oxidation sensitized by the NOM itself under visible light. The rationale is for prevention of disinfection by-product (DBPs) formation as naturally occurring organic matter (NOM) reacts with disinfectants (primarily chlorine) to produce harmful halogenated byproducts (DBPs). Fulvic acid (FA) is the main humic component of dissolved NOM (DOM). A well-characterized Suwannee river fulvic acid (SRFA) serves as a useful model compound for research. Photocatalytic advanced oxidation using TiO₂ is known to degrade NOM efficiently under UV irradiation, subsequently reducing DBP formation. This present study explores the scope of 'self-sensitization' by NOM acting as a 'dye sensitizer' allowing TiO₂ application under visible light such as cool white fluorescent lamps or sunlight. Model studies with well-characterized Suwannee river fulvic acid (SRFA) are reported. These are then extended to treated municipal

¹ See Appendix-1B

wastewater samples and samples of source water from drinking water systems in two Southern Alberta small communities. In all cases, fate of species in solution was tracked by DOC, UV and fluorescence. Samples before and after irradiation are also evaluated for chloroform formation with 7-day chlorination test. Similar behavior is found between the SRFA model water and a wastewater sample, but the two drinking water samples, both of which are efficiently oxidized, differ significantly in spectroscopic character and propensity to lead to DBPs after treatment. This raises questions about the widely discussed humic model for the precursors to THM formation.

2.2 Introduction

Naturally occurring organic matter (NOM) can be described as heterogeneous blend of small molecules, oligomers and polymers pervasive in all natural water sources (surface water, surface affected ground water, and to a lesser extent, ground water). NOM components can be classified as humic substances (HS) and non-humic substances (NHS), where, NHS is commonly a hydrophilic component comprised mainly of carbohydrates, lipids, amino acids and other low molecular weight acids that are easily lost during biogeochemical degradation into the diverse NOM pool.

HS forms a major hydrophobic component of NOM, and as light absorbing substances, impart brownish yellow to black color to river waters and swamps^{1,2}. HS are ubiquitous, chemically functional, refractory organic left-overs or end-products of biochemical diagenesis. They modulate ecosystem function and elemental cycles in aquatic and terrestrial environments. Recent work with ICT-MS, NMR, and SEC reveal the presence of thousands of compounds with distinct molecular formulae with a wide array of functional groups (carboxylic, phenolic, hydroxyl, ketonic, aromatic carbon and conjugated double bonds) that can assemble polymers, oligomers, and small molecules into labile aggregates^{7,19-21,23,24}.

The origins of color of NOM remain somewhat obscure. The highly complex

chemical composition of NOM makes it difficult to analyse and define molar concentration hence the concentration of total organic carbon (TOC) is used to quantify the presence of NOM in water sources. TOC is comprised of both soluble (dissolved organic carbon, DOC) and insoluble (particulate organic carbon, POC) fractions¹. DOC is a fraction, which passes through a 0.45 µm filter while POC is a fraction, which is retained on the 0.45 µm filter. DOC forms the major fraction (90-95%) of TOC and is the main concern in drinking water of low turbidity. Approximately, 50% of the elemental composition of TOC compounds is typically the organic carbon measured as (DOC) in natural water sources⁴.

Fulvic acids are the HS fraction remaining soluble at neutral to acidic pH and the main humic contributor to DOC in aquatic systems¹⁴. Available well characterized FA samples are commonly used to model NOM chemistry. The presence of NOM in drinking water raises many concerns including: unacceptable color, taste and odor, increased coagulant and disinfectant dose leading to increased amount of sludge, irreversible membrane fouling, bacterial growth promotion in the distribution system, and increased levels of complex heavy metals and adsorbed organic pollutants⁸. However, the priority concern is the reaction of the DOC with the primary chloro disinfectants resulting in the formation of toxic disinfection by-products (DBPs)³⁴.

Health Canada has established drinking water guidelines for THMs at 0.1 mg/L, HAAs at 0.08 mg/L, bromate at 0.01 mg/L, chlorite at 1 mg/L⁸⁷. Trihalomethanes have been found to contribute most to the DBPs³⁸. The most common processes to remove DBP precursors (NOM/FA) are coagulation and flocculation followed by sedimentation/flotation and sand filtration⁴¹. The main drawback of these processes is that they do not lead to degradation or mineralization into CO₂ and relocate the NOM to a solid medium. Moreover, they are not uniformly or widely implemented in the 80% of Canadian drinking water systems that serve small and remote communities.

Hence, there is interest in “advanced oxidation technologies (AOT)” for the treatment of NOM to produce more biodegradable compounds or mineralization into CO₂. Heterogeneous photocatalysis using TiO₂, is one such AOT^{43,44}. The common mechanism of photocatalysis using semiconductor catalysts involves an input of photon energy greater than band gap energy to the particle thereby promoting a valence band electron to the conduction band leaving a hole in the valence band⁴⁹. At the surface of the TiO₂ particle these carriers can participate in the oxidation-reduction reactions. The, TiO₂ band gap energy is in the UV ($\lambda \leq 385$ nm) and the useful UV intensity is only 3-5% of the total solar intensity. Hence, a TiO₂ semiconductor absorbs only that small portion of the solar spectrum in the UV region and practically restricts its ability to absorb visible

light of wavelength ($\lambda > 400$ nm).

Sensitization of TiO_2 by various dyes has been extensively studied for application to removal of colored dyes using visible light^{60,61,63,64}. The colored dye acts as both a sensitizer and a substrate, an analogous approach can be considered for the degradation of brownish yellow colored organic matter (e.g. NOM/HS/FA)^{65,70}. Cho and Choi⁷⁰ have demonstrated this with a commercial humic acid. In the present case, NOM/ TiO_2 /visible light, NOM acts as a sensitizer and substrate as well, thereby achieving “Self-Sensitization”. In self-sensitization, reaction is initiated by the adsorption of NOM on the surface of TiO_2 . Subsequently, when NOM is irradiated with visible light, an electron is excited to the lowest unoccupied molecular orbital (LUMO) state of NOM. An electron can then be injected from the excited state of NOM into the TiO_2 lower energy conduction band (CB). NOM oxidation is initiated, yielding a cationic radical. The electron may be captured by the surface sorbed oxygen, resulting in the formation of superoxide radical anion as a reactive oxygen species (ROS).

The objective here is to study a well-characterized FA sample as a reference point for real water samples from drinking water source water and a treated wastewater stream. We examine the self-sensitized oxidation of the FA and the changes in potential for CHCl_3 formation as a model system and compare real samples.

2.3 Materials and Methods

2.3.1 Materials

Suwannee river fulvic acid (SRFA) standard II was obtained from the International Humic Substances Society (IHSS) materials collection, St. Paul, MN, USA. Treated wastewater was obtained from Bonnybrook Wastewater Treatment Plant, Calgary, AB after biological treatment but before final UV disinfection. The other two real or natural water samples were sampled in May 2011, from town of 'Standard' and village of 'Gleichen' drinking water treatment plant surface source waters in Southern Alberta. The samples were immediately stored on ice, transported to the lab, maintained at 4 °C. Chlorinated organic for standardization purpose were obtained from AccuStandard Inc., CT, USA. Degussa P25 was obtained from Degussa Corporation, Germany. The filters of size 0.45 µ were obtained from FP Vericel® PVDF Membrane Filters, Pall® Life Sciences. pH of the water samples was measured by Fisher Scientific Accumet pH meter 25. Eight watt, cool white (CW) ordinary fluorescent lamps (F8T5/CW) (simulating solar light to a satisfactory approximation) were obtained from Philips, Philips Electronics Ltd., Markham, ON, Canada.

2.3.2 Reagents used

Acetic acid (glacial), potassium iodide (KI), sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$), anhydrous potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), concentrated sulphuric acid (H_2SO_4), thyodene indicator, sodium hypochlorite solution reagent grade (available chlorine 10-15%) (NaOCl), ethylenediamine tetra acetic acid (EDTA), magnesium sulphate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), ammonium chloride (NH_4Cl), ammonium hydroxide (NH_4OH), calcium carbonate (CaCO_3), sodium bicarbonate (NaHCO_3), calcium chloride (CaCl_2), hydrochloric acid (HCl), sodium carbonate (Na_2CO_3), eriochrome black T indicator, potassium dihydrogen phosphate (KH_2PO_4), sodium hydroxide (NaOH), sodium sulphite (Na_2SO_3), pentane, acetone were used as purchased from EMD and Sigma Aldrich Canada Co., ON, Canada. Milli-Q (Barnstead Easy Pure LF, 18.3 M Ω -cm grade water) water was used whenever required in the experiments. Prior to performing an experiment or an analysis, glassware were washed with detergent, rinsed with Milli-Q water and acetone and placed in an oven at 150 °C for 4-5 hours.

2.3.3 Preparation of Model Water

10 mg/L or 10 ppm of “Model Water” was prepared. Milli-Q water used for the experiment was boiled to volatilize CO_2 present. After cooling down in a covered flask,

0.020 g of SRFA, 0.117 g of calcium chloride and 0.181 g of sodium bicarbonate was added to 2000 ml of Milli-Q water. The solution was mixed using a sonicator and pH was adjusted between 7.1-7.3 using 0.1 N or 1.0 N HCl or NaOH. The prepared stock solution was titrated for the detection of hardness and alkalinity targeted at 50 mg/L as calcium carbonate. Model water was prepared fresh for each set of experiments.

2.3.4 Irradiation Protocol

Model studies with well characterized SRFA based “Model water” was conducted, and then extended to “treated wastewater” and “real or natural water” samples from the sources in Southern Alberta using a batch experimental set up. All real water samples were used without adjusting pH or any other parameter.

2.3.4.1 Dark Adsorption and Irradiation experiments

A slurry consisting of 1.5 g of Degussa P25 (TiO₂ photocatalyst) in 150 ml of water sample (model water, treated wastewater, town of Standard water and village of Gleichen water) sample was contained in 250 ml conical flask and covered with a stopper as the solution inside was saturated with air. The slurry was first kept in dark for an adsorption measurement for a period of 30 minutes. The dark adsorption period was

followed by irradiation in a Rayonet® photoreactor equipped with 14 cool white, 8 Watt (F8T5/CW) fluorescent lamps. Irradiation was continued for increasing periods corresponding to increasing light dosages measured in joule (35, 75, 110, 150, 260, 370, 519, and 739 J). The slurry was stirred vigorously with a magnetic stirrer and stir bar. At the bottom of the reactor a fan was operated. The intensity of light entering the conical flask was measured using ferrioxalate actinometry, following Parker's⁸⁸, that measures the integrated intensity for UV~ 520 nm. The intensity of light (for 14 visible lamps) entering 150ml of the solution was measured to be $4.7 \pm 0.2 \times 10^{16}$ photons per second over the range of ferrioxalate (UV~520 nm)^{56,88}. Since NOM/HS/FA absorbance rises steeply and smoothly into the UV, the intensity upto 520 nm accounts for most light absorption by NOM/HS/FA.

After irradiation, the slurry sample was collected and centrifuged to separate TiO₂ particles. The supernatant was filtered through a 0.45 µm polycarbonate filter (to minimize adsorption) prior to all analysis. In all cases, the fate of species in solution was tracked. Experiments with model water sample were performed in triplicate whereas experiments with treated wastewater, town of Standard and village of Gleichen water samples were performed in duplicate. A control experiment was also performed on lab based and real water samples in the absence of irradiation and TiO₂ photocatalyst. Real

water samples are heterogeneous and the reproducibility of photocatalytic reaction rate is limited to approximately $\pm 6\%$.

2.3.5 Sample Chlorination

The samples before and after irradiation were evaluated for chloroform formation with a 7-day chlorination test. In accordance with *Standard Method 5710B-00*⁸⁹ sample chlorination was performed and subsequently concentrations of trichloromethane formed were measured. A diluted solution of sodium hypochlorite was used as the source of hypochlorite ion for the chlorine-dosing solution. The chlorine concentration was determined to be 90 mgCl₂/ml by titration to the starch-iodide endpoint, *Standard Method 4500-Cl-B-00*⁸⁹. The chlorine dosing solution was maintained in an amber glass bottle with Teflon septa, headspace-free, at 4 °C until used. A chlorine-demand test was performed on the samples collected before and after irradiation. The resulting chlorine concentration of the samples was determined by titration to the starch iodide endpoint, after 4 hours of chlorination on the samples (before and after irradiation water samples), using *Standard Method 4500-Cl-B-00*⁸⁹. The dose recommended by *Standard Method 5710B-00*⁸⁹ for chlorine demand resulted in chlorine residual after 4 hours of chlorination. From this analysis, chlorine-dosing was determined and the required

amount of the chlorine dose was added to the sample bottles (sample bottles also contained 1ml of phosphate buffer) and pH was maintained at 6.8-7.2. Chlorine dosed sample bottles were immediately transferred to the incubator and maintained in darkness at 25 ± 2 °C for 7 days. After the 7-day incubation period, the test samples were removed from the incubator, and an aliquot of the sample was collected for residual chlorine analysis according to *Standard Method 4500-Cl-G-00*⁸⁹. After collection of an aliquot for residual chlorine, the remainder of the sample was tested for pH, and sodium sulfite solution was added to each vial to stop the chlorination. THM (chloroform) analysis was performed within the accepted 7-day holding time after reaction quenching. THMs (chloroform) were extracted with 4 ml of pentane added to 32 ml of chlorinated water sample. The pentane phase for each sample was analyzed for THMs (trihalomethane or chloroform).

2.3.6 Analysis of the Sample

2.3.6.1 Determination of DOC

DOC concentrations were monitored by using a Teledyne Tekmar Apollo 9000 TOC analyzer with duplicate runs. Data acquisition and quantification were obtained by

using TOC talk 4.22.109.7 software. Calibration gave a linear relationship between peak area and DOC concentration. Small blank corrections were significant.

2.3.6.2 UV-VIS Absorption Spectrum

UV-Visible absorption spectra of all the water samples (before and after irradiation) were recorded at room temperature with a Hewlett-Packard 8452-A diode array spectrophotometer equipped with a computer for the data acquisition using Milli-Q water as a reference. A 1.0 cm quartz cell was used.

2.3.6.3 Fluorescence Measurements

Fluorescence measurements were carried out with a Varian Cary Eclipse fluorescence spectrophotometer equipped with a computer for data acquisition. The samples were analyzed in standard 1.0 cm quartz cuvette. The slit width was 5 mm both for excitation and emission. The photomultiplier was set to operate at low to high voltage. The start wavelength of the emission scans at each excitation wavelength was offset by 10 nm (excitation wavelength = 350 nm).

2.3.6.4 Chloroform Analysis

For halocarbon (chloroform) analysis, a 1.0 μl aliquot of the sample was analyzed in an Agilent 6890 series Gas Chromatograph (GC) with an electron capture detector (ECD). A Zebron ZB-1MS column (30 m length, 250 μm ID, and 1 μm film thickness) was used. Helium was the carrier gas at a flow rate of 1 ml/min. The make-up gas was nitrogen. Samples injection used a splitless mode. The GC-ECD temperature programming was set up as follows: The initial starting temperature set for each run was 35 $^{\circ}\text{C}$, which was ramped to 150 $^{\circ}\text{C}$ at 6 $^{\circ}\text{C}$ per minute. Beyond 150 $^{\circ}\text{C}$ the temperature was further ramped at 3 $^{\circ}\text{C}$ per minute to a final temperature of 340 $^{\circ}\text{C}$ where it was held for 15 minutes. Data accumulation and analysis were performed using “Chem Station” software from Agilent. Standard reference materials were processed for calibration. Duplicate injections were performed for all samples, standards, and quality checks.

2.4 Results and Discussion

No single analytical tool can provide definitive structural or functional information about NOM degradation because of its heterogeneous and poorly defined character. Hence, combined applications of a variety of spectroscopic and wet-chemical techniques have been applied.

2.4.1 DOC Analysis

The overall removal of DOC is indicated by the changes observed with the TOC analyzer. The initial concentration decreased during the dark equilibration of samples prior to irradiation. This is attributed to adsorption of NOM on the TiO₂ surface. Thus there are two zero irradiation points on each curve in Figure 2.1, before and after equilibration. Following that all samples did show extensive DOC loss after an irradiation dose of < 1 kJ. The experimental error related with DOC analysis was approximately ±6%.

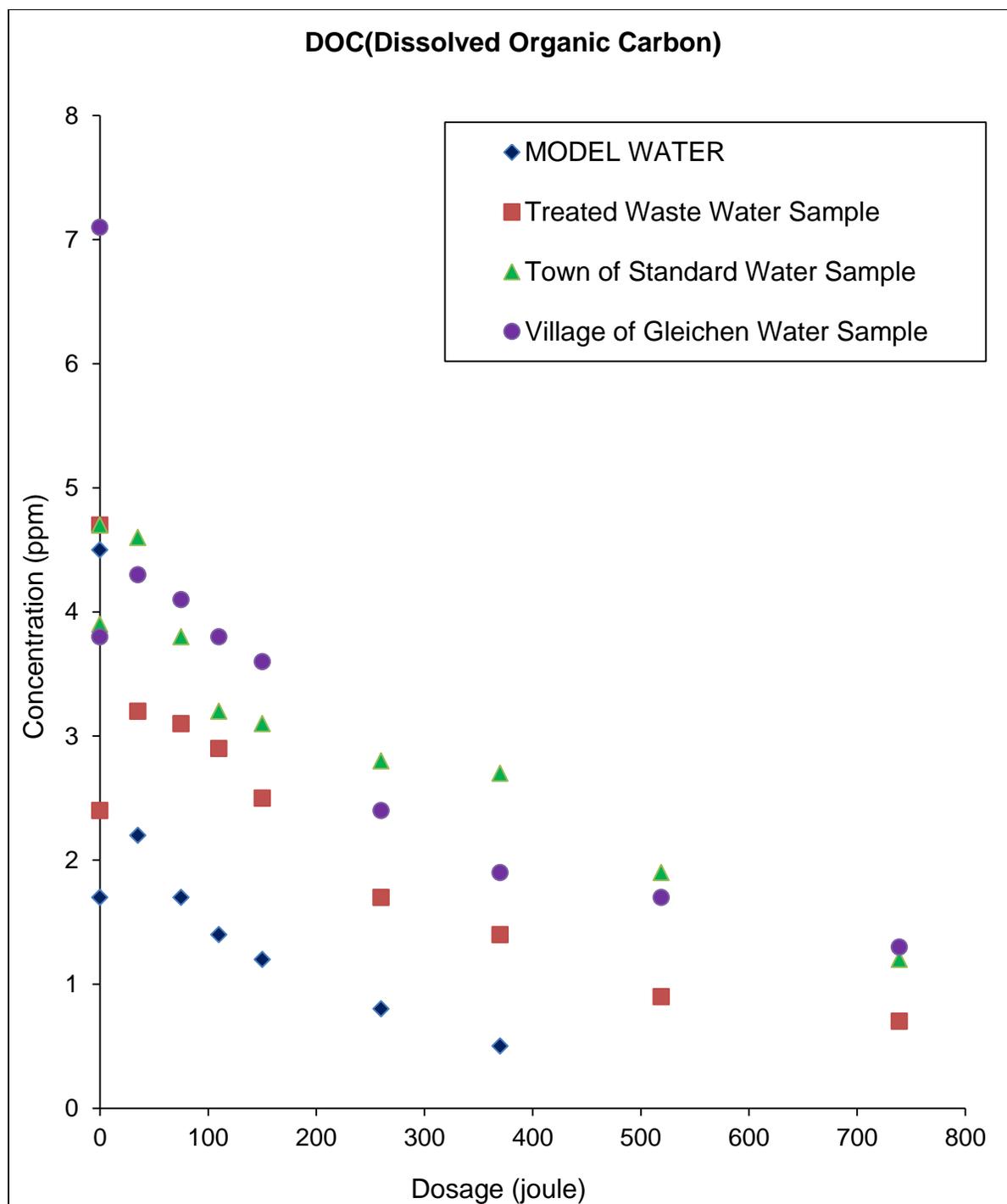


Figure 2.1. Change in the concentration of DOC in various water samples as a function of light dosage. The TiO₂ loading is 1 g/100 ml.

The extent of dark adsorption varied among the samples more than the initial DOC values. The model water at pH 6.8-7.2 shows 62% decrease, treated wastewater at pH 6.9-7.4 shows 38% decrease, village of Gleichen at pH 7.3-7.6 shows 46% decrease and town of Standard at pH 7.9-8.3 shows 17% decrease. Wiszniowski et al.⁹⁰ used diffuse reflectance FTIR to demonstrate adsorption via the interaction with carboxylate groups on the HA molecules at acidic pH. Some adsorption of NOM/HS/FA onto the surface of TiO₂ is essential to facilitate an efficient 'dye' sensitization for electron transfer to TiO₂. That all 'real' water samples adsorb less than the model suggests that the humic content of the organic matter is an important variable. Below the point of zero charge at pH = 6.7 the TiO₂ surface carries a positive charge which is favorable to anion adsorption.

As reported earlier for purified humic acid, irradiation into the visible absorption bands of the NOM of all of these samples leads to transformations of the NOM (Figure 2.1)⁷⁰. Picosecond resolved transient spectroscopy has verified electron transfer to the conduction band^{82,83}. This leaves a reactive organic cation radical, and O₂ scavenging of the electrons yields ·O₂⁻ which can react with organics and disproportionate to produce other reactive oxygen species. In the initial stage of reaction, there is a small increase in measured TOC, probably reflecting release of some less strongly adsorbed degradation intermediates⁹¹. Further irradiation produces a continuous decrease in the DOC. Irradiation eventually leads to mineralization or conversion (to CO₂ and H₂O). Model water sample shows 90% decrease with the light dosage of 370 J. The real samples were less reactive. The treated wastewater sample showed an 85% decrease,

town of Standard water sample showed 74% decrease, and village of Gleichen water sample showed 82% decrease in DOC concentration with the light dosage of 740 J.

2.4.2 UV-Visible Spectra

The UV-VIS spectra of fulvic acids are broad, featureless showing no maxima or minima and monotonically decrease with increasing wavelength. Several absorption wavelengths have been assigned as indicators of the spectral characteristics of humic substances⁹². UV absorbance at 254 nm was taken to represent total NOM content or humification and its aromatic and hydrophobic nature. UV absorbance at 280 nm represents total aromaticity for humic substances. UV absorbance at 400 nm and 436 nm is taken to represent humic color removal⁹².

The higher UV₂₅₄ absorbance values arise because of the presence of substituted chromophoric groups in humic substances and especially aromatic compounds substituted with COOH and OH groups. Lab based model water sample prepared by using SRFA, shows higher absorbance values at UV₂₅₄ when compared to the real or natural water samples at similar TOC. SRFA is extracted by resin fractionation XAD methods from mainly natural aquatic sources (Okefenokee swamp in Georgia), which contains humified plant material leached out organic rich layers of soil. Hence, increased UV~254 nm absorbance values in model water suggest a higher degree of humification. The humic substances or NOM from wastewater treatment is mainly composed of anthropogenic organic matter and microorganisms. Hence comparatively decreased absorbance represents lesser degree of humification. The other two samples of natural water sources collected from the Southern parts of Alberta came from the

Bow river via the irrigation district canals and are believed to be of partly urban origin. Specifically, when water is diverted at the Western Irrigation District Weir or Western Irrigation Headworks (inside the City of Calgary limits, north of Inglewood and south of the junction of Deerfoot Trail and Memorial Drive). It then flows to Chestermere Lake and through canals to both communities. The UV_{254} spectrum of samples from natural water sources shows decreased absorbance representing a relatively lower degree of humification. The water samples from the Bow river/canal aquatic systems (town of Standard and village of Gleichen) display a deviation from the typical humic substances characteristics. The experimental error related with spectrophotometric analysis was approximately $\pm 3\%$.

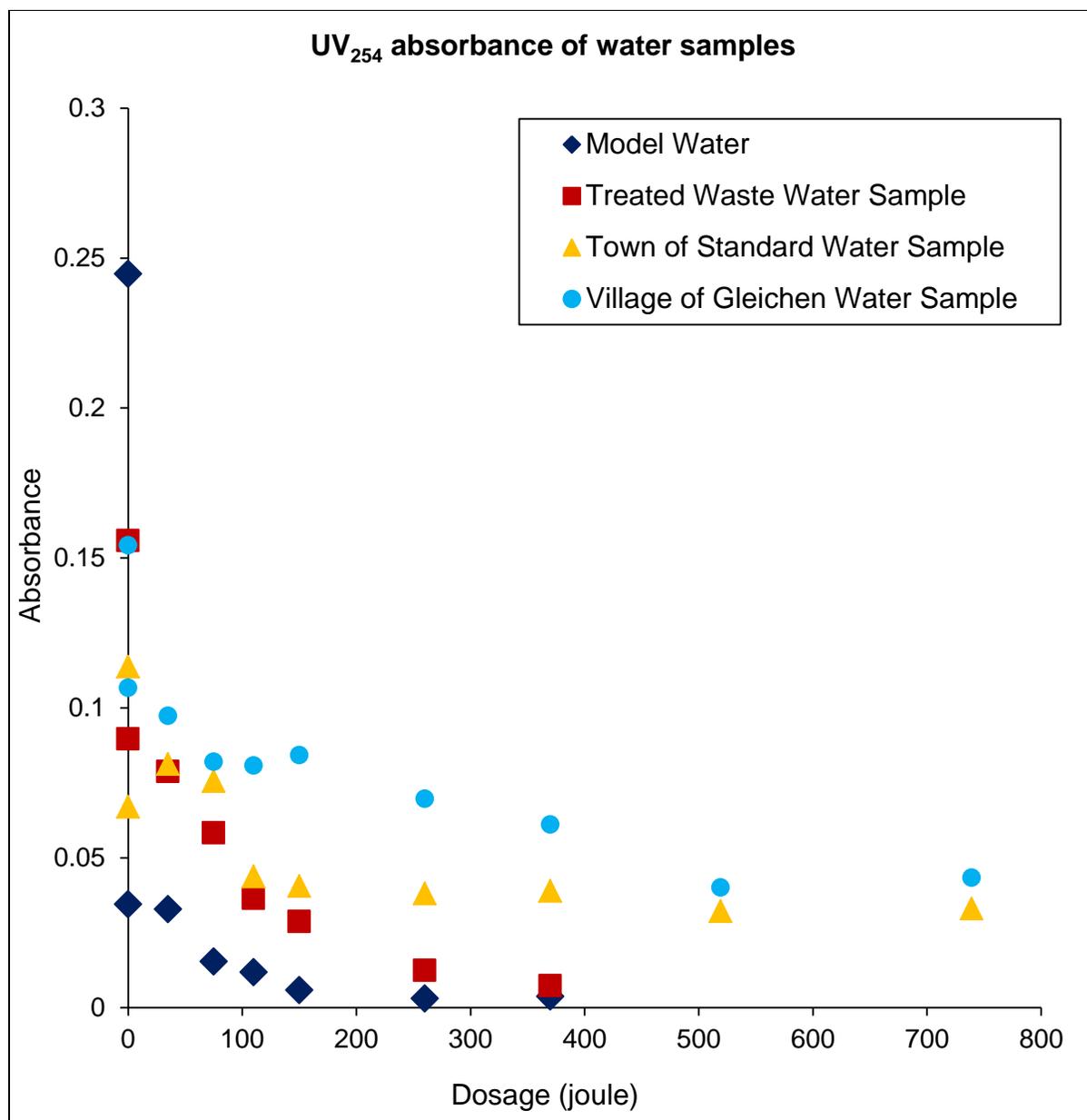


Figure 2.2. UV₂₅₄ absorbance spectra of various water samples containing NOM as a function of light dosage. The loading of TiO₂ is 1 g/100 ml. Model water is a lab based water sample prepared by adding Suwannee River Fulvic Acid. The rest of the water samples are natural water samples. Samples are irradiated under cool white fluorescent lamps.

Photosensitized degradation of NOM/HS/FA was tracked by measuring UV absorbance of all NOM samples at UV 254 nm. The percentage decrease in absorbance due to dark adsorption was 86% in model water followed by treated wastewater (42%), town of Standard water (41%), village of Gleichen water (31%) samples. This limited the sensitivity of spectra as probes of subsequent degradation kinetics. The dark adsorption decrease was followed by a continuous decrease in the absorbance values with increasing light dosage. In contrast to DOC, no early short-term increase in absorbance values was observed, suggesting that the intermediate oxidation products released had exhibited loss of aromaticity of the dissolved humic aggregates⁹¹. An exception to this observation was the town of Standard water sample. The percentage decrease in absorbance during dark adsorption in the town of Standard water sample was followed by an intermittent increase in the absorbance before finally decreasing continuously with increasing light dosage. This small increase in absorbance in the initial stages of irradiation reaction indicates release of some less strongly adsorbed degradation intermediates that have not lost their aromaticity.

Figure 2.2 shows the measured absorbance at 254 nm as a function of light dosage during irradiation. More than 95% decrease in the absorbance was observed with the increasing light dosage in all cases. The trend of absorbance decay was similar to measured DOC, but the percentage removal of 254 nm absorbance was relatively higher than that of total DOC, for model water sample (99%) and treated wastewater sample (95%) at the light dosage of 370 joule (5 hours of irradiation). However, removal of UV 254 nm was observed to be relatively lower in town of Standard water sample (71%) and village of Gleichen water sample (72%) with the light dosage of 740 joule (10

hours of irradiation). This difference is consistent with a less 'humic' composition. A higher removal rate at 365 nm or 436 nm absorbance with respect to the removal rates at 254 nm is observed. The bulk behavior of NOM (or HS) may differ significantly from that of individual NOM (or FA) components.

2.4.3 Fluorescence Spectrum

Before irradiation, the fluorescence spectra of humic substances are generally characterized by broad peaks. Since NOM is a very complex mixture, these broad peaks are probably the sum of the spectra of many different fluorophores present in NOM. The relatively sharp peak observed in the region within 50 nm of the excitation wavelength is the peak for water Raman scattering. The relative fluorescence intensities can be judged by comparison to the Raman band which remains constant. The model water sample shows a fairly intense characteristic humic peak and village of Gleichen water sample shows a relatively low intensity. The lowest intensity is shown by treated waste water and town of Standard water samples. Chen et al.⁹³ attributed the low emission intensity, to the depletion of aromatic or polyphenolic content and also due to the enrichment of its carbohydrate materials which do not give fluorescence.

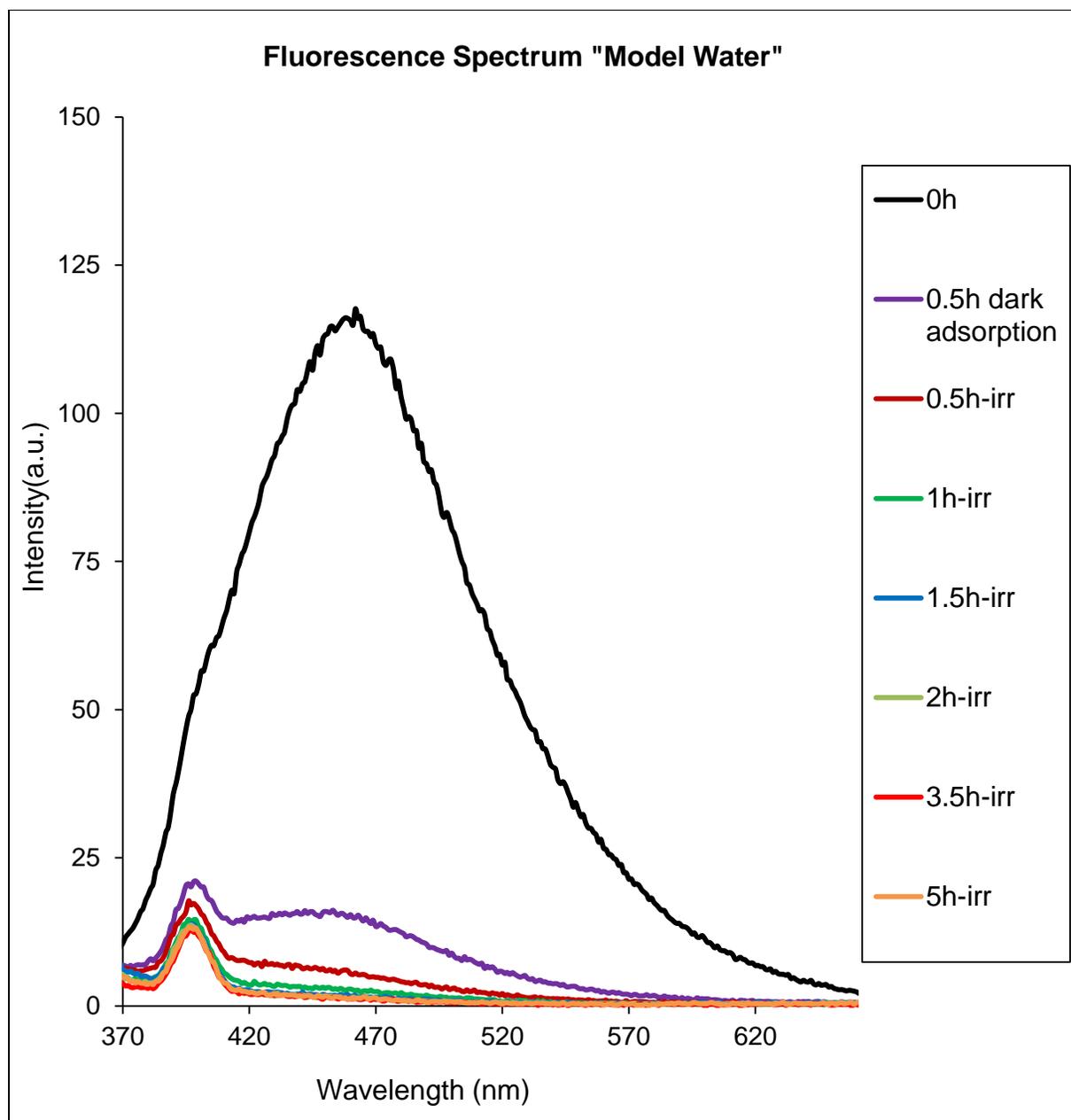


Figure 2.3. Fluorescence emission intensity of NOM/FA present in the “Model Water” water sample with excitation at 350 nm over the extent of irradiation periods. Note narrow Raman band near 400 nm. Relative intensity is indicated by the relative intensity of the constant water Raman band serving as internal standard.

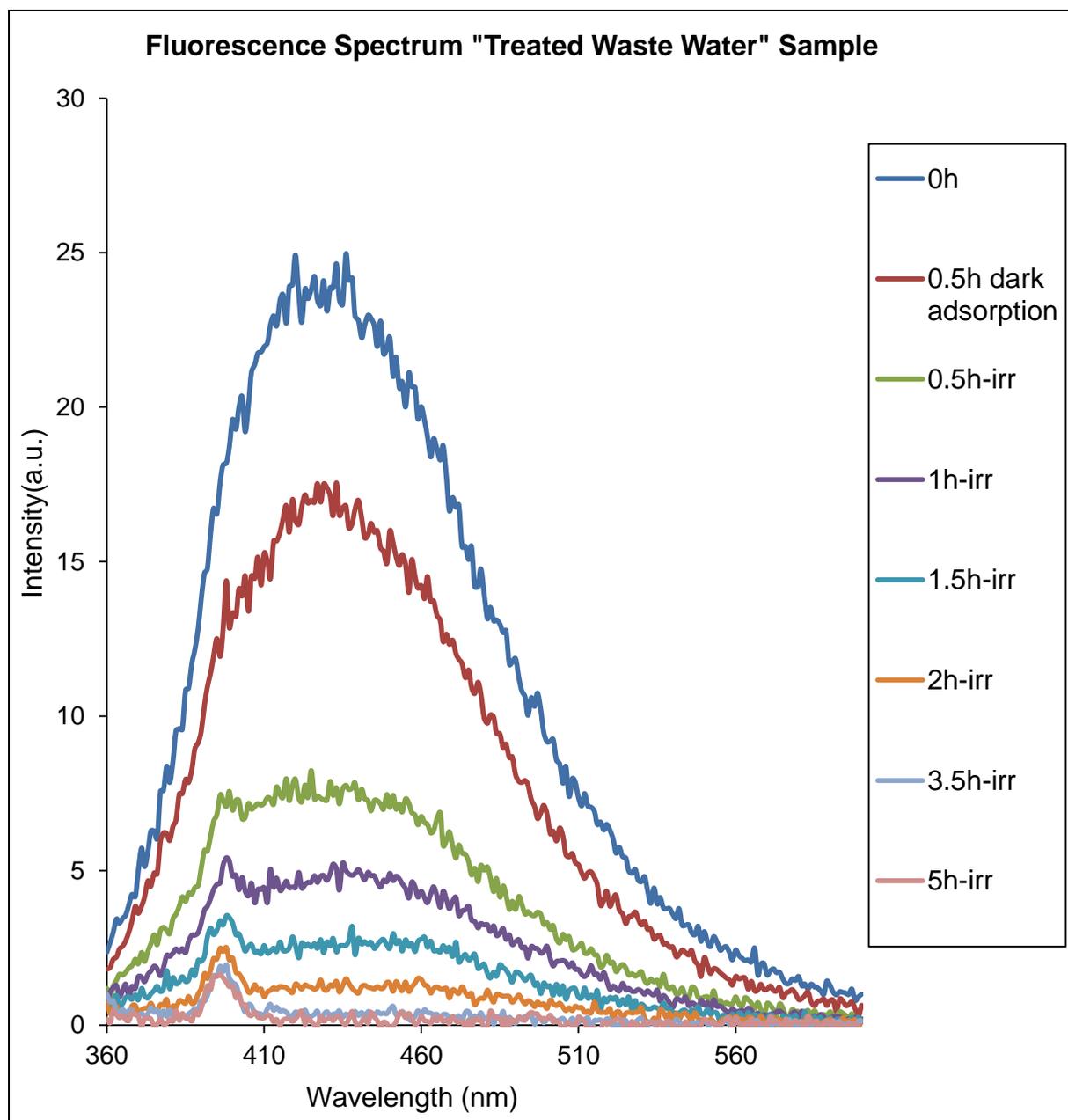


Figure 2.4. Fluorescence emission intensity of NOM present in the “Treated Waste Water” sample with excitation at 350 nm over the extent of irradiation periods. Note narrow Raman band near 400 nm. Relative intensity is indicated by the relative intensity of the constant water Raman band serving as internal standard.

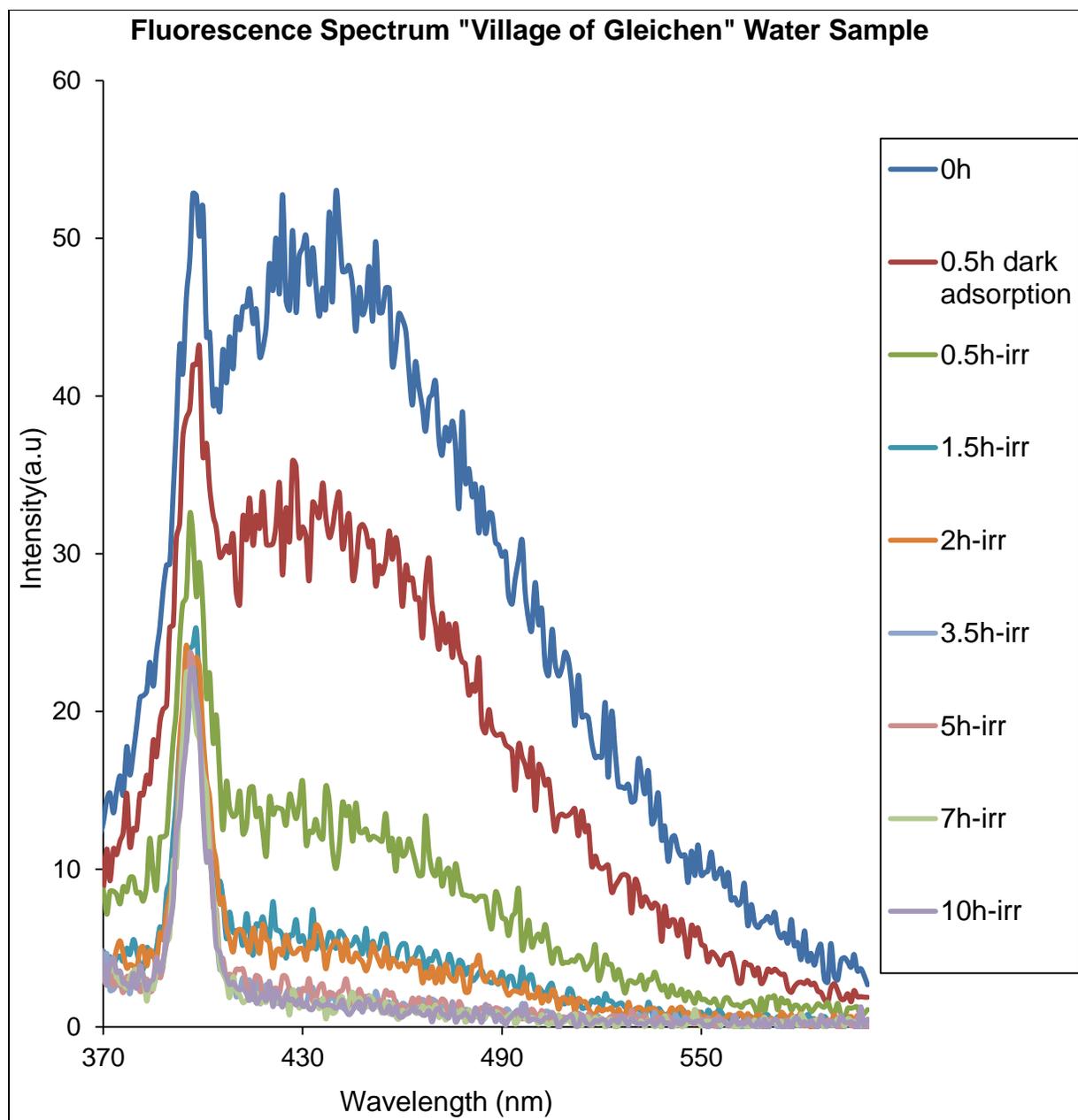


Figure 2.5. Fluorescence emission intensity of NOM present in the “Village of Gleichen” water sample with excitation at 350 nm over the extent of irradiation periods. Note narrow Raman band near 400 nm. Relative intensity is indicated by the relative intensity of the constant water Raman band serving as internal standard.

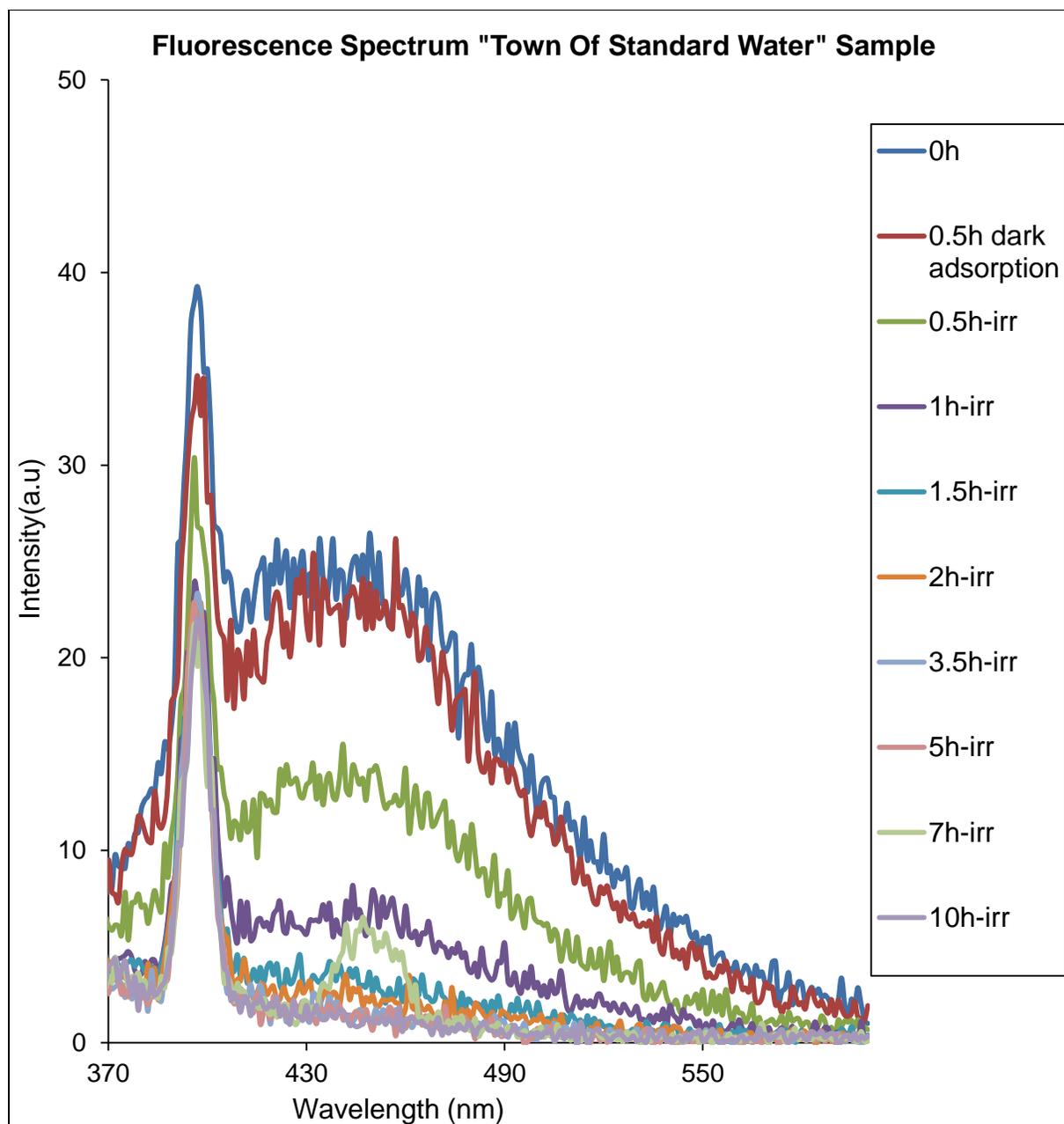


Figure 2.6. Fluorescence emission intensity of NOM present in the “Town of Standard” water sample with excitation at 350 nm over the extent of irradiation periods. Note narrow Raman band near 400 nm. Relative intensity is indicated by the relative intensity of the constant water Raman band serving as internal standard.

Before irradiation, model water sample shows, when excited at 350 nm, a typical humic emission peak at wavelengths around 450-470 nm. The relatively low intensity of village of Gleichen water sample peak is shifted to shorter wavelengths of 420-440 nm. Treated waste water and town of Standard water samples show lowest intensity at the shorter wavelength of 420-440 nm. The shift of peaks towards shorter wavelength region indicates the different composition of NOM in real or natural water samples as compared to the model water sample (containing Suwannee River fulvic acid, standard II). This order of intensity is not explained by variation of DOC, where model water, treated waste water and town of Standard water samples contain nearly equal amount of DOC (~4.5 ppm) before irradiation and village of Gleichen water sample contains relatively higher amount of DOC (~7.2 ppm) before irradiation. In real water samples, the shifted maximum and intensity variation with DOC, indicates the presence of hydrophilic NOM^{13,94,95} in addition to the presence of hydrophobic aromatic compounds (major contribution to THM formation) and hence influencing the fluorescence spectrum.

Upon dark adsorption, the intensity of characteristic humic peak in model water sample shows a large decrease when compared to the real water samples. Treated waste water and village of Gleichen water samples show a small decrease in the intensity of the characteristic peak, and town of Standard water sample shows negligible decrease in the intensity upon dark adsorption.

Upon irradiation, the characteristic peak around 470 nm decays in intensity and is undetectable after 5hrs of irradiation in model water. The same behavior is observed in treated waste water sample after 5 hours of irradiation. Village of Gleichen and town of Standard water samples also show the same behavior but after 10 hours of irradiation.

The significantly different behavior of the NOM from the Alberta sources, including a blue shifted maximum and a different pattern of decline under irradiation, emphasizes the limitations of the humic models that have so often been postulated as DBP precursors⁹⁶⁻⁹⁹. Decreased adsorption on TiO₂, reduced UV absorbance at 254 nm and the fluorescence shift combine to suggest reduced humic character, aromaticity in the Alberta NOM samples.

2.4.4 Chloroform (CHCl_3) Concentration

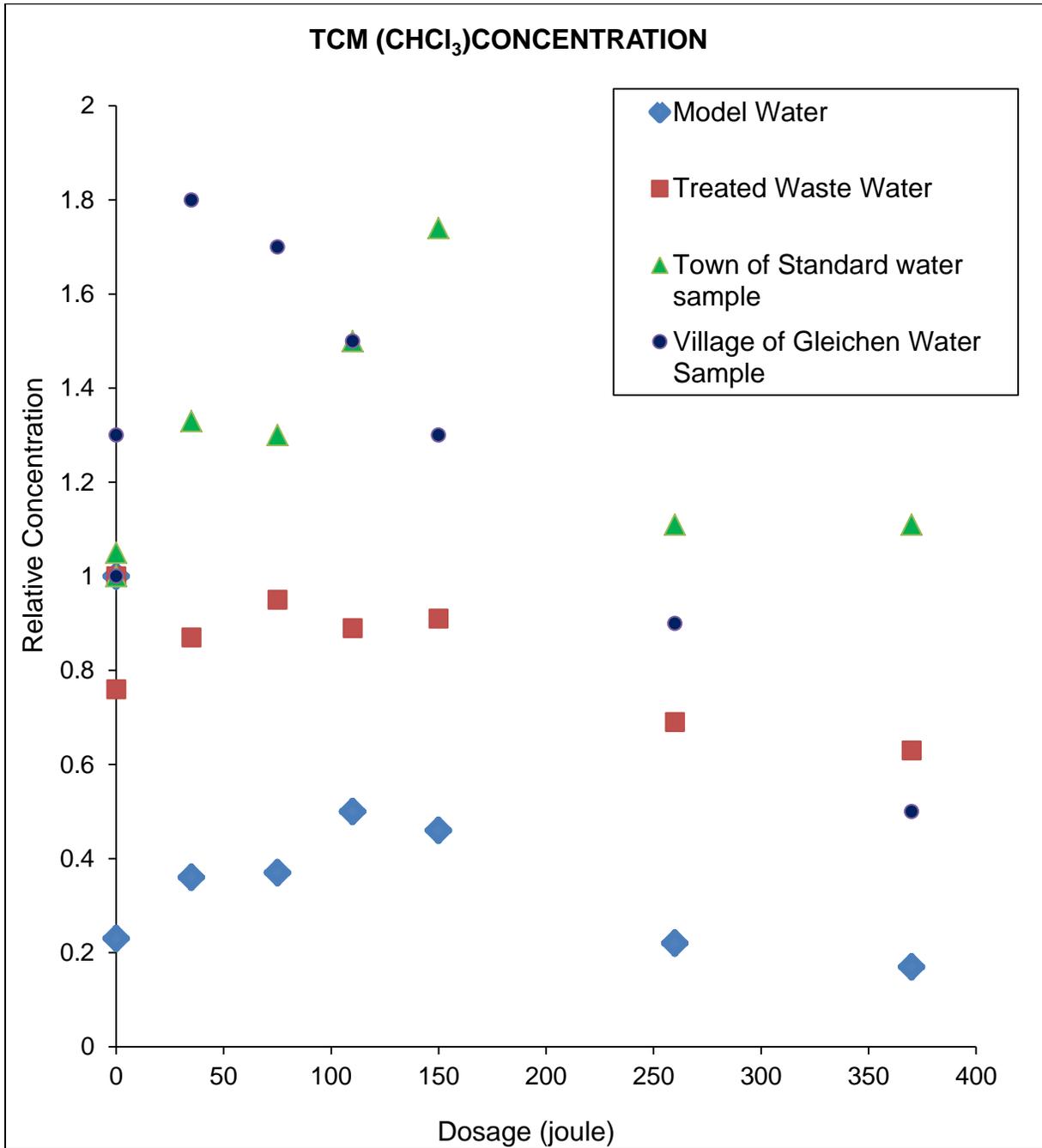


Figure 2.7. Trichloromethane formation in various water samples after moderate light doses.

The most consistently observable trihalomethane was chloroform (trichloromethane). Figure 2.7 shows the relative trichloromethane (CHCl_3) concentration as a function of moderate light dosage (400 J) to NOM in various water samples. Other THMs including brominated ones were not formed or were below the detection limit. In recent years, most studies of experimental chlorination have focused on THMs (especially CHCl_3) because they are the most extensively regulated^{38,100}. Consistent with the observations made in TOC analysis and UV absorbance, model water and treated wastewater samples have shown the initial decrease prior to irradiation in concentration of CHCl_3 formed as a consequence of dark adsorption of NOM limiting its reactivity. This was not clearly observable for town of Standard and village of Gleichen water samples. This emphasizes the distinctive behavior of the two samples with least spectroscopic resemblance to humic materials. Clearly, poorly adsorbed components can make significant contributions to THM formation. This challenges suggestions that the THM precursors are mainly humic like hydrophobic acid organic matter¹⁰¹. Liang et al.¹⁰² also suggested that aliphatic structures may play an important role in THM formation in addition to the aromatic moieties. These data emphasize that possibility. The experimental error related with the TCM analysis was approximately $\pm 8\%$.

On initiation of irradiation, an early increase in CHCl_3 formation is observed in all the photocatalytically treated water samples. This is most easily understood by recognizing that oxidative reactions will produce oxygen bearing, more polar, intermediates that will be less strongly adsorbed on the TiO_2 . Consistent with the significantly reduced DOC concentration and UV absorbance after photocatalytic

oxidation, all samples exhibit significant decrease, if variable, in chloroform formation after a 400 J light dosage. A distinctive pattern was observed in each of the drinking water samples, suggesting that formation of DBPs depends primarily on source water characteristics. Although complete mineralization of NOM was not achieved with the 400 J dose, the photocatalytic oxidation induces favorable changes to the precursors. The self-sensitization process appears efficient in removing the hydrophobic NOM molecules that are readily adsorbed. However, the sample exhibiting least initial dark adsorption, (town of Standard) showed no more than marginal decrease in CHCl_3 at large irradiation dose. In contrast, source water from the village of Gleichen exhibited the greatest proportional decrease in CHCl_3 at even lower irradiation dose.

2.5 Conclusions

The visible light (including sunlight) self-sensitized degradation of naturally occurring organic matter (NOM) using a TiO_2 photocatalyst was investigated with a view to its potential for prevention of DBPs formation. The photocatalytic oxidation process was able to reduce DOC levels by 80% in 'real' or natural water samples and up to 90% in the SRFA model water with light dose < 1 kJ. 254 nm UV spectra show about 98% decrease in absorbance in the model water sample and 72% decrease in absorbance in real water samples. Fluorescence spectra show the different behavior of natural water samples when compared to the model water sample. In the two drinking water source samples there are significant shifts in wavelength distribution of emission from that characteristic of humic substances under 350 nm excitation. Sufficient oxidative NOM reduction can eliminate THM formation. However, 'real' or natural water samples show

this can be less effective than humic models suggest. In agreement with the fluorescence evidence for differences, the observed kinetics of THM formation differ significantly from a fulvic acid model. In the case of the town of Standard source water, THM formation persists after significant reduction of DOC. In the case of village of Gleichen source water, THM formation decreases monotonically from early in irradiation with approximate zero order kinetics. Clearly, light dosages must be adjusted to variations in source water. These results raise questions about the generality of a hydrophobic aromatic model of the key DPB precursors^{13,94,95}.

This project is part of the work of the RES'EAU Waternet strategic network for advancing technologies for small and remote water systems. In this context, compact low maintenance technologies requiring minimal operator attention have been a priority. Visible light treatment might be implemented in a pretreatment step, which could be a compact reactor requiring no added chemicals and little operator attention that is based on common fluorescent lamps or LED light sources that are energy efficient and long lived⁶⁵. Alternatively where there is a pond (reservoir) it might be implemented on floating catalyst coated spheres as described by Heller^{103,104}.

Chapter 3

Coliform Inhibition by Natural Organic Matter (NOM) Sensitized

Photocatalysis Under Visible light²

3.1 Abstract

This study investigated visible light induced inactivation of total coliforms and E.coli in a wastewater sample by heterogeneous TiO₂ photocatalysis using NOM as a sensitizer. Natural Organic Matter (NOM) is adsorbed on the surface of TiO₂ and acts as a sensitizer. Analogously to dyes used for visible region sensitization, an excited state of the NOM transfers an electron to TiO₂ CB. The NOM undergoes an initial oxidative step and the conduction band electron will be captured by oxygen sorbed on TiO₂, resulting in the formation of superoxide radical anion and other reactive oxygen species (ROS) through its disproportionation reactions. The ROS may aid lysis of bacterial cell wall eventually leading to cell death or inactivation. This NOM sensitized visible light photocatalytic oxidation shows the capacity to inactivate total coliform and E.coli in a wastewater sample simultaneously. Three to four log reductions were achieved with an energy requirement < 0.22 kWhr per cubic meter.

² See Appendix-1B

3.2 Introduction

Naturally occurring organic matter (NOM) containing humic substances is colored yellow by a complex mixture of small molecules, oligomers, and polymers ubiquitously present in natural water sources (especially surface water and surface impacted ground water). But, the presence of NOM leads to the formation of disinfection by products (DBPs) upon chlorination and DBPs are strictly regulated in drinking water^{34,87}. Cho et al.⁷⁰ for humic acid models and Chamoli et al.¹⁰⁵ have shown that NOM functioning as a “dye” sensitizes TiO₂ under visible light irradiation and undergoes photocatalytic oxidative degradation (here termed ‘self-sensitization’). This is not limited to model humic samples but is applicable to various NOM including ones that differ in character from humic models¹⁰⁵. This leads to the present question: can visible light photocatalysis self-sensitized by NOM concurrently inhibit microorganism growth as it is reducing NOM concentration? This initial study focuses on coliform organisms (Total coliform and Escherichia coli) since they are the primary indicator organisms for drinking water contamination. Choosing samples from drinking water systems was not feasible since coliform counts are too small for quantification of the treatment. Consequently, the samples reported here are from an Alberta wastewater treatment plant. Health Canada drinking water guidelines set the maximum acceptable concentration (MAC) of E.coli in drinking water as **none** detectable per 100 ml and our target is defined by this regulation⁸⁷.

3.3 Materials and Methods

3.3.1 Materials

Treated wastewater prior to the final UV step was sampled from the Bonnybrook Wastewater Treatment Plant, Calgary, AB. All water samples were dispensed into sterile Nalgene[®] polyethylene bottles (1L). The samples were immediately stored on ice, transported to the lab, maintained at 4 °C and used within 24-48 hours. pH of the water samples was measured by Fisher Scientific Accumet pH meter 25. Colilert[®]-18 tests served total coliform and E.coli detection. A Colilert[®]-18 sampling kit was used including; Defined Substrate Technology[®] (DST[®]) containing nutrient indicators Ortho-Nitrophenyl- β -D-galactopyranoside (ONPG) and 4-methyl-umbelliferyl- β -D-glucuronide (MUG), The Quanti-Tray[®]/2000 Comparator, Quanti-Tray[®]/2000, Quanti-Tray[®]/2000 Rubber Insert, Quanti-Tray[®] Sealer, IDEXX Quanti Tray/2000 Most Probable Number (MPN) table or multi well card and a 6-Watt 365 nm UV lamp (to observe fluorescence), were all purchased from IDEXX Reference Laboratories Ltd., Markham, ON, Canada. Degussa P25 was obtained from Degussa Corporation, Germany. Cool white ordinary fluorescent lamps (F8T5/CW), 8 Watt were obtained from Philips, Philips Electronics Ltd., Markham, ON, Canada. Milli-Q (Barnstead Easy Pure LF, 18.3 M Ω ·cm grade water) water with a resistivity of 18.3 M Ω ·cm was used whenever required in the experiments. NaHCO₃ was purchased from Sigma Aldrich Canada Co., ON, Canada. The glassware used for the experiment was washed, sterilized and autoclaved for 45 minutes.

3.3.2 *Experimental Protocol*

A slurry consisting of 1.0 g Degussa P25 (photocatalyst) in 100 ml of water sample (treated wastewater), was contained in a 200 ml conical flask and covered with a stopper, the solution inside was pre-saturated with air. In all the experiments, the samples were diluted with Milli-Q water by a dilution factor of 2. No pH adjustment was made to the water samples before starting dark and irradiation experiments. In all the experiments, the suspension was magnetically stirred for 30 min in the dark to ensure complete equilibration of adsorption/desorption interaction of total coliform and E.coli bacteria with the catalyst surface prior to the light source being turned on. Surface interaction may produce changes in apparent viability arising from the adsorptive interaction between TiO₂ and the cell walls. The dark adsorption period was followed by irradiation in a Rayonet® photoreactor equipped with 14 cool white, 8 Watt (F8T5/CW) ordinary fluorescent lamps. The irradiation experiments were performed for different light dosages measured in joule (6, 12, 24, 30, 35, and 75). All the while, the slurry was being stirred using a magnetic stirrer and magnetic stir bar. A fan at the bottom of the reactor was used to maintain the temperature. The intensity of light entering the conical flask was measured using ferrioxalate actinometry, following Parker's⁸⁸, that senses the integrated blue end light up to ~ 520 nm¹⁰⁶. Typical intensity of light (for 14 lamps) entering 100 ml of the solution was measured to be $4.7 \pm 0.1 \times 10^{16}$ photons per second over the ferrioxalate range (to 520 nm). After performing the visible light irradiation experiments, the samples were in each case protected from any other light source interference by covering the conical flask with aluminium foil. After irradiation, a slurried sample of water and catalyst was collected and prepared for incubation immediately.

The slurried sample was mixed with the IDEXX's patented Defined Substrate Technology[®] (DST[®]) and the mixture was shaken gently by hand for 2 minutes or until dissolved. The mixture was poured into a Quanti-Tray/2000 and sealed in a Quanti-Tray Sealer. In addition to the seal, the Quanti-Tray/2000, the sealer also uniformly distributed the mixture in small wells (#48) and large wells (#49) of Quanti-Tray/2000. The sealed tray was placed in an incubator maintained at 35±0.5 °C for 18 hours.

To confirm complementary chemistry of a model chemical pollutant, photolysis in the same apparatus was conducted on 30 ppm of 4-chlorophenol (4-CP) with 10 mg/L of the humic fraction, Suwannee River fulvic acid (SRFA), acting as the sensitizer. The degradation of 4-CP was monitored by decrease of its UV bands over 210 minutes of irradiation.

3.3.3 *Recovery Experiments*

After the sampling on terminating irradiation, the residual sample was kept in an incubator at temperature 35±0.2 °C for an additional 48 hours in dark and then quantified for the presence of total coliform and E.coli. A control experiment was also run with Milli-Q water for the same set of experimental conditions. Also, dark equilibrated samples were centrifuged and Milli-Q water was added to TiO₂ after removal of the supernatant to test for reversal of the adsorption process of organisms.

3.3.4 *Total Coliform and E.coli enumeration*

Colilert[®]-18 is the U.S. EPA¹⁰⁷⁻¹¹⁰ approved method and 18-hour enzyme based test for drinking water analysis. It is also included in the Standard Methods for Examination of Water and Wastewater¹¹¹. Results were interpreted conventionally by comparing the color appearance of small and large wells of Quanti-Tray/2000 to the Quanti-Tray/2000 Comparator. The result will be negative for total coliform and E.coli, if the color (both small and large wells) of the Quanti-Tray/2000 is less yellow than the comparator. The result will be positive for total coliform in a well, if the color (both small and large wells) of the Quanti-Tray/2000 is yellow equal to or greater than the comparator. The result will be positive for E.coli, if the color (both small and large wells) of the Quanti-Tray/2000 is yellow and fluoresce equal to or greater than the comparator is observed. The number of positive small and large wells were counted (using a UV lamp for fluorescence) and referred to the IDEXX Quanti Tray/2000 Most Probable Number (MPN) table or multi well card available from the manufacturer to obtain a Most Probable Number (MPN). MPN is a statistical method that enumerates the number of cells by their patterns of growth in liquid culture media. It is interpreted to estimate count of viable cells that can be cultured or are metabolically active. The detection limit for total coliforms and E.coli is 1 organism per 100 ml.

3.4 Results

Total coliform count and E.coli counts were monitored during the photocatalytic oxidation of NOM of pre-UV Treated Wastewater. Attempts to examine source water from two Southern Alberta small systems (town of Standard and village of Gleichen) source waters were defeated by results at detection limit.

A loading of 1 g/100 ml TiO₂ under ordinary fluorescent lamps with an intensity of about 0.24 mW/cm² resulted in the inactivation to below the detection limit of bacteria (total coliform and E.coli) with a dose ≤ 80 J (Figure 3.1 and Figure 3.2). Blank experiments were carried out in the absence of photocatalyst. Repeat experiments produced parallel data with some differences in counts resulting from initial counts from the samples changing with time. Results of these experiments are also shown in Figure 3.1 and 3.2.

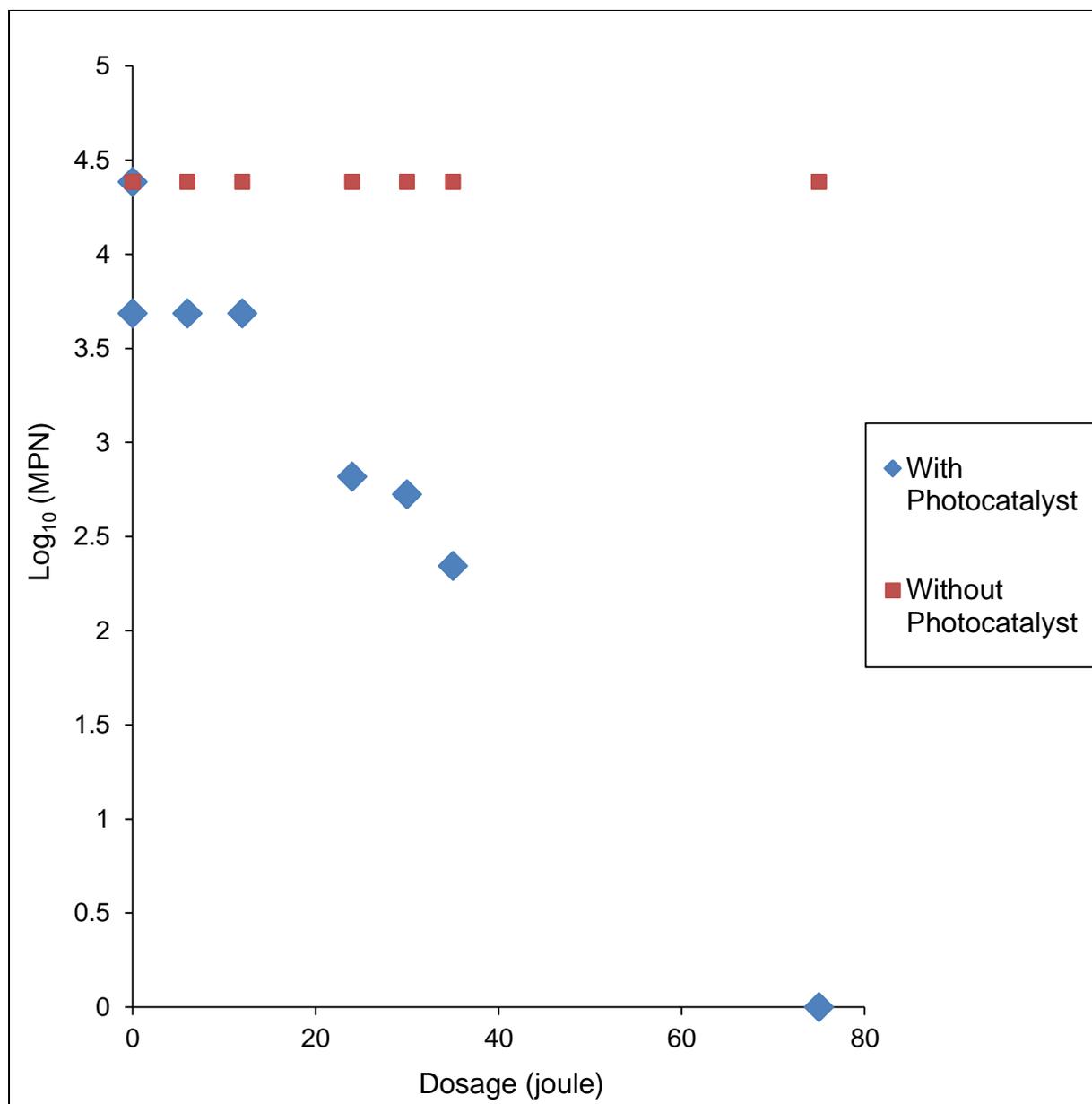


Figure 3.1. Inactivation of Total coliform (a) ◆ with TiO₂ photocatalyst and (b) ■ without TiO₂ photocatalyst. The loading of TiO₂ photocatalyst is 1 g/100 ml. Water samples have been diluted with a dilution factor of 2. Samples are irradiated under cool white fluorescent lamps.

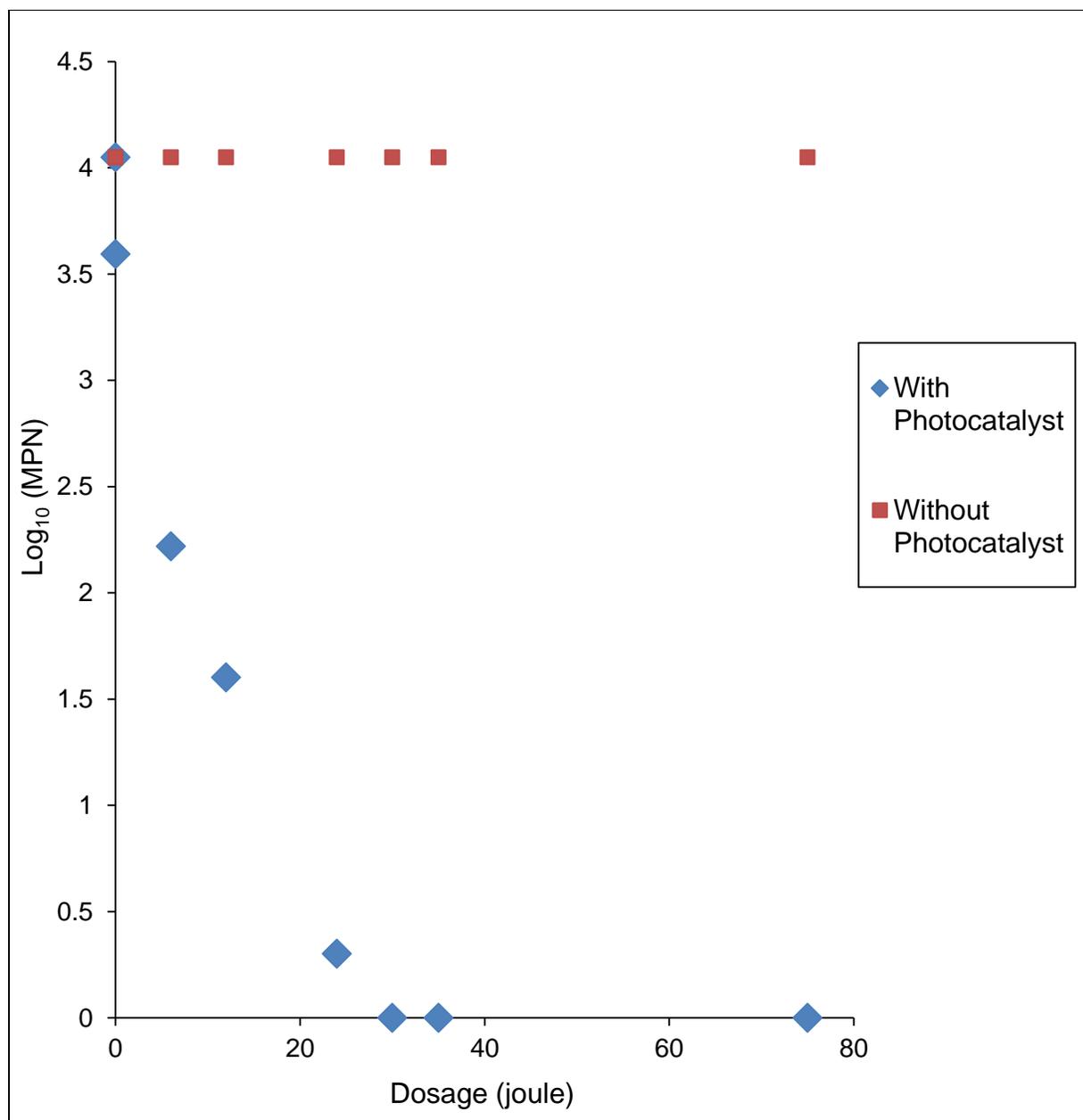


Figure 3.2. Inactivation of E.coli \blacklozenge with TiO_2 photocatalyst and \blacksquare without TiO_2 photocatalyst. The loading of TiO_2 photocatalyst is 1 g/100 ml. Water samples have been diluted with a dilution factor of 2. Samples are irradiated under cool white fluorescent lamps.

The extent of bacteria adsorption/desorption interaction with the TiO₂ surface was estimated by magnetically stirring the sample in the dark for 30 minutes. The dark adsorption shows as much as a 60-70% decrease in the count of total coliform and E.coli respectively. The bacterial population did not change beyond 30 minutes in the dark in wastewater sample demonstrating that the adsorption-desorption equilibrium with the TiO₂ surface is complete. These results are similar to those of Venieri et al.¹¹² using *Enterococcus faecalis* as a target pathogen and inactivating by UV and solar light TiO₂ photocatalysis. Adsorption plays an important role in the photocatalysis process and the decrease in the count can be explained by the adsorption of total coliform and E.coli at the surface of TiO₂. It was found that 5% of coliform and E.coli were able to reactivate metabolic activity after extraction from TiO₂ with Milli-Q water. Unfortunately this measurement does not distinguish between the extents of irreversibility of the adsorption interaction vs. the extent of bacterial inactivation as illustrated by the following two studies^{113,114}. Gogniat et al.¹¹³ reported that culturability of *E. coli* decreased in the presence of TiO₂ only after the commencement of irradiation but depended upon cells adsorbing on the photocatalyst. Especially since the Gogniat et al. experiments used UV light, generating the more oxidizing valence band hole in the photocatalyst. In contrast, Paleologou et al.¹¹⁴ reported that *E.coli* interacted with the catalyst surface in the dark and this interaction results in 61% loss of viability suggesting that the comparable loss observed here is a consequence of adsorption interaction which may, in part, be irreversible adsorption.

Post irradiation, recovery of organisms inactivated by photocatalysis was estimated by reanalyzing samples after 48 hour post irradiation equilibration in the dark at 35 °C. A

12% apparent recovery was observed for total coliform and 3% apparent recovery was observed for E.coli.

Having demonstrated that NOM adsorption and visible light absorption can sensitize inactivation of coliforms, the question arises whether there is other chemistry that might also accompany the self-sensitized oxidation of NOM (humics). Ghosh et al.⁶⁵ demonstrated coumarin dye sensitized degradation of the common pollutant model 4-chlorophenol (4-CP) under visible irradiation. Thus, an interesting question to complement the present results is a test of humic sensitized degradation of 4-CP. To answer this question degradation of 4-CP was monitored using P25 under visible light irradiation. With the aid of Dr. Maryam Izadifard, an experiment in the presence of 10 mg/L of the well characterized Suwannee river fulvic acid (SRFA) humic fraction was conducted. The results (Figure 3.3) show successful degradation of 4-CP monitored by decrease of its UV absorption bands, which was sensitized by FAs present in the system. This is a case of oxidative degradation of 4-CP; which is via superoxide radical anion production after transferring of the photoexcited electron to adsorbed molecular oxygen⁶⁵.

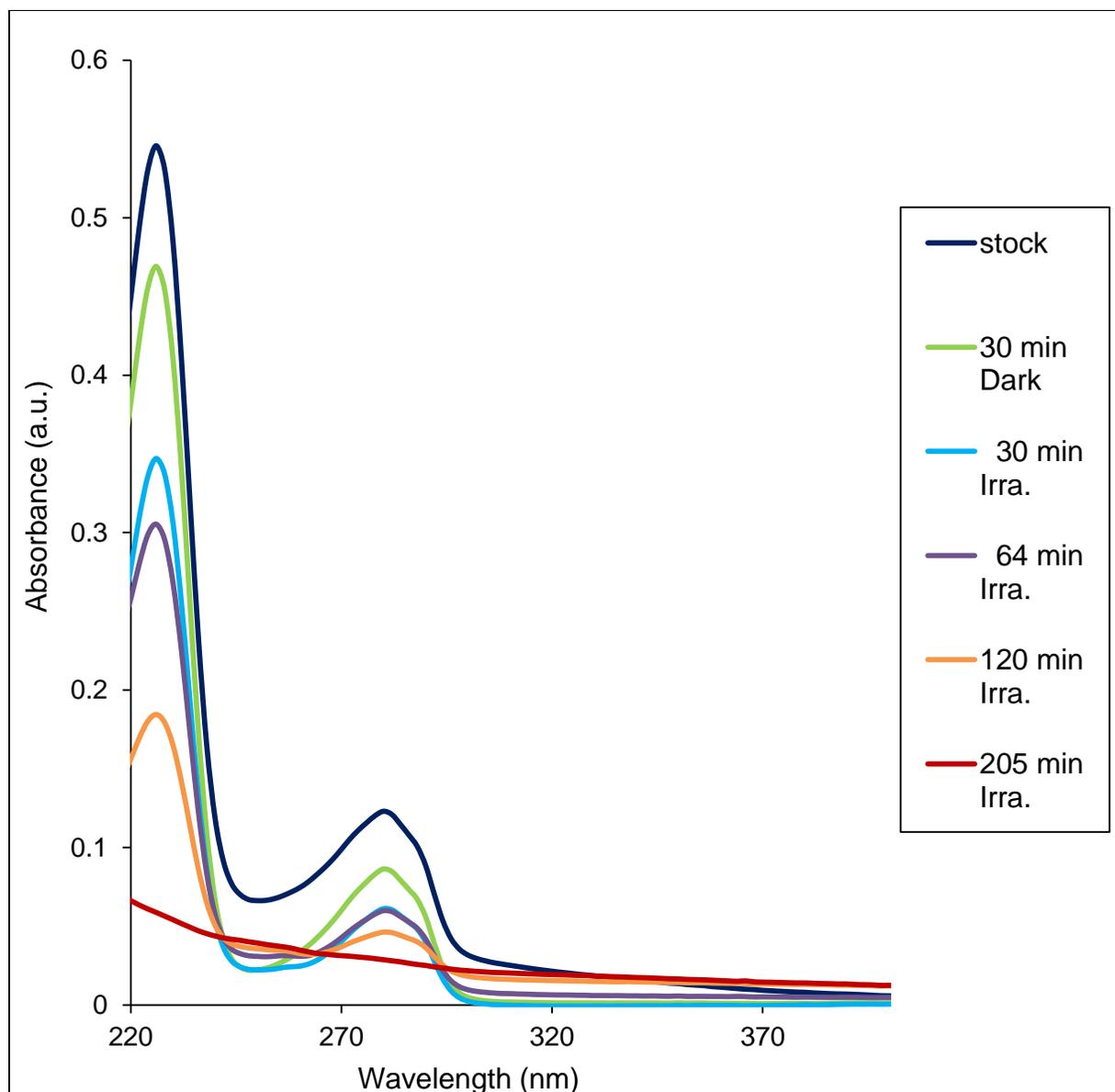


Figure 3.3. Changes in absorption spectra of 4-CP (33 ppm) upon irradiation with visible lamps in presence of FA (10 ppm) and Degussa P25 TiO₂. (From data collected by Dr. Maryam Izadifard “Application of photocatalysts and LED sources in drinking water treatment, Dr. Maryam Izadifard, Dr. Gopal Achari, Dr. C. H. Langford, submitted to Catalyst”)

3.5 Discussion

Typical curves (Figure 3.1 and 3.2 one for each target) showing the dark adsorption and irradiation effect over the period of irradiation characterizes the decrease in cell viability. There is some evidence for an induction period in the total coliform plot. During the first 10–15 min, inactivation is negligible, but subsequent decay seems to follow a log linear or first order kinetic form. Induction is expected until damage accumulates to overcome self-defense and auto repair mechanisms of bacteria involving the enzymes, catalase and superoxide dismutase (SOD)¹¹⁵. The induction period seems to be small in the E.coli curve where continuous inactivation is observed soon after irradiation initiation.

It has been generally accepted that hydroxyl radicals, derived from disproportionation of superoxide radical anion ($\cdot\text{O}_2^-$), are powerful oxidative species that can attack total coliform and E.coli cells¹¹⁶. However, literature also suggests that the other reactive species generated photocatalytically during the photosensitization with NOM, such as perhydroxyl radicals, singlet oxygen, hydrogen peroxide (H_2O_2) and organic radical cations could also contribute to inactivation¹¹⁷⁻¹¹⁹.

A straightforward mechanism for cell destruction can be postulated for this non-specific oxidative attack. Lu et al.¹²⁰ demonstrated that K^+ ion leakage was consistent with the decomposition of the cell wall and the cell membrane resulting in the loss of cell viability. If this is generalizable, cells in the presence of illuminated TiO_2/NOM , suffer outer membrane damage resulting in the increase in permeability, leakage of intracellular molecules and final cell death^{121,122}.

An effort to appraise adsorbed bacterial species residual viability was attempted by

extraction from the surface of TiO₂ and incubation. Simple bacterial cell co-aggregation with TiO₂ particles has been suggested to decrease cell survival in some species in the dark, but recovery of only a small percentage of viable cells from the surface renders the present situation ambiguous because it was not feasible to determine if all cells were separated from the TiO₂ by the wash¹¹⁴.

Repair mechanisms (photoreactivation and dark repair) have also been reported in the coliform and e.coli species resulting in their reactivation after the DNA damage caused particularly by UV 254 nm irradiation^{123,124}. When UV light (low or medium pressure mercury lamps) is used for achieving disinfection, it results in DNA damage in the bacterial cell (coliform and E.coli) leading to cell death or inactivation. But, DNA repair mechanisms have been reported¹²³. The presence of bacterial DNA repair mechanisms, which come into action upon further exposure to near UV or visible light (called photoreactivation), and lead to the reactivation and increase the number of viable microorganisms in the finished water supply even after the completion of UV-disinfection treatment process. In addition to the light repair mechanisms, dark repair mechanisms (also called nucleotide excision repair mechanism) have also been suggested to be responsible for dark DNA repair to UV- damaged cells.

In the present study of photocatalytic degradation of coliform and E.coli in visible light, cell death or inactivation has been suggested to be the result of the overall cell membrane damage. Once leakage is *sufficient*, permanent inactivation or death of cells leave no mechanism for repair as cell permeability and integrity has been lost. Nevertheless, apparent recovery has been observed for total coliform and E.coli, to the extent of 12% and 3% respectively. Obviously some initial inactivation is occurring

without cell death as just described. Another aspect to this recovery is the pathogenicity of recovered microorganisms, which was not studied in the current research work. Guo et al.¹²⁴ in their study reported percent photoreactivation for amp-resistant E.coli and the fluorescent E.coli to be 1% and 46% respectively. They observed the photoreactivated amp-resistant E.coli and fluorescent E.coli showed similar behavior when compared with the untreated bacteria.

3.6 CONCLUSIONS

The major feature identified here is the destructive effect of reactive oxygen species produced by the sensitization by natural organic matter (NOM) with TiO₂ under visible light. A significant decrease in the total coliform and E.coli count was observed in conjunction with sensitized degradation of NOM with TiO₂ photocatalyst using visible light. Upon irradiation of the TiO₂-wastewater sample, with a light dosage of < 0.8 kJ (corresponding to 0.22 kWhr/m³), total coliform and E.coli count were reduced to below detection level. There was no decrease or change observed in the count of total coliform and E.coli, when the wastewater sample was irradiated with only visible light in the absence of a TiO₂ photocatalyst. Sensitization by NOM has extended the light absorption range of TiO₂ into the visible region. This in turn produces reactive oxygen species which inactivate total coliform and E.coli. The visible light induced disinfection seems to be a promising approach in wastewater disinfection, also eliminating NOM and to some degree disinfection by-product formation, simultaneously by self-sensitization *via* NOM¹⁰⁵.

Chapter 4

Conclusions and Future Research Directions

The overarching aim of the work carried out in this thesis is to contribute to the existing state-of-the-art technology used in controlling the concentration of natural organic matter (NOM) present in drinking water. The presence of NOMs in fresh water may result in carcinogenic by products which are increasingly stringently regulated, when treated with primary disinfectants (Cl_2), thus leaving it unsuitable for drinking purposes. In addition, the work also focuses on developing novel techniques for disinfection of drinking water in small-scale water treatment units. Major conclusions and outcomes of this study are summarized below:

4.1 Self-sensitized Photocatalysis

The first part of this study investigated the degradation of NOM using TiO_2 photocatalysis under visible light (simulating solar light to a satisfactory approximation). The presence of NOM causes many undesirable physico-chemical changes in the water treatment units. In particular, it is the reaction with disinfectants (primarily Cl_2) that make NOM's presence an unwanted entity in the drinking water units. The Cl_2 reaction leads to the formation of DBPs, which are carcinogenic in nature and are regulated by Health Canada in drinking water supplies. We followed a strategy to limit the concentration of NOM (FA, a component of NOM, is reported to be a key precursor of DBPs) from various types of water sources, both lab models and real water sources from Southern Alberta³¹⁻³³. Heterogeneous photocatalysis, based on TiO_2 was applied to degrade

NOM and hence reduce the formation of DBPs. The scheme adopted in this work is an advancement on the conventional dye sensitization-TiO₂ photocatalytic process to achieve reaction under visible light.

When dyes are used for TiO₂ sensitization the excited state of the dye transfers an electron to the conduction band of TiO₂. In this study, NOM is adsorbed on the surface and acts as a sensitizer as well as the pollutant (a process here called self-sensitization). In this process, the NOM undergoes an initial oxidative step upon visible light irradiation and transfers an electron to the TiO₂ conduction band. The electron released can be captured by oxygen, resulting in the formation of superoxide radical anion, which can aid in the degradation of NOM.

Model water sample shows >90% DOC loss at irradiation dose < 1 kJ. Real water samples show reduced loss in comparison. That all “real” water samples adsorb less than the model suggests that the humic content and character of the organic matter is an important variable. The extent of dark adsorption onto TiO₂ appears to be proportional to the extent of degradation or loss of DOC upon irradiation. UV₂₅₄ absorbance values for model water sample are higher than real water samples suggesting a higher degree of aromaticity and humification. Real water samples collected from Bow river/canal aquatic systems display a deviation from the typical humic substances characteristics. This may be related to the exposure of the water to urban inputs as described in chapter 2. The weaker fluorescence spectral intensity shows a blue shifted maximum and a different pattern of decline under irradiation for NOM from the Alberta water sampling sources indicating the different composition in real or natural water samples as compared to the Model water sample. Despite the fact

that DOC concentration was reduced by 80% in all the water samples and UV₂₅₄ spectra show about 85-90% irradiation decrease in the (humic indicator) absorbance of water samples, Fluorescence spectra of two natural water sources show significant shifts from wavelength distribution of emission under 350 nm excitation characteristic of humic substances.

Photocatalytic oxidation of NOM can result in decreased THM formation. The NOM in real or natural water samples show different THM formation behavior when compared to the humic models itself. Source water from the village of Gleichen exhibited the greatest proportional decrease in THM at even lower irradiation dose. In contrast, Town of Standard water sample shows noisy and initially elevated levels of THM formation even after significant reduction of DOC. Very long irradiation was required to achieve overall significant THM prevention. This indicates that poorly TiO₂ adsorbed components can make significant contributions to THM formation (as in case of Town of Standard water sample). These poorly adsorbed components can be hydrophilic organic matter which in addition to the hydrophobic organic matter can contribute to the THM formation. These suggestions challenge that the THM precursors are mainly humic like hydrophobic acid organic matter. The wide use of humic substances as a model of photochemical degradation is not general and does not imply that all the THM precursors in natural water sources are parallel or comparable or have the same origin.

4.2 Coliform Reduction

The second part of this study sought to utilize the aforementioned process of NOM sensitization to generate reactive oxygen species and in turn inactivate pathogenic bacteria. Disinfection is the highest priority in the drinking water treatment plant and our goal was to determine if NOM reduction was accompanied by coliform reduction, allowing reduced subsequent chlorine application. Total coliform and E.coli were used as test organisms in the experiments. Most E.coli strains itself are harmless, but indicate the presence of pathogenic microorganisms since they are characteristic inhabitants of mammalian gut. The measure of hazard is recognized by this indicator parameter. A water sample contaminated with total coliform and E.coli was collected from the Bonnybrook wastewater treatment plant after biological treatment but before final UV disinfection. Water sampled from the surface water inputs to two Southern Alberta drinking water plants gives *nil* coliform counts. Initial studies have shown that NOM sensitized TiO₂ photocatalysis in the visible light was able to inactivate e.coli and total coliform to a not-detectable limit. Hence the net outcome of water treatment by the self-sensitization of NOM using TiO₂ with visible light is:

- Decrease in chlorine requirement, after decrease in NOM, which leads to reduction in DBPs concentration following treatment.
- Decrease in the coliform indicator, suggesting further decrease in chlorine requirement.

4.3 Future Research Directions

4.3.1 The process of self-sensitized / TiO_2 photocatalysis can be a potentially progressive technology for the degradation/elimination of light absorbing contaminants/pollutants (like NOM) in wastewater. In order to evaluate the applicability of self-sensitization process, a lab based experiment on waste water from a pulp and paper mill would be a good representative. The pulp and paper mill waste mostly contain recalcitrant organic matter exhibiting similar characteristics to those of humic substances (light absorbing substances / color producing compounds) and elevated levels of BOD, COD and TOC¹²⁵.

Carvalho et al.¹²⁵ have reported the effect of solar radiation on the degradation of the lignin derived organic matter from a pulp and paper industry effluent. The pulp and paper mill in this case has been using a biological wastewater treatment system based on the activated sludge process. For their research study, Carvalho et al.¹²⁵ used fulvic acid extracted from the final effluent from a kraft pulp mill and treated it with exposure to solar radiation. They analysed the degradation of humic substances by UV-VIS and fluorescence spectroscopy. They observed a typical decrease in the UV-VIS absorbance and Fluorescence spectra of the treated water suggesting the selective photodegradation of lignin derived organic compounds (humic-like substances).

The biodegradation methods currently used for treating waste are not sufficient to help pulp and paper industry. In that case, pulp mill waste containing light absorbing substances, can be treated by following the same approach as in dye sensitization / NOM self-sensitization with TiO_2 photocatalysis/visible light. The remediation method

adopted by Carvalho et al.¹²⁵ can be supplemented by the self-sensitization/TiO₂ photocatalysis/visible light for an effective and efficient degradation of the pollutants in wastewater from pulp and paper industry.

4.3.2 A properly immobilized TiO₂ photocatalyst can also improve the effectiveness of NOM self-sensitization process. The concept/approach is based on Heller and Brock's¹⁰³ coated "cenospheres", where TiO₂ was mounted by coating/immobilizing on a support like hollow glass or glass ceramic microspheres. The microbeads/microspheres were buoyant, appeared like fine sand, and were resistant to self-oxidation. These coated microspheres were used for photocatalytic oxidation of a strongly UV-absorbing crude oil layer on water. They observed 70% loss of the organic matter. They applied TiO₂ coated microspheres photocatalytic oxidation for cleaning up oil spills on water¹⁰³. We suspect self-sensitization played significant role in the Heller et al. studies. The applicability of this mounted TiO₂ photocatalyst in our applications can be investigated by an experimental bench scale set up comprising wastewater (coming from wastewater treatment plant or pulp mill waste disposal) and floating TiO₂ coated microspheres under cool white fluorescent lamps or sunlight.

4.3.3 *Potential for practical Implementation*

a) After analyzing bench scale operations for suitably mounted TiO₂/self-sensitization process on various wastewater samples with cool white fluorescent lamps or sunlight, the scheme can be practically implemented to the drinking water treatment facilities with small reservoirs.

Floating coated TiO_2 microspheres can be used in small reservoirs for drinking water treatment. Bowen Island (a small island in the regional district of Greater Vancouver has a population of 3,402 that is supplemented by another ~1500 visitors per year) is a typical example of an establishment, which can be competently served by small-scale water treatment systems (http://www.bimbc.ca/municipal_water_systems). Bowen island municipality owns and operates seven water systems around the island, serving up to 1,000 connections each. Out of seven water systems, only two of them use a shallow reservoir. In this particular case, coated TiO_2 microspheres can be spread all over the reservoir dimension and the effectiveness of NOM self-sensitization under sunlight can be determined. NOM present in water acts as a sensitizer as well as the pollutant and solar light as a source of photons. The absorption of light by NOM would trigger the sensitization process resulting in superoxide radical anion that would degrade NOM. As a result of aforementioned application to the water treatment units, lower amount of NOM will be present in the water undergoing chlorination resulting in lower amount of chlorine requirement and low concentration of DBPs in the treated drinking water going to distribution channels. With the application of self-sensitization, the reservoir water can be pre-treated with coated TiO_2 microspheres/NOM/sunlight “self-sensitization” process before sending it through the subsequent processes of water treatment.

b) A more generally useful system is possible where a pilot scale flow through reactor can be introduced and LEDs (a blue LED reactor) can be used. LEDs (light emitting diodes) are emerging technologies in the field of light sources that can be used as a much better choice over compact fluorescent lamps or cool white lamps (simulating

sunlight). LED based reactors are candidates to mitigate the high cost of electricity, the key operational variable in the widely used UV disinfection method. Major advantages of using LED light sources are it is inexpensive compact and robust of design, long lamp life, without toxic components (mercury free), no warm up time, high current to light conversion efficiency with little heating and smaller than comparable intensity lamp arrays^{65,126}. The power output and dollar cost get much more favourable as we go into the longer wavelength of LED light sources. They permit matching the output of the lamp to the absorption spectra of active species and would be very useful in a small-scale drinking water treatment unit because the size and unit cost of LED arrays scale linearly with size and don't exhibit high unit cost at small scale as do other technologies. Where the concentration of pollutant NOM is relatively low, usually between 5-7 ppm as it is in the surface water sources photochemical processes using LEDs are attractive options^{6,31}. For off grid operation in remote rural areas, a DC powered LED reactor can be powered by a photovoltaic battery set up that lasts for approximately 30 years. Higher efficiency, lower cost LEDs are available in the blue region/longer wavelength region than in the near UV, which make the use of LEDs appropriate in the aforementioned scheme of TiO₂ photocatalysis (visible illumination, self-sensitization). Design and demonstration of an LED reactor is a project in these laboratories.

c) As a supplement to existing biological treatment for industrial wastewater, Alfano et al.¹²⁷ built a useful simple low cost solar driven photocatalytic system for Volkswagen industrial waste. The present system would have an advantage of using larger part of solar spectrum. Almost a decade ago, the Volkswagen AG factories in Wolfsburg (Germany), installed a pilot plant to treat biologically pretreated industrial wastewaters

with high COD (chemical oxygen demand) and TOC (total organic carbon). The pilot plant was conceptualized on the basis of laboratory and bench-scale TiO₂ photocatalytic experiments performed by Dillert et al.¹²⁸ on the biologically pretreated industrial wastewater. In the Volkswagen AG pilot plant, the combination of solar light and TiO₂ photocatalyst-industrial wastewater slurry triggers the reaction process and after a desired time, a decrease in the concentration of the organic pollutants (COD & TOC) is observed. A pilot photoreactor system similar to the one used at Volkswagen plant in Germany and Brazil, can be applied to degrade NOM in small reservoirs for drinking water treatment or wastewater disposal from pulp and paper mill.

4.3.4 There is clear evidence showing the bacterial inactivation by solar photocatalytic technique. The solar TiO₂ photocatalysis demonstrates that the bacterial inactivation is a complementary advantage to the NOM degradation. The study done here was focused in controlling indicator microorganisms, i.e, total coliform and E.coli. A solar light/LED light-TiO₂ photocatalytic system should be evaluated for challenging microorganisms like *Bacillus subtilis*. The vegetative and spore forms of *Bacillus subtilis* are more resistant to treatment methods in drinking water treatment plants. A practical laboratory experimental design based on the application of TiO₂ photocatalysis/NOM self-sensitization/LED lamps would add significantly to evidence of capacity to disinfect water.

Supplementary Materials

Supplementary Material for Chapter II

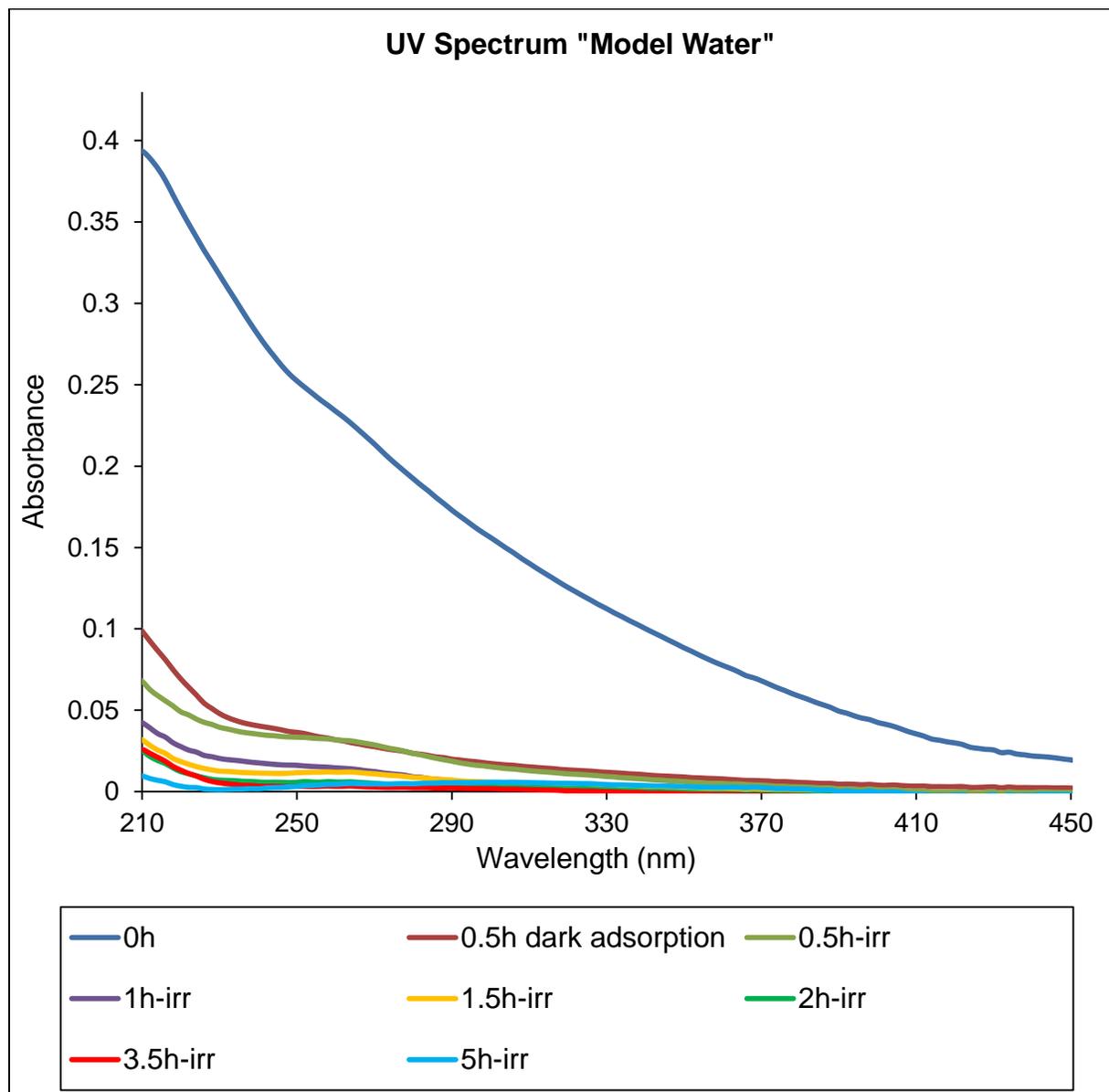


Figure 2. S1. UV absorbance spectra of “Model water” sample containing NOM as a function of wavelength. The loading of TiO_2 is 1 g/100ml. Model water is a lab based water sample prepared by adding Suwannee River Fulvic Acid (IHSS). Samples are irradiated under cool white fluorescent lamps.

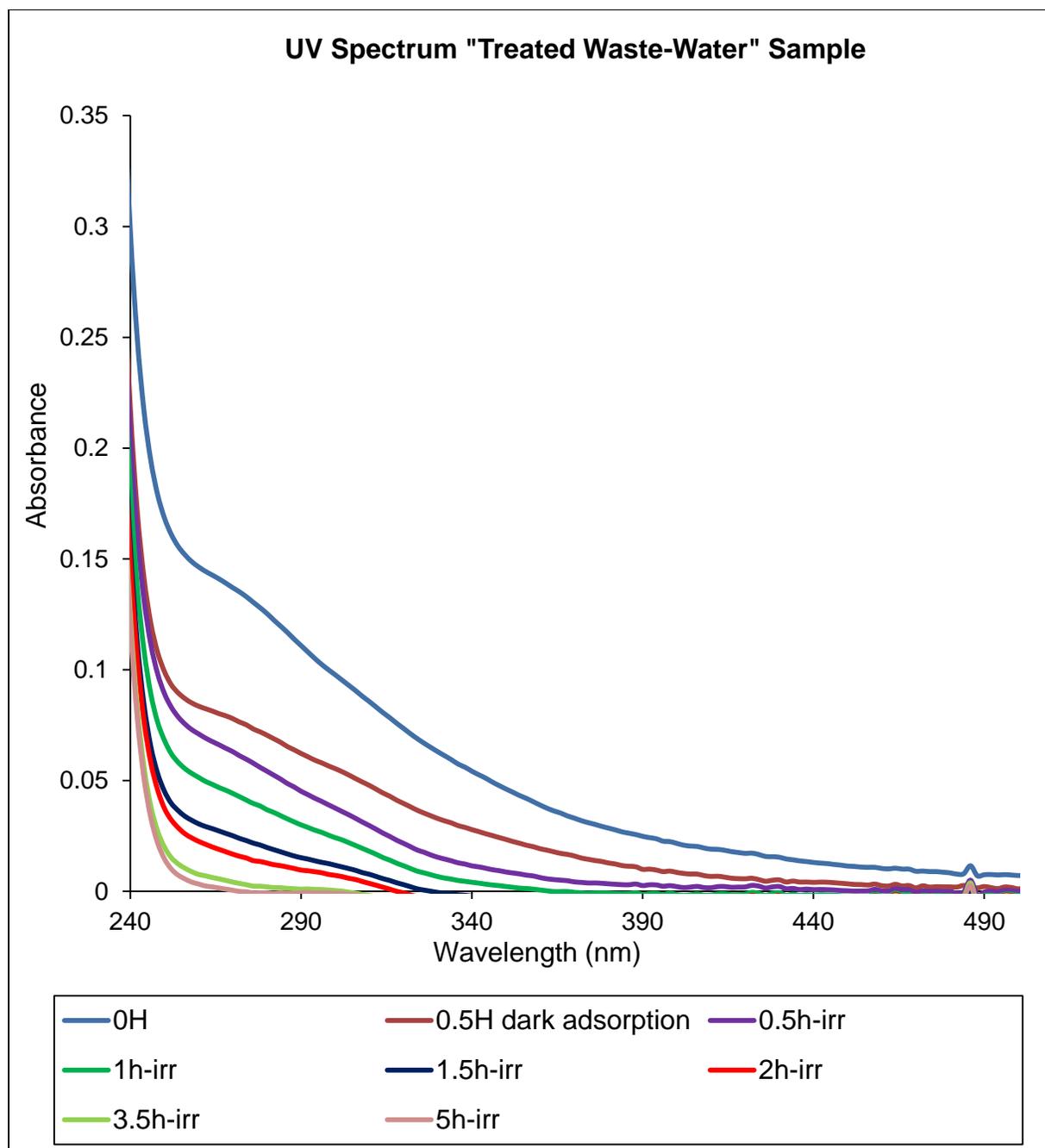


Figure 2. S2. UV absorbance spectra of “Treated waste water” sample containing NOM as a function of wavelength. The loading of TiO_2 is 1 g/100ml. Samples are irradiated under cool white fluorescent lamps.

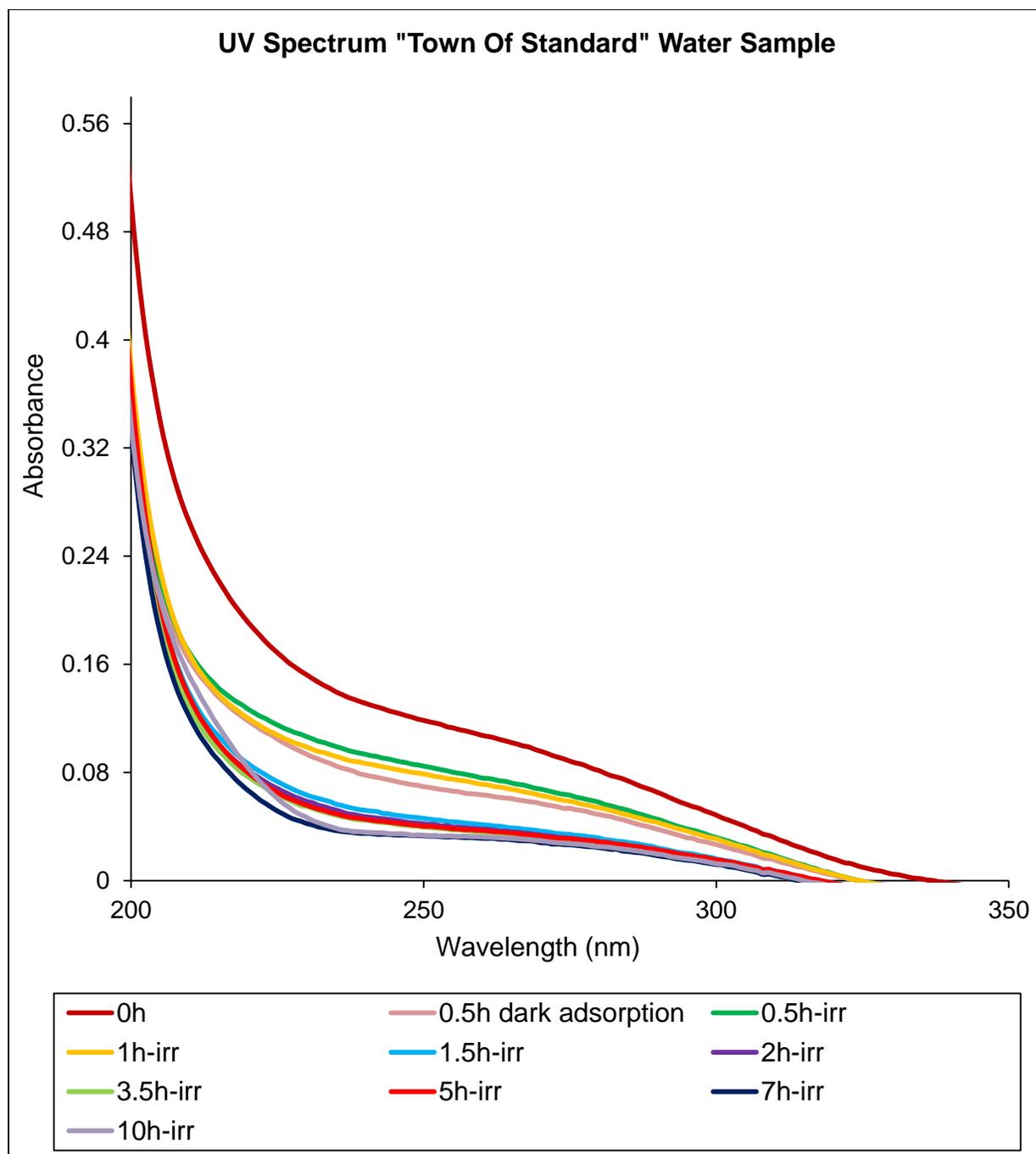


Figure 2. S3. UV absorbance spectra of “Town of Standard” water sample containing NOM as a function of wavelength. The loading of TiO_2 is 1 g/100ml. Samples are irradiated under cool white fluorescent lamps.

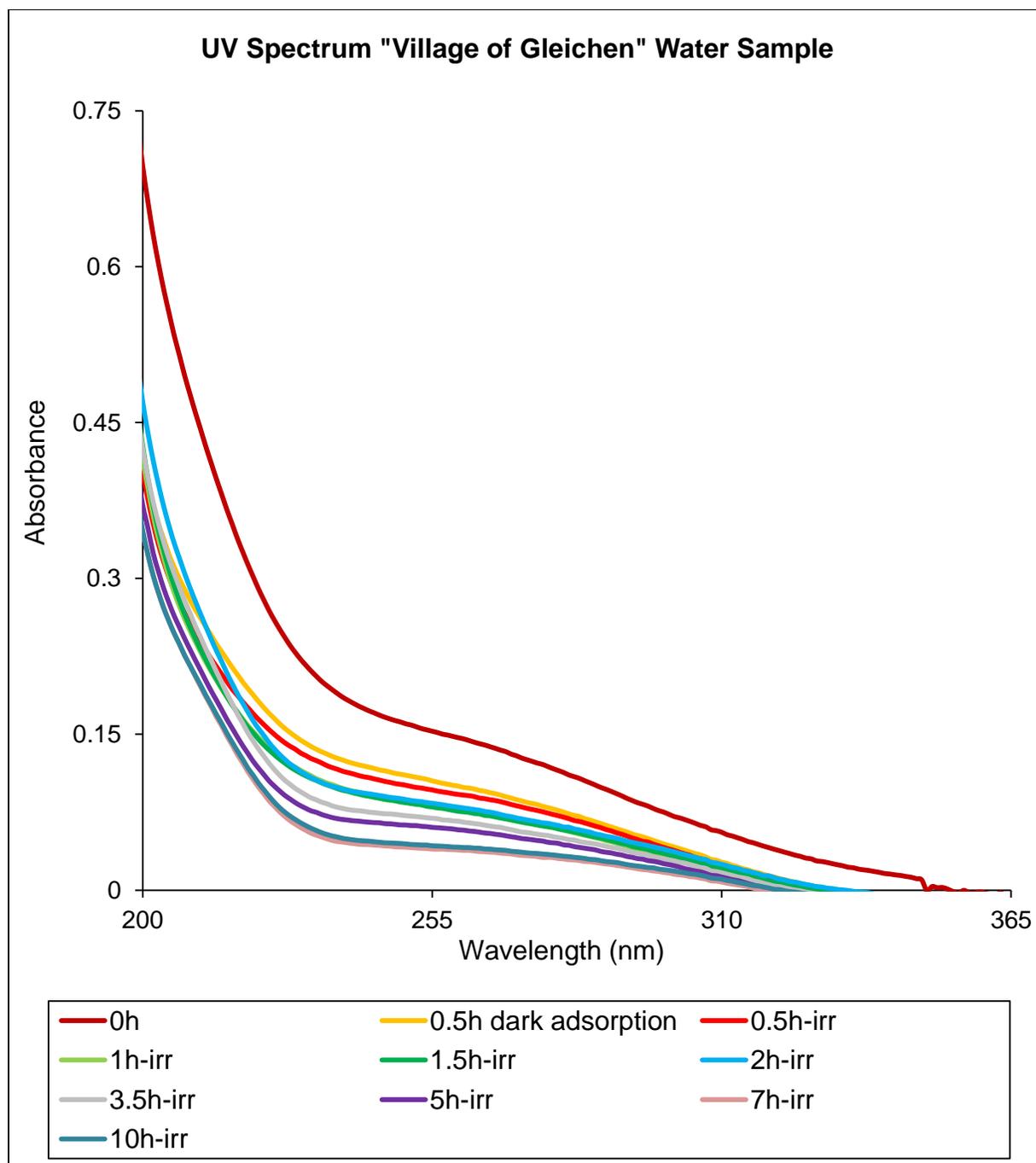


Figure 2. S4. UV absorbance spectra of "Village of Gleichen" water sample containing NOM as a function of wavelength. The loading of TiO_2 is 1 g/100ml. Samples are irradiated under cool white fluorescent lamps.

APPENDIX- 1A

Appendix- 1A provides some information about the preliminary experiments performed to analyze the role of desorbed species from the surface of TiO₂. The species adsorbed on the surface of TiO₂ were extracted using 0.1M sodium bicarbonate solution to give some understanding of materials adsorbed on the surface of TiO₂.

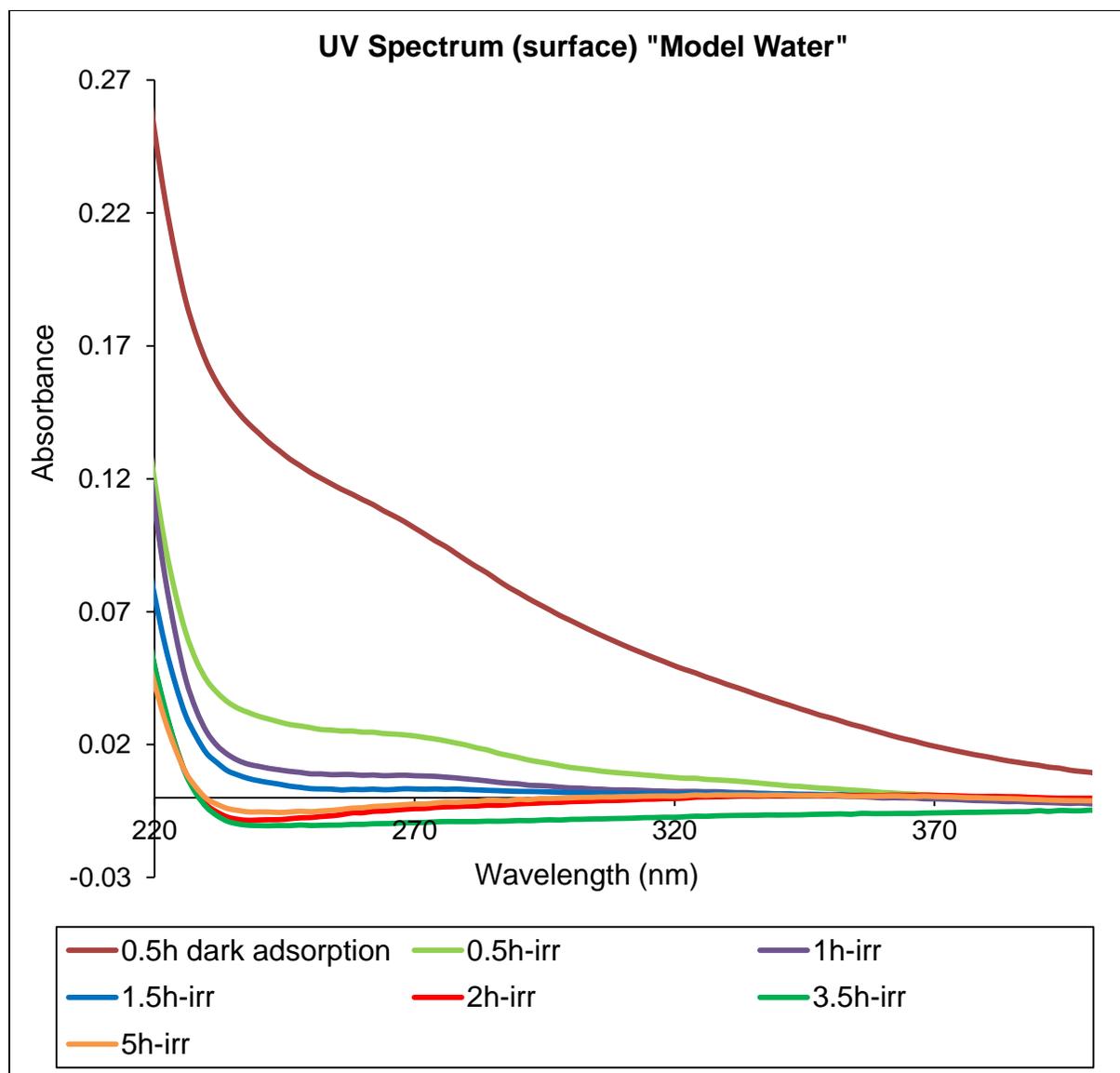


Figure 1A.1. UV absorbance spectra of “Model water” sample containing NOM (desorbed from the surface of TiO_2) as a function of wavelength. Model water is a lab based water sample prepared by adding Suwannee river fulvic acid (IHSS). The loading of TiO_2 is 1 g/100ml. Samples are irradiated under cool white fluorescent lamps. NOM species are desorbed from the TiO_2 surface using 0.1 M sodium bicarbonate.

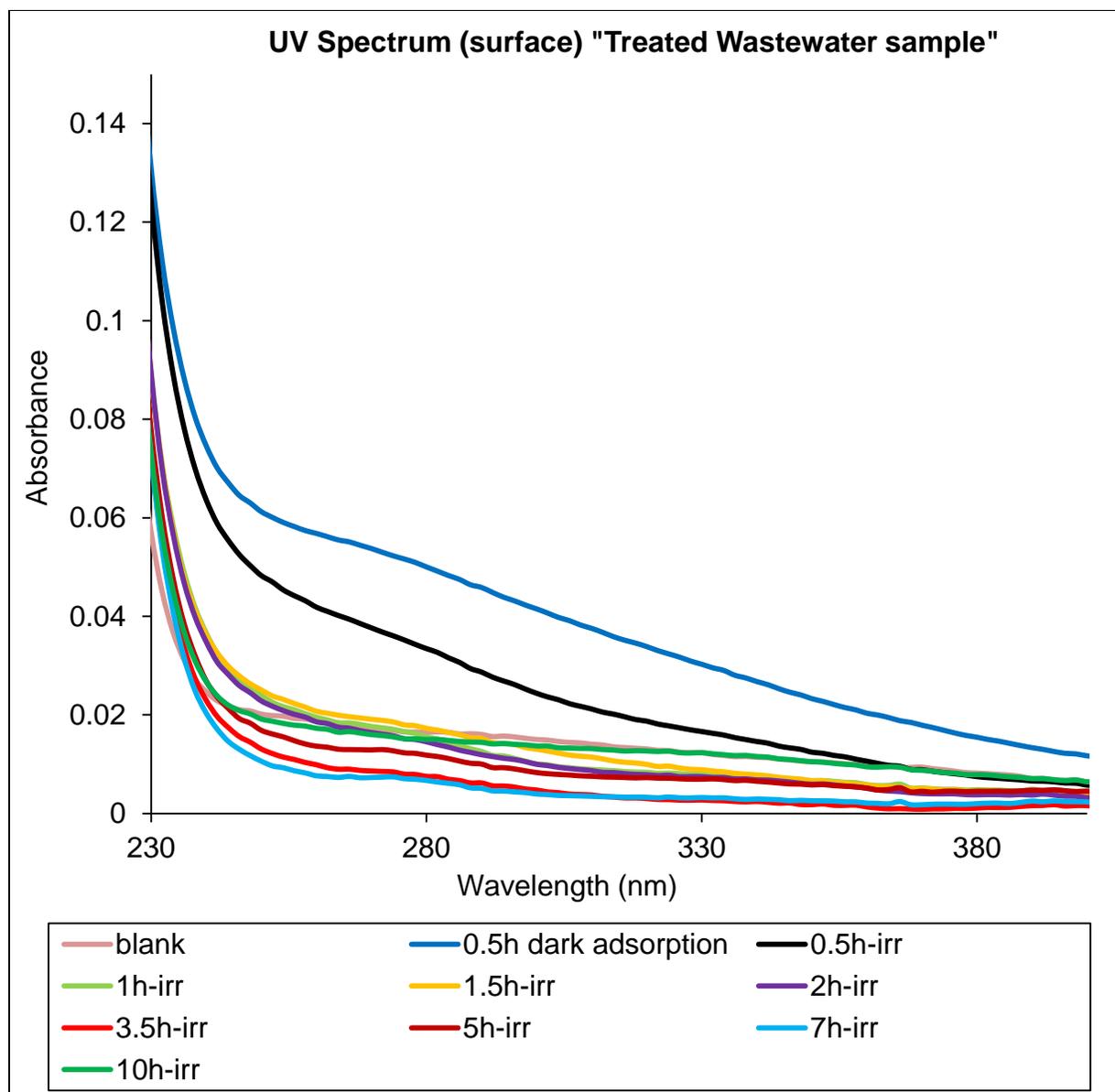


Figure 1A.2. UV absorbance spectra of “Treated wastewater” sample containing NOM (desorbed from the surface of TiO_2) as a function of wavelength. The loading of TiO_2 is 1 g/100 ml. Samples are irradiated under cool white fluorescent lamps. NOM species are desorbed from the TiO_2 surface using 0.1 M sodium bicarbonate.

APPENDIX- 1B

Appendix- 1B acknowledges the role of contributors to this work. Chapter 2 and 3 are co-authored by Dr. C. H. Langford and Dr. Gopal Achari. The co-authors contributed to the planning and interpretation of the research work performed. Experimental work except for 4-CP (pg. 92) were performed by the author, as was the drafting of the paper. 4-CP experiment was done by Dr. Maryam Izadifard.

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