

**ASSESSING THE PERFORMANCE OF A UV/H<sub>2</sub>O<sub>2</sub> PROCESS FOR REMOVING TOC  
FROM PETROLEUM REFINERY WASTEWATER AND THE RESPIROMETRIC  
EFFECTS OF ADDING UV/H<sub>2</sub>O<sub>2</sub> TREATED WASTEWATER TO ACTIVATED  
SLUDGE FROM THE REFINERY WWTP BIOLOGICAL TREATMENT PROCESS**

by

MARK KNIGHT, P.Eng.

B.Sc.E. in Chemical Engineering with Professional Internship

Queen's University, Kingston, Ontario, Canada, 2008

A Thesis

presented to Ryerson University

in partial fulfillment of the requirements

for the degree of

Master of Applied Science

in the Program of

Environmental Applied Science and Management

Toronto, Ontario, Canada, 2014

©Mark Knight, 2014

## **AUTHOR'S DECLARATION FOR ELECTRONIC SUBMISSION OF A THESIS**

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I authorize Ryerson University to lend this thesis to other institutions or individuals for the purpose of scholarly research.

I further authorize Ryerson University to reproduce this thesis by photocopying or by other means, in total or in part, at the request of other institutions or individuals for the purpose of scholarly research.

I understand that my thesis may be made electronically available to the public.

## ABSTRACT

### **Assessing the Performance of a UV/H<sub>2</sub>O<sub>2</sub> Process for Removing TOC from Petroleum Refinery Wastewater and the Respirometric Effects of Adding UV/H<sub>2</sub>O<sub>2</sub> Treated Wastewater to Activated Sludge from the Refinery WWTP Biological Treatment Process**

Mark Knight, P.Eng.

Master of Applied Science

Environmental Applied Science and Management

Ryerson University

2014

The treatment of petroleum refinery wastewater was studied using a bench scale ultraviolet/hydrogen peroxide (UV/H<sub>2</sub>O<sub>2</sub>) process. The highest treatment performance of the bench scale UV/H<sub>2</sub>O<sub>2</sub> process to reduce the total organic carbon (TOC) from the petroleum refinery wastewater took place at a reaction time of 45 min and a pH of 5.0. A three factor analysis of variance (ANOVA) analysis verified that the initial H<sub>2</sub>O<sub>2</sub>/TOC molar ratio did not have a significant effect on the bench scale UV/H<sub>2</sub>O<sub>2</sub> process treatment performance. The effects of adding UV/H<sub>2</sub>O<sub>2</sub> treated petroleum refinery wastewater to activated sludge microorganisms from the refinery WWTP biological treatment process was studied using respirometry. Overall, the UV/H<sub>2</sub>O<sub>2</sub> treated refinery wastewater inhibited the refinery activated sludge microorganisms. This occurred when the raw refinery wastewater was treated with a UV/H<sub>2</sub>O<sub>2</sub> process for 45 min, with an initial H<sub>2</sub>O<sub>2</sub>/TOC molar ratio of 1.7 mol H<sub>2</sub>O<sub>2</sub>/mol C, an initial H<sub>2</sub>O<sub>2</sub> concentration of 202 mg H<sub>2</sub>O<sub>2</sub>/L and a pH of either 5 or 7.

**Keywords:** Petroleum refinery wastewater treatment, UV/H<sub>2</sub>O<sub>2</sub> process, wastewater treatment performance, inhibition of activated sludge, respirometry

## **ACKNOWLEDGMENTS**

I would first like to acknowledge my supervisor, Dr. Mehrab Mehrvar, of the Department of Chemical Engineering at Ryerson University for his guidance, assistance and support through this research. I would also like to acknowledge the support of the Natural Sciences and Engineering Research Council of Canada (NSERC) and Ryerson University.

I would also like to thank everyone at Imperial Oil, Suncor Energy, GE Water & Process Technologies, and the Water Environment Association of Ontario (WEAO) who has and continues to support, mentor, and encourage me to pursue my passion.

Finally, I would like to thank my fiancée Brooke Harrison for her unwavering love and support over these past many years. I could not have done this without you.

## TABLE OF CONTENTS

AUTHOR'S DECLARATION FOR ELECTRONIC SUBMISSION OF A THESIS .....	ii
ABSTRACT.....	iii
ACKNOWLEDGMENTS .....	iv
TABLE OF CONTENTS.....	v
LIST OF TABLES .....	vii
LIST OF FIGURES .....	viii
INTRODUCTION .....	1
LITERATURE REVIEW .....	4
2.1 PETROLEUM REFINERY WATER USE AND WASTEWATER GENERATION .....	4
2.2 CURRENT CANADIAN REGULATIONS FOR REFINERY LIQUID EFFLUENTS.....	10
2.3 BIOLOGICAL WASTEWATER TECHNOLOGY FOR A REFINERY WWTP.....	14
2.4 ADVANCED OXIDATION PROCESS TECHNOLOGY FOR A REFINERY WWTP .....	15
MATERIALS AND METHODS.....	24
3.1 MATERIALS.....	24
3.1.1 Petroleum Refinery Wastewater and Activated Sludge Samples.....	24
3.1.2 Chemicals.....	25
3.2 EXPERIMENTAL LABORATORY SETUP.....	25
3.3 EXPERIMENTAL PROCEDURE AND ANALYTICAL TECHNIQUES .....	26
3.3.1 Experimental Procedure.....	26
3.3.2 Experimental Design.....	28
3.3.3. Respirometry Testing.....	29
RESULTS AND DISCUSSION .....	31
4.1 INITIAL EXPERIMENTAL TESTING OF A UV/H <sub>2</sub> O <sub>2</sub> PROCESS TO TREAT PETROLEUM REFINERY WASTEWATER .....	31
4.2 ADDITIONAL EXPERIMENTAL TESTING TO IMPROVE THE PERFORMANCE OF A UV/H <sub>2</sub> O <sub>2</sub> PROCESS TO TREAT PETROLEUM REFINERY WASTEWATER.....	38
4.3 ASSESSING THE EFFECTS OF ADDING UV/H <sub>2</sub> O <sub>2</sub> TREATED PETROLEUM REFINERY WASTEWATER TO REFINERY WWTP ACTIVATED SLUDGE .....	45
CONCLUSIONS AND RECOMMENDATIONS .....	60
5.1 CONCLUSIONS.....	60

5.2 RECOMMENDATIONS .....	63
APPENDICES .....	66
APPENDIX A: COD/TOC CORRELATION CALCULATIONS.....	66
APPENDIX B: CHARACTERISTICS OF PETROLEUM REFINERY WASTEWATER THROUGHOUT LITERATURE .....	68
APPENDIX C: RAW DATA FOR ONTARIO PETROLEUM REINERY’S AVERAGE MO NTHLY EFFLUENT TOC MASS LOADING.....	70
APPENDIX D: BIOLOGICAL TECHNOLOGY FOR PETROLEUM REFINERY WASTEWATER TREATMENT .....	72
APPENDIX E: CHEMICAL WASTEWATER TREATMENT TECHNOLOGY FOR PETROLEUM REFINERY WASTEWATER.....	74
APPENDIX F: AVERAGE CONCENTRATION CALCULATION .....	75
APPENDIX G: CONCENTRATION STANDARD DEVIATION CALCULATION .....	75
APPENDIX H: OUTLINE OF INITIAL EXPERIMENTAL TESTING RUNS .....	76
APPENDIX I: RAW TOC MEASUREMENT DATA FOR INITIAL EXPERIMENTS.....	76
APPENDIX J: OUTLINE OF INITIAL EXPERIMENTAL TESTING RUNS .....	77
APPENDIX K: RAW TOC MEASUREMENT DATA FOR ADDITIONAL EXPERIMENTS .....	78
APPENDIX L: OXIDATION OF SULPHIDE COMPOUNDS .....	80
APPENDIX M: FOOD TO MICROORGANISM (F/M) RATIO CALCULATION.....	83
APPENDIX N: SUNCOR MISSISSAUGA REINERY’S AVERAGE EFFLUENT TOC CONCENTRATION.....	83
REFERENCES .....	85

## LIST OF TABLES

Table 2.1: Petroleum Refinery Wastewater Types and Sources .....	4
Table 2.2: Biological Reactions That Can Occur During a BOD Test .....	6
Table 2.3: Overview of Characteristic BOD Curves (Eckenfelder, 2000).....	6
Table 2.4: Summary of Characteristics of Petroleum Refinery Wastewater Throughout Literature .....	8
Table 2.5: Canadian Petroleum Refinery Wastewater Regulations .....	10
Table 2.6: Recommended Petroleum Refinery Wastewater Treatment Technology .....	10
Table 2.7: Biological Technology for Petroleum Refinery Wastewater Treatment .....	14
Table 2.8: Overview of Chemical Wastewater Treatment Technology for Petroleum Refinery Wastewater .....	16
Table 2.9: Organic Compound Degradation Types .....	17
Table 2.10: Theoretical Fractionation between Carbonic Acid, Bicarbonate and Carbonate Ions .....	19
Table 3.1: Typical Range of Wastewater Parameters for Mississauga Refinery WWTP Biological Treatment Unit .....	25
Table 3.2: 2 <sup>3</sup> Factorial Design Input Data for the Initial Experimental Testing of a UV/H <sub>2</sub> O <sub>2</sub> Process to Treat Petroleum Refinery Wastewater .....	28
Table 3.3: 3 <sup>3</sup> Factorial Design Input Data for the Additional Experimental Testing of a UV/H <sub>2</sub> O <sub>2</sub> Process to Treat Petroleum Refinery Wastewater .....	29
Table 3.4: Respirometry Testing Experimental Design .....	30
Table 4.1: 3 Factor ANOVA Analysis Results for the Initial Experimental Testing of a UV/H <sub>2</sub> O <sub>2</sub> Process to Treat Petroleum Refinery Wastewater .....	33
Table 4.2: 3 Factor ANOVA Analysis Results for the Additional Experimental Testing of a UV/H <sub>2</sub> O <sub>2</sub> Process to Treat Petroleum Refinery Wastewater .....	41
Table 4.3: Respirometry Testing and Experimental Results .....	48

## LIST OF FIGURES

Figure 2.1: Characteristic BOD Curves (Adapted from Eckenfelder, 2000) .....	7
Figure 2.2: Relationship between Oxygen and Carbon Wastewater Characterization Parameters (Ford <i>et al.</i> 1971) .....	9
Figure 2.3: Typical Configuration of a Petroleum Refinery WWTP (Adapted from WEF 2008).....	11
Figure 2.4: Ontario Petroleum Refineries Average Effluent TOC Mass Loading from 2008 through 2011 .....	13
Figure 2.5: Theoretical Fractionation between Carbonic Acid, Bicarbonate and Carbonate Ions (Adapted from Chapra, 2008).....	21
Figure 3.1: Laboratory Set-up of UV/H <sub>2</sub> O <sub>2</sub> Process .....	26
Figure 4.1: TOC Removal of Petroleum Refinery Wastewater Treated by a UV/H <sub>2</sub> O <sub>2</sub> Process during the Initial Experiments.....	32
Figure 4.2: Main Effects Plot for the Reaction Time, Initial H <sub>2</sub> O <sub>2</sub> /TOC molar ratio, and pH for the Initial Experimental Testing of a UV/H <sub>2</sub> O <sub>2</sub> Process to Treat Petroleum Refinery Wastewater .....	34
Figure 4.3: Interaction Effect Plot for the Reaction Time, Initial H <sub>2</sub> O <sub>2</sub> /TOC molar ratio, and pH for the Initial Experimental Testing of a UV/H <sub>2</sub> O <sub>2</sub> Process to Treat Petroleum Refinery Wastewater .....	35
Figure 4.4: TOC Removal of Petroleum Refinery Wastewater Treated by a UV/H <sub>2</sub> O <sub>2</sub> Process during Additional Experiments .....	40
Figure 4.5: Main Effects Plot for the Reaction Time, Initial H <sub>2</sub> O <sub>2</sub> /TOC molar ratio, and pH for the Additional Experimental Testing of a UV/H <sub>2</sub> O <sub>2</sub> Process to Treat Petroleum Refinery Wastewater .....	42
Figure 4.6: Interaction Effect Plot for the Reaction Time, Initial H <sub>2</sub> O <sub>2</sub> /TOC molar ratio, and pH for the Additional Experimental Testing of a UV/H <sub>2</sub> O <sub>2</sub> Process to Treat Petroleum Refinery Wastewater .....	43
Figure 4.7: Respirometry Experimental Results. ....	47
Figure 4.8: Summary of Respirometry Experimental Results. ....	49
Figure 4.9: Suncor Mississauga Refinery's Average Effluent TOC from 2004 through 2011 .....	58



# CHAPTER 1

## INTRODUCTION

Petroleum refineries use large quantities of water for cooling processes, desalting processes and stripping steam (Al Zarooni and Elshorbagy, 2006; Llop *et al.* 2009) which in turn generate large volumes of wastewater (Rebhun and Galil, 1988). Refinery wastewater can contain a variety of biodegradable, inhibitory and toxic organic and inorganic pollutants (Coe, 1952; Ruggles, 1959; Mahendrakarn and Viraraghavan, 1996; Juang *et al.* 1997; Al Zarooni and Elshorbagy, 2006; Wagner and Nicell, 2001; Galil and Wolf, 2001; Shokrollahzadeh *et al.*, 2008; Llop *et al.* 2009) so a refinery's liquid effluent is regulated to meet a specific quality standard before it can be discharged to the environment. The main effluent regulation for refineries in Ontario is Ontario Regulation 537/93 the Municipal Industrial Strategy for Abatement (MISA) Effluent Monitoring and Effluent Limits for the Petroleum Sector.

The two main goals of Ontario's MISA regulations were to create a comprehensive pollution control program to reduce all municipal and industrial waste loadings and to virtually eliminate the discharge of toxic contaminants to Ontario's waterways (Ontario, 1988). MISA is a command-and-control policy where a permit is issued by the provincial government to each industrial facility that discharges effluent to a body of surface water (MacDonald and Lintner, 2010). MISA is also a technology based standard (TBS) since each permit is based on pollution control technologies for a specific industry (Dupuy, 1997).

A typical petroleum refinery wastewater treatment plant (WWTP) uses a series of physical, chemical and biological treatment technologies to remove contaminants from the wastewater. Biological treatment by an activated sludge process is commonly used to treat petroleum refinery wastewater since it is generally the most economical method for reducing both wastewater toxicity and dissolved organic constituents (Qin *et al.* 2007). However, petroleum refinery wastewater often contains a high concentration of compounds that could be toxic or inhibit the microorganisms in the biological treatment unit (Juang *et al.* 1997). A sudden load of high strength, non-biodegradable or toxic wastewater can lead to a WWTP discharging effluent that exceeds regulatory limits or even results in the failure of the biological treatment unit. This would require long periods of time to re-establish a reliable activated sludge which can impact the throughput of upstream refinery production units (Tyagi *et al.* 1992; Chavan and Mukherji, 2008). Therefore, additional advanced treatment technology may be required to degrade these types of compounds. One promising area of research is the set of advanced oxidation processes (AOPs).

AOPs are a type of advanced wastewater technology that are effective at treating wastewater that contains non-biodegradable, inhibitory, or toxic compounds (Tabrizi and Mehrvar, 2004). The main advantage of AOPs is that the organic compounds in the wastewater can be completely converted to water and carbon dioxide without generating a residual solid waste by-product (Tabrizi and Mehrvar, 2004). An important disadvantage of AOPs is that the capital and operating costs are usually much higher when compared to conventional biological treatment processes (Tabrizi and Mehrvar, 2004).

While the literature does show that AOPs are effective at treating industrial wastewater, there are very few examples of treating actual petroleum refinery wastewater, none of this

literature is from Canada, and none of this literature assesses the effects of adding UV/H<sub>2</sub>O<sub>2</sub> treated petroleum refinery wastewater to activated sludge microorganisms from the refinery WWTP biological treatment process (Niegowski, 1956; Juang *et al.* 1997; Adeyinka and Rim-Rukeh, 1999; Huang *et al.* 1999; Andereozzi *et al.* 2000; Lin *et al.* 2001; Wagner and Nicell, 2001; Stepnowski *et al.* 2002; Mohammadzadeh *et al.* 2004; Chidambara and Quen, 2005; Saïen and Nejati, 2007; Ting *et al.* 2007).

There are two objectives to this work in order to evaluate if a UV/H<sub>2</sub>O<sub>2</sub> process could be used as a pre-treatment process for a biological treatment unit at a refinery WWTP. The first objective is to assess the performance of a UV/H<sub>2</sub>O<sub>2</sub> process to treat actual petroleum refinery wastewater. This will be accomplished by treating actual petroleum refinery wastewater with a bench scale UV/H<sub>2</sub>O<sub>2</sub> process. The performance of the UV/H<sub>2</sub>O<sub>2</sub> process will be assessed as its ability to remove soluble organic compounds measured as total organic carbon (TOC). The other objective is to assess the effects of adding UV/H<sub>2</sub>O<sub>2</sub> treated petroleum refinery wastewater to activated sludge microorganisms from the refinery WWTP biological treatment process. The effects of adding the UV/H<sub>2</sub>O<sub>2</sub> treated petroleum refinery wastewater will be assessed as the amount of oxygen consumed by the activated sludge microorganisms using respirometry.

# CHAPTER 2

## LITERATURE REVIEW

### 2.1 PETROLEUM REFINERY WATER USE AND WASTEWATER GENERATION

Petroleum refineries use large quantities of water for cooling processes, desalting processes and stripping steam (Al Zarooni and Elshorbagy, 2006; Llop *et al.* 2009) which in turn generate large volumes of wastewater (Rebhun and Galil, 1988). Since the volume and composition of wastewater depends on the refinery size and process configuration (Al Zarooni and Elshorbagy, 2006), sources of refinery wastewater can be classified as either clean water, oily water, or process water (McKinney, 1967). Details of each source are outlined in Table 2.1.

**Table 2.1: Petroleum Refinery Wastewater Types and Sources**

(Adapted from Coe, 1952; Ruggles, 1959; McKinney, 1967; Mahendrakarn and Viraraghavan, 1996; Galil and Wolf, 2001; Wagner and Nicell, 2001; Al Zarooni and Elshorbagy, 2006; Chavan and Mukherji, 2008; Shokrollahzadeh *et al.* 2008; WEF 2008; Llop *et al.* 2009).

WATER TYPE	WATER SOURCES	PRIMARY CONSTITUENTS
Clean Water	<ul style="list-style-type: none"><li>• Cooling Water</li><li>• Boiler Blow Down</li><li>• Storm Water</li></ul>	Soluble and Non-soluble Inorganic Compounds
Oily Water	<ul style="list-style-type: none"><li>• Tank Drainage</li><li>• Equipment Leaks/Spills</li><li>• Vessel Washings</li></ul>	Non-soluble Organic Compounds
Process Water	<ul style="list-style-type: none"><li>• Desalting Wash Waters</li><li>• Stripped Sour Water</li><li>• Catalytic Cracking Rundown</li><li>• Reformer Regenerator Wash Waters</li><li>• Isomerization Caustic Wash Waters</li><li>• Process Leaks and Drainage</li></ul>	Soluble and Non-soluble Biodegradable, Recalcitrant and Toxic Organic and Inorganic Compounds

Refinery wastewater can contain a variety of biodegradable, inhibitory and toxic organic and inorganic pollutants including alkanes (C10-C21), aromatic hydrocarbons (benzene, toluene, xylene, styrene, benzaldehyde, phenol and phthalates) polyaromatic hydrocarbons (cyclopentane and cyclohexane naphthenes), nitrogen compounds (ammonia, amines), sulfur compounds (sulphides and mercaptans), greases, calcium chlorides, magnesium chlorides, carboxylic acids, carbonates, cyanides, chromium, lead, arsenic, nickel, zinc, phosphates, esters, ethers, ketones, and aldehydes (Coe, 1952; Ruggles, 1959; Mahendrakar and Viraraghavan, 1996; Juang *et al.* 1997; Al Zarooni *et al.* 2006; Wagner *et al.* 2001; Galil and Wolf, 2001; Shokrollahzadeh *et al.* 2008; Llop *et al.* 2009). Due to the large variety of compounds within petroleum refinery wastewater, the organic fraction is typically estimated using bulk parameter such as the biochemical oxygen demand (BOD), chemical oxygen demand (COD), or total organic carbon (TOC) concentration.

BOD is an estimate of the amount of oxygen required to oxidize biodegradable organic materials by a heterogeneous microbial population (Ford *et al.* 1971). During a BOD test, three distinct biological reactions can occur as outlined in Table 2.2. Tracking the shape of the measured BOD curve also gives insight to how the microbial population is responding to the specific wastewater being tested. Figure 2.1 shows the characteristic BOD curves while Table 2.3 describes each curve. Typically, the BOD is measured after 5 days of incubation and reported as the BOD<sub>5</sub> (Eckenfelder, 2000). In industrial wastewater, other compounds that can be oxidized may also need to be accounted for in the BOD test including sulfides, sulfites and oxidizable nitrogen (Eckenfelder, 2000).

COD measures the amount of oxygen it takes to oxidize organic and inorganic substances using potassium dichromate in a sulphuric acid solution (Ford *et al.* 1971).

**Table 2.2: Biological Reactions That Can Occur During a BOD Test**

(Adapted from Metcalf and Eddy, 2003 where the compound COHNS is used to represent a general organic waste compound made up of carbon, oxygen, hydrogen, nitrogen and sulphur and the term  $C_5H_7NO_2$  is used to represent the cell tissue of a general microorganism)

REACTION:	DESCRIPTION
Oxidation	A portion of the organic waste compounds are oxidized to end products in order to obtain energy for microbial cell maintenance and the synthesis of new microbial cell tissue. The following equation outlines the general chemical reaction: $COHNS + O_2 + \text{bacteria} \rightarrow CO_2 + H_2O + NH_3 + \text{other end products} + \text{energy} \quad (2.1)$
Synthesis	A portion of the organic waste compounds are converted into new cell tissue using part of the energy released during the oxidation step. The following equation outlines the general chemical reaction: $COHNS + O_2 + \text{bacteria} + \text{energy} \rightarrow C_5H_7NO_2 \quad (2.2)$
Endogenous Respiration	The bacteria consume their own cell tissue to obtain energy for cell maintenance when there are no more available organic waste compounds. The following equation outlines the general chemical reaction: $C_5H_7NO_2 + 5O_2 \rightarrow 5CO_2 + NH_3 + H_2O \quad (2.3)$

**Table 2.3: Overview of Characteristic BOD Curves (Eckenfelder, 2000)**

Curve	Description
A	BOD curve using activated sludge which is fully acclimatized to the wastewater. Oxidation and Synthesis are the dominant biological reactions occurring.
B	BOD curve using activated sludge which is slowly acclimatized to the wastewater. Oxidation and Synthesis are the dominant biological reactions after acclimatization phase is complete.
C	BOD curve using activated sludge which is not acclimatized to the wastewater. Endogenous Respiration is the dominant biological reaction occurring.
D	BOD curve using wastewater which is inhibitory or toxic to the activated sludge. No significant biological reactions are occurring.

It should be noted that the COD is usually higher than the BOD when testing refinery wastewater since organic compounds that are oxidized by dichromate may be a mixture of readily biodegradable, slowly biodegradable or recalcitrant compounds (Ford *et al.* 1971; Metcalf and Eddy, 2003). Inorganic substances such as sulfides, sulfites, thiosulfates, nitrites, and ferrous iron are also oxidized by dichromate (Eckenfelder, 2000).

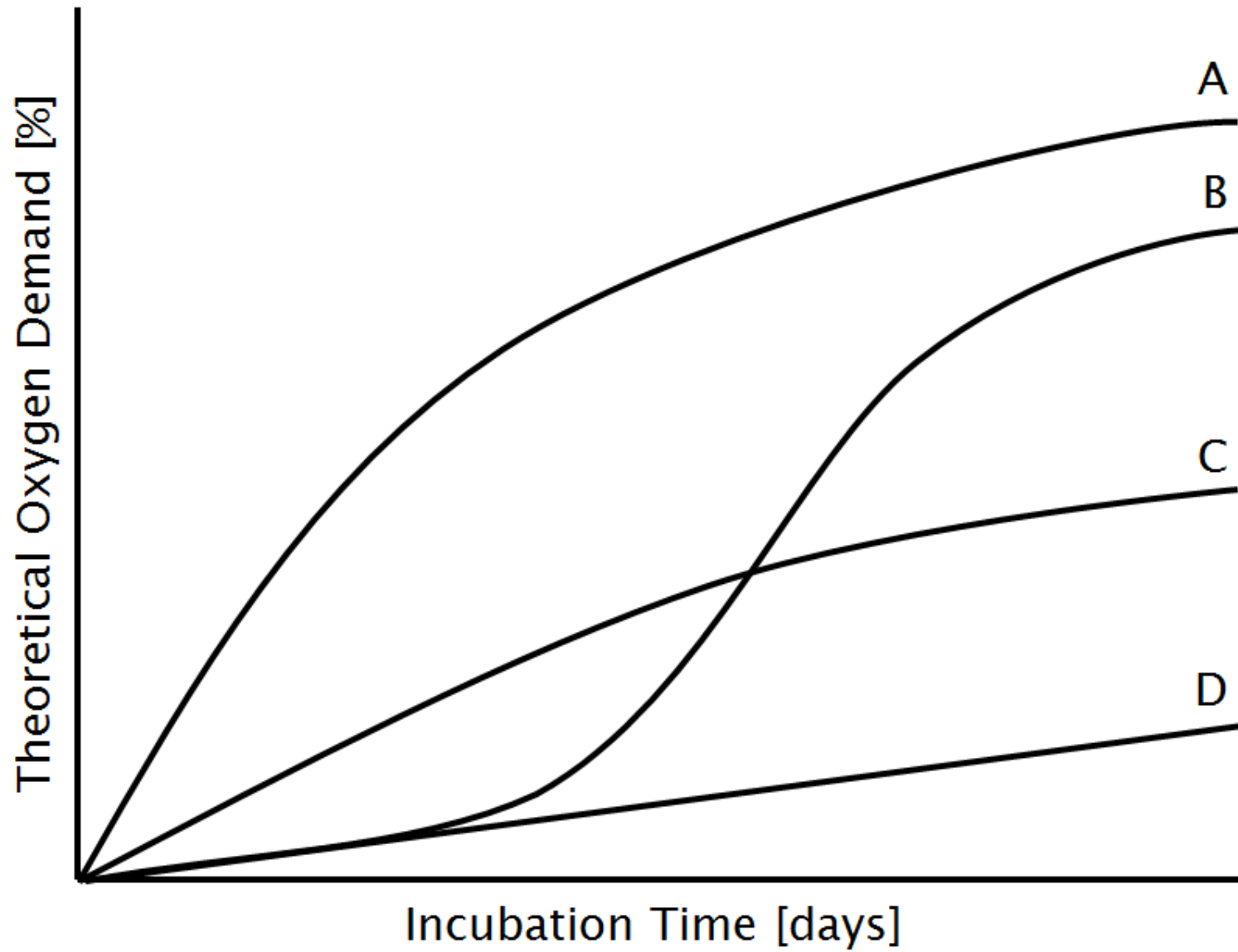


Figure 2.1: Characteristic BOD Curves (Adapted from Eckenfelder, 2000)

TOC measures the amount of carbon in a water sample by measuring the carbon dioxide generated from combustion of the water sample (Ford *et al.* 1971). It should be noted that biodegradable, slowly biodegradable or even recalcitrant compounds cannot be distinguished with the TOC test (Orhon *et al.* 1999). The TOC test also does not indicate the oxidation state of the compounds in the sample so the result cannot be used as a direct balance between substrate utilized, biomass generated and oxygen consumed (Orhon *et al.* 1999).

Correlations between BOD, COD and TOC are often developed due to the differences in the testing methods and the results generated (Eckenfelder, 2000). A correlation between COD and TOC is outlined in Appendix A. The relationship between the BOD, COD and TOC tests is shown in Figure 2.2. A review of refinery wastewater characterization throughout literature is summarized in Table 2.4 and the complete information is outlined in Appendix B.

**Table 2.4: Summary of Characteristics of Petroleum Refinery Wastewater Throughout Literature**

PARAMETER	RANGE
Flow (gpm)	37 – 1,284
Temperature (°C)	25 – 60
pH	1.6 – 10.4
COD (mg/L)	74 – 350,000
BOD <sub>5</sub> (mg/L)	56 – 62,000
TOC (mg/L)	33 – 160,000
TKN (mg/L)	1.2 – 253.0
NH <sub>3</sub> (mg/L)	0.2 – 132.0
PO <sub>4</sub> (mg/L)	7 – 227

Due to the various compounds in refinery wastewater, the effluent must meet a specific quality standard before it can be discharged to the environment as regulated by both the Canadian federal and provincial governments.



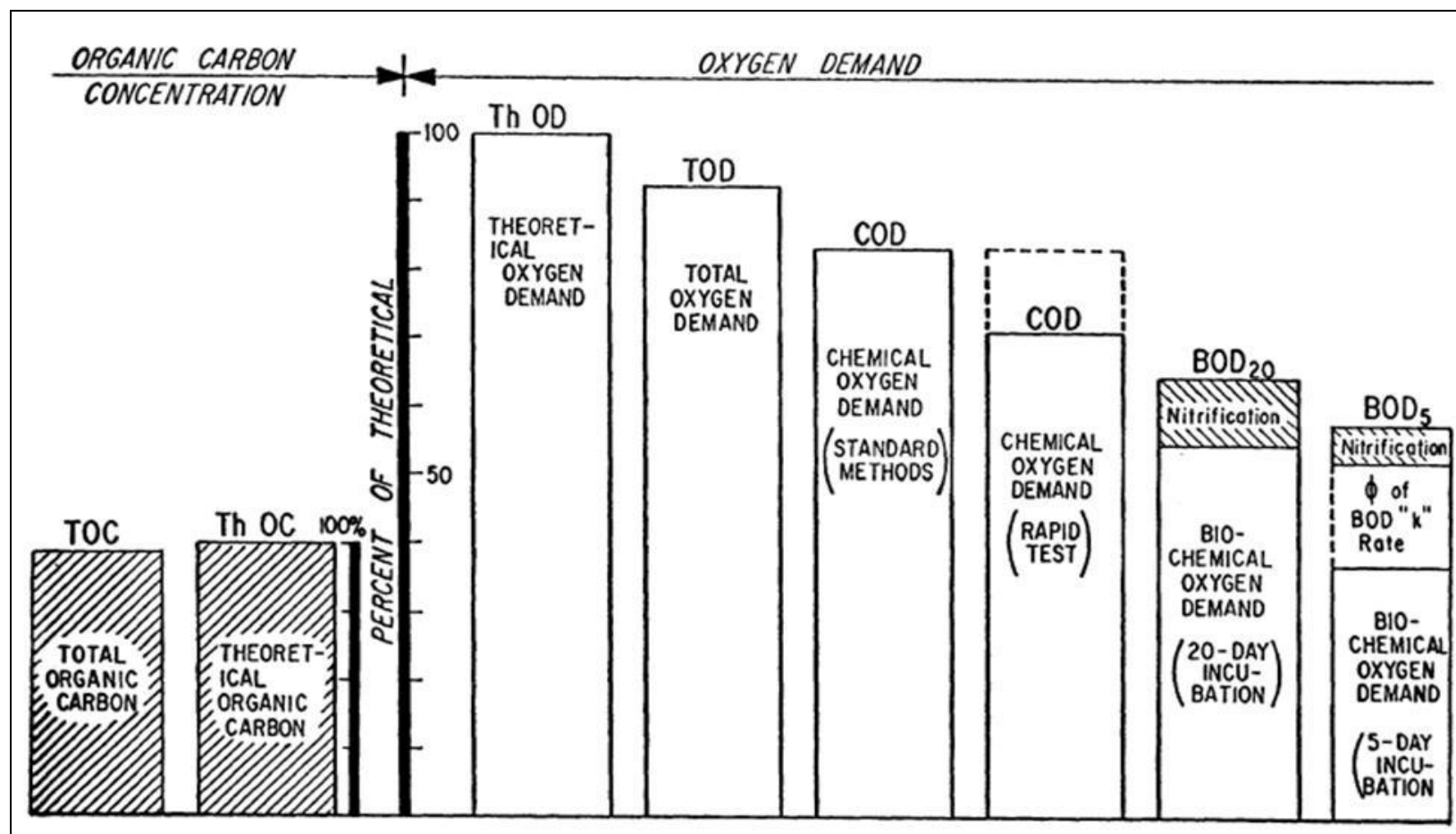


Figure 2.2: Relationship between Oxygen and Carbon Wastewater Characterization Parameters (Ford *et al.* 1971)

## 2.2 CURRENT CANADIAN REGULATIONS FOR REFINERY LIQUID EFFLUENTS

The Canadian federal and provincial governments are enabled by the Canadian Fisheries Act to have the authority to regulate effluent water pollution from petroleum refineries. These regulations are outlined in Table 2.5.

**Table 2.5: Canadian Petroleum Refinery Wastewater Regulations**

GOVERNMENT LEVEL	GOVERNMENT AGENCY	REGULATION	REFERENCE
Federal	Environment Canada	Petroleum Refinery Liquid Effluent Regulations and Guidelines	Environment (1974)
Provincial	Ministry of the Environment (MOE)	Liquid Effluent Guidelines for the Petroleum Refining Industry	Ontario (1977)
Provincial	Ministry of the Environment (MOE)	Municipal Industrial Strategy for Abatement (MISA) Effluent Monitoring Regulations for the Petroleum Refining Sector	Ontario (1988)

These regulations also include the government recommended wastewater treatment technology for Canadian petroleum refineries. The specific technologies are outlined in Table 2.6.

**Table 2.6: Recommended Petroleum Refinery Wastewater Treatment Technology**

(Adapted from Environment 1974 and Ontario 1977)

TECHNOLOGY	FUNCTION
Equalization and Storm Water Diversion	Managing Flow and Contaminant Variations
Gravity Separators	Primary Insoluble Oil and Solids Removal
Air Flotation	Intermediate Insoluble Oil and Solids Removal
Biological Treatment	Dissolved Organic Constituent Removal
Granular Media Filtration	Final Polishing

Table 2.6 shows that petroleum refinery wastewater is often treated by a series of physical, chemical and biological treatment technologies. A typical petroleum refinery WWTP flow diagram is shown in Figure 2.3.

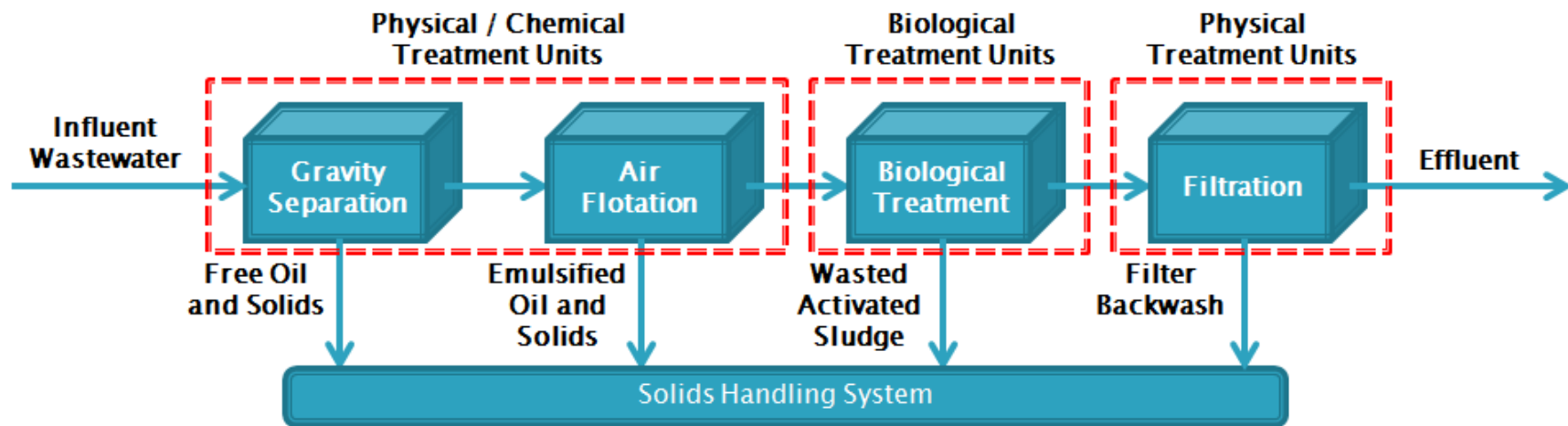


Figure 2.3: Typical Configuration of a Petroleum Refinery WWTTP (Adapted from WEF 2008)

The two main goals of Ontario's Municipal Industrial Strategy for Abatement (MISA) regulations was to create a comprehensive pollution control program to reduce all municipal and industrial waste loadings, and to virtually eliminate the discharge of toxic contaminants to Ontario's waterways (Ontario, 1988). MISA is a command-and-control policy where a permit is issued by the provincial government to each industrial facility that discharges liquid effluent to a body of surface water (MacDonald and Lintner, 2010). MISA is also a technology-based standard (TBS) since each permit is based on pollution control technologies for a specific industry (Dupuy, 1997).

It should be noted that all six of Ontario's refineries upgraded their WWTP's to the recommended pollution control technology in order to comply with the MISA regulations (MacDonald and Lintner, 2010). Therefore, all six of Ontario's refineries should be consistently meeting their respective effluent limits. Figure 2.4 shows the average monthly effluent TOC mass loadings from 2008 through 2011 for all six of Ontario's petroleum refinery's (Ontario, 2013). The raw data is outlined in Appendix C. The average monthly effluent TOC mass loadings for all six of Ontario's petroleum refineries have always been below the regulated limits of 167 kg/day for IOL Nanticoke, 859 kg/day for IOL Sarnia, 256 kg/day for Nova Corunna, 214 kg/day for Shell Sarnia, 220 kg/day for Suncor Mississauga and 214 kg/day for Suncor Sarnia (Ontario, 1993; Ontario, 2013).

When a regulation is in the process of being amended, it must also clearly align with other current regulations as well as emerging regulations. In the case of a TBS like the MISA regulations, one such regulation that needs to be considered is Ontario Regulation 455/09 the Toxics Reduction Act (TRA).

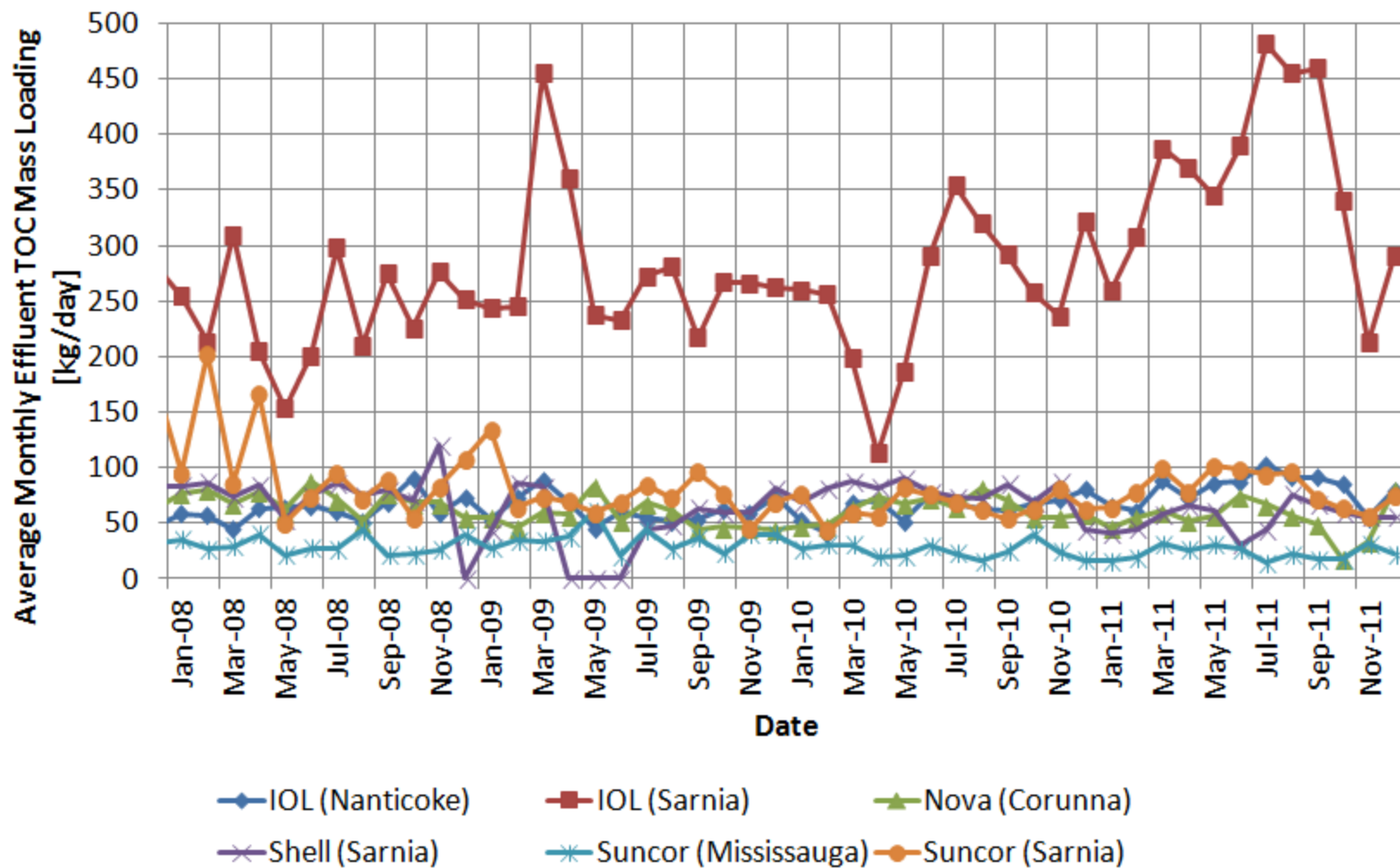


Figure 2.4: Ontario Petroleum Refineries Average Effluent TOC Mass Loading from 2008 through 2011

The main purpose of the TRA is to prevent pollution and protect human health and the environment by reducing the use and creation of toxic substances (Ontario, 2009a). The TRA regulation lists 47 compounds with multiple sub-compounds that need to be considered when reviewing a TBS like the MISA regulations (Ontario 2009b). Future regulations must also now consider the use and creation of toxic substances when using new technology.

### 2.3 BIOLOGICAL WASTEWATER TECHNOLOGY FOR A REFINERY WWTP

Biological treatment by an activated sludge process is an established practice used to treat refinery wastewater since it is usually the most economical method for reducing both wastewater toxicity and dissolved organic constituents (Qin *et al.* 2007). Activated sludge processes are classified as either suspended growth or supported growth systems and can operate under aerobic or anaerobic conditions (Tyagi *et al.* 1992, Rebhun and Galil, 1988). A review of biological treatment technology for petroleum refinery wastewater throughout literature is summarized in Table 2.7 and the complete information is outlined in Appendix D.

**Table 2.7: Biological Technology for Petroleum Refinery Wastewater Treatment**

PARAMETER	RANGE
Hydraulic Retention Time (hr)	0.3 – 240.0
Temperature (°C)	15 – 40
pH	2.5 – 10.4
BOD (mg/L)	69 – 3,160
COD (mg/L)	220 – 142,000
Phenol (mg/L)	9 – 100
TSS (mg/L)	5 – 900
Ammonia (mg/L)	4.7 – 24.0
Oil & Grease (mg/L)	2 – 90

Refinery wastewater often contains a high concentration of compounds that could be toxic to or inhibit the microorganisms in the biological treatment unit (Juang *et al.*, 1997). A

sudden load of high strength, non-biodegradable or toxic wastewater can lead to a WWTP discharging effluent that exceeds regulatory limits or even result in the failure of the biological treatment unit. This would require long periods of time to re-establish a reliable activated sludge which can impact the throughput of upstream refinery production units (Tyagi *et al.* 1992; Chavan and Mukherji, 2008). Therefore, additional advanced treatment technology may be required to degrade these types of compounds. One promising area of research is advanced oxidation processes (AOPs).

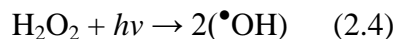
## **2.4 ADVANCED OXIDATION PROCESS TECHNOLOGY FOR A REFINERY WWTP**

Advanced oxidation processes (AOPs) are a type of advanced technology which are effective at treating wastewaters that contains non-biodegradable, inhibitory, or toxic compounds (Tabrizi and Mehrvar, 2004). The main advantage of AOPs is that the organic compounds in the wastewater could be completely converted to water and carbon dioxide without generating a residual solid waste by-product (Tabrizi and Mehrvar, 2004). An important disadvantage of AOPs is that the capital and operating costs are usually much higher when compared to conventional biological treatment processes (Tabrizi and Mehrvar, 2004). Therefore, AOPs are typically used as either a pre-treatment to enhance the biodegradability of the wastewater before the biological treatment process or as a post-treatment after the biological treatment process to remove any remaining compounds that were not degraded (Juang *et al.* 1997; Tabrizi and Mehrvar, 2004). Some examples of AOPs include UV, UV/H<sub>2</sub>O<sub>2</sub>, UV/O<sub>3</sub>, UV/H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>, and UV/TiO<sub>2</sub> (Tabrizi and Mehrvar, 2004). A review of AOP treatment technology for petroleum refinery wastewater throughout the literature is summarized in Table 2.8 and the complete information is outlined in Appendix E.

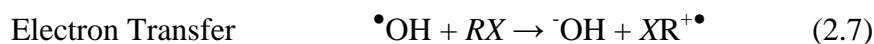
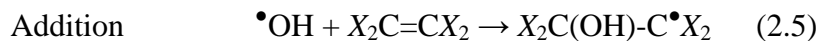
**Table 2.8: Overview of Chemical Wastewater Treatment Technology for Petroleum Refinery Wastewater**

PARAMETER	RANGE
Time (hr)	0.25 – 12.00
Temperature (°C)	20 – 50
pH	2.1 –11.0
COD (mg/L)	96 –5,500
TOC (mg/L)	133 –1,200
Phenol (mg/L)	38 – 80

AOPs use an oxidant (H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, etc.) and energy or a catalyst to produce highly reactive hydroxyl radicals (•OH) which are able to oxidize almost all organic pollutants (Tabrizi and Mehrvar, 2004). For example, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) may generate hydroxyl radicals in the presence of UV light with the wavelength of less than 254 nm based on Equation 2.4 (Tabrizi and Mehrvar, 2004):



These hydroxyl radicals are able to degrade pollutants by addition to double bonds, abstraction of a hydrogen atom, or transferring an electron to a compound according to Equations 2.5, 2.6 and 2.7 (Tabrizi and Mehrvar, 2004):



The products of degrading organic molecules could be intermediate molecules or final stage compounds such as HCO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, CO<sub>2</sub>, or H<sub>2</sub>O (Tabrizi and Mehrvar, 2004). AOPs are able to completely degrade organic compounds in water without transferring them to another



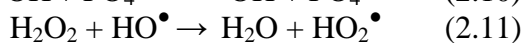
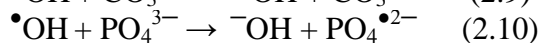
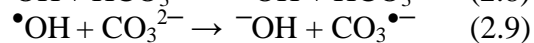
medium or generating a secondary waste that requires additional disposal (Tabrizi and Mehrvar, 2004). Hydroxyl radicals non-selectively oxidize organic compounds so AOPs are effective at treating recalcitrant, inhibitory and toxic compounds (Tabrizi and Mehrvar, 2004). The degradation types are outlined in Table 2.9.

**Table 2.9: Organic Compound Degradation Types**

(Adapted from Tabrizi and Mehrvar, 2004)

DEGRADATION TYPE	DESCRIPTION
Satisfactory	The molecular structure of the parent compound changes in a way which reduces the toxicity of the compound or increases the biodegradability of the compound.
Improper	The molecular structure of the parent compound changes in a way which increases the toxicity of the compound or decreases the biodegradability of the compound.
Complete Mineralization	The organic compound is completely degraded into the final products of carbon dioxide and water.

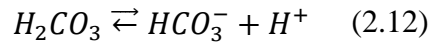
One of the issues with AOPs is that the hydroxyl radical can be consumed by reacting with inorganic constituents in wastewater including bicarbonates, carbonates, phosphates, reduced cations such as iron and excessive amounts of hydrogen peroxide (Hernandez *et al.* 2002; Tabrizi and Mehrvar, 2004). These “scavenging reactions” can significantly reduce the efficiency of an AOP to oxidize the target constituents and are outlined in Equations 2.8 through 2.11 (Andreozzi *et al.* 1999; Hernandez *et al.* 2002).



Wastewater with high alkalinity must have the pH adjusted before treatment with an AOP to minimize these scavenging reactions (Juang *et al.* 1997; Andreozzi *et al.* 1999). Juang *et al.*

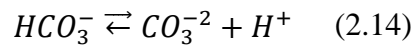
(1997) found that when the pH of the petrochemical wastewater was kept at 8.5, there was a large H<sub>2</sub>O<sub>2</sub> consumption with very little COD or TOC removal. When the pH was adjusted down to 3, the carbonate and bicarbonate molecules formed carbonic acid which is not a hydroxide radical scavenger and the COD and TOC removal significantly increased to 69.9% and 55.5% respectively. It was also found that a high concentration of hydrogen ions at a low pH also scavenges hydroxyl radicals as indicated by decreasing treatment performance at lower pH's (Juang *et al.* 1997). Andreozzi *et al.* (1999) also mentioned that a pH between 3 and 5 typically results in the highest efficiency of constituent destruction.

Water can be resistant to pH changes due to buffering related to the dissolved inorganic carbon species of carbon dioxide, bicarbonate ions and carbonate ions (Chapra, 2008). Carbon dioxide combines with water to form carbonic acid which the dissociates into its ionic form as shown in equation 2.12 with an equilibrium constant shown in equation 2.13 (Chapra, 2008):



$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} \quad (2.13)$$

The bicarbonate ion the dissociates to a carbonate ion as shown in equation 2.14 with an equilibrium constant shown in equation 2.15 (Chapra, 2008):



$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \quad (2.15)$$

The fraction of the three inorganic carbon species can be calculated according to equations 2.16, 2.17, and 2.18 (Chapra, 2008):

$$F_{H_2CO_3} = \frac{[H^+]^2}{[H^+]^2 + K_1[H^+] + K_1K_2} \quad (2.16)$$

$$F_{HCO_3^-} = \frac{K_1[H^+]}{[H^+]^2 + K_1[H^+] + K_1K_2} \quad (2.17)$$

$$F_{CO_3^{2-}} = \frac{K_1K_2}{[H^+]^2 + K_1[H^+] + K_1K_2} \quad (2.18)$$

Assuming the initial temperature of the water was 20°C, the equilibrium constants would be (Metcalf and Eddy, 2003):

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 4.169 \times 10^{-7}$$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 4.169 \times 10^{-11}$$

The calculated fractionation of the three inorganic carbon species is outlined in Table 2.10. The data in Table 2.10 is displayed in Figure 2.5.

**Table 2.10: Theoretical Fractionation between Carbonic Acid, Bicarbonate and Carbonate Ions**

pH	Carbonic Acid	Bicarbonate	Carbonate
0.0	100.00%	0.00%	0.00%
0.5	100.00%	0.00%	0.00%
1.0	100.00%	0.00%	0.00%
1.5	100.00%	0.00%	0.00%
2.0	100.00%	0.00%	0.00%
2.5	99.99%	0.01%	0.00%
3.0	99.96%	0.04%	0.00%
3.5	99.87%	0.13%	0.00%
4.0	99.58%	0.42%	0.00%
4.5	98.70%	1.30%	0.00%
5.0	96.00%	4.00%	0.00%
5.5	88.35%	11.65%	0.00%
6.0	70.58%	29.42%	0.00%

6.5	43.13%	56.86%	0.01%
7.0	19.34%	80.63%	0.03%
7.5	7.04%	92.84%	0.12%
8.0	2.33%	97.26%	0.41%
8.5	0.74%	97.97%	1.29%
9.0	0.23%	95.78%	3.99%
9.5	0.07%	88.29%	11.64%
10.0	0.02%	70.56%	29.42%
10.5	0.00%	43.13%	56.86%
11.0	0.00%	19.35%	80.65%
11.5	0.00%	7.05%	92.95%
12.0	0.00%	2.34%	97.66%
12.5	0.00%	0.75%	99.25%
13.0	0.00%	0.24%	99.76%
13.5	0.00%	0.08%	99.92%
14.0	0.00%	0.02%	99.98%

There are a number of examples in the literature showing that AOPs are effective at treating industrial wastewater. Niegowski (1956) used ozone to treat refinery wastewater containing phenols. Farooq and Misbahuddin (1991b) treated wastewater through a combination of activated carbon adsorption and ozonation. Juang *et al.* (1997) used a laboratory scale UV/H<sub>2</sub>O<sub>2</sub> system to treat petrochemical wastewater as pre-treatment or post-treatment for a refinery WWTP biological treatment unit. Adeyinka and Rim-Rukeh (1999) treated effluent from a petrochemical plant in bench scale tests with alum and hydrogen peroxide. Huang *et al.* (1999) treated the effluent from a refinery WWTP biological treatment unit using various chemical oxidants including O<sub>3</sub>, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, sodium hypochlorite, and Fenton's reagent. Andereozzi *et al.* (2000) used combinations of AOPs (O<sub>3</sub>/UV, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>) to treat mineral oil contaminated wastewater at ambient conditions as well as developing a kinetic model for both O<sub>3</sub>/UV and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> systems.

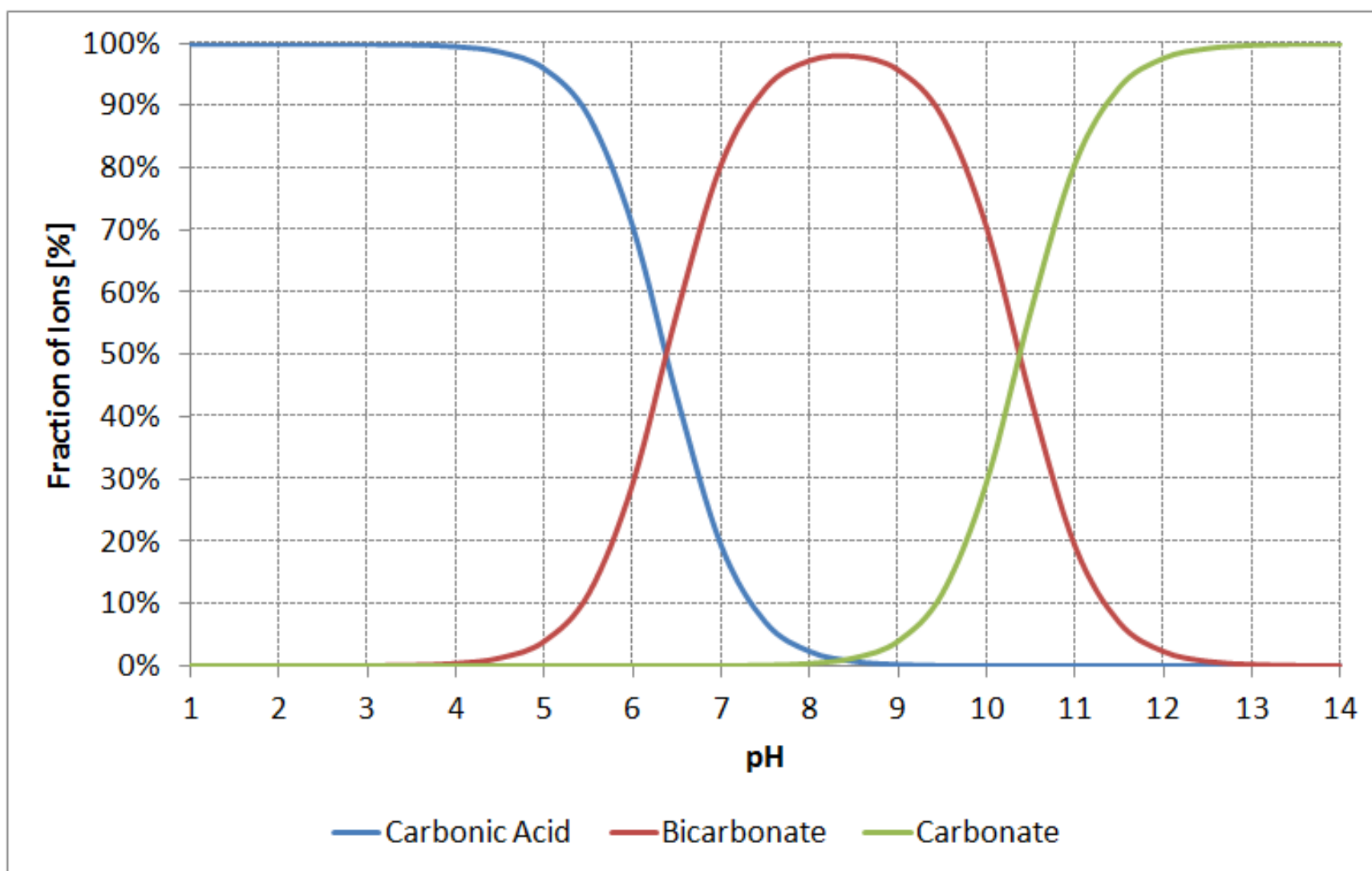


Figure 2.5: Theoretical Fractionation between Carbonic Acid, Bicarbonate and Carbonate Ions (Adapted from Chapra, 2008)

Lin *et al.* (2001) treated petrochemical wastewater in a laboratory scale test that combined pre-ozonation and a lifted moving-bed biological activated carbon process. Wagner and Nicell (2001) treated refinery wastewater containing phenols using horseradish peroxidase and hydrogen peroxide. Stepnowski *et al.* (2002) treated refinery wastewater with UV/H<sub>2</sub>O<sub>2</sub> as a pre-treatment to the refinery WWTP biological treatment unit and found that additional UV irradiation only slightly increased the degradation process. Mohammadzadeh *et al.* (2004) treated phenol-rich olefin plant wastewater using O<sub>3</sub> in a bench scale semi-batch system and a pilot scale unit. Chidambara and Quen (2005) optimized a UV/H<sub>2</sub>O<sub>2</sub> process that was integrated with a biological treatment unit using Taguchi's orthogonal design and found that a single dose of H<sub>2</sub>O<sub>2</sub> was more effective than several smaller doses, the circulation rate was insignificant and the molar ratio between H<sub>2</sub>O<sub>2</sub> used per TOC degradation was 1:1 for pre-treatment and 4:1 for post-treatment. Saïen and Nejati (2007) treated refinery wastewater containing aliphatic and aromatic compounds using a circulating photocatalytic reactor with TiO<sub>2</sub> catalyst. Ting *et al.* (2007) treated the effluent from a refinery WWTP biological treatment unit with a batch scale and pilot scale electro-Fenton process. Sun *et al.* (2008) used microwave assisted catalytic wet air oxidation at low temperature and pressure to treat refinery wastewater.

While the literature does show that AOPs are effective at treating industrial wastewater, there are very few examples of treating actual petroleum refinery wastewater, none of this literature is from Canada, and none of this literature uses respirometry to assess the effects of adding UV/H<sub>2</sub>O<sub>2</sub> treated petroleum refinery wastewater to activated sludge microorganisms from the refinery WWTP biological treatment process (Niegowski, 1956; Juang *et al.* 1997; Adeyinka and Rim-Rukeh 1999; Huang *et al.* 1999; Andereozzi *et al.* 2000; Lin *et al.* 2001; Wagner and

Nicell 2001; Stepnowski *et al.* 2002; Mohammadzadeh *et al.* 2004; Chidambara and Quen 2005; Saïen and Nejati 2007; Ting *et al.* 2007).

This research is similar to the work from Juang *et al.* (1997) and Stepnowski *et al.* (2002) since both of these works also used a UV/H<sub>2</sub>O<sub>2</sub> process to treat petroleum refinery wastewater. However, this research is still significantly different from these other studies. Juang *et al.* (1997) and Stepnowski *et al.* (2002) used actual wastewater from a petroleum refinery in Taiwan and Poland respectively, whereas this research used wastewater from a petroleum refinery in Canada. Stepnowski *et al.* (2002) also examined the degradation of specific compounds where as this research examined the degradation of all soluble organic carbon species as measured by the total organic carbon (TOC). This research is also significantly different since respirometry was used to assess the effects of adding UV/H<sub>2</sub>O<sub>2</sub> treated petroleum refinery wastewater to activated sludge microorganisms from the refinery WWTP biological treatment process.

# CHAPTER 3

## MATERIALS AND METHODS

### 3.1 MATERIALS

#### 3.1.1 Petroleum Refinery Wastewater and Activated Sludge Samples

Wastewater and activated sludge samples were collected from the Suncor Mississauga refinery WWTP.

The Suncor Mississauga refinery has a combined sewer system where all of the clean water, oily water and process wastewater sources all combine into a single influent wastewater stream for the WWTP. The combined influent wastewater first passes through an American Petroleum Institute (API) gravity separator in order to remove free oil and solid particles. The wastewater then is pumped to an equalization tank to minimize fluctuations in wastewater temperature and contaminant concentrations. The wastewater then passes through dissolved air flotation (DAF) units to remove emulsified oil and solid particles. The wastewater is then treated in the activated sludge biological treatment units.

Batch wastewater samples were collected from a sample point between the DAF units and the biological treatment units. Operations staff at the Suncor Mississauga refinery WWTP collect samples from this location twice a day to monitor the water quality entering the biological treatment units. Operations staff at the Suncor Mississauga refinery WWTP do not collect composite samples since the upstream equalization tank minimizes any wastewater temperature



or contaminant concentration fluctuations. The batch samples collected accurately reflect the water quality entering the biological treatment units throughout the 12 hours between samples. Table 3.1 outlines the typical contaminant concentrations for the influent wastewater to the biological treatment units.

Activated sludge samples were collected from the Suncor Mississauga refinery WWTP biological treatment unit since the microorganisms would already be acclimatized to the influent wastewater.

**Table 3.1: Typical Range of Wastewater Parameters for Mississauga Refinery WWTP Biological Treatment Unit**

Parameter	Typical Range
Temperature (°C)	20 – 30
pH	6.8 – 7.8
Chemical Oxygen Demand (mg/L)	50 – 200
Ammonia (mg/L)	3 – 10
Phosphate (mg/L)	1 – 5
Sulphide (mg/L)	0 – 15
Alkalinity (mg/L measured as CaCO <sub>3</sub> )	90 – 170

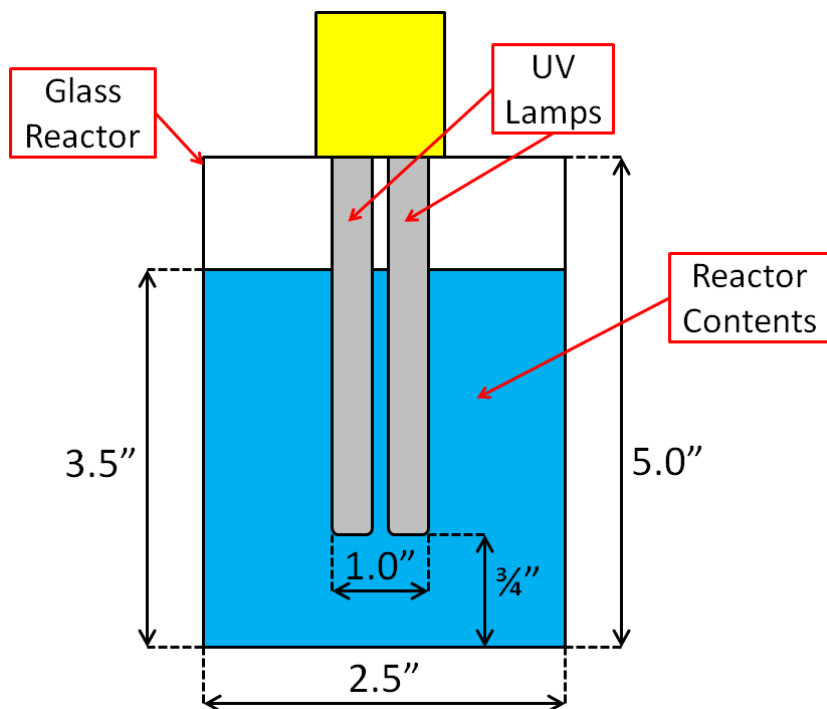
### 3.1.2 Chemicals

A 30% w/w solution of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) with a density of 1,110 g/L was used as the chemical oxidant in the UV/ H<sub>2</sub>O<sub>2</sub> process. A 1N solution of sulphuric acid and a 50% solution of sodium hydroxide were used to adjust the pH in the UV/H<sub>2</sub>O<sub>2</sub> process. Distilled Toronto municipal city water was used in the respirometric experiments.

## 3.2 EXPERIMENTAL LABORATORY SETUP

The refinery wastewater was placed in a bench scale cylindrical glass reactor vessel that was 5.0 inches tall and had a diameter of 2.5 inches as shown in Figure 3.1. The reactor was

placed on a VWR Stir Plate Model 365 with a magnetic stir bar to ensure that the water and chemicals were well mixed. The UV light was generated using a Philips PL-S9W/TUV UV-C 9 WATT lamp. The reactor was also covered in aluminum foil to ensure the UV energy is contained inside the reactor.



**Figure 3.1: Laboratory Set-up of UV/H<sub>2</sub>O<sub>2</sub> Process**

### **3.3 EXPERIMENTAL PROCEDURE AND ANALYTICAL TECHNIQUES**

#### **3.3.1 Experimental Procedure**

250 mL of raw petroleum refinery wastewater was first added to a bench scale reactor. The stir plate was then turned on. The pH of the petroleum refinery wastewater was measured using a Thermo Orion Model 230A+ pH meter. This instrument has a pH resolution of 0.01 and a pH accuracy of  $\pm 0.02$ . The pH meter was calibrated using a pH 4.01, 7.00 and 10.00 buffer

solution at a room temperature of approximately 20°C. Sulphuric acid was then added to adjust the pH from the initial 7.5 down to a minimum of 4.0. H<sub>2</sub>O<sub>2</sub> was then added as the chemical oxidant where the concentration varied from an initial H<sub>2</sub>O<sub>2</sub>/TOC molar ratio of 1.7-8.6 mol H<sub>2</sub>O<sub>2</sub>/mol C. The UV lamp was then placed on top of the reactor submerging the UV bulb directly into the reactor contents. The treatment time varied from 10 to 45 min to assess the effect of reaction time on the TOC removal. The temperature of the wastewater was not controlled during the experiments. This is due to the fact that the treatment kinetics were not evaluated as part of this study. The wastewater treatment began at the ambient temperature of the lab which was approximately 20°C. Throughout the treatment, the temperature of the wastewater would have increased due to the heat generated from the UV bulb. It can be assumed that the degradation rate of the contaminants would increase as the temperature increases (Tabrizi and Mehrvar, 2004). The final temperature was not recorded since this study focused on the final TOC concentration achieved from treatment using a UV/H<sub>2</sub>O<sub>2</sub> process, not the treatment kinetics of the process. As shown in Appendix E, Juang *et. al.* (1997) controlled the temperature of the reaction at 30°C and Stepnowski *et. al.* (2002) did not even mention the process temperature. After the specified reaction time, the UV lamp was turned off, the mixer was turned off and the treated wastewater was sampled for total organic carbon (TOC) testing. Sodium hydroxide was added to UV/H<sub>2</sub>O<sub>2</sub> treated water to adjust the pH back up to 7.0 for specific respirometry tests. The TOC concentration of the sample was measured using a Teledyne Tekmar Apollo 9000 Combustion TOC/TN Analyzer equipped with an automated sampler. The TOC was tested in triplicate for each sample.

### 3.3.2 Experimental Design

There were two phases to the bench scale experiments. The first phase was an initial screening of how the reaction time, the initial  $\text{H}_2\text{O}_2/\text{TOC}$  molar ratio, and the system pH affected the treatment of petroleum refinery wastewater using a UV/ $\text{H}_2\text{O}_2$  process. The second phase used the results of the first phase to further improve the UV/ $\text{H}_2\text{O}_2$  process to treat petroleum refinery wastewater.

A  $2^3$  factorial design with a center point run was used in the first phase or the screening phase of the experiments. A  $2^3$  factorial design means that all three parameters are tested at their lower and upper values. The three parameters are the reaction time, the initial  $\text{H}_2\text{O}_2/\text{TOC}$  molar ratio, and the system pH as indicated in Table 3.2.

**Table 3.2:  $2^3$  Factorial Design Input Data for the Initial Experimental Testing of a UV/ $\text{H}_2\text{O}_2$  Process to Treat Petroleum Refinery Wastewater**

Parameter	Lower Value	Middle Value	Upper Value
Reaction Time (min)	10	20	30
Initial $\text{H}_2\text{O}_2$ / TOC Molar Ratio (mol $\text{H}_2\text{O}_2$ /mol C)	2.9	5.8	8.6
pH	4.0	6.0	7.5

The center point run took place at the middle values where the reaction time was 20 min, the initial  $\text{H}_2\text{O}_2/\text{TOC}$  molar ratio was 5.8, and the system pH was 6.0.  $2^3$  or eight distinct tests were completed since three parameters are being tested at the lower and upper values. An additional test at the center point was completed which equals a total of nine tests for the first phase of experiments. The experimental parameters which resulted in the highest TOC removal were used as the basis for the second phase of testing.

The second phase of testing used a  $3^3$  factorial design where the basis used was the highest performance result from the first phase of testing. A  $3^3$  factorial design means that all three parameters will be tested at their lower, middle and upper values. The three parameters are once again the reaction time, the initial  $\text{H}_2\text{O}_2$ /TOC molar ratio, and the system pH as indicated in Table 3.3.  $3^3$  or 27 distinct tests will be completed since three parameters are being tested at the lower, middle and upper values.

**Table 3.3:  $3^3$  Factorial Design Input Data for the Additional Experimental Testing of a UV/ $\text{H}_2\text{O}_2$  Process to Treat Petroleum Refinery Wastewater**

Parameter	Lower Value	Middle Value	Upper Value
Reaction Time (min)	15	30	45
Initial $\text{H}_2\text{O}_2$ / TOC Molar Ratio (mol $\text{H}_2\text{O}_2$ /mol C)	1.7	2.8	3.9
pH	4.0	5.0	6.0

Each experiment was replicated three separate times in order to determine the average and standard deviation of the wastewater TOC. The methods to calculate the average and standard deviation are outlined in Appendix F and G.

### 3.3.3. Respirometry Testing

The effects of adding raw and UV/ $\text{H}_2\text{O}_2$  treated petroleum refinery wastewater to activated sludge microorganisms from the refinery WWTP biological treatment process were tested using a Bioscience BI-2000 Electrolytic Respirometer. Half of the 1 L respirometer reactors were seeded with activated sludge resulting in an initial mixed liquor volatile suspended solids concentration of 1,000 mg VSS/L. The other half of the respirometer reactors did not contain any activated sludge since they acted as an abiotic control. The abiotic reactors were

used to assess the background oxygen consumption. The respirometer reactors, either seeded or not seeded, were then filled with either municipal tap water, untreated refinery wastewater or refinery wastewater treated by a UV/H<sub>2</sub>O<sub>2</sub> process. The pH of the UV/H<sub>2</sub>O<sub>2</sub> treated wastewater was either left at 5.0 or it was increased back to 7.0 to assess if there were any pH impacts to the activated sludge microorganisms in the reactor. In summary, eight different experimental combinations were tested using the respirometers as shown in Table 3.4.

**Table 3.4: Respirometry Testing Experimental Design**

<b>Water Type</b>	<b>Seeded With Activated Sludge or Blank</b>	<b>pH</b>
Untreated Refinery Wastewater	Seeded (Biotic)	7.5
	Blank (Abiotic)	7.5
Municipal Tap Water	Seeded (Biotic)	7.2
	Blank (Abiotic)	7.2
UV/H <sub>2</sub> O <sub>2</sub> Treated Refinery Wastewater	Seeded (Biotic)	5.0
	Blank (Abiotic)	5.0
UV/H <sub>2</sub> O <sub>2</sub> Treated Refinery Wastewater	Seeded (Biotic)	7.0
	Blank (Abiotic)	7.0

It should be also noted that each experiment was replicated three separate times in order to determine the average and standard deviation of the wastewater TOC as outlined in Appendix F and G.

# CHAPTER 4

## RESULTS AND DISCUSSION

### 4.1 INITIAL EXPERIMENTAL TESTING OF A UV/H<sub>2</sub>O<sub>2</sub> PROCESS TO TREAT PETROLEUM REFINERY WASTEWATER

The first phase of experiments was an initial screening of how the reaction time, the initial H<sub>2</sub>O<sub>2</sub>/TOC molar ratio and the system pH affected the treatment of petroleum refinery wastewater using a UV/H<sub>2</sub>O<sub>2</sub> process. A 2<sup>3</sup> factorial design with a center point run at a reaction time of 20 min, an initial H<sub>2</sub>O<sub>2</sub>/TOC molar ratio of 5.8 mol H<sub>2</sub>O<sub>2</sub>/mol C, and a pH of 6.0 was used as outlined in Table 3.2. Figure 4.1 shows the TOC removal results from the experimental testing outlined in Table 3.2.

As stated previously in Section 3.3.2, a total of nine tests were completed. Four of the tests took place at a pH of 4.0 where the lower and upper reaction times and initial H<sub>2</sub>O<sub>2</sub>/TOC molar ratios were tested. Four of the tests took place at an initial pH of 7.5 where the lower and upper reaction times and initial H<sub>2</sub>O<sub>2</sub>/TOC molar ratios were tested. The final test took place at the center point at the middle values where the reaction time was 20 min, the initial H<sub>2</sub>O<sub>2</sub>/TOC molar ratio was 5.8, and the system pH was 6.0. This is why Figure 4.1 has four bars at a pH of 4.0, four bars at a pH of 7.5 and only one bar at a pH of 6.0.

It should also be noted that the average initial TOC was 42.0 mg C/L for all experiments. The initial H<sub>2</sub>O<sub>2</sub> concentration for the experiments were 345, 690 and 1,023 mg H<sub>2</sub>O<sub>2</sub>/L for an initial H<sub>2</sub>O<sub>2</sub>/TOC molar ratio of 2.9, 5.8, and 8.6 mol H<sub>2</sub>O<sub>2</sub>/mol C respectively.

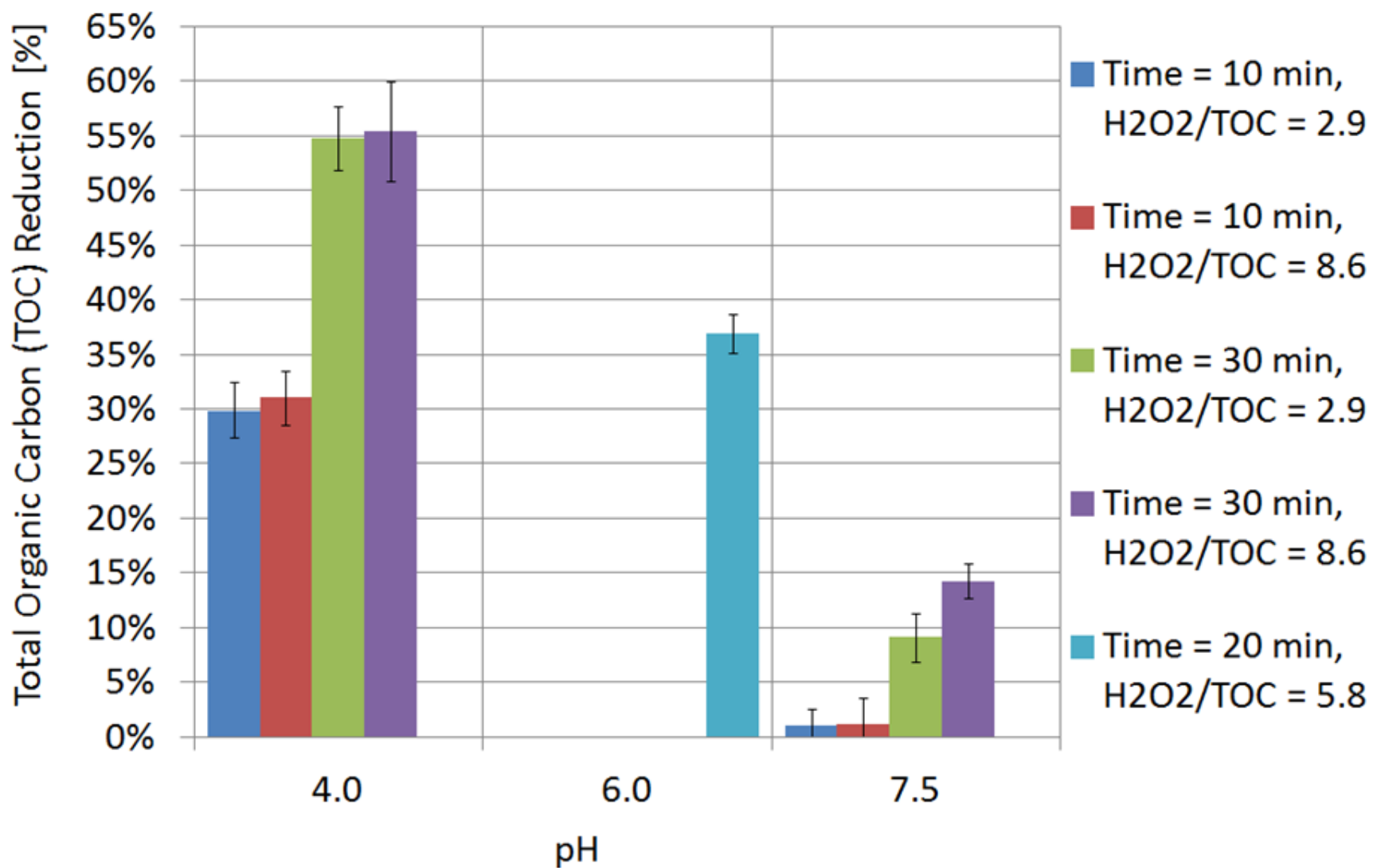


Figure 4.1: TOC Removal of Petroleum Refinery Wastewater Treated by a UV/H<sub>2</sub>O<sub>2</sub> Process during the Initial Experiments



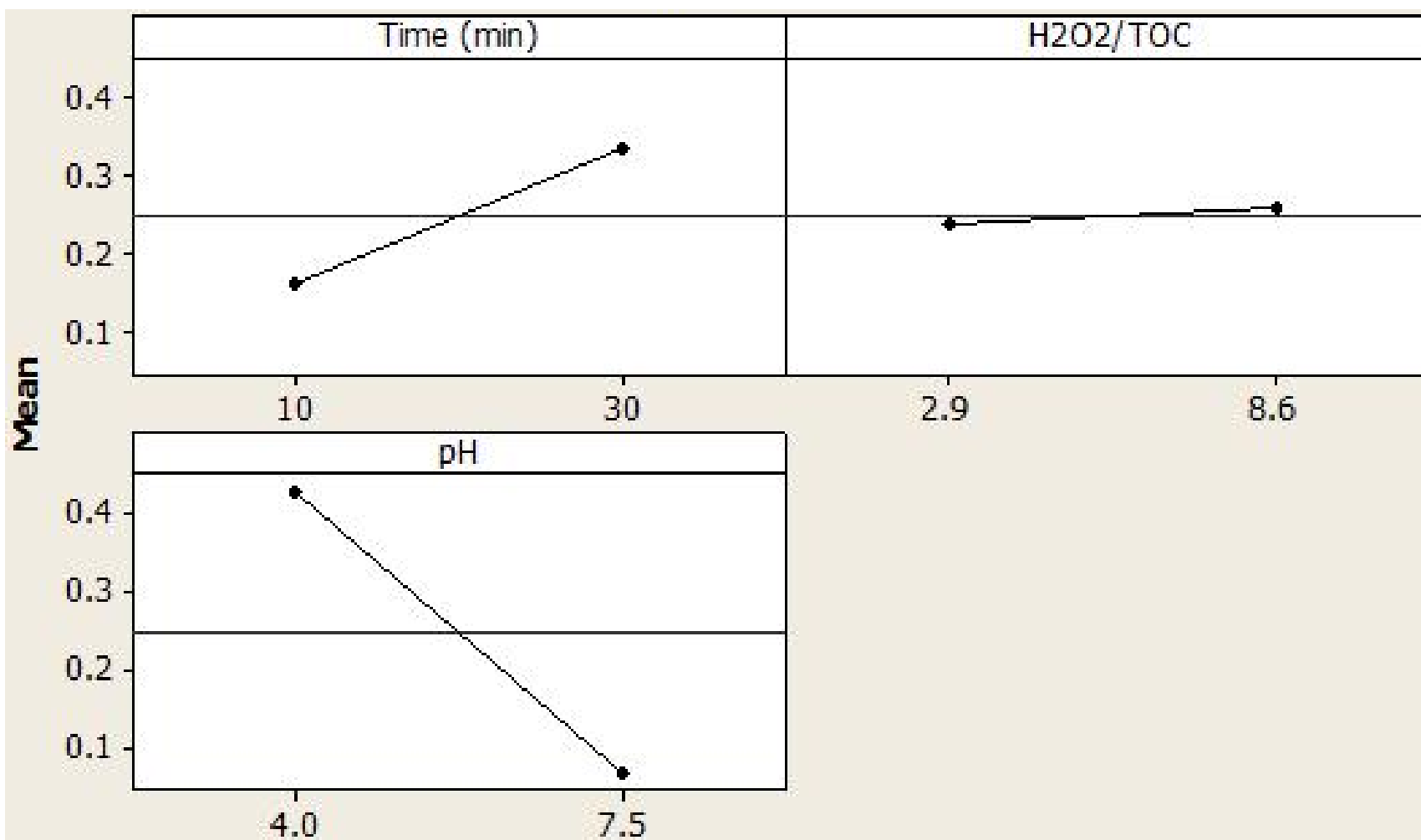
A detailed outline of each experimental run is in Appendix H. The measured TOC concentration data output from the TOC analyzer is presented in Appendix I.

Figure 4.1 shows that a UV/H<sub>2</sub>O<sub>2</sub> process to treat petroleum refinery wastewater is significantly more effective at reducing the TOC when the pH is lowered and the reaction time is increased. This confirms the work previously completed by Juang *et al.* (1997) and Stepnowski *et al.* (2002) as discussed in Section 2.4. When the pH was kept at the initial value of 7.5, the resulting TOC reduction was less than 20% when the reaction time was either 10 or 30 min or when the H<sub>2</sub>O<sub>2</sub>/TOC molar ratio was 2.9 or 8.6 mol H<sub>2</sub>O<sub>2</sub>/mol C. When the pH was reduced to 4.0, the TOC reduction significantly increased to approximately 30% and 55% when the reaction time was 10 and 30 min, respectively.

A three factor ANOVA analysis was also completed to identify which parameters and parameter interactions had a significant effect in the initial experimental results. Table 4.1 summarizes the results of a three factor ANOVA analysis while Figure 4.2 and 4.3 display the main effects and interaction effects plots respectively. The center point result was not included to maintain a balanced ANOVA analysis.

**Table 4.1: 3 Factor ANOVA Analysis Results for the Initial Experimental Testing of a UV/H<sub>2</sub>O<sub>2</sub> Process to Treat Petroleum Refinery Wastewater**

Source Of Variation	Degrees Of Freedom	Sum Of Squares	Mean Square	F-Ratio	Critical F-Ratio ( $\alpha=0.01$ )
(Time)	1	0.17677	0.17677	123.454	8.531
(H <sub>2</sub> O <sub>2</sub> /TOC)	1	0.00232	0.00232	1.620	8.531
(pH)	1	0.77436	0.77436	540.801	8.531
(Time) x (H <sub>2</sub> O <sub>2</sub> /TOC)	1	0.00005	0.00005	0.035	8.531
(Time) x (pH)	1	0.03346	0.03346	23.368	8.531
(H <sub>2</sub> O <sub>2</sub> /TOC) x (pH)	1	0.00176	0.00176	1.229	8.531
(Time) x (H <sub>2</sub> O <sub>2</sub> /TOC) x (pH)	1	0.00087	0.00087	0.608	8.531
Error	16	0.02291	0.00143	-	-
Total	23	1.01249	-	-	-



**Figure 4.2: Main Effects Plot for the Reaction Time, Initial H<sub>2</sub>O<sub>2</sub>/TOC molar ratio, and pH for the Initial Experimental Testing of a UV/H<sub>2</sub>O<sub>2</sub> Process to Treat Petroleum Refinery Wastewater**

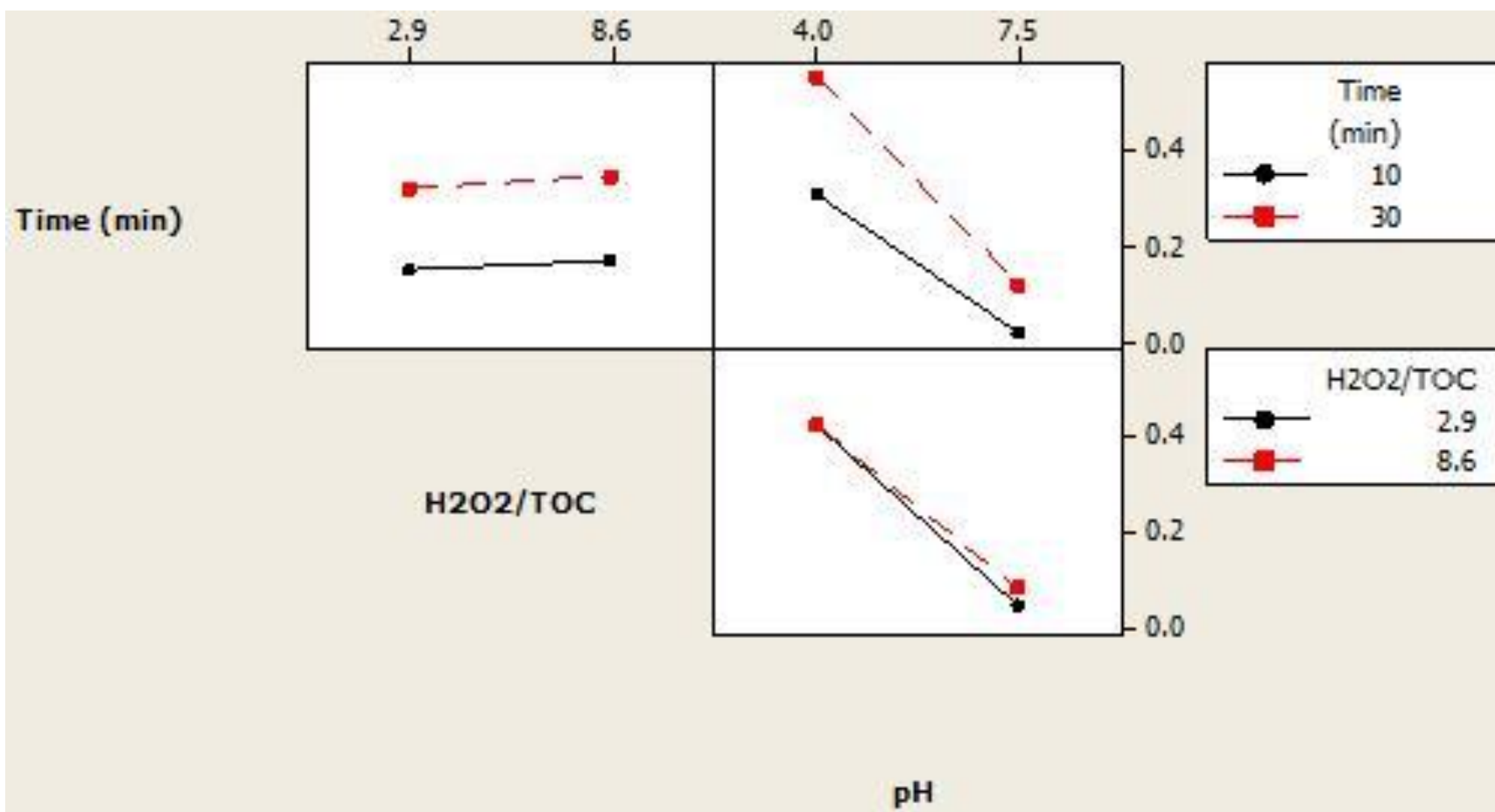


Figure 4.3: Interaction Effect Plot for the Reaction Time, Initial H<sub>2</sub>O<sub>2</sub>/TOC molar ratio, and pH for the Initial Experimental Testing of a UV/H<sub>2</sub>O<sub>2</sub> Process to Treat Petroleum Refinery Wastewater

The three factor ANOVA analysis confirms that a UV/H<sub>2</sub>O<sub>2</sub> process to treat petroleum refinery wastewater was significantly more effective at reducing the TOC when the pH is lowered and the reaction time is increased. Adjusting the pH was significant since the F-ratio of 540.801 was higher than the critical F-ratio of 8.531 at F<sub>0.01,1,16</sub>. Adjusting the reaction time was also significant since the F-ratio of 123.454 was higher than the critical F-ratio of 8.531 at F<sub>0.01,1,16</sub>. Figure 4.2 and Figure 4.3 both show that the treatment performance increases when the pH is lowered and the reaction time is increased. The interaction between the pH and the reaction time is also significant since the F-ratio of 23.368 was higher than the critical F-ratio of 8.531 at F<sub>0.01,1,16</sub>. Adjusting the initial H<sub>2</sub>O<sub>2</sub>/TOC molar ratio was not significant since the F-ratio of 1.620 was lower than the critical F-ratio of 8.531 at F<sub>0.01,1,16</sub>. Figure 4.2 and Figure 4.3 both show that the treatment performance does not significantly change when the initial H<sub>2</sub>O<sub>2</sub>/TOC molar ratio is adjusted. All of the other interactions between the reaction time, initial H<sub>2</sub>O<sub>2</sub>/TOC molar ratio and pH were also not significant since the F-ratio's were lower than the corresponding critical F-ratio's.

Lowering the pH consumed alkalinity in the wastewater which minimizes hydroxyl radical scavenging reactions as previously described in Section 2.4. Minimizing hydroxyl radical scavenging reactions results in a higher UV/H<sub>2</sub>O<sub>2</sub> process treatment performance. Table 2.1 shows that one of the main sources of water to a refinery WWTP is clean water sources including cooling water, boiler blow down, and storm water. All three of these sources contain some form of alkalinity. The refinery, where the wastewater and activated sludge were collected from, measures the alkalinity of the influent wastewater to the biological treatment units on a daily basis using Standard Methods for the Examination of Water and Wastewater Method #2320B (American, 1999) in order to monitor nitrification in the biological treatment units.

When the wastewater samples were collected from the refinery WWTP, the refinery measured the alkalinity as 142 mg/L measured as  $\text{CaCO}_3$ . This measurement is similar to the results found by McKinney R.E. (1967) who found that the average alkalinity in a number of refinery WWTP's was 180 mg/L measured as  $\text{CaCO}_3$ .

As previously described in Section 2.4, carbonate and bicarbonate ions scavenge hydroxyl radicals and decrease the performance of a UV/ $\text{H}_2\text{O}_2$  process while carbonic acid does not scavenge hydroxyl radicals (Juang *et al.* 1997). As Table 2.10 shows, theoretically 92.9% of the inorganic carbon ions are hydroxyl radical scavengers which explain the very low treatment performance at the initial wastewater with the pH of 7.5. When the pH was reduced from 7.5 to 6.0, the theoretically concentration of hydroxyl radical scavengers was reduced by approximately a factor of 3.2 from 92.9% to 29.4% and resulted in a higher treatment performance. When the pH was further reduced to 4.0, the theoretically concentration of hydroxyl radical scavengers was reduced by approximately a factor of 221.3 from 92.9% to 0.4% and resulted in an even higher treatment performance.

There may be also other compounds present in the refinery wastewater which could scavenge hydroxyl radicals and decrease the performance of a UV/ $\text{H}_2\text{O}_2$  process including chlorides and various weak acids. It is recommended to further investigate the composition of refinery wastewater to identify other compounds that would scavenge hydroxyl radicals and affect the performance of a UV/ $\text{H}_2\text{O}_2$  process.

Overall, a UV/ $\text{H}_2\text{O}_2$  process to treat petroleum refinery wastewater is significantly more effective at reducing the TOC in the wastewater when the pH is decreased from 7.5 to 4.0 and the reaction time is increased from 10 to 30 min. This result confirms the work previously

completed by Juang *et al.* (1997) and Stepnowski *et al.* (2002) as discussed in Section 2.4. Decreasing the pH consumes alkalinity in the wastewater which minimizes hydroxyl radical scavenging reactions and results in a higher UV/H<sub>2</sub>O<sub>2</sub> process treatment performance. Increasing the reaction time allows for more time for the reaction to take place which also results in a higher UV/H<sub>2</sub>O<sub>2</sub> process treatment performance (Scott and Ollis, 1995).

As mentioned previously in section 3.3.2, the basis for the second phase of experimental testing used the best performance result from the initial experimental testing. Lowering the pH to 4.0 and increasing the reaction time to 30 min significantly increased the TOC reduction as indicated from the three factor ANOVA analysis. Therefore, the best treatment performance took place at a reaction time of 30 minutes and a pH of 4.0. There was no significant difference in TOC reduction if the experiment took place at an initial H<sub>2</sub>O<sub>2</sub>/TOC molar ratio of either 2.9 or 8.6 mol H<sub>2</sub>O<sub>2</sub>/mol C as indicated from the three factor ANOVA analysis. The lower initial H<sub>2</sub>O<sub>2</sub>/TOC molar ratio of 2.9 mol H<sub>2</sub>O<sub>2</sub>/mol C was chosen as the best performance since a lower initial H<sub>2</sub>O<sub>2</sub>/TOC molar ratio means less H<sub>2</sub>O<sub>2</sub> was being used in the treatment process. Using less H<sub>2</sub>O<sub>2</sub> in the treatment process would reduce the cost of the UV/H<sub>2</sub>O<sub>2</sub> process. Therefore, the best performance for the initial experimental testing was chosen at a reaction time of 30 min, an initial H<sub>2</sub>O<sub>2</sub>/TOC molar ratio of 2.9 mol H<sub>2</sub>O<sub>2</sub>/mol C, and a pH of 4.0.

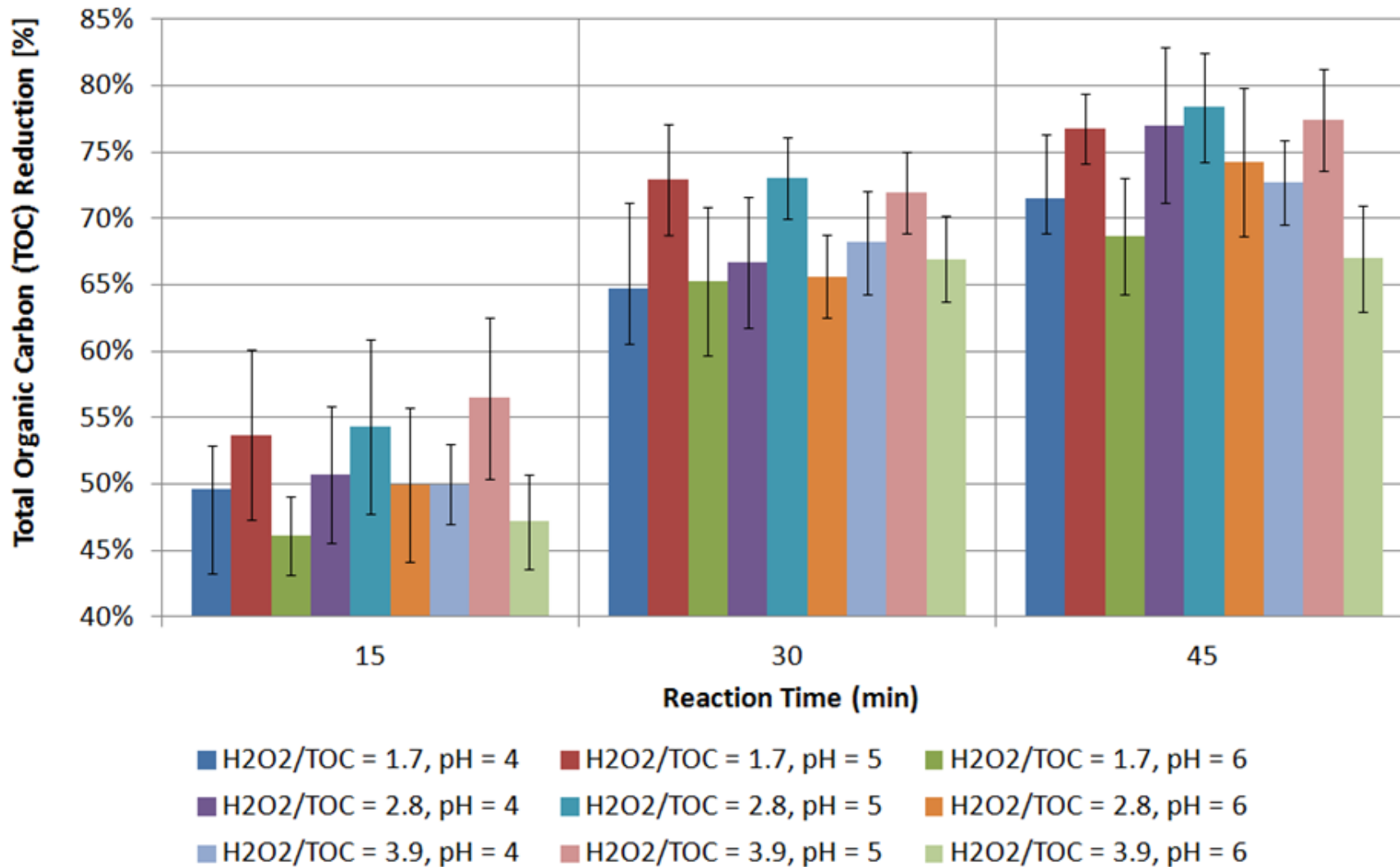
#### **4.2 ADDITIONAL EXPERIMENTAL TESTING TO IMPROVE THE PERFORMANCE OF A UV/H<sub>2</sub>O<sub>2</sub> PROCESS TO TREAT PETROLEUM REFINERY WASTEWATER**

A second phase of experiments was performed to improve the performance of a UV/H<sub>2</sub>O<sub>2</sub> process to treat petroleum refinery wastewater. As mentioned previously, the basis for the second phase of experimental testing used the best performance result from the initial

experimental testing where the reaction time was 30 min, the initial  $\text{H}_2\text{O}_2/\text{TOC}$  molar ratio was 2.9 mol  $\text{H}_2\text{O}_2/\text{mol C}$ , and the pH was 4.0. A reaction time of 30 min would be the basis so the lower and higher values were set at  $\pm 50\%$  of the base value which means the experimental reaction times would be 15, 30, and 45 min. An initial  $\text{H}_2\text{O}_2/\text{TOC}$  molar ratio of 2.8 mol  $\text{H}_2\text{O}_2/\text{mol C}$  would be the basis so the lower and higher values were set at  $\pm 40\%$  of the base value which means the experimental initial  $\text{H}_2\text{O}_2/\text{TOC}$  molar ratios would be 1.7, 2.8, and 3.9 mol  $\text{H}_2\text{O}_2/\text{mol C}$ . A  $\pm 40\%$  was selected based on the ability to accurately measure and add the required amount  $\text{H}_2\text{O}_2$  to meet the required initial  $\text{H}_2\text{O}_2/\text{TOC}$  molar ratio. The minimum pH was established at 4.0 since that was the lowest calibrated value on the pH meter. The middle and higher values were set at one standard unit higher at a pH of 5.0 and 6.0 respectively.

A  $3^3$  factorial design was used in the second phase of experiments as outlined in Table 3.3. Figure 4.4 shows the TOC removal results from the experimental testing outlined in Table 3.3. It should also be noted that the average initial TOC was 42.7 mg C/L for all experiments. The initial  $\text{H}_2\text{O}_2$  concentration for the experiments were 202, 333 and 464 mg  $\text{H}_2\text{O}_2/\text{L}$  for an initial  $\text{H}_2\text{O}_2/\text{TOC}$  molar ratio of 1.7, 2.8, and 3.9 mol  $\text{H}_2\text{O}_2/\text{mol C}$  respectively. A detailed outline of each experimental run is in Appendix J. The measured TOC concentration data output from the TOC analyzer is presented in Appendix K.

Figure 4.4 shows that the average TOC removal was 51, 68 and 74% at a reaction time of 15, 30, and 45 min, respectively. The treatment at a wastewater pH of 5.0 was also on average 6% higher compared to treatment at a wastewater pH of 4.0 or 6.0 for the same reaction time and initial  $\text{H}_2\text{O}_2/\text{TOC}$  molar ratio. This observation aligns with the literature since it has been found that the highest treatment performance of an AOP typically occurs at a pH between 3.0 and 5.0 (Andreozzi *et al.* 1999).



**Figure 4.4: TOC Removal of Petroleum Refinery Wastewater Treated by a UV/H<sub>2</sub>O<sub>2</sub> Process during Additional Experiments**

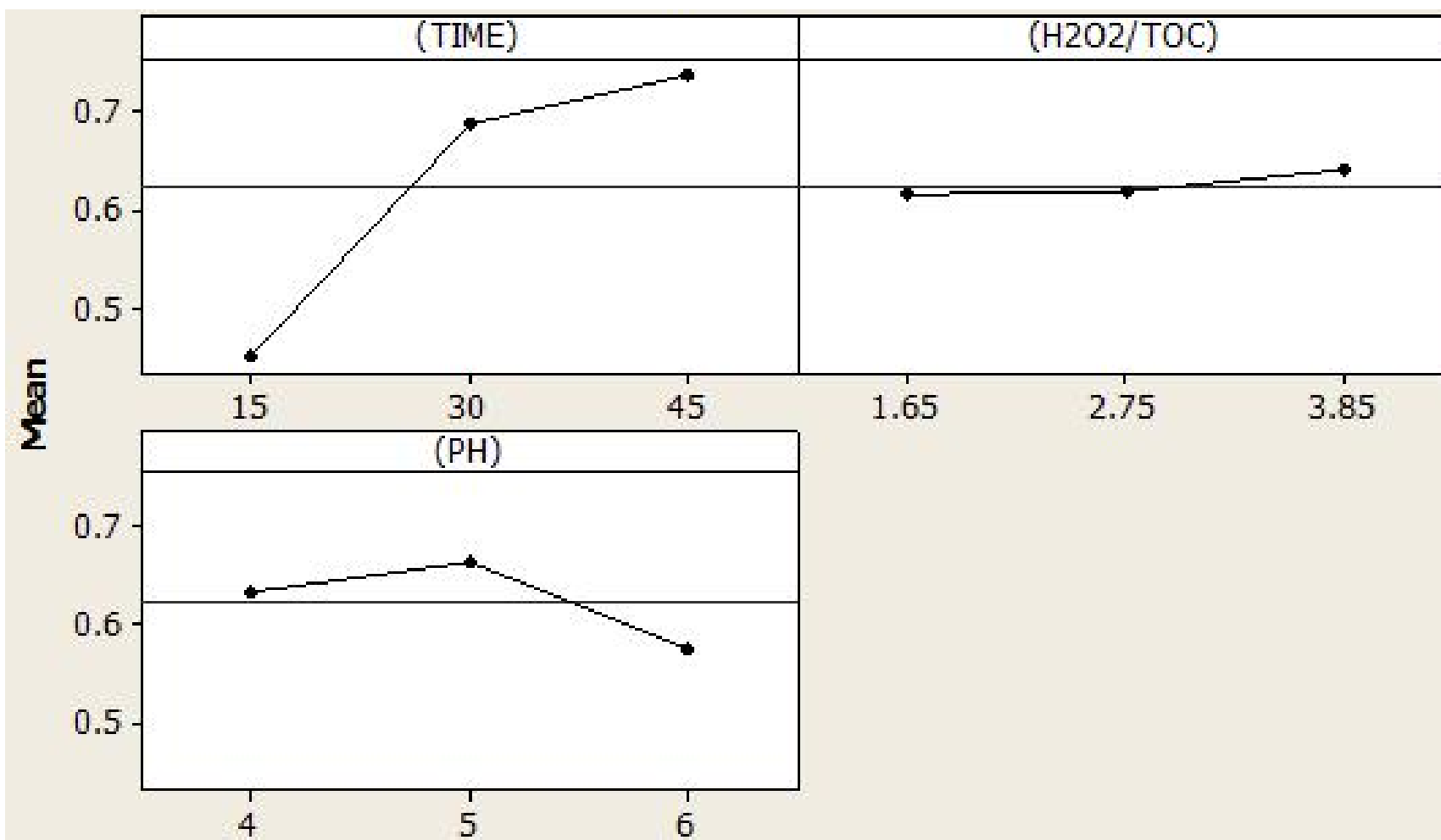


A three factor ANOVA analysis was also completed to identify which parameters and parameter interactions had a significant effect in the additional experimental results. Table 4.2 summarizes the results of a three factor ANOVA analysis while Figure 4.4 and 4.5 display the main effects and interaction effects plots.

**Table 4.2: 3 Factor ANOVA Analysis Results for the Additional Experimental Testing of a UV/H<sub>2</sub>O<sub>2</sub> Process to Treat Petroleum Refinery Wastewater**

Source Of Variation	Degrees Of Freedom	Sum Of Squares	Mean Square	F-Ratio	Critical F-Ratio ( $\alpha=0.01$ )
(Time)	2	1.270019	0.635010	74.944	5.021
(H <sub>2</sub> O <sub>2</sub> /TOC)	2	0.010271	0.005136	0.606	5.021
(pH)	2	0.110581	0.055291	6.525	5.021
(Time) x (H <sub>2</sub> O <sub>2</sub> /TOC)	4	0.055657	0.013914	1.642	3.688
(Time) x (pH)	4	0.041709	0.010427	1.231	3.688
(H <sub>2</sub> O <sub>2</sub> /TOC) x (pH)	4	0.052897	0.013224	1.561	3.688
(Time) x (H <sub>2</sub> O <sub>2</sub> /TOC) x (pH)	8	0.173799	0.021725	2.564	2.860
Error	54	0.457546	0.008473	-	-
Total	80	2.172480	-	-	-

The three factor ANOVA analysis confirmed again that a UV/H<sub>2</sub>O<sub>2</sub> process to treat petroleum refinery wastewater was significantly more effective at reducing the TOC when the pH is lowered and the reaction time was increased. Adjusting the reaction time was significant since the F-ratio of 74.944 was higher than the critical F-ratio of 5.021 at  $F_{0.01,2,54}$ . Adjusting the pH was also significant since the F-ratio of 6.525 was higher than the critical F-ratio of 5.021 at  $F_{0.01,2,54}$ . Figure 4.4 and Figure 4.5 both show that the treatment performance increases when the reaction time is increased. Figure 4.4 and Figure 4.5 also both show that the treatment performance increases when the pH is reduced from 6.0 to 5.0, but then the treatment performance decreases when the pH is further reduced from 5.0 to 4.0. Once again, the initial H<sub>2</sub>O<sub>2</sub>/TOC molar ratio was not significant since the F-ratio of 0.606 was lower than the critical F-ratio of 5.021 at  $F_{0.01,2,54}$ . Figure 4.4 and Figure 4.5 both show that the treatment performance does not significantly change when the initial H<sub>2</sub>O<sub>2</sub>/TOC molar ratio is adjusted.



**Figure 4.5: Main Effects Plot for the Reaction Time, Initial H<sub>2</sub>O<sub>2</sub>/TOC molar ratio, and pH for the Additional Experimental Testing of a UV/H<sub>2</sub>O<sub>2</sub> Process to Treat Petroleum Refinery Wastewater**

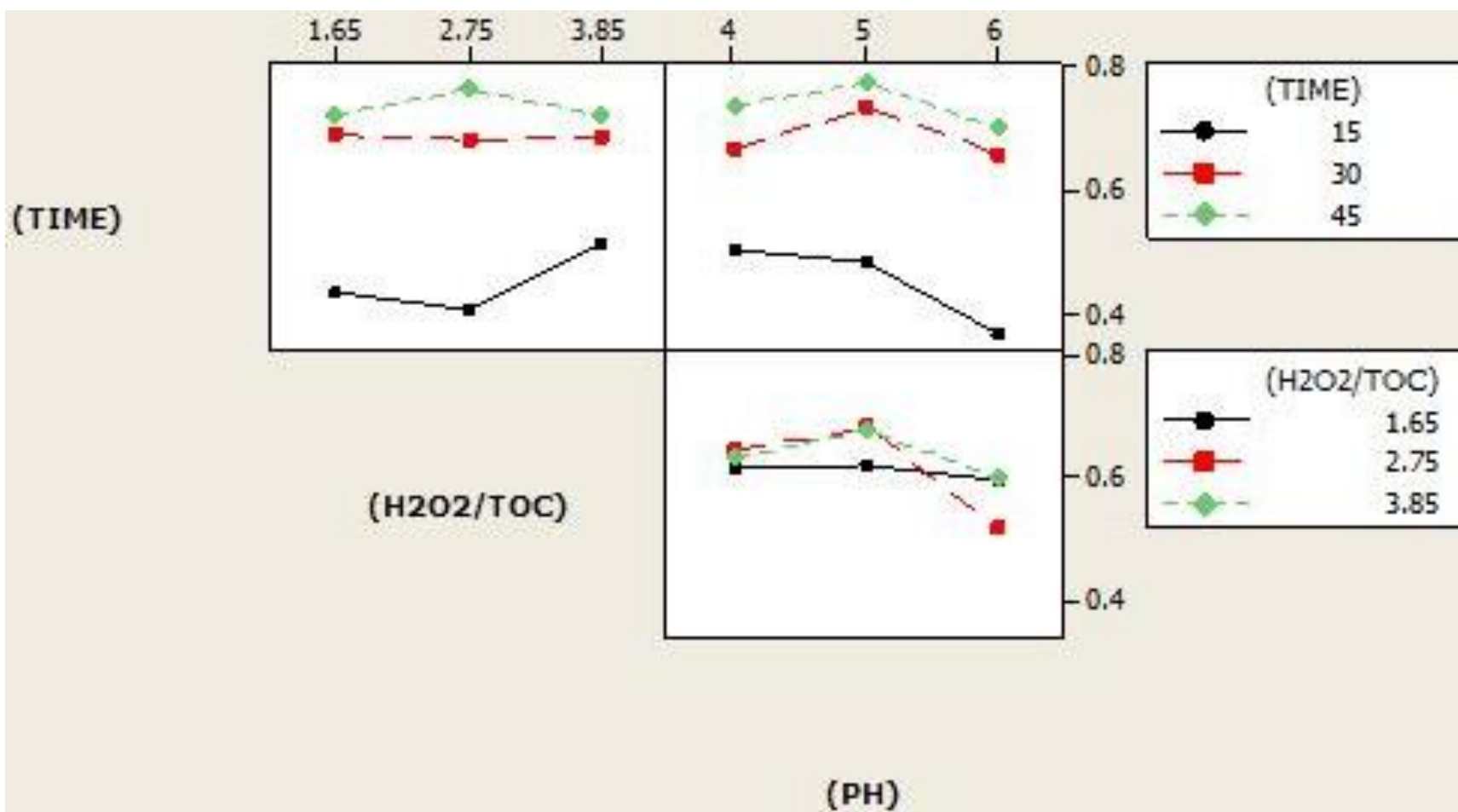


Figure 4.6: Interaction Effect Plot for the Reaction Time, Initial H<sub>2</sub>O<sub>2</sub>/TOC molar ratio, and pH for the Additional Experimental Testing of a UV/H<sub>2</sub>O<sub>2</sub> Process to Treat Petroleum Refinery Wastewater

All of the other interactions between the reaction time, initial  $\text{H}_2\text{O}_2/\text{TOC}$  molar ratio and pH were also not significant since the F-ratio's were lower than the corresponding critical F-ratio's.

Therefore, the best treatment performance took place at a reaction time of 45 minutes and a pH of 5.0. There was no significant difference in TOC reduction if the experiment took place at an initial  $\text{H}_2\text{O}_2/\text{TOC}$  molar ratio of either 1.7, 2.8 or 3.9 mol  $\text{H}_2\text{O}_2/\text{mol C}$  as indicated from the three factor ANOVA analysis. The lower initial  $\text{H}_2\text{O}_2/\text{TOC}$  molar ratio of 1.7 mol  $\text{H}_2\text{O}_2/\text{mol C}$  was chosen as the best performance since a lower initial  $\text{H}_2\text{O}_2/\text{TOC}$  molar ratio would result in less  $\text{H}_2\text{O}_2$  being used. Using less  $\text{H}_2\text{O}_2$  in the process would reduce the cost of the UV/ $\text{H}_2\text{O}_2$  process. Therefore, the best performance was chosen at a reaction time of 45 min, an initial  $\text{H}_2\text{O}_2/\text{TOC}$  molar ratio of 1.7 mol  $\text{H}_2\text{O}_2/\text{mol C}$ , and a pH of 5.0. These parameters will be used in assessing the effects of adding UV/ $\text{H}_2\text{O}_2$  treated petroleum refinery wastewater to activated sludge microorganisms from the refinery WWTP biological treatment process.

As previously described in Section 2.4, carbonate and bicarbonate ions scavenge hydroxyl radicals and decrease the performance of a UV/ $\text{H}_2\text{O}_2$  process while carbonic acid does not scavenge hydroxyl radicals (Juang *et al.* 1997). As Table 2.10 shows, theoretically 29.42% of the inorganic carbon ions are hydroxyl radical scavengers at a pH of 6.0. When the pH was reduced to 5.0, the theoretically concentration of hydroxyl radical scavengers was reduced by approximately a factor of 7.4 from 29.4% to 4.0%. When the pH was further reduced to 4.0, the theoretically concentration of hydroxyl radical scavengers was reduced by approximately a factor of 70.1 from 29.4% to 0.4%.

As previously mentioned, there may also be other compounds present in the refinery wastewater which could scavenge hydroxyl radicals and decrease the performance of a UV/ $\text{H}_2\text{O}_2$  process including chlorides and various weak acids. It is recommended to further investigate the

composition of refinery wastewater to identify other compounds that would scavenge hydroxyl radicals and affect the performance of a UV/H<sub>2</sub>O<sub>2</sub> process.

The TOC removal performance may start to decrease below a pH of 5 since a high concentration of hydrogen ions consumes hydrogen peroxide without generating hydroxyl radicals (Juang *et al.* 1997). Decreasing the wastewater pH from 5.0 to 4.0 increases the concentration of hydrogen ions in the wastewater. Therefore, lowering the pH from 5.0 to 4.0 may increase the concentration of hydrogen ions which consumes hydrogen peroxide beyond any benefit gained from further decreasing the concentration of bicarbonate ions which scavenges hydroxyl radicals (Juang *et al.* 1997). It is recommended to further examine why the treatment performance of a UV/H<sub>2</sub>O<sub>2</sub> process may start to decrease as the pH continues to decrease by measuring the initial and final concentrations of TOC, pH, alkalinity and residual H<sub>2</sub>O<sub>2</sub>.

Once again, increasing the reaction time also allows for more time for the reaction to take place which also results in a higher UV/H<sub>2</sub>O<sub>2</sub> process treatment performance (Scott and Ollis, 1995).

#### **4.3 ASSESSING THE EFFECTS OF ADDING UV/H<sub>2</sub>O<sub>2</sub> TREATED PETROLEUM REFINERY WASTEWATER TO REFINERY WWTP ACTIVATED SLUDGE**

The other objective of this work was to assess the effects of adding UV/H<sub>2</sub>O<sub>2</sub> treated petroleum refinery wastewater to activated sludge microorganisms from the refinery WWTP biological treatment process. The effects of UV/H<sub>2</sub>O<sub>2</sub> treated petroleum refinery wastewater will be assessed as the amount of oxygen consumed by the activated sludge microorganisms from the refinery WWTP using respirometry. The petroleum refinery wastewater was treated using the

best treatment performance parameters of 45 min reaction time, an initial  $\text{H}_2\text{O}_2/\text{TOC}$  molar ratio of 1.7 mol  $\text{H}_2\text{O}_2/\text{mol C}$  and a pH of 5.0. Figure 4.7 outlines the measured oxygen demand results from the respirometry experiments. Table 4.3 summarizes the respirometry experimental results. Figure 4.8 displays the results from Table 4.3.

Figure 4.8 and Table 4.3 show that the untreated refinery wastewater was very biodegradable by the activated sludge microorganisms from the refinery WWTP. The average initial TOC of the untreated refinery wastewater was 42.4 mg C/L. As outlined in Appendix A, an initial TOC of 42.4 mg C/L would have an estimated COD of 112.9 mg  $\text{O}_2/\text{L}$  using a COD/TOC ratio of 2.67 mg  $\text{O}_2/\text{mg C}$ . This estimated COD is similar to the measured oxygen demand of  $117.0 \pm 11.8$  mg  $\text{O}_2/\text{L}$ . These experiments were the biotic control since activated sludge was added to the respirometry reactors.

Figure 4.8 and Table 4.3 also show that the untreated refinery wastewater without activated sludge added had a measured oxygen demand of  $29.8 \pm 4.2$  mg  $\text{O}_2/\text{L}$ . These experiments were the abiotic control since activated sludge was not added to the respirometry reactors. Therefore, this oxygen demand would most likely correspond to the presence of reducing compounds in the wastewater such as sulphides and also the leak rate of the respirometry equipment.

The refinery, where the wastewater and activated sludge were collected from, measures the sulphide concentration of the influent wastewater on a daily basis using the Standard Methods for the Examination of Water and Wastewater Method #4500S (American, 1999). The sulphide concentration of the influent wastewater was 9.6 mg S/L on the day the samples were collected which corresponds to an estimated COD of 19.2 mg  $\text{O}_2/\text{L}$  as calculated in Appendix L.

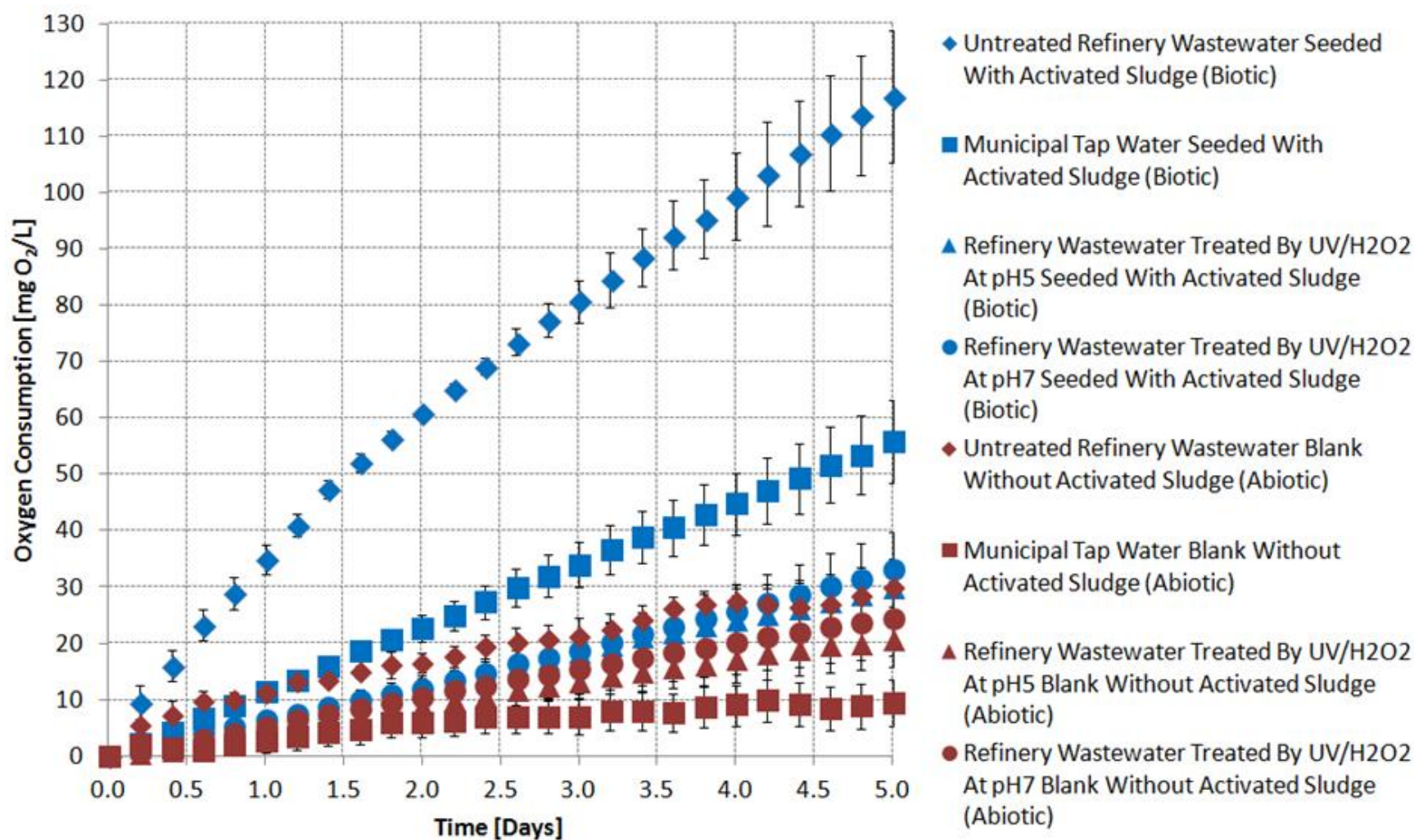
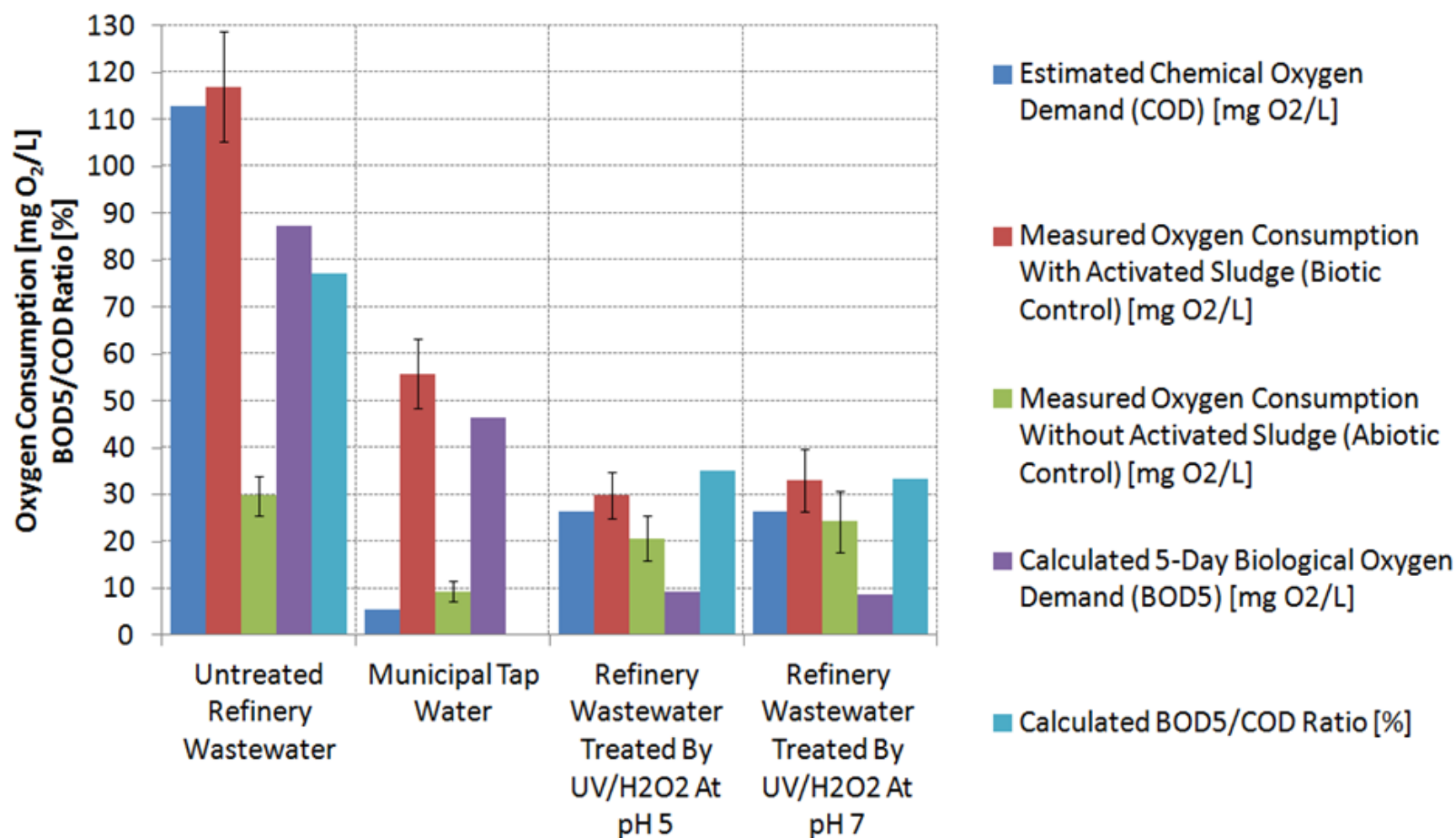


Figure 4.7: Respirometry Experimental Results.

**Table 4.3: Respirometry Testing and Experimental Results**

<b>Water Type</b>	<b>Seeded With Activated Sludge or Blank</b>	<b>pH</b>	<b>Initial Average TOC Concentration [mg C/L]</b>	<b>Estimated Chemical Oxygen Demand (COD) [mg O<sub>2</sub>/L]</b>	<b>Measured Oxygen Consumption [mg O<sub>2</sub>/L]</b>	<b>Calculated 5 Day Biological Oxygen Demand (BOD<sub>5</sub>) [mg O<sub>2</sub>/L]</b>	<b>BOD<sub>5</sub> / COD Ratio [%]</b>	<b>Initial F/M Ratio [kg COD/ kg VSS]</b>	<b>BOD Curve Produced</b>
Untreated Refinery Wastewater	Seeded (Biotic)	7.5	42.4	112.9	117.0±11.8	87.2	77.2%	0.113	A
	Blank (Abiotic)	7.5	42.4	112.9	29.8±4.2	-	-	-	-
Municipal Tap Water	Seeded (Biotic)	7.2	2.1	5.5	55.8±7.5	46.4	-	0.005	C
	Blank (Abiotic)	7.2	2.1	5.5	9.4±2.3	-	-	-	-
UV/H <sub>2</sub> O <sub>2</sub> Treated Refinery Wastewater	Seeded (Biotic)	5.0	9.9	26.4	29.9±5.0	9.3	35.2%	0.026	D
	Blank (Abiotic)	5.0	9.9	26.4	20.6±4.8	-	-	-	-
UV/H <sub>2</sub> O <sub>2</sub> Treated Refinery Wastewater	Seeded (Biotic)	7.0	9.9	26.4	33.1±6.7	8.8	33.3%	0.026	D
	Blank (Abiotic)	7.0	9.9	26.4	24.3±6.6	-	-	-	-





**Figure 4.8: Summary of Respirometry Experimental Results.**

Therefore, the remaining 9.6 mg O<sub>2</sub>/L of the background oxygen demand would be made up of oxygen leaking into the respirometry equipment through joint connections and any other reducing compounds that may be present in the wastewater.

Figure 4.8 and Table 4.3 also show that the calculated BOD<sub>5</sub> for the untreated refinery wastewater was 87.2 mg O<sub>2</sub>/L. The BOD<sub>5</sub> was calculated by subtracting the background oxygen demand of 29.8 mg O<sub>2</sub>/L from the measured oxygen demand of 117.0 mg O<sub>2</sub>/L. The BOD<sub>5</sub>/COD ratio was also 77.2% which indicates a majority of the organics in the wastewater are easily degraded by the activated sludge microorganisms.

The estimated COD of 112.9 mg O<sub>2</sub>/L also resulted in an initial food to microorganism (F/M) ratio of approximately 0.113 kg COD/kg VSS, as calculated in Appendix M. This F/M ratio aligns with respirometry tests found throughout literature (Orhon *et al.* 1999; Strotmann *et al.* 1999) and a typical biological treatment system (Metcalf and Eddy, 2003). Figure 4.7 also shows that an A type BOD curve was produced as displayed in Figure 2.1. Overall, the untreated refinery wastewater was very biodegradable by the activated sludge from the refinery WWTP.

Figure 4.8 and Table 4.3 show that the refinery WWTP activated sludge microorganisms were also viable and active. The average initial TOC of the municipal tap water was 2.1 mg C/L which resulted in an estimated COD of 5.5 mg O<sub>2</sub>/L as calculated in Appendix A. This estimated COD was much lower than the measured oxygen demand of 55.8±7.5 mg O<sub>2</sub>/L. These experiments were the biotic control since activated sludge was added to the respirometry reactors.

Figure 4.8 and Table 4.3 also show that the municipal tap water without activated sludge added had a measured oxygen demand of 9.4±2.3 mg O<sub>2</sub>/L. These experiments were the abiotic control since activated sludge was not added to the respirometry reactors. Therefore, this oxygen

demand would most likely correspond to the leak rate of the respirometry equipment. This leak rate was very similar to the previously calculated 9.6 mg O<sub>2</sub>/L for the background oxygen demand which was made up of equipment leaks and any other reducing compounds that may be present in the wastewater.

Figure 4.8 and Table 4.3 also show that the calculated BOD<sub>5</sub> for the municipal tap water was 46.4 mg O<sub>2</sub>/L. The BOD<sub>5</sub> was calculated by subtracting the background oxygen demand of 9.4 mg O<sub>2</sub>/L from the measured oxygen demand of 55.8 mg O<sub>2</sub>/L.

The estimated COD of 5.5 mg O<sub>2</sub>/L also resulted in an initial F/M ratio of approximately 0.006 kg COD/kg VSS, as calculated in Appendix M which would result in a higher rate of endogenous respiration (Metcalf and Eddy, 2003). Figure 4.7 also shows that a C type BOD curve was produced as displayed in Figure 2.1. Table 2.2 shows that endogenous respiration requires more oxygen relative to typical oxidation and synthesis biological reactions which explains why the measured oxygen demand was much higher compared to the estimated COD. Overall, the refinery WWTP activated sludge microorganisms were viable and active due to endogenous respiration.

Figure 4.8 and Table 4.3 show that the refinery wastewater which was treated with a UV/H<sub>2</sub>O<sub>2</sub> process inhibited the refinery WWTP activated sludge microorganisms. The average initial TOC of the refinery wastewater which was treated with a UV/H<sub>2</sub>O<sub>2</sub> process was 9.9 mg C/L which indicates that there were still organic compounds left in the treated wastewater so complete mineralization of the organics did not occur. The average initial TOC also results in an estimated COD of 26.4 mg O<sub>2</sub>/L as calculated in Appendix A. This estimated COD was similar to the measured oxygen demand of 29.9±5.0 mg O<sub>2</sub>/L. These experiments were the biotic control since activated sludge was added to the respirometry reactors.

Figure 4.8 and Table 4.3 also show that the refinery wastewater which was treated with a UV/H<sub>2</sub>O<sub>2</sub> process without activated sludge added had a measured oxygen demand of 20.6±4.8 mg O<sub>2</sub>/L. These experiments were the abiotic control since activated sludge was not added to the respirometry reactors. Therefore, this oxygen demand would most likely correspond to the presence of reducing compounds in the wastewater and also the leak rate of the respirometry equipment.

Figure 4.8 and Table 4.3 also show that the calculated BOD<sub>5</sub> for the refinery wastewater which was treated with a UV/H<sub>2</sub>O<sub>2</sub> process was 9.3 mg O<sub>2</sub>/L. The BOD<sub>5</sub> was calculated by subtracting the background oxygen demand of 20.6 mg O<sub>2</sub>/L from the measured oxygen demand of 29.9 mg O<sub>2</sub>/L. The BOD<sub>5</sub>/COD ratio was also 35.2% which indicates a majority of the organics in the wastewater were not degradable by the activated sludge microorganisms. This BOD<sub>5</sub> was also much lower compared to the BOD<sub>5</sub> for the activated sludge treating either untreated petroleum refinery wastewater or municipal tap water.

The estimated COD of 26.4 mg O<sub>2</sub>/L also resulted in an initial F/M ratio of approximately 0.026 kg COD/kg VSS, as calculated in Appendix M. This F/M ratio was below typical biological treatment guidelines and should have resulted in a higher rate of endogenous respiration (Metcalf and Eddy, 2003). A B type BOD curve was expected where the residual organic compounds were degraded through oxidation and synthesis biological reactions after which endogenous respiration would take place and result in an increased oxygen consumption. However, endogenous respiration did not occur since Figure 4.7 shows that a D type BOD curve was produced which indicates that the wastewater was inhibitory or toxic to the activated sludge microorganisms. The UV/H<sub>2</sub>O<sub>2</sub> treated refinery wastewater had a pH of 5.0 which was below the optimum pH for bacteria growth typically between 6.5 and 7.5 (Metcalf and Eddy, 2003).

Therefore, another set of respirometry experiments were completed where the pH of the UV/H<sub>2</sub>O<sub>2</sub> treated refinery wastewater was increased to 7.0 before being added to the respirometer reactor to assess if the pH of the wastewater was affecting the activated sludge microorganisms.

Figure 4.8 and Table 4.3 show that the refinery wastewater which was treated with a UV/H<sub>2</sub>O<sub>2</sub> process and then had the pH increased to 7.0 before being added to the respirometer reactors also inhibited the refinery WWTP activated sludge microorganisms. The average initial TOC of the refinery wastewater which was treated with a UV/H<sub>2</sub>O<sub>2</sub> process and then had the pH increased to 7.0 before being added to the respirometer reactors was 9.9 mg C/L which indicates that there were still organic compounds left in the treated wastewater so complete mineralization of the organics did not occur. The average initial TOC also results in an estimated COD of 26.4 mg O<sub>2</sub>/L as calculated in Appendix A. This estimated COD was similar to the measured oxygen demand of 33.1±6.7 mg O<sub>2</sub>/L. These experiments were the biotic control since activated sludge was added to the respirometry reactors.

Figure 4.8 and Table 4.3 also show that the refinery wastewater which was treated with a UV/H<sub>2</sub>O<sub>2</sub> process and then had the pH increased to 7.0 before being added to the respirometer reactors without activated sludge had a measured oxygen demand of 24.3±6.6 mg O<sub>2</sub>/L. These experiments were the abiotic control since activated sludge was not added to the respirometry reactors. Therefore, this oxygen demand would most likely correspond to the presence of reducing compounds in the wastewater and also the leak rate of the respirometry equipment.

Figure 4.8 and Table 4.3 also show that the calculated BOD<sub>5</sub> for the refinery wastewater which was treated with a UV/H<sub>2</sub>O<sub>2</sub> process and then had the pH increased to 7.0 before being added to the respirometer reactors was 8.8 mg O<sub>2</sub>/L. The BOD<sub>5</sub> was calculated by subtracting

the background oxygen demand of 24.3 mg O<sub>2</sub>/L from the measured oxygen demand of 33.1 mg O<sub>2</sub>/L. This shows that the BOD<sub>5</sub> did not improve when the pH was adjusted from 5.0 to 7.0. The BOD<sub>5</sub>/COD ratio was also 33.3% which indicates a majority of the organics in the wastewater were not degradable by the activated sludge microorganisms. This BOD<sub>5</sub> was also much lower compared to the BOD<sub>5</sub> for the activated sludge treating either untreated petroleum refinery wastewater or municipal tap water.

The estimated COD of 26.4 mg O<sub>2</sub>/L also resulted in an initial F/M ratio of approximately 0.026 kg COD/kg VSS, as calculated in Appendix M. This F/M ratio was below typical biological treatment guidelines and should have resulted in a higher rate of endogenous respiration (Metcalf and Eddy, 2003). A B type BOD curve was expected where the residual organic compounds were degraded through oxidation and synthesis biological reactions after which endogenous respiration would take place and result in an increased oxygen consumption. However, endogenous respiration did not occur since Figure 4.7 shows that a D type BOD curve was produced which indicates that the wastewater was inhibitory or toxic to the activated sludge microorganisms. The UV/H<sub>2</sub>O<sub>2</sub> treated petroleum refinery wastewater had a pH of 7.0 which is within the optimum pH for bacteria growth (Metcalf and Eddy, 2003). Therefore, the pH of the wastewater did not have an effect on the activated sludge microorganisms since the BOD<sub>5</sub> did not improve when the pH was adjusted from 5.0 to 7.0.

This once again shows that untreated refinery wastewater was very biodegradable and the refinery wastewater which was treated with a UV/H<sub>2</sub>O<sub>2</sub> process was inhibitory to the activated sludge from the refinery WWTP. The treated wastewater was inhibitory due to either improper degradation of the wastewater organics where the new intermediate compound structures increased the toxicity of the wastewater, the activated sludge microorganisms were not

acclimatized to the new intermediate compounds or the residual  $\text{H}_2\text{O}_2$  concentration was toxic to the activated sludge microorganisms.

The UV/ $\text{H}_2\text{O}_2$  treated wastewater was not biodegradable since it most likely inhibited the activated sludge microorganisms. One reason for a low oxygen uptake by the activated sludge was improper degradation of the organics where the structure of the compounds changed in a way that increases the toxicity of the wastewater (Tabrizi and Mehrvar, 2004). This study did not include analyzing the molecular structure of the wastewater constituents. Therefore, it is recommended to further investigate the molecular structure of the initial, intermediate and final wastewater constituents during biological, UV/ $\text{H}_2\text{O}_2$  and combined process treatments.

The activated sludge microorganisms may not have been acclimatized to the new intermediate compounds in the UV/ $\text{H}_2\text{O}_2$  treated wastewater. Combining a UV/ $\text{H}_2\text{O}_2$  and biological treatment process may require re-acclimatization since the activated sludge may not have the specific microorganisms present in the microbial community or enzymes required to degrade the new intermediate compounds (Scott and Ollis, 1995). It is recommended to further evaluate combining chemical and biological treatment process to assess if the overall treatment of petroleum refinery wastewater can be improved

High concentrations of  $\text{H}_2\text{O}_2$  can also adversely affect the activated sludge microorganisms. As stated previously, the initial  $\text{H}_2\text{O}_2$  concentration was between 202 and 1,023 mg  $\text{H}_2\text{O}_2$ /L. This initial  $\text{H}_2\text{O}_2$  concentration range was much lower than what was found in literature since a similar study treating refinery wastewater with a UV/ $\text{H}_2\text{O}_2$  process used an initial  $\text{H}_2\text{O}_2$  concentration of 1,000 mg/L for pre biological treatment and 5,000 mg/L for post biological treatment (Juang *et al.* 1997). Typically, an initial concentration of approximately 100 mg  $\text{H}_2\text{O}_2$ /L adversely affects the activated sludge microorganisms due to a high residual

concentration of  $\text{H}_2\text{O}_2$  (Scott and Ollis, 1995). It has been shown that a residual  $\text{H}_2\text{O}_2$  concentration of 3 – 7 mg  $\text{H}_2\text{O}_2/\text{L}$  did not affect activated sludge microorganisms (Laera *et al.* 2012). This study did not include measuring the residual concentration of  $\text{H}_2\text{O}_2$  in the UV/ $\text{H}_2\text{O}_2$  treated wastewater. Therefore, it is recommended to further investigate how residual  $\text{H}_2\text{O}_2$  affects the activity of the activated sludge microorganisms.

It should also be highlighted that there is always risk of equipment failing or not working properly during normal operation. In this case, since the wastewater was required to be acidified down to 5.0 which was below the optimum pH range of 6.5 and 7.5 for biological treatment, it is assumed that the pH would have to be adjusted back up to the optimum biological treatment operating range (Metcalf and Eddy, 2003). In the event that the caustic addition fails, the acidic water would pose a risk to the biological treatment unit as previously described.

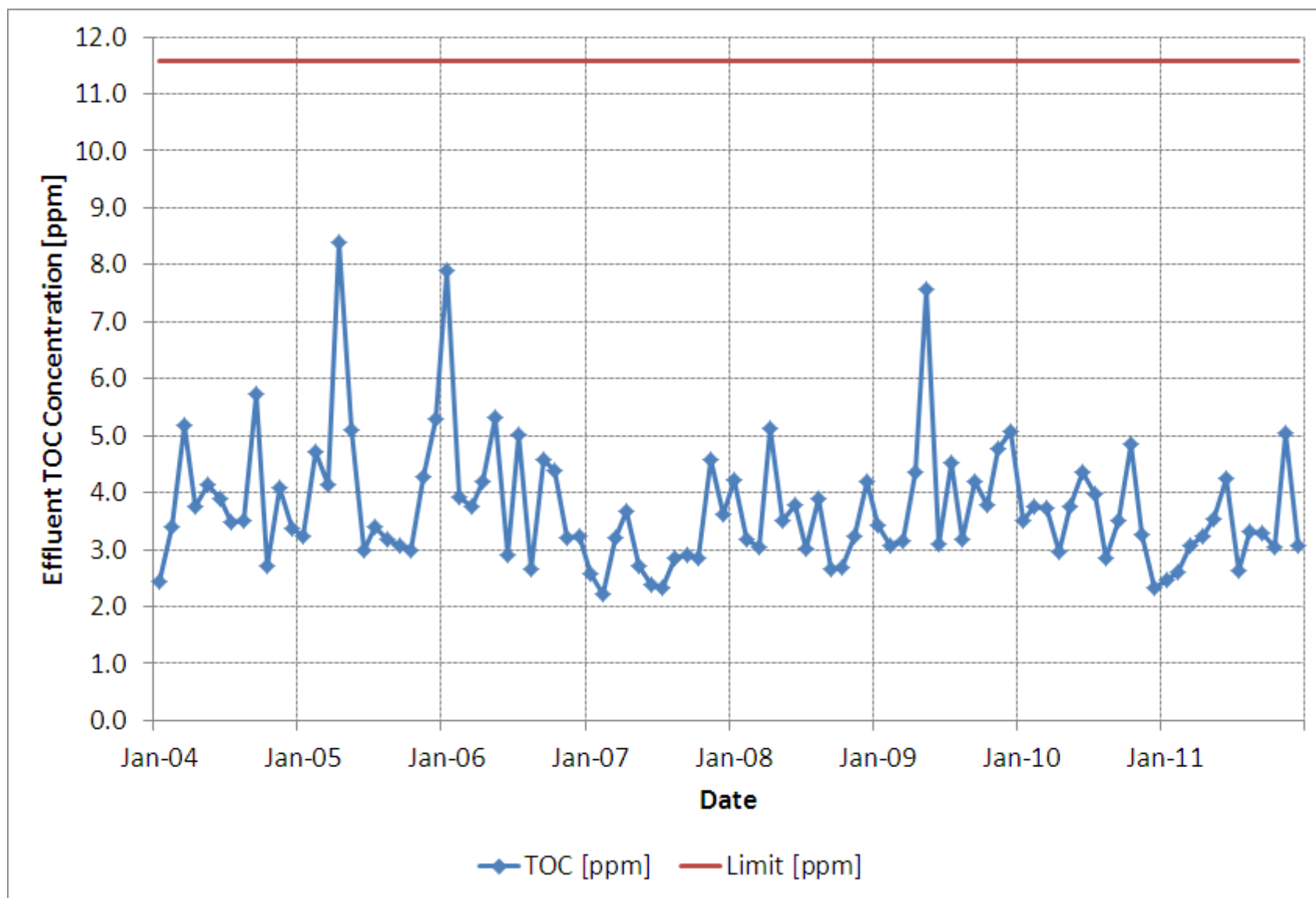
Overall, a UV/ $\text{H}_2\text{O}_2$  process was currently not suitable as a pre-treatment for the biological treatment unit since the UV/ $\text{H}_2\text{O}_2$  treated refinery wastewater inhibited the refinery activated sludge microorganisms. This occurred when the raw refinery wastewater was treated with a UV/ $\text{H}_2\text{O}_2$  process for 45 min, with an initial  $\text{H}_2\text{O}_2/\text{TOC}$  molar ratio of 2.8 mol  $\text{H}_2\text{O}_2/\text{mol C}$ , an initial  $\text{H}_2\text{O}_2$  concentration of 202 mg  $\text{H}_2\text{O}_2/\text{L}$  and a pH of either 5 or 7.

Using a UV/ $\text{H}_2\text{O}_2$  process as a post-treatment after the biological treatment unit at a refinery WWTP was not examined. The refinery where the wastewater and activated sludge was collected from did not have an issue meeting the regulated effluent TOC limit so it was deemed unnecessary to test this scenario.



Figure 4.9 shows that the average WWTP effluent TOC concentration from the Suncor Mississauga Refinery between January 2004 and December 2011 has not exceeded the regulated effluent TOC concentration limit (Ontario, 2013). The average effluent TOC concentration between January 2004 and December 2011 was 3.7 mg C/L which was approximately 32% of the regulated effluent concentration of 11.6 mg C/L (Ontario, 2011). The raw data and the calculated regulated effluent concentration limit are outlined in Appendix N. It should also be noted, that the highest treatment performance of a UV/H<sub>2</sub>O<sub>2</sub> process to treat refinery wastewater resulted in a final TOC concentration of 9.9 mg C/L as shown in Table 4.3 which was approximately 85% of the regulated effluent concentration of 11.6 mg C/L (Ontario, 2011). Therefore, a bench scale UV/H<sub>2</sub>O<sub>2</sub> process was not able to even achieve a treatment efficiency comparable to the current refinery WWTP biological treatment process.

A UV/H<sub>2</sub>O<sub>2</sub> process must be used with caution at a petroleum refinery WWTP since it contradicts the purpose of the current MISA regulation. There is always a risk of equipment failing or not working properly. The UV/H<sub>2</sub>O<sub>2</sub> process required the wastewater to be acidified down to 5.0 which is below the regulated effluent pH range 6.0 to 9.5 as required by Ontario Regulation 537/93 the MISA Effluent Monitoring and Effluent Limits for the Petroleum Sector (Ontario, 1993). The effluent pH would have to be adjusted back up to a regulated effluent limit of 6.0 to 9.5 before being discharged out to the environment to maintain regulatory compliance. In the event that the caustic addition fails, the acidic water would violate the regulated MISA effluent quality and produce a toxic effluent which goes against the purpose of the MISA regulation and result in financial penalties from the Ontario Ministry of the Environment due to regulatory non-compliance.



**Figure 4.9: Suncor Mississauga Refinery's Average Effluent TOC from 2004 through 2011**

It should also be noted that installing a new UV/H<sub>2</sub>O<sub>2</sub> process at a petroleum refinery WWTP would be in contravention of the current Ontario Regulation 455/09 or Toxic Reduction Act (TRA) regulation. The pH of the wastewater was required to be decreased for a UV/H<sub>2</sub>O<sub>2</sub> process to actually remove organic compounds. In a full scale application, a UV/H<sub>2</sub>O<sub>2</sub> process would require the addition of an acid such a sulphuric acid or even hydrochloric acid. However, both sulphuric acid and hydrochloric acid are listed in the TRA. Instead of reducing the use of these toxic substances, using a UV/H<sub>2</sub>O<sub>2</sub> process to treat petroleum refinery wastewater requires more use of a toxic substance which does not comply with O. Reg 455/09.

# CHAPTER 5

## CONCLUSIONS AND RECOMMENDATIONS

### 5.1 CONCLUSIONS

The first phase of experiments was an initial screening of how the reaction time, the initial  $\text{H}_2\text{O}_2/\text{TOC}$  molar ratio and the system pH affected the treatment of petroleum refinery wastewater using a UV/ $\text{H}_2\text{O}_2$  process. Lowering the pH to 4.0 and increasing the reaction time to 30 min significantly increased the TOC reduction as indicated from the three factor ANOVA analysis. There was no significant difference in TOC reduction if the experiment took place at an initial  $\text{H}_2\text{O}_2/\text{TOC}$  molar ratio of either 2.9 or 8.6 mol  $\text{H}_2\text{O}_2/\text{mol C}$  as indicated from the three factor ANOVA analysis. The lower initial  $\text{H}_2\text{O}_2/\text{TOC}$  molar ratio of 2.9 mol  $\text{H}_2\text{O}_2/\text{mol C}$  was chosen as the best performance since a lower initial  $\text{H}_2\text{O}_2/\text{TOC}$  molar ratio means less  $\text{H}_2\text{O}_2$  was being used in the treatment process. Therefore, the best performance for the initial experimental testing was chosen at a reaction time of 30 min, an initial  $\text{H}_2\text{O}_2/\text{TOC}$  molar ratio of 2.9 mol  $\text{H}_2\text{O}_2/\text{mol C}$ , and a pH of 4.0.

The second phase of experiments was performed to improve the performance of a UV/ $\text{H}_2\text{O}_2$  process to treat petroleum refinery wastewater. A three factor ANOVA analysis confirmed again that a UV/ $\text{H}_2\text{O}_2$  process to treat petroleum refinery wastewater was significantly more effective at reducing the TOC when the reaction time was increased. The three factor ANOVA analysis also indicated that the treatment performance increases when the pH is reduced from 6.0 to 5.0, but then the treatment performance decreases when the pH is further

reduced from 5.0 to 4.0. Therefore, the best treatment performance took place at a reaction time of 45 minutes and a pH of 5.0. There was no significant difference in TOC reduction if the experiment took place at an initial  $\text{H}_2\text{O}_2/\text{TOC}$  molar ratio of either 1.7, 2.8 or 3.9 mol  $\text{H}_2\text{O}_2/\text{mol C}$  as indicated from the three factor ANOVA analysis. The lower initial  $\text{H}_2\text{O}_2/\text{TOC}$  molar ratio of 1.7 mol  $\text{H}_2\text{O}_2/\text{mol C}$  was chosen as the best performance since a lower initial  $\text{H}_2\text{O}_2/\text{TOC}$  molar ratio would result in less  $\text{H}_2\text{O}_2$  being used. Using less  $\text{H}_2\text{O}_2$  in the process would reduce the cost of the UV/ $\text{H}_2\text{O}_2$  process. Therefore, the best performance was chosen at a reaction time of 45 min, an initial  $\text{H}_2\text{O}_2/\text{TOC}$  molar ratio of 1.7 mol  $\text{H}_2\text{O}_2/\text{mol C}$ , and a pH of 5.0. Decreasing the pH consumed alkalinity in the wastewater which minimized hydroxyl radical scavenging reactions and resulted in a higher UV/ $\text{H}_2\text{O}_2$  process treatment performance. Increasing the reaction time allowed for more time for the reaction to take place and also resulted in a higher UV/ $\text{H}_2\text{O}_2$  process treatment performance. Overall, these results confirm and support the work previously completed by Juang *et al.* (1997) and Stepnowski *et al.* (2002).

A UV/ $\text{H}_2\text{O}_2$  process was found not to be suitable as a pre-treatment process for the refinery biological treatment unit since the UV/ $\text{H}_2\text{O}_2$  treated refinery wastewater inhibited the refinery activated sludge microorganisms. This occurred when the raw refinery wastewater was treated with a UV/ $\text{H}_2\text{O}_2$  process at the best treatment parameters of 45 min, with an initial  $\text{H}_2\text{O}_2/\text{TOC}$  molar ratio of 1.7 mol  $\text{H}_2\text{O}_2/\text{mol C}$ , an initial  $\text{H}_2\text{O}_2$  concentration of 202 mg  $\text{H}_2\text{O}_2/\text{L}$  and a pH of either 5 or 7. The effects of untreated petroleum refinery wastewater were tested using respirometry and was found to be very biodegradable by the activated sludge from the petroleum refinery WWTP since the  $\text{BOD}_5$  was 87.2 mg  $\text{O}_2/\text{L}$  and the measured oxygen demand displayed a characteristic A type BOD curve due to active microorganisms. Municipal tap water was then seeded with activated sludge from the petroleum refinery WWTP and respirometry was

used to show that active microorganisms were present since the BOD<sub>5</sub> was 46.4 mg O<sub>2</sub>/L and the measured oxygen demand displayed a characteristic C type BOD curve due to endogenous respiration. The petroleum refinery wastewater which was treated with a UV/H<sub>2</sub>O<sub>2</sub> process was inhibitory to the activated sludge microorganisms from the refinery WWTP since the BOD<sub>5</sub> measured was only 9.3 and 8.8 mg O<sub>2</sub>/L at a pH of 5.0 or 7.0 respectively. The oxygen demand also displayed a characteristic D type BOD curve due to microbial inhibition. Therefore, the UV/H<sub>2</sub>O<sub>2</sub> treated petroleum refinery wastewater had an inhibitory effect on the refinery WWTP activated sludge microorganisms. The treated wastewater was inhibitory due to either improper degradation of the wastewater organics where the new intermediate compound structures increased the toxicity of the wastewater, the activated sludge microorganisms were not acclimatized to the new intermediate compounds or the residual H<sub>2</sub>O<sub>2</sub> concentration was toxic to the activated sludge microorganisms.

Finally, a UV/H<sub>2</sub>O<sub>2</sub> process is currently not suitable for full scale application in a petroleum refinery WWTP due to the incompatibility with current environmental regulations. The UV/H<sub>2</sub>O<sub>2</sub> process required the pH of the wastewater to be decreased to 5.0 which was well below the optimum pH range of 6.5 and 7.5 for activated sludge microorganisms. This poses a risk to the biological treatment unit which can result in discharging effluent that exceeds regulatory limits and result in financial penalties from the Ontario MOE due to regulatory non-compliance. Decreasing the pH to 5.0 was also below the regulated effluent pH range 6.0 to 9.5 as required by Ontario Regulation 537/93 the MISA Effluent Monitoring and Effluent Limits for the Petroleum Sector. Equipment failure could result in violating the regulated MISA effluent quality and result in financial penalties from the Ontario MOE due to regulatory non-compliance. It should also be noted that using a UV/H<sub>2</sub>O<sub>2</sub> process would also be in contravention with

Ontario Regulation 455/09, the Toxic Reduction Act. Instead of reducing the use of toxic substances such as sulphuric acid, using a UV/H<sub>2</sub>O<sub>2</sub> process to treat refinery wastewater requires more use of toxic substances and in turn does not comply with O. Reg 455/09.

## 5.2 RECOMMENDATIONS

The following are a list of recommendations from this work:

- There may be also other compounds present in the refinery wastewater which could scavenge hydroxyl radicals and decrease the performance of a UV/H<sub>2</sub>O<sub>2</sub> process including chlorides and various weak acids. It is recommended to investigate the composition of refinery wastewater to identify other compounds that would scavenge hydroxyl radicals and affect the performance of a UV/H<sub>2</sub>O<sub>2</sub> process. Identifying the specific compounds in refinery wastewater was not within the scope of this work. Compounds can be identified using analytical tools such as gas chromatography–mass spectrometry (GC-MS).
- There appeared to be a maximum treatment performance at a pH of 5. The literature does state that the treatment performance maximum for a UV/H<sub>2</sub>O<sub>2</sub> process is typically between a pH of 3 and 5. However, the references to those specific works were not accessible since Ryerson does not have a license for the required journal or text book. It is recommended to further examine why the treatment performance of a UV/H<sub>2</sub>O<sub>2</sub> process may start to decrease as the pH continues to decrease. This can be accomplished by measuring the initial and final concentrations of TOC, pH, alkalinity and residual

H<sub>2</sub>O<sub>2</sub> to track how they change at various pH values. These additional measurements were not within the scope of this work.

- One reason for a low oxygen uptake by the activated sludge would be improper degradation of the organics where the structure of the compounds changed in a way that increases the toxicity of the wastewater. Analyzing the molecular structure of the wastewater constituents was not within the scope of this work. It is recommended to investigate the molecular structure of the initial, intermediate and final wastewater constituents during biological, UV/H<sub>2</sub>O<sub>2</sub> and combined process treatments. Compounds can be identified using analytical tools such as gas chromatography–mass spectrometry (GC-MS).
- Combining a UV/H<sub>2</sub>O<sub>2</sub> and biological treatment process may require re-acclimatization of the activated sludge since the activated sludge may not have the specific microorganisms present in the microbial community or enzymes required to degrade the new intermediate compounds. It is recommended to evaluate combining chemical and biological treatment processes to assess if the overall treatment of petroleum refinery wastewater can be improved. This can be done by settling up a lab scale AOP reactor connected to a lab scale biological treatment unit and running continuous experiments. This type of additional experimentation was not within the scope of this work.
- High concentrations of H<sub>2</sub>O<sub>2</sub> can also adversely affect the activated sludge microorganisms. Measuring the residual concentration of H<sub>2</sub>O<sub>2</sub> in the UV/H<sub>2</sub>O<sub>2</sub> treated wastewater was not within the scope of this work. It is recommended to investigate how residual hydrogen peroxide affects the activity of the activated sludge microorganisms.



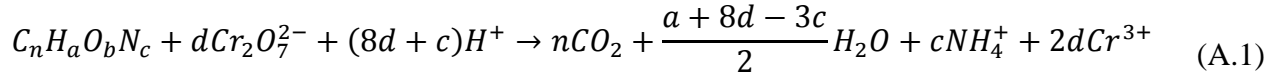
This can be done by dosing activated sludge with wastewater containing measured residual concentrations of  $\text{H}_2\text{O}_2$  and measuring the oxygen uptake through respirometry.

- There is potential to develop a model of a combined UV/ $\text{H}_2\text{O}_2$  and biological treatment process. The model should include 4 different function including treatment performance, regulated effluent limits, operating cost and toxicity. These four functions can then be solved simultaneously to identify how a combined UV/ $\text{H}_2\text{O}_2$  and biological treatment system can be operated in order to maximize treatment performance, stay within regulated effluent limits, minimize operating costs and minimize toxicity. Developing a model was not within the scope of this work since it requires a lot of additional research into combined treatment performance, combined operating costs, and toxicity limits.

# APPENDICIES

## APPENDIX A: COD/TOC CORRELATION CALCULATIONS

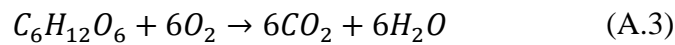
The following equation outlines how the organic material is converted to carbon dioxide (Metcalf and Eddy, 2003):



Where

$$d = \frac{2n}{3} + \frac{a}{6} - \frac{b}{3} - \frac{c}{2} \quad (A.2)$$

Developing a correlation between COD and TOC is important since the COD can be estimated by measuring the TOC of a wastewater and multiplying the result by a developed correlation (Eckenfelder, 2000). This correlation is essentially a carbon-oxygen balance (Eckenfelder, 2000). For example, a simple organic compound such as glucose would have a COD/TOC ratio of 2.67 mg COD/mg TOC. The calculation is as follows:



$$\frac{COD}{TOC} = \frac{6(M_{O_2})}{6(M_C)} = \frac{6\left(32 \frac{g}{mol} O_2\right)}{6\left(12 \frac{g}{mol} C\right)} = 2.67 \frac{mg \text{ COD}}{mg \text{ TOC}} \quad (A.4)$$

Where,

$M_{O_2}$  = molar mass of molecular oxygen ( $O_2$ ) = 32 g / mol  $O_2$

$M_C$  = molar mass of carbon = 12 g / mol C

The COD/TOC ratio will change based on the characteristics of the wastewater especially if it contains aromatic and nitrogen-containing compounds (Eckenfelder, 2000). However, an

initial COD/TOC ratio estimate of 2.67 mg COD/mg TOC is typically used for industrial wastewater until a plant specific COD/TOC ratio can be developed (Eckenfelder, 2000). Eckenfelder (2000), also found that the typical COD/TOC ratio for a petrochemical refinery was 2.70 mg COD/mg TOC which is close to the recommended initial estimate COD/TOC ratio of 2.67 mg COD/mg TOC.

## APPENDIX B: CHARACTERISTICS OF PETROLEUM REFINERY WASTEWATER THROUGHOUT LITERATURE

Type:	Flow (gpm)	Temp (°C)	pH	COD (mg/L)	BOD <sub>5</sub> (mg/L)	TOC (mg/L)	TKN (mg/L)	NH <sub>3</sub> (mg/L)	PO <sub>4</sub> (mg/L)	Reference:
Petroleum Refinery wastewater effluent	-	-	8	96	-	-	-	-	-	Adeyinka and Rim-rukeh, 1999
Petroleum Refinery wastewater influent to CPL	-	-	-	420	140 - 350	-	60	-	-	Al Zarooni and Elshorbagy, 2006
Petroleum Refinery Wastewater	-	-	7.5 - 8.5	300 - 1,050	650 - 1,600	-	30 - 40	20 - 30	30	Coe, 1952
Petrochemical Wastewater	-	-	6.5 - 8.5	800	350	-	-	-	-	Demirci <i>et al.</i> 1998
Petroleum Refinery wastewater from condensates, quenches and wash waters.	100 - 350	-	-	500 - 2,800	230 - 440	-	-	-	-	Elkin, 1959
Petrochemical Wastewater	881	30	6.2 - 7.6	74 - 386	56 - 84	33 - 119	1.2 - 3.8	0.2 - 2.4	11 - 28	Farooq and Misbahuddin, 1991a
Various chemical, petrochemical & polymer refineries.	-	-	-	192 - 350,000	850 - 62,000	110 - 160,000	-	-	-	Ford <i>et al.</i> 1971
Petroleum Refinery wastewater effluent from API separator.	-	-	-	351 - 790	-	-	-	-	-	Galil and Wolf, 2001
Petroleum Refinery wastewater influent to activated sludge system.	-	-	6.5 - 8.0	5,200	3,160	2,943	-	-	-	Guan <i>et al.</i> 2000
Petrochemical Wastewater	-	-	8.1	510	-	-	-	-	-	Jou and Huang, 2003
Petrochemical Wastewater	-	-	8.3 - 8.6	4,400 - 5,130	-	1,100 - 1,300	180 - 253	21 - 29	-	Juang <i>et al.</i> 1997
Terephthalic acid (PTA) Wastewater	-	40 - 50	3.0 - 5.0	720 - 1,840	-	-	-	-	-	Kleerebezem <i>et al.</i> 1997
Olefin Process Wastewater and Petrochemical Wastewater from process streams.	-	-	9.0 - 10.0	-	-	250 - 850	-	-	-	Llop <i>et al.</i> 2009
Terephthalic acid (PTA)	-	-	4.5	9,000	5,500	-	-	-	-	Macarie <i>et al.</i> 1992
Chemical and Petrochemical Wastewaters treated by Anaerobic Treatment Technology	-	-	-	650 - 50,000	-	-	-	-	-	Macarie, 2000

Type:	Flow (gpm)	Temp (°C)	pH	COD (mg/L)	BOD <sub>5</sub> (mg/L)	TOC (mg/L)	TKN (mg/L)	NH <sub>3</sub> (mg/L)	PO <sub>4</sub> (mg/L)	Reference:
Petroleum Refinery wastewater influent to API separator.	-	-	7.6 - 7.8	146.5 - 151.5	-	-	-	-	-	Mahendra Kaenrd and Viraraghavan, 1996
Petrochemical Wastewater	1,284	32 - 40	-	1000 - 2700	-	-	-	-	-	Maqueda <i>et al.</i> 2006
Average Refinery Wastewater Characteristics from 12 Refineries	1,100	31	8.4	320	160	-	-	87	49	McKinney, 1967
Petroleum Refinery wastewater influent to API separator. Petroleum Refinery wastewater effluent from API separator.	37 - 46	35 30	-	450 160	300 80	250 45	-	-	-	Meier and Nikolic, 1995
Olefin Process Wastewater	-	25 - 30	5.8 - 6.0	-	-	-	-	-	-	Mohammadzadeh <i>et al.</i> 2004
Terephthalic acid (PTA) Wastewater	1,013	50 - 60	3.0 - 5.0	4,000 - 12,000	-	-	-	-	-	Noyola <i>et al.</i> 2000
Petrochemical Wastewater	-	-	4.3 - 5.2	4,120 - 4,950	1,150 - 1,360	-	20 - 25	-	7 - 10	Park <i>et al.</i> 1996
Wastewater from the Gujarat State Fertilizer Company of Baroda	-	-	2.5 - 2.7	5,500 - 6,000	3,000 - 3,200	-	50 - 212	-	102 - 227	Patel and Madamwar, 2002
Petroleum Refinery wastewater influent to activated sludge system.	-	34	7	319	121	-	205	-	-	Pinzon Pardo <i>et al.</i> 2007
Petroleum Refinery wastewater influent to activated sludge system.	-	26	6.4 - 10.4	720 - 1,590	-	-	-	56-132	8.5 - 10.1	Qin <i>et al.</i> 2007
Petrochemical Wastewater from DAF to Activated Sludge System	-	-	8.1 - 8.8	625 - 637	180 - 268	-	-	4.7 - 21	-	Rebhun and Galil, 1988
Petroleum Refinery wastewater influent to activated sludge system.	-	-	6.5 - 7.5	170 - 180	-	-	-	-	-	Saien and Nejati, 2007
Dimethyl Terephthalate (DMT) Wastewater	-	-	2	110,000 - 162,000	-	-	-	-	-	Shah <i>et al.</i> 1998
Dimethyl Terephthalate (DMT) Wastewater	-	-	1.6 - 2.5	130,000 - 142,000	-	-	-	-	-	Sharma <i>et al.</i> 1994
Petroleum Refinery wastewater influent to activated sludge system.	-	25 - 37	7.1 - 7.4	200 - 850	-	-	-	-	-	Shokrollahzadeh <i>et al.</i> 2008
Petroleum Refinery wastewater effluent from API & DAF process.	-	-	7.3	628	118	-	-	24	-	Tyagi <i>et al.</i> 1992

## APPENDIX C: RAW DATA FOR ONTARIO PETROLEUM REINERY'S AVERAGE MONTHLY EFFLUENT TOC MASS LOADING

The following data was collected from Ontario (2013):

**Table C.1: Average Effluent TOC Mass Loading for Ontario's Petroleum Refinery's**

Refinery	TOTAL ORGANIC CARBON [PPM]					
	IOL (Nanticoke)	IOL (Sarnia)	Nova (Corunna)	Shell (Sarnia)	Suncor (Mississauga)	Suncor (Sarnia)
Jan-08	59	255	77	84	35	95
Feb-08	57	213	80	87	27	202
Mar-08	45	309	68	73	29	86
Apr-08	63	204	78	84	40	166
May-08	64	153	62	53	21	50
Jun-08	66	201	88	75	27	73
Jul-08	60	298	72	86	27	95
Aug-08	51	210	51	75	44	72
Sep-08	69	275	77	80	21	89
Oct-08	90	226	68	71	22	55
Nov-08	59	276	68	120	26	83
Dec-08	74	251	55	0	39	108
Jan-09	53	243	55	42	28	134
Feb-09	73	245	46	86	34	64
Mar-09	89	455	60	83	34	73
Apr-09	69	361	58	0	38	69
May-09	45	237	84	0	61	60
Jun-09	60	233	52	0	20	69
Jul-09	55	272	68	45	44	84
Aug-09	51	280	61	48	26	73
Sep-09	53	218	44	64	36	96
Oct-09	63	267	47	60	23	76
Nov-09	59	266	46	59	40	45
Dec-09	73	262	45	81	40	68
Jan-10	52	260	47	69	27	76
Feb-10	40	255	48	81	30	43
Mar-10	68	198	63	87	31	60
Apr-10	70	112	73	82	20	56
May-10	52	186	68	90	21	82
Jun-10	76	290	72	78	30	76
Jul-10	67	353	65	74	23	69

Aug-10	63	319	81	72	16	62
Sep-10	62	292	71	85	25	54
Oct-10	67	257	55	69	40	62
Nov-10	71	237	56	87	25	80
Dec-10	81	322	59	45	17	62
Jan-11	66	259	45	41	16	64
Feb-11	61	308	56	45	19	78
Mar-11	88	387	61	58	31	99
Apr-11	73	369	52	66	26	78
May-11	86	345	57	62	31	102
Jun-11	87	389	75	31	26	98
Jul-11	103	481	67	44	14	93
Aug-11	91	455	57	76	22	96
Sep-11	92	460	49	67	17	72
Oct-11	85	340	18	60	18	63
Nov-11	55	213	34	56	31	56
Dec-11	80	290	80	56	22	74

## APPENDIX D: BIOLOGICAL TECHNOLOGY FOR PETROLEUM REFINERY WASTEWATER TREATMENT

Technology:	Details	HRT: [h]	Temp: [°C]	pH:	Contaminants:	Parameter:	Initial [mg/L]	Final [mg/L]	Reduction:	Reference:
Activated Sludge	-	4-18	21-25	6-10	Petrochemical Wastewater	BOD COD Phenol	1,100 500 100	-	87-93% 70-75% 90-94%	Coe 1952
Activated Sludge	-	10-30	-	8.0 - 8.8	Petrochemical Wastewater	TSS VSS COD BOD Phenols Ammonia	46-98 25-65 625-637 180-268 9-22 4.7-21	47-52 26-34 230-400 19-30 0.2-0.8 0.5-13	-	Rebhun and Galil, 1988
Aerated Fixed-film	Various packing ratios were used.	-	18-27	4.3- 5.2	Petrochemical Wastewater	COD	4,120-4,950	-	92-97%	Park <i>et al.</i> 1996
Attached/ Fixed Film	Batch & continuous with porous plastic BSP	6 -12	-	7	Dimethyl Terephthalate (DMT)	COD	2,000 - 14,000	-	86-90%	Shah <i>et al.</i> 1998
Biologically Activated Carbon (BAC)	Pilot Scale BAC system.	12 – 24	15-25	-	Diesel & Gasoline	Oil	2 - 5	-	-	Kliaugaite <i>et al.</i> 2008
Fixed Film Bioreactor	Plastic pall rings as packing material.	8	-	6.5- 7.5	Petrochemical Wastewater	COD Phenol	510 30	-	85-90% 99%	Jou and Huang, 2003
Membrane Bioreactor (MBR)	MBR Pilot Plant. Membranes were made from chlorinated polyethylene.	5-12.5	-	9-10	Olefin Process & Petrochemical Wastewater	COD TOC SS	- 250-850 5-110	-	84-90% 90-92% 92-98%	Llop <i>et al.</i> 2009
Membrane Bioreactor (MBR)	Lab scale MBR with anoxic/aerobic treatment with MF membrane.	13-19	26	6.4- 10.4	Petrochemical Wastewater	COD Oil & Grease	720-1590 14-20	38-78 1-4	-	Qin <i>et al.</i> 2007
Rotating Biological Contactor (RBC)	RBC modified With Polyurethane foam disks.	7 - 30	27-30	7.3	Petrochemical Wastewater	COD BOD Oil Phenol TSS Ammonia	628 118 64 38 85 24	90 0 3 2 18 0	86% 99% 95% 94% 79% 96%	Tyagi <i>et al.</i> 1993
Rotating Biological Contactor (RBC)	Phototrophic Microorganisms Used.	21	28	7.5	Diesel	TPH COD	1,654-6,615 2,677-5,406	-	95-99% 79-92%	Chavan and Mukherji, 2008
Sequencing Batch Reactors (SBR)	-	0.33 - 1.33	30	6.2- 7.6	Petrochemical Wastewater	BOD COD	69 220	-	94% 87%	Farooq and Misbahuddin 1991a



Technology:	Details	HRT: [h]	Temp: [°C]	pH:	Contaminants:	Parameter:	Initial [mg/L]	Final [mg/L]	Reduction:	Reference:
Attached/ Fixed Film	Biomass support particles (BSP)	240	35	7	Dimethyl Terephthalate (DMT)	COD SS	130,000 -142,000 900	- 180	5-10% -	Sharma <i>et al.</i> 1994
Pond	Three stage process with two covered basins and a UASB reactor.	-	40	4.5	Terephthalic acid (PTA)	COD	5900	-	47%	Noyola <i>et al.</i> 2000
Upflow Anaerobic Sludge Blanket (UASB) Reactor	-	43	35	6	Petrochemical Wastewater	COD	12,885	-	83%	Nel <i>et al.</i> 1984
UASB	-	24	30	-	Terephthalic acid (PTA)	-	720 - 1840	-	-	Kleerebezem <i>et al.</i> 1997
UASB	-	6-24	27	-	Tetrachloroethylene (PCE)	COD	2000	-	94%	Prakash and Gupta, 2000
UASB	-	19	-	6.0- 7.7	Nitro-organic Effluent	COD	15,000 - 20,000	-	90%	Stergar <i>et al.</i> , 2003
UASB & Aeration Basin	Flow to Anaerobic UASB then Aeration Basin	4-24	35	-	Petrochemical Wastewater	COD BOD <sub>5</sub> TOC Oil	886-5,200 474-3,160 365-2,743 8-90	-	83-93% 85-94% 90% 91-96%	Guan <i>et al.</i> 2000
Upflow Fixed-film Reactor	-	36-360	37	2.5 - 2.7	Petrochemical Wastewater	COD	5,500 – 6,000	-	90-95%	Patel and Madamwar, 2002
Down flow Fixed-film Reactor	-	82	33	-	Terephthalic acid (PTA)	COD TSS	6477 704	-	84% 80%	Macarie <i>et al.</i> 1992

## APPENDIX E: CHEMICAL WASTEWATER TREATMENT TECHNOLOGY FOR PETROLEUM REFINERY

### WASTEWATER

<u>Technology:</u>	<u>Configuration:</u>	<u>Ozone:</u>	<u>H<sub>2</sub>O<sub>2</sub>:</u>	<u>Time:</u>	<u>Temp:</u>	<u>pH:</u>	<u>Parameter:</u>	<u>Initial:</u> <u>[mg/L]</u>	<u>Reduction:</u>	<u>Reference:</u>
O <sub>3</sub> /UV/H <sub>2</sub> O <sub>2</sub>	O <sub>3</sub> /UV	11 mg/L	-	30 min	25°C	4.9	COD	-	90%	Andreozzi <i>et al.</i> 2000
	O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>		2x10 <sup>-2</sup> mol/L	120 min						
Horseradish Peroxidase and H <sub>2</sub> O <sub>2</sub> .	Horseradish Peroxidase and H <sub>2</sub> O <sub>2</sub> .	-	0.6 mM	12h	20°C	8.6	COD	300	58%	Wagner <i>et al.</i> 2001
							BOD <sub>5</sub>	93.7	78%	
							Toxicity	-	95%	
O <sub>3</sub>	Batch	-	-	15 min	21°C	11	Phenol	80	>99%	Mohammadzadeh <i>et al.</i> 2004
	Continuous	65 g/m <sup>3</sup>		3.5 h	25-30°C	6	Phenol	38	88%	
							COD	274	40%	
UV/H <sub>2</sub> O <sub>2</sub>	Post biotreatment.	-	1000 mg/L	250 min	30°C	3	TOC	133	55%	Juang <i>et al.</i> 1997
	Pre biotreatment.		5000 mg/L				COD	365	69%	
							TOC	1,200	12%	
							COD	4,400	42%	
Catalytic wet air oxidation (CWAO)	Microwaves	-	-	30 min	150°C	-	COD	5,500	92%	Sun <i>et al.</i> 2008
UV/H <sub>2</sub> O <sub>2</sub>	-	-	1 – 12 mM	24h	-	7.0 – 8.9	TPH	1,534	90%	Stepnowski <i>et al.</i> 2002
TiO <sub>2</sub>	Circulating and direct irradiation reactor	-	-	4 h	45°C	3	COD	170 - 180	90%	Saien and Nejati, 2007
O <sub>3</sub> / BAC	Ozone pretreatment to BAC	100 – 200 mg/h	-	30 min / 6h	-	7	COD	200 - 900	70-95%	Lin <i>et al.</i> 2001
Alum / H <sub>2</sub> O <sub>2</sub>	Alum and H <sub>2</sub> O <sub>2</sub> then filtered through activated clay.	-	40 mg/L	20 min	-	6.8	TSS	48	70%	Adeyinka and Rim-Rukeh, 1999
							COD	96	46%	
Electro-Fenton	Bench Scale	-	600 mg/L	2 h	-	3	COD	200 – 225	80%	Ting <i>et al.</i> 2007
	Pilot Scale	-	940 mg/L	-	-	3	COD	336	58%	
Electro-Fenton	Bench Scale	-	600 mg/L	2 h	-	3	COD	255	81%	Huang <i>et al.</i> 1999
	Pilot Scale	-	774 mg/L	3 h	-	2.1 - 3.3	COD	307 - 420	58%	

## APPENDIX F: AVERAGE CONCENTRATION CALCULATION

Each experiment was replicated three separate times in order to determine the average and standard deviation of the wastewater TOC. The average or mean value ( $\bar{X}$ ) of the sample TOC was calculated as follows:

$$\bar{X} = \frac{\sum_{i=1}^n (X_i)}{n} \quad (\text{F.1})$$

Where,

$\bar{X}$  = mean value of the sample observations

$n$  = sample size

$X_i$  = observed values of the sample items ( $X_1, X_2, \dots, X_n$ )

## APPENDIX G: CONCENTRATION STANDARD DEVIATION CALCULATION

Each experiment was replicated three separate times in order to determine the average and standard deviation of the wastewater TOC. The sample standard deviation ( $s$ ) of the sample TOC was calculated as follows:

$$s = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (X_i - \bar{X})^2} \quad (\text{G.1})$$

Where,

$s$  = sample standard deviation

$n$  = sample size

$X_i$  = observed values of the sample items ( $X_1, X_2, \dots, X_n$ )

$\bar{X}$  = mean value of the sample observations

## APPENDIX H: OUTLINE OF INITIAL EXPERIMENTAL TESTING RUNS

**Table H.1: 2<sup>3</sup> Factorial Design Input Data for the Initial Experimental Testing of a UV/H<sub>2</sub>O<sub>2</sub> Process to Treat Petroleum Refinery Wastewater**

Experiment #	Experimental Reaction Time [min]	Initial H <sub>2</sub> O <sub>2</sub> / TOC Molar Ratio [mol H <sub>2</sub> O <sub>2</sub> /mol C]	pH
1	10	2.9	4.0
2	10	2.9	7.5
3	10	8.6	4.0
4	10	8.6	7.5
5	20	5.8	6.0
6	30	2.9	4.0
7	30	2.9	7.5
8	30	8.6	4.0
9	30	8.6	7.5

## APPENDIX I: RAW TOC MEASUREMENT DATA FOR INITIAL EXPERIMENTS

**Table I.1: TOC Measurement Data for Initial UV/H<sub>2</sub>O<sub>2</sub> Experiments**

Exp #	Time (min)	H <sub>2</sub> O <sub>2</sub> /TOC Molar Ratio	pH	Experimental Run	Initial TOC Measurement (mg/L)			Final TOC Measurement (mg/L)		
					1	2	3	1	2	3
1	30	8.6	7.5	1	42.6641	42.2853	40.0447	35.4779	38.0628	36.1965
				2	41.8988	41.1559	43.5544	34.9498	37.8976	30.5810
				3	42.8482	40.7983	42.7180	37.8212	37.0334	35.9912
2	10	8.6	7.5	1	42.6641	42.2853	40.0447	42.5590	38.5733	36.3171
				2	41.8988	41.1559	43.5544	46.0867	39.9687	36.5048
				3	42.8482	40.7983	42.7180	45.4650	46.8783	41.1609
3	30	2.9	7.5	1	42.6641	42.2853	40.0447	39.3509	41.7025	31.6053
				2	41.8988	41.1559	43.5544	35.5470	41.5719	35.1189
				3	42.8482	40.7983	42.7180	40.3708	37.7495	40.5784
4	10	2.9	7.5	1	42.6641	42.2853	40.0447	40.8434	39.1192	46.1643
				2	41.8988	41.1559	43.5544	41.4442	39.7337	42.0510
				3	42.8482	40.7983	42.7180	44.9030	44.2725	46.4774
5	30	8.6	4.0	1	42.6641	42.2853	40.0447	17.9975	22.7820	20.9859
				2	41.8988	41.1559	43.5544	16.7710	19.9653	18.2749
				3	42.8482	40.7983	42.7180	15.3866	19.9939	18.8451
6	10	8.6	4.0	1	42.6641	42.2853	40.0447	26.9599	27.9257	25.7187
				2	41.8988	41.1559	43.5544	25.9436	33.1180	28.1069
				3	42.8482	40.7983	42.7180	29.2434	33.4613	30.2791

7	30	2.9	4.0	1	42.6641	42.2853	40.0447	17.5780	24.0040	20.8208
				2	41.8988	41.1559	43.5544	12.1718	19.7451	17.8490
				3	42.8482	40.7983	42.7180	15.8936	20.9208	19.4860
8	10	2.9	4.0	1	42.6641	42.2853	40.0447	24.7417	29.3899	27.8417
				2	41.8988	41.1559	43.5544	25.6500	32.1967	30.8008
				3	42.8482	40.7983	42.7180	29.1427	34.9468	30.4771
9	20	5.8	6.0	1	42.6641	42.2853	40.0447	25.5619	29.3828	25.1966
				2	41.8988	41.1559	43.5544	28.1226	28.2397	26.9161
				3	42.8482	40.7983	42.7180	23.2202	25.5356	26.4982

## APPENDIX J: OUTLINE OF INITIAL EXPERIMENTAL TESTING RUNS

**Table J.1: 3<sup>3</sup> Factorial Design Input Data for the Additional Experimental Testing to Improve UV/H<sub>2</sub>O<sub>2</sub> Process to Treat Refinery Wastewater**

Experiment #	Experimental Reaction Time [min]	Initial H <sub>2</sub> O <sub>2</sub> / TOC Molar Ratio [mol-H <sub>2</sub> O <sub>2</sub> / mol-C]	pH
1	15	1.7	4
2	15	1.7	5
3	15	1.7	6
4	15	2.8	4
5	15	2.8	5
6	15	2.8	6
7	15	3.9	4
8	15	3.9	5
9	15	3.9	6
10	30	1.7	4
11	30	1.7	5
12	30	1.7	6
13	30	2.8	4
14	30	2.8	5
15	30	2.8	6
16	30	3.9	4
17	30	3.9	5
18	30	3.9	6
19	45	1.7	4
20	45	1.7	5
21	45	1.7	6
22	45	2.8	4
23	45	2.8	5
24	45	2.8	6
25	45	3.9	4
26	45	3.9	5
27	45	3.9	6

## APPENDIX K: RAW TOC MEASUREMENT DATA FOR ADDITIONAL EXPERIMENTS

**Table K.1: TOC Measurement Data for Additional UV/H<sub>2</sub>O<sub>2</sub> Experiments**

Exp #	Time (min)	H <sub>2</sub> O <sub>2</sub> /TOC Molar Ratio	pH	Experimental Run	Initial TOC Measurement (mg/L)			Final TOC Measurement (mg/L)		
					1	2	3	1	2	3
1	15	1.65	6	1	39.5273	42.6099	39.0323	20.3804	22.6930	22.8662
				2	38.9745	45.1661	45.2037	23.9007	24.1190	25.6918
				3	39.9194	46.3612	47.4755	21.6434	27.0543	18.9270
2	15	1.65	5	1	39.5273	42.6099	39.0323	13.6273	18.2853	30.3995
				2	38.9745	45.1661	45.2037	13.3962	22.6069	24.8169
				3	39.9194	46.3612	47.4755	19.7457	18.4191	16.6375
3	15	1.65	4	1	39.5273	42.6099	39.0323	18.0950	17.8123	19.5703
				2	38.9745	45.1661	45.2037	21.0991	22.9245	26.3007
				3	39.9194	46.3612	47.4755	21.3376	23.8158	22.7036
4	15	2.75	6	1	39.5273	42.6099	39.0323	20.3914	23.6283	26.2906
				2	38.9745	45.1661	45.2037	19.1766	30.2239	15.0384
				3	39.9194	46.3612	47.4755	18.9414	23.3078	15.4819
5	15	2.75	5	1	39.5273	42.6099	39.0323	13.8549	19.5272	29.8863
				2	38.9745	45.1661	45.2037	12.1925	19.4657	18.8336
				3	39.9194	46.3612	47.4755	18.5792	26.4945	16.6337
6	15	2.75	4	1	39.5273	42.6099	39.0323	19.1449	22.0483	28.4857
				2	38.9745	45.1661	45.2037	19.4134	18.1521	25.3431
				3	39.9194	46.3612	47.4755	15.4834	24.9220	16.4409
7	15	3.85	6	1	39.5273	42.6099	39.0323	22.6550	19.2837	22.6855
				2	38.9745	45.1661	45.2037	26.4778	23.5655	25.6616
				3	39.9194	46.3612	47.4755	22.3572	16.4778	23.9290
8	15	3.85	5	1	39.5273	42.6099	39.0323	10.1919	17.2957	25.4139
				2	38.9745	45.1661	45.2037	11.8874	20.4680	24.2639
				3	39.9194	46.3612	47.4755	22.1963	17.9960	17.5654
9	15	3.85	4	1	39.5273	42.6099	39.0323	18.8859	18.8089	22.5836
				2	38.9745	45.1661	45.2037	23.6594	20.4756	24.5561
				3	39.9194	46.3612	47.4755	17.3855	21.9341	23.8996
10	30	1.65	6	1	39.5273	42.6099	39.0323	13.2635	13.3375	10.9897
				2	38.9745	45.1661	45.2037	9.6154	14.5192	26.1910
				3	39.9194	46.3612	47.4755	14.0697	14.5638	16.8833

11	30	1.65	5	1	39.5273	42.6099	39.0323	9.4840	7.3826	18.3599
				2	38.9745	45.1661	45.2037	8.2836	7.6618	11.2847
				3	39.9194	46.3612	47.4755	10.8116	6.3788	9.3801
12	30	1.65	4	1	39.5273	42.6099	39.0323	10.5457	10.4638	13.5012
				2	38.9745	45.1661	45.2037	11.2748	16.7723	27.4110
				3	39.9194	46.3612	47.4755	11.0750	16.3829	18.2627
13	30	2.75	6	1	39.5273	42.6099	39.0323	14.1711	19.3728	17.2219
				2	38.9745	45.1661	45.2037	16.7919	12.4540	12.5567
				3	39.9194	46.3612	47.4755	13.0476	11.4738	14.9420
14	30	2.75	5	1	39.5273	42.6099	39.0323	13.1617	9.2856	8.9921
				2	38.9745	45.1661	45.2037	9.0509	14.3520	12.9293
				3	39.9194	46.3612	47.4755	8.0188	14.3728	13.3593
15	30	2.75	4	1	39.5273	42.6099	39.0323	8.4250	15.3636	16.2934
				2	38.9745	45.1661	45.2037	17.2857	15.6691	19.3321
				3	39.9194	46.3612	47.4755	7.2361	11.3983	17.0100
16	30	3.85	6	1	39.5273	42.6099	39.0323	16.4299	11.3829	13.2113
				2	38.9745	45.1661	45.2037	15.8936	19.9923	12.8084
				3	39.9194	46.3612	47.4755	12.2473	12.3845	12.7129
17	30	3.85	5	1	39.5273	42.6099	39.0323	13.8268	10.0288	18.2343
				2	38.9745	45.1661	45.2037	14.1462	11.2099	11.5419
				3	39.9194	46.3612	47.4755	10.5953	10.2743	12.8909
18	30	3.85	4	1	39.5273	42.6099	39.0323	16.5532	10.1998	14.2309
				2	38.9745	45.1661	45.2037	16.9336	15.2836	11.2234
				3	39.9194	46.3612	47.4755	7.4493	13.5640	16.7152
19	45	1.65	6	1	39.5273	42.6099	39.0323	14.3939	11.4682	9.9650
				2	38.9745	45.1661	45.2037	10.5369	10.2696	18.2353
				3	39.9194	46.3612	47.4755	9.7693	17.9922	17.9390
20	45	1.65	5	1	39.5273	42.6099	39.0323	8.7296	8.2293	8.1129
				2	38.9745	45.1661	45.2037	8.9861	14.2845	10.2295
				3	39.9194	46.3612	47.4755	12.0373	11.1986	7.4515
21	45	1.65	4	1	39.5273	42.6099	39.0323	8.2009	17.1825	15.0096
				2	38.9745	45.1661	45.2037	6.9877	16.2616	13.9312
				3	39.9194	46.3612	47.4755	6.1404	14.0678	11.6251

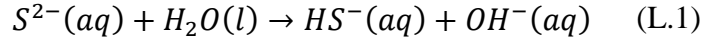
22	45	2.75	6	1	39.5273	42.6099	39.0323	8.3148	9.2846	22.7407
				2	38.9745	45.1661	45.2037	7.9687	12.3391	6.8281
				3	39.9194	46.3612	47.4755	9.1817	10.5785	11.8250
23	45	2.75	5	1	39.5273	42.6099	39.0323	9.7210	12.5398	12.2133
				2	38.9745	45.1661	45.2037	6.4213	6.4927	15.7175
				3	39.9194	46.3612	47.4755	7.0728	6.3627	6.5577
24	45	2.75	4	1	39.5273	42.6099	39.0323	8.5385	11.3855	6.6941
				2	38.9745	45.1661	45.2037	6.3504	8.2366	21.4908
				3	39.9194	46.3612	47.4755	5.9576	6.3747	13.2285
25	45	3.85	6	1	39.5273	42.6099	39.0323	10.4621	16.2713	14.9307
				2	38.9745	45.1661	45.2037	12.8340	9.1374	19.0671
				3	39.9194	46.3612	47.4755	10.8483	17.3371	16.0336
26	45	3.85	5	1	39.5273	42.6099	39.0323	12.2182	6.3568	12.7637
				2	38.9745	45.1661	45.2037	9.2379	15.7275	7.8105
				3	39.9194	46.3612	47.4755	9.3128	7.2364	6.1403
27	45	3.85	4	1	39.5273	42.6099	39.0323	8.3873	12.5019	12.7502
				2	38.9745	45.1661	45.2037	8.0455	13.6131	13.3530
				3	39.9194	46.3612	47.4755	8.0367	15.0073	13.1695

## APPENDIX L: OXIDATION OF SULPHIDE COMPOUNDS

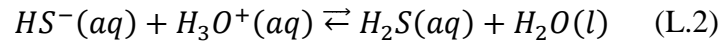
Refinery hydrocarbon feedstocks contain varying amounts of sulphur. Refinery processes, specifically hydroprocessing units, convert the sulphur atoms into sulphide ( $S^{2-}$ ) ions. Sulphides must be removed from the process streams in order to prevent excessive corrosion and plugging of refinery equipment as well as to meet regulated product quality specifications such as ultra-low sulphur diesel. Hydroprocessing reactor effluent streams are washed with water to dilute and dissolve the sulphide ions from the hydrocarbon phase into the water phase. This sour water is then separated from the hydrocarbon stream and is sent to the WWTP for further treatment.



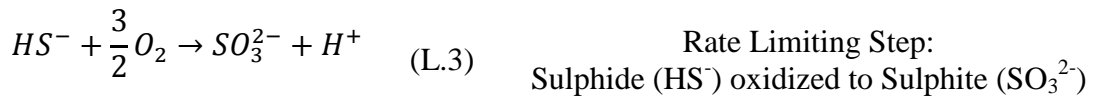
Sulphide ( $S^{2-}$ ) ions are a very strong base and will completely react with water according to equation L.1 (Oxtoby *et al.* 2002).



The dissociation constant ( $K_b$ ) for the reaction L.1 is on the order of  $10^5$  (Oxtoby *et al.* 2002). This means that essentially there are no  $S^{2-}$  sulphide ions present in an aqueous solution (Oxtoby *et al.* 2002). At a neutral and basic pH, only  $HS^{-}$  sulphide ions will be present in an aqueous solution (Oxtoby *et al.* 2002). As the pH of the aqueous solution starts to decrease, the concentration of  $OH^{-}$  species will also decrease (Oxtoby *et al.* 2002). The addition of  $H_3O^{+}$  will decrease the concentration of  $HS^{-}$  sulphide ions of the aqueous solution since the equilibrium would shift to the right in reaction L.2 (Oxtoby *et al.* 2002).



The oxidation of sulphide ( $HS^{-}$ ) by oxygen ( $O_2$ ) in an aqueous solution takes place according to reactions L.3, L.4 and L.5 (Avrahami and Golding, 1968).



The calculation to estimate the chemical oxygen demand (COD) associated with oxidizing sulphides follows equation L.6.

$$C_{COD} \left[ \frac{mg O_2}{L} \right] = C_{HS^-} \left[ \frac{mg S^{2-}}{L} \right] \times \frac{2 [mol O_2]}{1 [mol S^{2-}]} \times \frac{M_{O_2} \left[ \frac{g}{mol O_2} \right]}{M_{HS^-} \left[ \frac{g}{mol S^{2-}} \right]} \quad (L.6)$$

Where,

$C_{COD}$  = Estimated Chemical oxygen demand (COD) concentration  $[mg O_2/L]$

$C_{S^{2-}}$  = Sulphide concentration  $[mg S^{2-}/L]$

$M_{O_2}$  = Oxygen Molar Mass  $[g/mol O_2] = 32 g/mol O_2$

$M_{S^{2-}}$  = Sulphide Molar Mass  $[g/mol S^{2-}] = 32 g/mol S^{2-}$

Therefore, equation L.6 can be simplified as equation L.7.

$$C_{COD} \left[ \frac{mg O_2}{L} \right] = 2 \left[ \frac{mg O_2}{mg S^{2-}} \right] \times C_{HS^-} \left[ \frac{mg S^{2-}}{L} \right] \quad (L.7)$$

Avrahami and Golding (1968), did not determine the rate of the reaction for reactions L.3, L.4 or L.5. The following table outlines various reaction rates throughout literature.

**Table L.1: Literature Review of Oxidation of Sulphide Reaction Rates**

Equation	Units	Initial Sulphide Conc.	Oxygen Conc.	pH	Temperature	Reference
$R = 1.44[S]^{1.02}[O]^{0.80}$	M/min	0.022 – 1.21 mM	0.21 – 1.1 mM	7.55	25°C	O'Brien and Birkner (1977)
$R = 67.6[S]^{1.15}[O]^{0.69}$	M/min	0.05 – 0.2 mM	0.6 mM	7.0	Not Mentioned	Jolley and Forster (1985)
$R = k[S][O]$ Where: $\log k = 11.78 - \frac{3000}{T} + 0.44I^{0.5}$ Where the ionic strength (I) was between 0 and 6 M.	M/h	0.025 mM	Air Saturated	8.0	5 - 65°C	Millero <i>et al.</i> (1987)
$R = 0.055[S]^{0.38}[O]^{0.21}$	mg/L min	0.09 – 0.3 mM	0.16 – 0.62 mM	7.0	20°C	Wilmot <i>et al.</i> (1988)
$R = 0.57[S]^{0.41}[O]^{0.39 \log[S]}$	mg/L min	0.15 – 28.0 mM	0.25 mM	8.0	25°C	Buisman <i>et al.</i> (1990)

## APPENDIX M: FOOD TO MICROORGANISM (F/M) RATIO CALCULATION

The Food to Microorganism (F/M) Ratio is a process parameter commonly used to characterize a biological wastewater treatment system (Metcalf and Eddy, 2003). The calculation is as follows:

$$\frac{F}{M} \left[ \frac{kg \text{ COD}}{kg \text{ VSS}} \right] = \frac{C_{COD} \left[ \frac{kg \text{ COD}}{L} \right]}{C_{VSS} \left[ \frac{kg \text{ VSS}}{L} \right]} \quad (M.1)$$

Where,

$C_{COD}$  = Chemical oxygen demand (COD) concentration [ $kg \text{ COD}/L$ ]

$C_{VSS}$  = Biomass Volatile Suspended Solids (VSS) concentration [ $kg \text{ VSS}/L$ ]

## APPENDIX N: SUNCOR MISSISSAUGA REINERY'S AVERAGE EFFLUENT TOC CONCENTRATION

The effluent TOC concentration limit was calculated using data collected from Ontario (2011):

$$\frac{220 \text{ kg}}{\text{day}} \times \frac{1000 \text{ g}}{\text{kg}} \times \frac{1000 \text{ mg}}{\text{g}} \times \frac{\text{sec}}{220 \text{ L}} \times \frac{\text{min}}{60 \text{ sec}} \times \frac{\text{hr}}{60 \text{ min}} \times \frac{\text{day}}{24 \text{ hr}} = 11.574 \text{ mg/L}$$

The following data was collected from Ontario (2013):

**Table N.1: Average Effluent TOC Concentration for Suncor Mississauga Refinery**

TOTAL ORGANIC CARBON [PPM]								
	2004	2005	2006	2007	2008	2009	2010	2011
January	2.4	3.2	7.9	2.6	4.2	3.4	3.5	2.5
February	3.4	4.7	3.9	2.2	3.2	3.1	3.8	2.6
March	5.2	4.1	3.7	3.2	3.1	3.1	3.7	3.1
April	3.7	8.4	4.2	3.7	5.1	4.4	3.0	3.2

May	4.1	5.1	5.3	2.7	3.5	7.6	3.8	3.5
June	3.9	3.0	2.9	2.4	3.8	3.1	4.4	4.2
July	3.5	3.4	5.0	2.3	3.0	4.5	4.0	2.6
August	3.5	3.2	2.7	2.9	3.9	3.2	2.9	3.3
September	5.7	3.1	4.6	2.9	2.6	4.2	3.5	3.3
October	2.7	3.0	4.4	2.8	2.7	3.8	4.9	3.0
November	4.1	4.3	3.2	4.6	3.2	4.8	3.3	5.0
December	3.4	5.3	3.2	3.6	4.2	5.1	2.3	3.1

# REFERENCES

- Adeyinka J.S. and Rim-Rukeh A. 1999. Effect of Hydrogen Peroxide on Industrial Waste Water Effluents: A Case Study of Warri Refining and Petrochemical Industry. *Environmental Monitoring and Assessment*. 59:249-256.
- Al Zarooni M. and Elshorbagy W. 2006. Characterization and assessment of Al Ruwais refinery wastewater. *Journal of Hazardous Materials*. A136:398-405.
- American Public Health Association (APHA), the American Water Works Association (AWWA), and the Water Environment Federation (WEF). 1999. *Standard Methods for the Examination of Water and Wastewater*. 20<sup>th</sup> Edition. ISBN-10: 0875532357. APHA.
- Andreozzi R., Caprio V., Insola A. and Marotta R. 1999. Advanced oxidation processes (AOP) for water purification and recovery. *Catalysis Today*. 53:51-59.
- Andreozzi R., Caprio V., Insola A., Marotta R. and Sanchirico R. 2000. Advanced Oxidation Processes for the Treatment of Mineral Oil-contaminated Wastewaters. *Water Research*. 34 (2):620-628.
- Avrahami M. and Golding R.M. 1968. The Oxidation of the Sulphide Ion at Very Low Concentrations in Aqueous Solutions. *Journal of the Chemical Society A: Inorganic, Physical, Theoretical*. 647-651.
- Buisman C., Jspeert P.I., Janssen A., and Lettinga G. 1990. Kinetics of Chemical and Biological Sulphide Oxidation in Aqueous Solutions. *Water Research*. 24(5):667-671.
- Chapra S.C. 2008. *Surface Water-Quality Modeling*. Waveland Press, Inc.
- Chavan A. and Mukherji S. 2008. Treatment of Hydrocarbon-rich wastewater using oil degrading bacteria and phototrophic microorganisms in rotating biological contactor: Effect of N:P ratio. *Journal of Hazardous Materials*. 154:63-72.
- Chidambara Raj C.B. and Quen H.L. 2005. Advanced Oxidation Processes for Wastewater Treatment: Optimization of UV/H<sub>2</sub>O<sub>2</sub> Process Through a Statistical Technique. *Chemical Engineering Science*. 60:5305-5311.
- Coe R.H. 1952. Bench-Scale Biological Oxidation of Refinery Wastes with Activated Sludge. *Sewage and Industrial Wastes*. 24 (6):731-749.

- Demirci S., Erdogan B. and Ozcimder R. 1998. Wastewater treatment at the Petroleum Refinery, Kirikkale, Turkey using some coagulants and Turkish clays as coagulant aids. *Water Resesearch*. 32(11):3495-3499.
- Dupuy D. 1997. Technological Change and Environmental Policy: The Diffusion of Environmental Technology. *Growth and Change*. 28:49-66.
- Eckenfelder W.W. 2000. *Industrial Water Pollution Control*. McGraw-Hill. Third Edition.
- Elkin H. F. 1959. Condensates, Quenches and Wash Waters as Petrochemical Waste Sources. *Sewage and Industrial Wastes*. 31(7):836-840.
- Environment Canada. 1974. *Petroleum Refinery Effluent Regulations and Guidelines. Regulations, Codes and Protocols Report EPS 1-WP-74-1*. Water Pollution Control Directorate. Information Canada. Ottawa, Canada. Retrieved November 22, 2013, from [http://laws.justice.gc.ca/PDF/C.R.C.,\\_c.\\_828.pdf](http://laws.justice.gc.ca/PDF/C.R.C.,_c._828.pdf)
- Farooq S. and Misbahuddin M. 1991a. Biological Treatment of a Petrochemical Wastewater Using Sequencing Batch Reactors. *Environmental Technology*. 12:131-145.
- Farooq S. and Misbahuddin M. 1991b. Activated Carbon Adsorption and Ozone Treatment of Petrochemical Wastewater. *Environmental Technology*. 12:147-159.
- Ford D. L., Eller J. M. and Gloyne E. F. 1971. Analytical Parameters of Petrochemical and Refinery Wastewaters. *Journal of Water Pollution Control Federation*. 43(8):1712-1723
- Galil N.I. and Wolf D. 2001. Removal of hydrocarbons from petrochemical wastewater by dissolved air flotation. *Water Science and Technology*. 43 (8):107-113.
- Guan W., Lei Z. and Zhu J. 2000. Petro-chemical wastewater treatment by biological process. *Journal of Environmental Science*. 12(2):220-224.
- Hernandez R., Zappi M., Colucci J. and Jones R. 2002. Comparing the performance of various advanced oxidation processes for treatment of acetone contaminated water. *Journal of Hazardous Materials* 92:33-50.
- Huang Y., Chou S., Perng M., Huang G. and Cheng S. 1999. Case Study on the Bioeffluent of Petrochemical Wastewater by Electro-Fenton Method. *Water Science Technology*. 39 (10-11): 145-149.
- Jolley R.A. and Forster C.F. 1985. The kinetics of sulphide oxidation. *Environmental Technology Letters*. 6:1-10.

- Jou C.G. and Huang G.C. 2003. A Pilot Study for Oil Refinery Wastewater Treatment Using a Fixed-film Bioreactor. *Advances in Environmental Research*. 7:463-469.
- Juang L., Tseng D. and Yang S. 1997. Treatment of Petrochemical Wastewater by UV/H<sub>2</sub>O<sub>2</sub> Photodecomposed System. *Water Science Technology*. 36 (12): 357-365.
- Kleerebezem R., Mortier J., Hulshoff L., Lettinga G. 1997. Anaerobic Pre-Treatment of Petrochemical Effluents: Terephthalic Acid Wastewater. *Water Science Technology*. 36(2-3):237-248.
- Kliaugaite D., Jankunaite D. and Racys V. 2008. Factor Influencing Treatment of Petroleum Polluted Wastewater Using Biologically Activated Carbon. *The 7th International Environmental Engineering Conference*. 569-575.
- Laera G., Cassano D., Lopez A., Pinto A., Pollice A., Ricco G., and Mascolo G. 2012. Removal of Organics and Degradation Products from Industrial Wastewater by a Membrane Bioreactor Integrated with Ozone or UV/ H<sub>2</sub>O<sub>2</sub> Treatment. *Environmental Science & Technology*. 46:1010-1018.
- Lin C., Tsai T., Liu J. and Chen M. 2001. Enhanced Biodegradation of Petrochemical Wastewater Using Ozonation and BAC Advanced Treatment System. *Water Research*. 35 (3):699-704.
- Llop A., Pocurull E. and Borrull F. 2009. Evaluation of the Removal of Pollutants from Petrochemical Wastewater Using a Membrane Bioreactor Treatment Plant. *Water Air Soil Pollution*. 197:349-359.
- Macarie H., Noyola A. and Guyot J.P. 1992. Anaerobic Treatment of a Petrochemical Wastewater from a Terephthalic Acid Plant. *Water Science Technology*. 25(7):223-235.
- Macarie H. 2000. Overview of the application of anaerobic treatment to chemical and petrochemical wastewaters. *Water Science Technology*. 42(5-6):201-214.
- MacDonald E and Lintner A. 2010. Summary of Concerns: Municipal Industrial Strategy for Abatement (MISA) Regulations. Great Lakes United and Environmental Defence. Retrieved November 22, 2013, from <http://www.ecojustice.ca/publications/submissions/EBR%20AfR%20MISA%20Regulation%20Summary%20of%20Concerns.pdf>

- Mahendrakar V. and Viraraghavan T. 1996. Respirometric Evaluation of Comparative Biodegradability of Municipal and Petroleum Refinery Wastewaters. *Water Quality Research*. 31 (2):283-304
- Maqueda M.A.M., Martinez S.A., Narvaez D., Rodriguez M.G., Aguilar R. and Herrero V.M. 2006. Dynamical modeling of an activated sludge system of a petrochemical plant operating at high temperatures. *Water Science Technology*. 53(11):135-142.
- McKinney R.E. 1967. Biological Treatment Systems for Refinery Wastes. *Water Pollution Control Federation*. 39 (3):346-359.
- Meier A.L. and Nikolic O. 1995. Croatian Refiner Meets Waste Water Treatment Standards, Reduces Fines. *Oil & Gas Journal*. 70-72.
- Metcalf and Eddy. 2003. *Wastewater Engineering, Treatment and Reuse*. McGraw-Hill. Fourth Edition.
- Millero F.J., Hubinger S., Fernandez M. and Garnett S. 1987. Oxidation of H<sub>2</sub>S in seawater as a function of temperature, pH, and ionic strength. *Environmental Science and Technology*. 21:439-443.
- Mohammadzadeh, J.S., Khoshfetrati A.B. and Kaynejad M.A. 2004. Pilot Scale System for Removal of Phenol in Phenolic Wastewater of Olefin Plant. *Process Safety and Environmental Protection*. 82 (B5):365-370.
- Nel L.H., De Haast J. and Britz T.J. 1984. Anaerobic Digestion of a Petrochemical Effluent Using an Upflow Anaerobic Sludge Blanket Reactor. *Biotechnology Letters*. 6(11):741-746.
- Niegowski S.J. 1956. Ozone Method for Destruction of Phenols in Petroleum Waste Waters. *Sewage and Industrial Wastes*. 28 (10):1266-1272.
- Noyola A., Macarie H., Varela F., Landrieu S., Marcelo R., and Rosas M.A. 2000. Upgrade of a petrochemical wastewater treatment plant by an upflow anaerobic pond. *Water Science and Technology*. 42(5-6):269-276.
- O'Brien D.J. and Birkner F.B. 1977. Kinetics of oxygenation of reduced sulfur species in aqueous solution. *Environmental Science and Technology*. 11:1114-1120.
- Ontario Ministry of the Environment. 1977. *Liquid Effluent Guidelines for the Petroleum Refining Industry*. TD 899.P4.O75. Retrieved November 22, 2013, from <http://www.archive.org/details/liquideffluentgu00onta>



- Ontario Ministry of the Environment. 1988. Municipal Industrial Strategy for Abatement (MISA) Effluent Monitoring Regulations for the Petroleum Refining Sector. ISBN: 0-7729-4100-9. Retrieved November 22, 2013, from <http://www.archive.org/details/effluentpetroleum00ontauoft>
- Ontario Ministry of the Environment. 1993. Effluent Monitoring and Effluent Limits for the Petroleum Sector. Retrieved November 22, 2013, from [http://www.e-laws.gov.on.ca/html/regs/english/elaws\\_regs\\_930537\\_e.htm](http://www.e-laws.gov.on.ca/html/regs/english/elaws_regs_930537_e.htm)
- Ontario Ministry of the Environment. 2009a. Toxics Reduction Act. Retrieved November 22, 2013, from [http://www.e-laws.gov.on.ca/html/statutes/english/elaws\\_statutes\\_09t19\\_e.htm](http://www.e-laws.gov.on.ca/html/statutes/english/elaws_statutes_09t19_e.htm)
- Ontario Ministry of the Environment. 2009b. Ontario Regulation 455/09. Retrieved November 22, 2013, from [http://www.e-laws.gov.on.ca/html/regs/english/elaws\\_regs\\_090455\\_e.htm](http://www.e-laws.gov.on.ca/html/regs/english/elaws_regs_090455_e.htm)
- Ontario Ministry of the Environment. 2011. Amended Certification of Approval: Industrial Sewage Works Number 0697-8FLQ78. April 29, 2011.
- Ontario Ministry of the Environment. 2013. Resources, Collection, Data Downloads. Retrieved November 22, 2013, from [http://www.ene.gov.on.ca/environment/en/resources/collection/data\\_downloads/index.htm#MISA](http://www.ene.gov.on.ca/environment/en/resources/collection/data_downloads/index.htm#MISA)
- Orhon, D., Genceli E.A. and Cokgor E.U. 1999. Characterization and modeling of activated sludge for tannery wastewater. *Water Environment Research*. 71(1):50-63
- Oxtoby D.W., Gillis H.P., and Nachtrieb N. H. 2002. *Principles Of Modern Chemistry*. Thomson Learning, Inc. Fourth Edition.
- Park, T.J., Lee, K.H., Kim D.S. and Kim C.W. 1996. Petrochemical Wastewater Treatment with Aerated Submerged Fixed-film Reactor (ASFFR) Under High Organic Loading Rate. *Water Science and Technology*. 34(10):9-16.
- Patel H. and Madamwar D. 2002. Effects of temperature and organic loading rates on biomethanation of acidic petrochemical wastewater using an anaerobic upflow fixed-film reactor. *Bioresource Technology*. 82:65-71.
- Pinzon Pardo A.L., Brdjanovic D., Moussa M.S., Lopez-Vazquez C.M., Meijer S.C.F., Van Straten H.H.A., Janssen A.J.H., Amy G., Van Loosdrecht M.C.M. 2007. Modelling of an oil refinery wastewater treatment plant. *Environmental Technology*. 28:1273-1284.

- Prakash S.M. and Gupta S.K. 2000. Biodegradation of Tetrachloroethylene in Upflow Anaerobic Sludge Blanket Reactor. *Bioresource Technology*. 72:47-54.
- Qin J., Oo M.H., Tao G. and Kekre K.A. 2007. Feasibility Study on Petrochemical Wastewater Treatment and Reuse Using Submerged MBR. *Journal of Membrane Science*. 293:161-166.
- Ramakrishna C. and Desai J.D. 1997. High Rate Anaerobic Digestion of a Petrochemical Wastewater Using Biomass Support Particles. *World Journal of Microbiology & Biotechnology*. 13:329-334.
- Rebhun M. and Galil N. 1988. Inhibition by Hazardous Compounds in an Integrated Oil Refinery. *Water Pollution Control Federation*. 60 (11):1953-1959.
- Ruggles W.L. 1959. Basic Petrochemical Processes as Waste Sources. *Sewage and Industrial Wastes*. 31 (3):274-281.
- Saien J. and Nejati H. 2007. Enhanced Photocatalytic Degradation of Pollutants in Petroleum Refinery Wastewater Under Mild Conditions. *Journal of Hazardous Materials*. 148:491-495.
- Scott J.P. and Ollis D.F. 1995. Integration of Chemical and Biological Oxidation Processes for Water Treatment: Review and Recommendations. *Environmental Progress*. 14(2):88-103.
- Shah S., Desai J, Ramakrishna C, Bhatt N. 1998. Aerobic Biotreatment of Wastewater from Dimethyl Terephthalate Plant Using Biomass Support Particles. *Journal of Fermentation and Bioengineering*. 86(2):215-219.
- Sharma S., Ramakrishna C, Desai J, Bhatt N.M. 1994. Anaerobic Biodegradation of a Petrochemical Waste-water Using Biomass Support Particles. *Applied Microbiology and Biotechnology*. 40:768-771.
- Shokrollahzadeh S., Azizmohseni F., Golmohammad F., Shokouhi H. and Khademhaghighat F. 2008. Biodegradation potential and bacterial diversity of a petrochemical wastewater treatment plant in Iran. *Bioresource Technology*. 99:6127-6133.
- Stepnowski P., Siedlecka E.M. Behrend P. and Jastorff B. 2002. Enhanced Photo-degradation of Contaminants in Petroleum Refinery Wastewater. *Water Research*. 36:2167-2172.
- Stergar V., Zagorc-Koncan J. and Zgajnar-Gotvanj A. 2003. Laboratory scale and pilot plant study on treatment of toxic wastewater from the petrochemical industry by UASB reactors. *Water Science and Technology*. 48(8):97-102.

- Strotmann U., Geldem A., Kuhn A., Gendig C. and Klein S. 1999. Evaluation of A Respirometric Test Method to Determine The Heterotrophic Yield Coefficient Of Activated Sludge Bacteria. *Chemosphere*. 38(15):3555-3570.
- Sun Y., Zhang Y. and Quan X. 2008. Treatment of petroleum refinery wastewater by microwave-assisted catalytic wet air oxidation under low temperature and low pressure. *Separation and Purification Technology*. 62:565-570.
- Tabrizi G.B. And Mehrvar M. 2004. Integration of Advanced Oxidation Technologies and Biological Processes: Recent Developments, Trends and Advances. *Journal of Environmental Science and Health*. A39 (11–12):3029–3081.
- Ting W., Huang Y. and Lu M. 2007. Catalytic Treatment of Petrochemical Wastewater by Electroassisted Fenton Technologies. *Reaction Kinetics and Catalysis Letters*. 92 (1):41-48.
- Tyagi R.D., F. T. Tran F.T. and Chowdhury A.K. 1992. Performance of RBC Coupled to a Polyurethane Foam to Biodegrade Petroleum Refinery Wastewater. *Environmental Pollution*. 76:61-70.
- Tyagi R.D., F. T. Tran F.T. and Chowdhury A.K. 1993. Biodegradation of petroleum refinery wastewater in a modified rotating Biological Contactor with Polyurethane Foam Attached to the Disks. *Water Research*. 27(1):91-99.
- Wagner M. and Nicell J.A. 2001. Peroxidase-catalyzed removal of phenols from a petroleum refinery wastewater. *Water Science and Technology*. 43 (2):253-260.
- Water Environment Federation (WEF). 2008. Manual of Practice (MOP) FD-3: Industrial Wastewater Management, Treatment, and Disposal. 3rd Edition.
- Wilmot P.D., Cadee K., Katinic J.J. and Kavanagh B.V. 1988. Kinetics of sulfide oxidation by dissolved oxygen. *Journal of the Water Pollution Control Federation*. 60:1264-1270.