

**COMBINED UV-C/H₂O₂/VUV PROCESSES FOR THE TREATMENT OF ACTUAL
SLAUGHTERHOUSE WASTEWATER**

by

KAMBIZ VAEZZADEH NADERI

B.Eng. in Chemical Engineering

University of Sistan and Baluchistan, Zahedan, Iran, 1988

A Thesis

presented to Ryerson University

in partial fulfilment of the requirements

for the degree of

Master of Applied Science

in the Program of

Environmental Applied Science and Management

Toronto, Ontario, Canada, 2016

© Kambiz Vaezzadeh Naderi, 2016

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

Combined UV-C/H₂O₂/VUV processes for the treatment of actual slaughterhouse wastewater

Kambiz Vaezzadeh Naderi

Master of Applied Science

Environmental Applied Science and Management

Ryerson University

2016

In this study, a three-factor, three-level Box-Behnken design with response surface methodology and quadratic programming were used to maximize the total organic carbon (TOC) removal and minimize the H₂O₂ residual in the effluent of the combined UV-C/H₂O₂/VUV system for the treatment of actual slaughterhouse wastewater. The initial TOC concentration (TOC_o), the initial concentration of H₂O₂, and the irradiation time were the three independent variables studied in the design of experiments. The multiple response approach was used to obtain desirability response surfaces at the optimum factor settings. Thus, the optimum conditions to achieve a maximum TOC removal of 46.19% and a minimum H₂O₂ residual of 1.05% were TOC_o of 213 mg/L, H₂O_{2,o} of 450 mg/L, and irradiation time of 9 min. The obtained optimal operating conditions were validated with an additional test. Consequently, maximum TOC removal of 45.68% and minimum H₂O₂ residual of 1.03% were obtained experimentally, confirming the reliability of the statistical model.

Keywords: Slaughterhouse Wastewater; Wastewater Treatment; UV-C/H₂O₂/VUV, Combined Processes; Design of Experiments; Optimization.

ACKNOWLEDGMENTS

I would like to express my sincere gratitude to my supervisor, Dr. Mehrab Mehrvar, of the Department of Chemical Engineering at Ryerson University, and my co-supervisor Dr. Mohammad Jafar Abdekhodaei of the Department of Chemical Engineering at Sharif University of Technology, Iran, for their guidance, and support throughout the successful completion of this research.

I would also like to acknowledge Ali Hemmati, Daniel Boothe, and Tondar Tajrobeikar, Engineering Technologists of the Department of Chemical Engineering, for their technical assistance on my experimental setup. Dr. Mehrvar's research group team with whom I shared many times of enlightenment and entertainment, and provided me with great support and encouragement. Special thanks to Ciro Fernando Bustillo-Lecompte for his unconditional help and support.

Finally yet importantly, I would like to thank my family, which without their support, I would have found this achievement much more difficult.

This thesis is dedicated to my wife, Akram Poorsamangol, whose love, patience, and sacrifice has made me the person I am today.

TABLE OF CONTENTS

	Page
AUTHOR’S DECLARATION FOR ELECTRONIC SUBMISSION OF A THESIS	ii
ABSTRACT	iii
ACKNOWLEDGMENTS	iv
TABLE OF CONTENTS	v
LIST OF TABLES	viii
LIST OF FIGURES	ix
CHAPTER 1 INTRODUCTION	1
Objectives	6
CHAPTER 2 LITERATURE REVIEW	8
2.1. Introduction	8
2.2. Slaughterhouse wastewater characteristics	8
2.2.1. Slaughterhouse wastewater guidelines and regulations	9
2.2.2. Environmental impacts	11
2.2.3. Health effects	12
2.3. Slaughterhouse wastewater treatment methods	14
2.4. Advanced oxidation processes for slaughterhouse wastewater treatment	15
2.4.1. UV/H ₂ O ₂ process	18
2.4.2. Photolysis of slaughterhouse wastewater by VUV	24
2.5. Need for combined UV-C/H ₂ O ₂ /VUV processes for slaughterhouse wastewater treatment	28
2.6. Concluding remarks	32
CHAPTER 3 MATERIALS AND METHODS	34
3.1. Introduction	34

3.2. Materials	34
3.2.1. Actual slaughterhouse wastewater	34
3.2.2. Experimental setup	35
3.3. Experimental procedure	38
3.4. Analytical techniques	39
3.4.1. Total organic carbon (TOC)	39
3.4.2. Biochemical oxygen demand (BOD)	40
3.5. Experimental design and optimization studies	41
3.5.1. Box-Behnken design	43
3.5.2. Multiple linear regression	45
3.6. Combined UV-C/H ₂ O ₂ /VUV treatment of SWW	46
CHAPTER 4 RESULTS AND DISCUSSION	48
4.1. Introduction	48
4.2. Preliminary experiments	48
4.3. Experimental design and statistical analysis	51
4.4. Individual effect of model parameters	55
4.5. Interaction of model parameters, 2D contour plots, and 3D response surface	58
4.6. Optimization of operating conditions and process parameters	66
4.7. Comparison between combined UV-C/H ₂ O ₂ /VUV processes and individual processes	67
4.8. Biodegradability of the actual SWW using Respirometry assays	71
CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS	73
5.1. Conclusions	73
5.2. Recommendations	75
NOMENCLATURE	76
Greek Letters	77
Acronyms	77

APPENDICES	79
Appendix A. Sample standard deviation	79
Appendix B. Relative error analysis.....	80
Appendix C. Relationship between oxygen and carbon parameters.	81
Appendix D. Raw data.....	82
REFERENCES	110

LIST OF TABLES

	Page
Table 2.1. General characteristics of slaughterhouse wastewater.	10
Table 2.2. Worldwide standards for slaughterhouse wastewater discharge.	11
Table 2.3. Recommendations for wastewater discharges from federal facilities.	13
Table 2.4. Standard electrode potential of selected oxidant species.	17
Table 2.5. Electromagnetic spectrum of ultraviolet light.	19
Table 2.6. Common reaction mechanisms in UV/H ₂ O ₂ processes.	21
Table 2.7. Selected studies on AOPs effectiveness in removing recalcitrant compounds from water and wastewater.	30
Table 3.1. Characteristics of the actual slaughterhouse wastewater from selected provincially licensed meat processing plants along with detection limits.	35
Table 3.2. Independent variables with coded levels based on a three-factor, three-level BBD.	41
Table 3.3. Balanced incomplete block design example.	43
Table 4.1. Three-factor, three-level BBD for RSM, along with the observed and predicted percent TOC removal and H ₂ O ₂ residual.	51
Table 4.2. ANOVA for results for prediction of percent TOC removal by quadratic modeling.	53
Table 4.3 ANOVA for results for prediction of percent H ₂ O ₂ residual by quadratic modeling.	54
Table D.1. Experimental runs for the Box-Behnken Design of Experiments. Every run was repeated in triplicates.	82
Table D.2. Experimental run tabulation for the Box-Behnken Design of Experiments. Mean and residual values for the TOC removal response.	99
Table D.3. Experimental run tabulation for the Box-Behnken Design of Experiments. Mean and residual values for the H ₂ O ₂ residual response.	102
Table D.4. Experimental run tabulation for the VUV process alone.	106
Table D.5. Experimental run tabulation for the VUV/H ₂ O ₂ process alone.	107
Table D.6. Experimental run tabulation for the UV-C/H ₂ O ₂ process alone.	108
Table D.7. Comparison between individual and combined UV-C/H ₂ O ₂ /VUV processes.	108

LIST OF FIGURES

	Page
Figure 2.1. Oxidation and mineralization of organic compounds by the VUV photolysis of water. RH: Aliphatic or aromatic hydrocarbons substrate; X^\bullet : halogen radical; ET: electron transfer to an acceptor molecule. (Adopted from Oppenländer, 2003).....	27
Figure 3.1. Schematic diagram of the experimental setup for the combined UV-C and VUV photochemical processes (a) front view and (b) rear view.	36
Figure 3.2. Lab view of the experimental setup for the combined UV-C and VUV photochemical processes.	37
Figure 3.3. Schematric representation of the Box-Behnken design for three factors.....	44
Figure 4.1. Profiles of TOC removal and H_2O_2 residual in a laboratory-scale batch recirculation UV-C/ H_2O_2 /VUV photoreactor for actual SWW treatment under different conditions of (a) initial concentration of TOC, (b) initial H_2O_2 concentration, (c) and irradiation time.	50
Figure 4.2. Validation of the percent TOC removal model using different plots: (a) internally studentized residuals versus predicted values, (b) normal probability, and (c) observed experimental data versus predicted values.	56
Figure 4.3. Validation of the percent H_2O_2 residual model using different plots: (a) internally studentized residuals versus predicted values, (b) normal probability, and (c) observed experimental data versus predicted values.	57
Figure 4.4. The individual effect of model parameters on the percent TOC removal: (a) initial concentration of TOC, (b) initial H_2O_2 concentration, (c) and irradiation time. The continuous lines represent model predicted values, whereas the dashed lines represent the 95% confidence interval bands.	59
Figure 4.5. The individual effect of model parameters on the H_2O_2 residual: (a) initial concentration of TOC, (b) initial H_2O_2 concentration, (c) and irradiation time. The continuous lines represent model predicted values, whereas the dashed lines represent the 95% confidence interval bands.	60
Figure 4.6. Interaction effects of different parameters on the percent TOC removal using 3D response surface and 2D contours: (a) initial concentration of TOC and H_2O_2 (X_1/X_2), (b) initial	

concentration of TOC and irradiation time (X_1X_3), and initial concentration of H_2O_2 and irradiation time (X_2X_3).....	62
Figure 4.7. Interaction effects of different parameters on the residual H_2O_2 using 3D response surface and 2D contours: (a) initial concentration of TOC and H_2O_2 (X_1X_2), (b) initial concentration of TOC and irradiation time (X_1X_3), and initial concentration of H_2O_2 and irradiation time (X_2X_3).	63
Figure 4.8. Desirability response surface, maximizing the percent removal of TOC and minimizing the H_2O_2 residual at optimum factor settings: (a) initial concentration of TOC and H_2O_2 interaction (X_1X_2) with optimum irradiation time (9.06 min), (b) initial concentration of TOC and irradiation time (X_1X_3) interaction with optimum initial H_2O_2 concentration (450.71 mg/L), and (c) initial concentration of H_2O_2 and irradiation time (X_2X_3) with optimum initial TOC concentration (213.01 mg/L).	69
Figure 4.9. Comparison of TOC removal and H_2O_2 residual using different processes for the treatment of actual slaughterhouse wastewater, including VUV alone, VUV/ H_2O_2 , UV-C/ H_2O_2 , and combined UV-C/ H_2O_2 /VUV processes.....	70
Figure 4.10. Respirometry testing results for different samples of actual SWW, treated SWW by combined UV-C/ H_2O_2 /VUV processes, and a blank. The initial TOC concentration is 450 mg/L. BOD_5 is obtained as the oxygen uptake at the five-day mark.....	72
Figure D.1. TOC removal profile in a laboratory-scale batch recirculation UV-C/ H_2O_2 /VUV photoreactor for actual SWW treatment at different initial concentrations of TOC.....	100
Figure D.2. TOC removal profile in a laboratory-scale batch recirculation UV-C/ H_2O_2 /VUV photoreactor for actual SWW treatment at different initial H_2O_2 concentrations.....	101
Figure D.3. TOC removal profile in a laboratory-scale batch recirculation UV-C/ H_2O_2 /VUV photoreactor for actual SWW treatment at different irradiation times.....	101
Figure D.4. TOC removal profile in a laboratory-scale batch recirculation UV-C/ H_2O_2 /VUV photoreactor for actual SWW treatment at different initial concentrations of TOC (Series 1), initial concentrations of H_2O_2 (Series 2), and irradiation times (Series 3).	102
Figure D.5. H_2O_2 residual profile in a laboratory-scale batch recirculation UV-C/ H_2O_2 /VUV photoreactor for actual SWW treatment at different initial concentrations of TOC.....	104
Figure D.6. H_2O_2 residual profile in a laboratory-scale batch recirculation UV-C/ H_2O_2 /VUV photoreactor for actual SWW treatment at different initial concentrations of H_2O_2	104
Figure D.7. H_2O_2 residual profile in a laboratory-scale batch recirculation UV-C/ H_2O_2 /VUV photoreactor for actual SWW treatment at different irradiation times.....	105

Figure D.8. H ₂ O ₂ residual profile in a laboratory-scale batch recirculation UV-C/H ₂ O ₂ /VUV photoreactor for actual SWW treatment at different initial concentrations of TOC (Series 1), initial concentrations of H ₂ O ₂ (Series 2), and irradiation times (Series 3).	105
Figure D.9. TOC calibration curve for the range of 1–400 mgTOC/L.	109

CHAPTER 1

INTRODUCTION

The limitation of freshwater resources and population growth in one hand and progressively stricter regulations on the quality of discharged effluent on the other hand makes the reuse of industrial and municipal wastewater crucial (US EPA, 2004; Environment Canada, 2012). Researchers are forced to develop and evolve novel technologies to accomplish higher mineralization rate with a lower amount of detectable contaminants (Feng et al., 2009). At present, the occurrence of emerging contaminants such as pharmaceutical compounds, slaughterhouse wastewater, pesticides, oil and gasoline by-products, among others in water sources is a great environmental concern. Based on different living standards, economic factors, types, and the amount of contaminants present in water bodies, diverse treatment methods have been applied to achieve clean and pure water (Daigger, 2009; Bustillo-Lecompte and Mehrvar, 2015).

Biological wastewater treatment, which is the use of bacteria and other microorganisms for reducing the pollution level of wastewater, is known as the most common and cost-effective method of treatment for almost all types of industrial wastewater (Edalatmanesh et al., 2008; Chan et al., 2009). Even though these methods are an economical choice of treatment, several types of industrial wastewater such as those from petrochemical, pharmaceutical, slaughterhouse, leather, dye, pulp and paper, and pesticide manufacturing plants, contain considerable amounts of nonbiodegradable organic compounds and refractory to microorganisms (Mowla et al., 2014). Conventional wastewater treatment plants such as biological wastewater treatment, including

active sludge, ultrafiltration or reverse osmosis cannot remove these pollutants; therefore, the standard regulations cannot be reached. Hence, physico-chemical processes provide a solution.

Physical processes are widely used in wastewater treatment plants. These processes are based on the separation of one or more compounds from the wastewater stream. The pollutant is transferred from one phase to another due to the separation process. As a result, further treatment is required for the degradation of contaminants in the second phase. Physical methods are employed mainly to separate large settleable and floating matter, to clarify turbid solutions, to recover and recycle valuable substances utilized in the main processes, and to separate inorganic materials.

Furthermore, the conventional and advanced physical techniques include filtration, adsorption, gas stripping, and others. Physical treatment methods can be used before or after the chemical processes depending on the influent nature and its concentration as well as the operation conditions. Solid matter and non-soluble compounds should be removed before applying chemical or biochemical treatment to prevent equipment damage. On the other hand, an increase in the size of the equipment will result in higher costs and lower process efficiency (Mohajerani et al., 2012)

Advanced oxidation processes (AOPs) have been proven to be efficient treatment methods for degrading resistant materials or mineralizing stable, inhibitory, or toxic contaminants (Tabrizi and Mehrvar, 2004). AOPs generate highly reactive intermediates, mainly hydroxyl radicals ($\cdot\text{OH}$), which oxidize most organic compounds and degrade them to intermediate products and ultimately to CO_2 and H_2O and inorganic ions.

AOPs such as ultraviolet (UV), UV/ H_2O_2 , Fenton ($\text{Fe}_2^+/\text{H}_2\text{O}_2$), sonolysis, among others are of great interest and were used by several researchers to treat different types of pollutants during the past few decades (Mehrvar and Tabrizi, 2006; Ghafoori et al., 2015). These processes

can be described as an oxidation method based on the production of an intermediary of highly reactive species such as hydroxyl radicals ($\bullet\text{OH}$ second highest powerful oxidant after fluorine), in a procedure leading to the degradation of the target contaminants (Comninellis et al., 2008). The degradation makes organic chemicals smaller and more biodegradable. Even though AOPs are very efficient in treating almost all organic compounds, some drawbacks prevent their commercial applications.

A high requirement of oxidant dosage, high electrical power consumption, and precise pH adjustment are some of these disadvantages, which increases the operational cost of AOPs (Klamerth et al., 2010). Therefore, combination of AOPs and physical treatments or biological treatments can be an ideal alternative to treat refractory components of wastewater (Hirvonen et al., 1998)

Meat is an important part of the daily diet in numerous countries worldwide. Therefore, meat processing plants (MPPs) produces large volumes of slaughterhouse wastewater (SWW). In the food and beverage industry, 24% of the total freshwater is used in the slaughtering of animals and cleaning of the slaughterhouse facilities (Table 1.1) and up to 29% of that consumed by the agricultural sector worldwide (Gerbens-Leenes et al., 2013).

SWW composition depends on the type of industry processes and specific water demand varies (Debik and Coskun, 2009). Consequently, SWW requires significant treatment for a safe and sustainable release to the environment (Salminen and Rintala, 2002; Mittal, 2006; Arvanitoyannis and Ladas, 2008; Franke-Whittle and Insam, 2013; Bustillo-Lecompte and Mehrvar, 2015).

Table 1.1. Fresh water consumption in the food and beverage manufacturing.

(Adopted from Bustillo-Lecompte and Mehrvar, 2015)

Food Industry	Water consumption (%)
<i>Meat Processing</i>	<i>24</i>
Beverages	13
Dairy	12
Other Food	11
Fruits and Vegetables	10
Bakery and Tortilla Products	9
Grain and Oilseeds	9
Sugar and Confectionary	5
Animal Food	5
Seafood	2

In Ontario, Canada, slaughterhouses and MPPs discharge the SWW into the municipal sewer system after onsite preliminary treatment and usually pay fines for the disposal (Mittal, 2006; Bustillo-Lecompte et al., 2013; Bustillo-Lecompte and Mehrvar, 2015). Due to a high level of organics and nutrients in SWW, it has been considered detrimental worldwide. Furthermore, the onsite treatment would be the best option to treat and disinfect the effluents before discharging into receiving waters (Debik and Coskun, 2009; Wu and Mittal, 2011; Bustillo-Lecompte et al., 2013, 2014; Bustillo-Lecompte and Mehrvar, 2015). The level of organics and nutrients in SWW are expressed as bulk components such as total suspension solids (TSS), biochemical oxygen demand (BOD), chemical oxygen demand (COD), and total organic carbon (TOC).

SWWs are typically treated in anaerobic reactors because of the high level of COD. Despite the efficiency of anaerobic treatment, complete degradation of the organic matter is not possible. The soluble organic matters remained in the effluent of anaerobic treatment are more suited for treatment by aerobic processes or anaerobic–aerobic systems (Gray, 2010). There are also instabilities in anaerobic treatment methods, which requires using aerobic treatment to meet

the standards (Chan et al., 2009). These instabilities include the low settling rate and the treatment of the ammonium ions (NH_4^+) and hydrogen sulphide (HS^-) in anaerobic treatment effluent (Heijnen et al., 1991; Cao and Mehrvar, 2011). Furthermore, a suitable combination of anaerobic and aerobic processes is required for the biological removal of nutrients N and P (Del Pozo and Diez, 2005). According to Aggelis et al. (2001), effluents produced by anaerobic or aerobic processes alone does not comply with discharge limits when treating high organic content wastewater. The use of combined processes can also lead to a reduction in operating costs when compared with aerobic treatment alone (Vera et al., 1999).

AOPs are more attractive alternatives to conventional treatment and also used as a complementary treatment option, either pretreatment or post-treatment, to biological processes for SWW treatment (De Sena et al., 2009; Luiz et al., 2009; Cao and Mehrvar, 2011; Bustillo-Lecompte et al., 2013, 2014; Bustillo-Lecompte and Mehrvar, 2015). Furthermore, AOPs may inactivate microorganisms without adding additional chemicals to the SWW, avoiding the formation of hazardous by-products (De Sena et al., 2009; Barrera et al., 2012; Bustillo-Lecompte et al., 2015).

The UV/ H_2O_2 process are discovered to be more efficient compared to the other processes, which have been tested for SWW treatment including ozonation, and gamma radiation (Millamena, 1992; Mittal, 2006; Melo et al., 2008; Bustillo-Lecompte and Mehrvar, 2015). Compared to the other technologies, the UV/ H_2O_2 process is five times faster in inactivation and inhibition of microorganisms as well as in degrading aromatic compounds (Luiz et al., 2009; De Sena et al., 2009; Cao and Mehrvar, 2011; Barrera et al., 2012; Bustillo-Lecompte et al., 2013, 2014; Bustillo-Lecompte and Mehrvar, 2015).

On the other hand, the vacuum–UV (VUV) photolysis is either an effective alternative or a complementary post-treatment method to the UV/H₂O₂ process since it avoids common drawbacks such as the need to use high amounts of H₂O₂ and to remove its residual concentrations after treatment. The VUV occurs within 100 to 200 nm range of the electromagnetic spectrum and the photons emitted within this range contain a greater amount of energy than those emitted from the rest of the UV electromagnetic spectra.

Several parameters including total organic contents, light source intensity, oxidant concentration, irradiation time, pH, reaction time, and output power are factors that are affecting AOP systems. Therefore, the characterization of such systems requires the consideration of cross-factor and single-factor effects using the design of experiments (DOE) to identify those factors that influence the multivariable system (Ghafoori et al., 2015; Bustillo-Lecompte et al., 2016).

Objectives

In this study, the effects of the irradiation time, the inlet concentrations of TOC and H₂O₂, and their interaction on the photochemical treatment of actual SWW in a combined UV-C/H₂O₂/VUV process were investigated to evaluate its applicability as a post-treatment method. DOE is used to overcome the limitations of conventional methods and consequently optimize the factors involved. Conversely, the response surface methodology (RSM) has been recognized to be statistically reliable to analyze multifactor systems in chemical treatment processes. The RSM considers cross-factor interactions to attain optimal responses using the minimum number of experiments (Ghafoori et al., 2012, 2014, 2015; Bustillo-Lecompte et al., 2016).

DOE was used to optimize the photochemical treatment of SWW using the combined UV-C/H₂O₂/VUV process in a batch recirculation system by maximizing the removal of TOC and

minimizing the H_2O_2 residual. The optimal parametric values for the DOE were obtained by a Box-Behnken design (BBD) using three factors at three levels combined with RSM.

A statistical quadratic regression model was also developed to predict both the percent TOC removal and the H_2O_2 residual as response variables by the combined UV-C/ H_2O_2 /VUV process. As a final point, the statistical model validated by an additional set of experiments carried out at optimum conditions according to the DOE results. In summary, the objectives of the present study are:

1. To evaluate the applicability of the combined UV-C/ H_2O_2 /VUV process as a post-treatment method of actual SWW.
2. To investigate the effects of the irradiation time, the initial concentrations of TOC and H_2O_2 , and their interaction on the photochemical treatment of SWW.
3. To optimize the combined UV-C/ H_2O_2 /VUV process as a post-treatment method of actual SWW by maximizing the percent TOC removal and minimizing the H_2O_2 residual using DOE, BBD, and RSM.
4. To develop statistical models to predict both percent TOC removal and H_2O_2 residual as response variables by the combined UV-C/ H_2O_2 /VUV process.

CHAPTER 2

LITERATURE REVIEW

2.1. Introduction

This chapter provides a comprehensive review of SWW treatment methods as well as the factors affecting their performance and a description of their mechanisms. This chapter also describes and reviews the characteristics, environmental impacts, health effects, and regulatory framework, including the current technologies for SWW treatment.

2.2. Slaughterhouse wastewater characteristics

According to the World Bank Group (2007), a meat processing plant, which is a slaughterhouse facility, consume between 2.5 and 40 m³/ton of water per metric ton of beef produced. More than 65% of the water used for three activities: cleaning, spraying and rinsing activities. The remaining 35% is associated with personal hygiene, tool sterilization, cooling water scald tank, animal handling facilities, and vehicles washing (Wang et al., 2009).

The washing and cleaning procedures bring about high loads of organic content such as large amounts of blood, fats and oils, body tissue, nitrogen (from blood), phosphorus, detergents from cleaning products, and salts (sodium) from protein recovery products such as sodium lignosulfonate, are released after washing and cleaning activities. The carcass and evisceration washing procedures are the main providers of organic content at slaughterhouse plants (Wang et al., 2009).

The composition of SWW characterized mostly by a complex mixture of proteins, fat, and fibers (Salminen and Rintala, 2002; Mittal, 2006; Arvanitoyannis and Ladas, 2008; Bustillo-Lecompte and Mehrvar, 2015). The United States Environmental Protection Agency (US EPA, 2004) has considered SWW as an industrial waste in the category of agricultural and food industries and classified as one of the most harmful wastes to the environment. The slaughterhouse effluent discharge causes deoxygenation of rivers and contamination of groundwater (Bustillo-Lecompte et al., 2013, 2014; Bustillo-Lecompte and Mehrvar, 2015).

The common characteristics of SWW in several studies are summarized in Table 2.1, in which their common ranges and averages including TSS, TOC, COD, BOD, total nitrogen (TN), and pH are presented (Debik and Coskun, 2009; Cao and Mehrvar, 2011; Barrera et al., 2012; Bustillo-Lecompte et al., 2013, 2014; Bustillo-Lecompte and Mehrvar, 2015). High concentrations of BOD, COD, and TSS in SWW containing flesh and blood have been reported to be 200,000 mg/L, 375,000 mg/L, and 2,800 mg/L or more, respectively (Debik and Coskun, 2009; Bustillo-Lecompte and Mehrvar, 2015).

2.2.1. Slaughterhouse wastewater guidelines and regulations

Meat processing plants (MPPs) effluent or SWW contain several constituents that may deplete oxygen in a body of water causing irreversible alterations to aquatic ecosystems and wildlife (Wang et al., 2009; U.S EPA, 2004). These components mainly are derived from fatty tissues, blood and different salts and detergents used in cleaning procedures of MPPs. The major concern of regulatory agencies in North America such as the U.S EPA, Canadian Environmental Agencies (Environment Canada and provincial Ministries of Environment), as well as the European

Environment Agency (EEA) is to limit the discharge of oxygen demand compounds, as BOD and COD concentrations to fresh water bodies.

Table 2.1. General characteristics of slaughterhouse wastewater.
(Adopted from Cao, 2011; Barrera et al., 2012; Bustillo-Leconte and Mehrvar, 2015)

Parameter	Range	Average
TSS (mg/L)	300–2800	1164
TOC (mg/L)	100–1200	546
COD (mg/L)	1250–15900	4221
BOD (mg/L)	610–1905	1209
P-PO ₄ (mg/L)	1.30–80	19
TN (mg/L)	50–785	427
Alkalinity (mg/L)	50–2100	450
pH	4.90–8.10	6.95
C/N	6.00–15	10

The treatment systems developed by industry are frequently regarded as a regulatory obligation, increasing capital and running costs, and yielding negative economic returns. Compliance with environmental legislation should not necessarily lead to the creation of additional expenses, but can instead provide a secondary source of income.

The standards and regulations governing slaughterhouses are different around the world mostly because of the differences between custom and traditions. However, two main kinds of meat processing systems are available everywhere, one that is produced in modern mechanized slaughterhouses and the other from local butcher shops.

The characteristics of the wastewater, the volume of organic concentration, the plant size, the availability of technology, and compliance with local regulations are the main parameters for selection of a particular wastewater treatment. There are instances that some MPPs are allowed to discharge their effluent into the municipal sewer system after demonstrating an adequate

reduction of BOD loads by preliminary treatment, such as storage tank, land application, lagoon systems, and dissolved air flotation (DAF) (Mittal, 2006; Bustillo-Lecompte and Mehrvar, 2015).

Table 2.2 describes the standard levels and concentration limits of organic constituents to be discharged into water bodies as recommended by different international agencies, including Environment Canada (2012), US EPA (2004), and the Council of the European Communities (CEC, 1991).

Table 2.2. Worldwide standards for slaughterhouse wastewater discharge.

Parameter	EU Standards¹	US Standards²	Canadian Standards³	Ontario Standards⁴
BOD ₅ (mg/L)	25	26	Freshwater lakes: 5. Rivers, streams, and estuaries: 20. Shoreline 30.	25
COD (mg/L)	125	n/a	n/a	n/a
TSS (mg/L)	35	30	Freshwater lakes: 5. Rivers, streams, and estuaries: 20. Shoreline 30.	25
TN (mg/L)	10	8	1	1.25

¹ CEC 1991; ² US EPA 2004; ³ Environment Canada 2012; ⁴ ECO 2010

2.2.2. Environmental impacts

Population growth and demand for animal products lead to the commercialization of animal products for consumption and the production of high waste volumes. The processes involved in the wastewater treatment depend on the strength and composition of pollutants (Bustillo-Lecompte and Mehrvar, 2015). The environment capacity to degrade organic matter is directly affected by high concentrations of organic matter present in SWW. Therefore, new treatment methods have to be developed for a more efficient management of waste products.

The results of the presence of organic constituents in natural source waters are eutrophication, temperature changes, and dissolved oxygen (DO) depletion, which will have a severe impact on the ecosystem (US EPA, 2004). For example, oxygen consumption of the biodegradable organic matter will result in the oxygen depletion for fish and other benthic organisms, leading to such problems as reproduction and developmental abnormalities, reduced levels of activity, or death of aquatic life (Torkian et al., 2003). The parameters used to determine the biodegradable organic compounds (BOCs) are biochemical oxygen demand (BOD), chemical oxygen demand (COD), and total suspended solids (TSS). The TSS represents the amount of insoluble organic and inorganic particles in the wastewater (Verheijen et al., 1996; Rajakumar et al., 2011).

High concentration of macronutrients such as nitrogen and phosphorous (N and P) may stimulate algal growth and cause eutrophication of the receiving water bodies. The mineralization of these algae may lead to the death of aquatic life because of oxygen depletion (Belsky et al., 1999). Finally, contaminants such as chromium and unionized ammonia are directly toxic to aquatic life (Verheijen et al., 1996; Bustillo-Lecompte and Mehrvar, 2015).

2.2.3. Health effects

Soil and groundwater pollution by nitrate, chloric anions, and many pathogenic microorganisms is the characteristic of SWW contamination. Pathogenic microorganisms from cattle wastes can be also transmitted to humans who are exposed to the water body, making those areas non-suitable for drinking or irrigation purposes (Benka-Coker and Ojior, 1995; Bustillo-Lecompte and Mehrvar, 2015).

Table 2.3 shows the standard levels recommended for slaughterhouse wastewater discharge in Canada (Environment Canada, 2012). They apply to direct discharges of treated effluents to surface water for general use.

Table 2.3. Recommendations for wastewater discharges from federal facilities.
(Adopted from Environment Canada, 2012)

Parameters	Water Bodies of Disposal	Disposal Recommendation
BOD (mg/L)	Freshwater lakes	5
	Rivers streams, and estuaries	20
	Shorelines	30
Fecal coliforms (MPN*/100mL)	All	100
Total coliform count (MPN*/100mL)	All	1000
TSS (mg/L)	Freshwater lakes	5
	Rivers, streams, and estuaries	20
	Shorelines	30
Reactive chlorine (mg/L)	All	0.01*
pH	All	6-9
Phenols (mg/L)	All	0.02
Oils and grease (mg/L)	All	5
Temperature (°C)	All	≥1
Ammonia (mg/L)	All	1
Nitrates (mg/L)	All	1
Phosphorus (mg/L)	All	1
Sulphurs (mg/L)	All	0.5
Chromium (mg/L)	All	0.05

* MPN: Most Probable Number or current detection limit.

Serious gastrointestinal diseases, bloody diarrhea, liver malfunctions, and in some cases, death associated with the presence of viruses, protozoa, helminthic eggs and bacteria in SWWs were reported in developed countries (Gopala Krishna et al., 2009; Feng et al., 2009; Bustillo-Lecompte and Mehrvar, 2015). To avoid environmental pollution and human health effects, SWW

must be treated efficiently before discharge into water bodies. (Belsky et al., 1999; Salminen and Rintala, 2002).

2.3. Slaughterhouse wastewater treatment methods

SWW treatment systems are similar to current methods used for municipal wastewater and may include preliminary, primary, secondary, and even tertiary treatment. Thus, SWW management methods after preliminary treatment are various, but they can be divided into five major subgroups: land application, physicochemical treatment, biological treatment, AOPs, and combined processes (Valta et al., 2015; Bustillo-Lecompte and Mehrvar, 2015). Each system has unique treatment advantages and disadvantages (Rajakumar et al., 2011). The feasibility of using individual or combined reactor types to treat SWW biologically has been examined in the past (Bustillo-Lecompte and Mehrvar, 2015).

The process of land application involves direct irrigation of the SWW onto agricultural land (Bull et al., 1982; Mittal, 2006). Physicochemical treatment involves the separation of the SWW into various components, typically the separation of solids from the liquor by sedimentation or coagulation/flocculation, and removal of pollutants using electrocoagulation (EC) and membrane technologies (Bull et al., 1982; Johns, 1995; Mittal, 2006; Eryuruk et al., 2014; Almandoz et al., 2015).

On the other hand, biological treatment can be divided into anaerobic and aerobic systems, and constructed wetlands (CWs). Aerobic systems are more frequently used since they operate at a higher rate than anaerobic systems. Anaerobic systems require less complex equipment since no aeration system is required. Both anaerobic and aerobic systems may be further sub-divided into

other processes, which have their own advantages and disadvantages (Bull et al., 1982; Tritt and Schuchardt, 1992; Johns, 1995; Mittal, 2006; Bugallo et al., 2014; Vymazal, 2014).

Moreover, AOPs, which are diverse and include UV/H₂O₂ and UV/O₃ for the oxidation and degradation of the organic and inorganic materials present in SWW through reactions with hydroxyl radicals ([•]OH) (Mittal, 2006; Melo et al., 2008; Luiz et al., 2009, 2011; Cao and Mehrvar, 2011; Barrera et al., 2012; Bustillo-Lecompte et al., 2013, 2014; Bustillo-Lecompte and Mehrvar, 2015).

Lastly, the use of combined processes is a cost-effective approach that can lead to a reduction in operating and maintenance costs when compared with individual processes (Tritt and Schuchardt, 1992; Chan et al., 2009; Luiz et al., 2011; Bustillo-Lecompte et al., 2013, 2014; Bustillo-Lecompte and Mehrvar, 2015).

2.4. Advanced oxidation processes for slaughterhouse wastewater treatment

The use of AOPs can also become an attractive alternative for post-treatment of biologically treated effluents. In this context, conventional biological processes do not always provide satisfactory results, especially for industrial and high-concentrated wastewater since many of the organic substances produced by various industries are toxic or resistant to conventional biological treatment (Steber and Wierich, 1986; Bowers et al., 1989; Adams et al., 1996; Pulgarín and Kiwi, 1996; García et al., 2001; Lapertot et al., 2006; Bustillo-Lecompte and Mehrvar, 2015). Therefore, one feasible option for such biologically persistent wastewater is the use of advanced oxidation technologies based on chemical oxidation widely recognized as a highly efficient treatment alternative for recalcitrant wastewater.

AOPs degrade organic pollutants by forming hydroxyl radicals ($\cdot\text{OH}$) (Balcioglu et al., 2001; Bhatkhande et al., 2002; Neyens and Baeyens, 2003; Gonze et al., 2003; Bustillo-Lecompte et al., 2013, 2014, 2015, 2016). $\cdot\text{OH}$ are highly reactive and non-selective. This species can degrade organic matter rapidly in comparison to those of ordinary chemical oxidation processes that may take months and even years to accomplish this. The fast oxidation, in terms of seconds, of the organic matter by the $\cdot\text{OH}$ species allows the use of the term “advanced” for this kind of process (Pera-Titus et al., 2004; Devipriyas and Yesodharan, 2005; Pignatello et al., 2006; Comninellis et al., 2008; Shannon et al., 2008; Bustillo-Lecompte et al., 2013, 2014, 2015, 2016).

AOPs include photochemical degradation processes, such as UV/ H_2O_2 , UV/ O_3 , and UV/ $\text{O}_3/\text{H}_2\text{O}_2$, in which UV radiation plays a secondary role in initiating the photoreaction in the presence of an auxiliary oxidant to produce $\cdot\text{OH}$ radicals; photocatalytic processes, such as TiO_2/UV and photo-Fenton reactors, in which a catalyst plays a secondary role in absorbing UV radiation to produce $\cdot\text{OH}$ radicals; and chemical oxidation, such as O_3 , $\text{O}_3/\text{H}_2\text{O}_2$ and $\text{H}_2\text{O}_2/\text{Fe}_2^+$ among others (Bustillo-Lecompte and Mehrvar, 2015).

The same principles of common chemical processes associated with redox reactions also govern AOPs, which involve the exchange of electrons between chemical species, leading to a change in the oxidation state of different compounds taking place in the process (Sawyer et al., 2002). In redox reactions, the compounds gaining electrons are known as oxidizing agents, while compounds losing electrons are known as reducing agents. Thus, $\cdot\text{OH}$ radicals, produced from AOPs, are strong oxidizing agents, which are highly reactive with organic matters.

The exchange of electrons between an oxidant and a reducer is spearheaded by the difference in their standard electrode potential (E°). $\cdot\text{OH}$ intermediates have one of the highest electrical oxidation potentials (EOP) (2.80V) among all typical chemical oxidizing agents used in

water and wastewater treatment technologies as shown in Table 2.4 (Barrera et al., 2012; Bustillo-Lecompte et al., 2013; Bustillo-Lecompte and Mehrvar, 2015).

Table 2.4. Standard electrode potential of selected oxidant species.
(Adopted from Tarr, 2003)

Oxidant	Electrical oxidation potentials (V)
Fluorine (F)	3.03
<i>Hydroxyl radical ($\cdot\text{OH}$)</i>	2.80
Atomic oxygen (O)	2.42
Ozone (O_3)	2.07
Hydrogen peroxide (H_2O_2)	1.77
Permanganate ion (MnO_4^{2-})	1.67
Hypochlorous acid (HClO)	1.49
Chlorine (Cl)	1.36
Chlorine dioxide (ClO_2)	1.27
Bromine (Br)	1.09

Furthermore, hydroxyl radicals ($\cdot\text{OH}$), which have a high oxidation potential, attack organic molecules by either abstracting or adding a hydrogen atom to double bonds, thus allowing their mineralization to non-toxic forms such as carbon dioxide and water. Studies carried out by Sigge et al. (2002) demonstrated the feasibility of this process in further reducing the TOC contents of anaerobic effluents, when using ozone and ozone/hydrogen peroxide in combination with a granular activated carbon contacting column. In one study, colour and COD reductions ranged from 66 to 90% and from 27 to 55%, respectively (Chernicharo, 2006). In some cases, the mineralization of an organic compound cannot be reached, but the toxicity of the parent compound is reduced and eventually it can be treated by cheaper methods such as biological treatment (Bustillo-Lecompte et al., 2014).

The chemical oxidation for complete mineralization is expensive because the oxidation intermediates, formed during treatment, tend to be more and more resistant to their total chemical degradation. Moreover, they all consume energy (e.g. UV radiation, ozone) and chemical reagents

like catalysts and oxidizers, which increase with treatment time. Appropriate techniques must be combined to provide technically and economically feasible options (Bustillo-Lecompte and Mehrvar, 2015). In combined chemical and biological wastewater treatment, it is very important to keep in mind how the characteristics of each treatment, such as the chemical oxidant to be used, can improve the destruction of a persistent contaminant (Liu et al., 2008; Comninellis et al., 2008; Klavarioti et al., 2009).

The rest of the aspects to be considered are also widely known: the chemical oxidation capacity (Jones et al., 1985; Lee and Carberry, 1992), its potential for forming toxic intermediates (Bowers et al., 1989; Barrera et al., 2012; Bustillo-Lecompte et al., 2014), a change in pollutant behaviour (Miller et al., 1988), the choice of biological agent, the comparison of different cultures (Lee and Carberry, 1992), the comparison of acclimated and non-acclimated cultures (Bowers et al., 1989; Hu and Yu, 1994), and the use of monospecific cultures and anaerobic cultures (Koyama et al., 1994; Adams et al., 1996). The measurement of the combined process efficiency depends on the purpose of the treatment, but normally requires the independent optimization of each chemical and biological step (Oller et al., 2011).

2.4.1. UV/H₂O₂ process

H₂O₂ and O₃ are chemical compounds that can be considered as auxiliary oxidants when coupled with UV radiation, usually under the UVC region of the electromagnetic spectrum between 200 to 280 nm as shown in Table 2.5 to produce [•]OH species. The UV/H₂O₂ process, one of the most widely AOPs, is an effective technology for industrial wastewater treatment (Tabrizi and Mehrvar, 2004; Aye et al., 2004; Edalatmanesh et al., 2008; Mohajerani et al., 2012). The degradation and disinfection of pollutants in the UV/H₂O₂ process rely on highly reactive species,

where $\cdot\text{OH}$ are produced from the reaction of the H_2O_2 with the UV light (Glaze, 1987; Edalatmanesh et al., 2008; Mohajerani et al., 2012).

Table 2.5. Electromagnetic spectrum of ultraviolet light.
(Adopted from Diffey, 2002)

Name	Abbreviation	Wavelength range (nm)	Energy per photon (eV)
Before UV spectrum; visible light	VIS	above 400	<3.10
Ultraviolet A, long wave, or black light	UVA	400–315	3.10–3.94
Near	NUV	400–300	3.10–4.13
Ultraviolet B or medium wave	UVB	315–280	3.94–4.43
Middle	MUV	300–200	4.13–6.20
Ultraviolet C, short wave, or germicidal	UVC	280–100	4.43–12.4
Far	FUV	200–122	6.20–10.2
Vacuum	VUV	200–100	6.20–12.4
Low	LUV	100–88	12.4–14.1
Super	SUV	150–10	8.28–124
Extreme	EUV	121–10	10.2–124
Beyond UV range	X-rays	below 10	>124

The UV/ H_2O_2 process uses ultraviolet radiation to cleave the O–O bond in hydrogen peroxide (H_2O_2) and generate hydroxyl radicals. The $\cdot\text{OH}$ can be then scavenged by an organic compound to initiate a radical chain degradation of H_2O_2 in the series of reactions shown below (Glaze, 1987; Andreozzie et al., 2000):



The quantum yield (ϕ) of a radiation-induced process can be defined as the number of molecules that react per photon absorbed by the system. This event may represent a chemical reaction and be calculable by Equations (2.6) and (2.7) (Zepp, 1978).

$$\phi[TOC] = \frac{-d[TOC]/dt}{k_{s(\lambda)}} \quad (2.6)$$

$$k_{s(\lambda)} = \frac{q_0 \varepsilon_\lambda [1 - 10^{-\alpha_\lambda (r - R_i)}]}{\alpha_\lambda (r - R_i)} \quad (2.7)$$

where,

$\phi[TOC]$ = quantum yield for TOC removal (mol/E);

t = time (s);

$k_{s(\lambda)}$ = specific rate of light absorption by TOC (E/mol.s);

q_0 = incident photon irradiance (E/cm².s);

ε_λ = molar absorption coefficient of TOC (1/M.cm);

α_λ = absorption coefficient (1/cm);

r = nominal radius of the photoreactor (cm); and

R_i = inner radius of the photoreactor (cm).

A recombination of hydroxyl radicals (Reaction 2.8) should be avoided by finding the optimum H₂O₂ concentration inherent to the specific contaminant and system configuration (Oppenländer, 2003).



In addition to radical recombination, the UVC/H₂O₂ process effectiveness is also delayed by the H₂O₂ low molar absorption coefficient, 18.6/M.cm at 254nm, which is responsible for large amounts of H₂O₂ being added to produce significant concentrations of •OH radicals within the system. Moreover, any post-treatment surplus of the H₂O₂ concentration should be removed from the effluent; otherwise, it could enter source waters, causing adverse effects on fish and other living communities due to the toxicity threshold of H₂O₂ (Barrera et al., 2012; Bustillo-Lecompte et al., 2014). The major photochemical and chemical reactions taking place in the UV/H₂O₂ process can be described as shown in Table 2.6.

Table 2.6. Common reaction mechanisms in UV/H₂O₂ processes.
(Adopted from Bustillo-Lecompte et al., 2016)

No.	Reaction	Rate constant	Reference
(2.9)	$H_2O_2 + hv \xrightarrow{\phi_1} 2 \cdot OH$	0.500 mol/E	Buxton et al. (1988)
(2.10)	$TOC + hv \xrightarrow{\phi_2} \dots \rightarrow CO_2 + H_2O$	0.032 mol/E	Barrera et al. (2012)
(2.11)	$H_2O_2 + \cdot OH \xrightarrow{k_1} HO_2\cdot + H_2O$	$k_1 = 2.7 \times 10^7$ 1/M.s	Christensen et al. (1982)
(2.12)	$\cdot OH + \cdot OH \xrightarrow{k_2} H_2O_2$	$k_2 = 5.0 \times 10^9$ 1/M.s	Staehelin et al. (1984)
(2.13)	$2 \cdot OH \xrightarrow{k_3} H_2O_2$	$k_3 = 6.0 \times 10^9$ 1/M.s	Staehelin et al. (1984)
(2.14)	$\cdot OH + HO_2\cdot \xrightarrow{k_4} H_2O_2 + O_2$	$k_4 = 8.3 \times 10^5$ 1/M.s	Bielski et al. (1985)
(2.15)	$2HO_2\cdot \xrightarrow{k_5} H_2O_2 + O_2$	$k_5 = 1.5 \times 10^6$ 1/M.s	Buxton et al. (1988)
(2.16)	$HO_2\cdot + \cdot OH \xrightarrow{k_6} H_2O + O_2$	$k_6 = 6.6 \times 10^9$ 1/M.s	Buxton et al. (1988)
(2.17)	$H_2O_2 + HO_2\cdot \xrightarrow{k_7} H_2O + O_2 + \cdot OH$	$k_7 = 3.0 \pm 0.6$ 1/M.s	Koppenol et al. (1978)
(2.18)	$HO_2\cdot + \cdot OH \xrightarrow{k_8} H_2O + O_2$	$k_8 = 7.1 \times 10^9$ 1/M.s	Sehested et al. (1968)
(2.19)	$HCO_3^- + \cdot OH \xrightarrow{k_9} CO_3^{\cdot -} + H_2O$	$k_9 = 8.5 \times 10^6$ 1/M.s	Buxton et al. (1988)
(2.20)	$CO_3^{\cdot -} + \cdot OH \xrightarrow{k_{10}} CO_3^{\cdot -} + OH^-$	$k_{10} = 3.9 \times 10^8$ 1/M.s	Buxton et al. (1988)
(2.21)	$CO_3^{\cdot -} + H_2O_2 \xrightarrow{k_{11}} HCO_3^- + HO_2\cdot$	$k_{11} = 4.3 \times 10^5$ 1/M.s	Crittenden et al. (1999)
(2.22)	$TOC + \cdot OH \xrightarrow{k_7} \dots \rightarrow CO_2 + H_2O$	$k_{12} = 7.0 \times 10^5$ 1/M.s	Barrera et al. (2012)
(2.23)	$TOC + \cdot OH \xrightarrow{k_{20}} intermediates \rightarrow CO_2 + H_2O$	$k_{13} = 7.0 \times 10^5$ 1/M.s	Cao and Mehrvar (2011)
(2.24)	$TOC_1 + \cdot OH \xrightarrow{k_{21}} \dots \rightarrow CO_2 + H_2O$	$k_{14} = 1.1 \times 10^5$ 1/M.s	Bustillo-Lecompte et al. (2016)

Bovine catalase is the most common compound used to remove excess H₂O₂, which converts H₂O₂ into water and oxygen, as shown in Reaction (2.25) (Chelikani et al., 2004). In

particular, the low molar absorption coefficient and the use of compounds to control the H₂O₂ concentration in the effluent have a significant impact on the total cost of the AOP process.



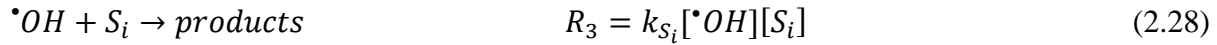
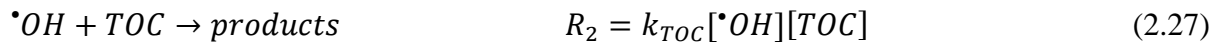
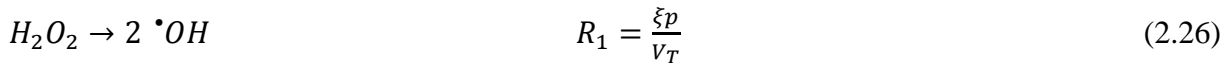
For a UV/H₂O₂ process to be efficient, the H₂O₂ concentration has to be at an optimal level to maximize the absorption of the incident photons, while the presence of other water compounds that may compete for the absorption of radiation must be minimized. The optimum H₂O₂ concentration also helps to minimize the recombination mechanisms as well as H₂O₂ effluent concentration surplus (Barrera et al., 2012).

The advantages of the UV/H₂O₂ process include a large range of applications, enhancing the degradation of pollutants, accelerating the rate of oxidation with great potentials for disinfection and comprehensive mineralization of pollutants in wastewater (Aye et al., 2004; Tabrizi and Mehrvar, 2004; Cao and Mehrvar, 2011; Barrera et al., 2012; Bustillo-Lecompte et al., 2013, 2014, 2016).

The successful applications of the UV/H₂O₂ process are shown in various wastewater treatment systems such as textile dye wastewater with an optimum H₂O₂ concentration of 510 mg/L (Aye et al., 2004), atrazine wastewater with 99% degradation in less than 15 min (Beltrán et al., 1993), linear alkyl benzene sulfonate (LAS) wastewater with an optimum H₂O₂ concentration of 5,000 mg/L (Venhuis and Mehrvar, 2005), LAS wastewater in a pilot-plant photoreactor with an optimum H₂O₂ concentration of 720 mg/L (Mehrvar and Tabrizi, 2006), cotton dyeing wastewater with 80% of TOC removal in 2 h with an optimum H₂O₂ concentration of 3,944 mg/L (Shu, 2006), and actual SWW with 81% TOC removal in a UV/H₂O₂ continuous

photoreactor with recycle using an optimum H₂O₂ concentration of 860 mg/L (Bustillo-Lecompte et al., 2016). In terms of disinfection the UV systems have been proved to be highly effective in bacteria inactivation with 99.9% of complete inhibition in 27.6 seconds (Barrera et al., 2012).

According to Bolton et al. (2001), the overall kinetics in terms of the rate of removal of a particular component, including TOC, can often be described by simple rate expressions that are either zero-order or first-order. Consequently, AOPs such as UV/H₂O₂ can be modeled by the following mechanisms:



where,

R_1 = reaction rate of $\cdot OH$ (mg/L.h);

R_2 = reaction rate of $\cdot OH$ with TOC (mg/L.h);

R_3 = reaction rate of $\cdot OH$ with a scavenger (S_i) (mg/L.h);

ξ = constant that depends on the type of AOP (mg/h.W)

p = power rating for the system (W);

V_T = treated SWW volume (L);

S_i = a scavenger for the $\cdot OH$, where $i = a, b, \dots, n$ (mg/L); and

k_{TOC} and k_{S_i} = second-order rate constants (L/mg.h).

According to Bolton et al. (2001), a steady-state analysis of this general mechanism yields the overall rate kinetic for the UV/H₂O₂ process as shown in Equation (2.29). This simple

mechanism is either zero- or first-order for TOC. If the concentration of TOC is high ($k_{TOC}[TOC] \gg \sum_i k_{S_i}[S_i]$), the reaction rate will be zero-order in TOC as shown in Equation (2.30). On the other hand, if the concentration of TOC is low ($k_{TOC}[TOC] \ll \sum_i k_{S_i}[S_i]$), the reaction rate will be first-order in TOC as shown in Equation (2.31). The difference between “high” and “low” concentration varies considerably with the system but is often approximately 100 mg/L.

$$-\frac{d[TOC]}{dt} = \frac{\xi p k_{TOC}[TOC]/V_T}{k_{TOC}[TOC] + \sum_i k_{S_i}[S_i]} \quad (2.29)$$

$$-\frac{d[TOC]}{dt} = \frac{\xi p}{V_T} \quad (2.30)$$

$$-\frac{d[TOC]}{dt} = \frac{\xi p k_{TOC}}{V_T \sum_i k_{S_i}[S_i]} \quad (2.31)$$

2.4.2. Photolysis of slaughterhouse wastewater by VUV

The VUV photolysis positions itself as an excellent alternative to the UV/H₂O₂ process since it avoids common drawbacks such as the need to use high amounts of H₂O₂ and to remove residual concentrations after treatment. The VUV occurs within 100 to 200 nm range of the electromagnetic spectrum and the photons emitted within this range contain a greater amount of energy than those emitted from the rest of the UV electromagnetic spectra (VIS, UVA, UVB, and UVC). For example, one mole of photons, emitted at 254 nm (UV-C), contains 471 kJ, while one mole of photons, at 185 nm (VUV), contains 647 kJ (U.S EPA, 1998).

The water molecule starts absorbing radiation from 498 kJ/mol and higher, the condition that is met by the high energy VUV photons, which causes the cleavage of the water molecule as shown in Reaction (2.32). As a result, hydroxyl (\bullet OH) and hydrogen ($H\bullet$) radicals are generated

as primary species (Barrera et al., 2012). In addition, hydrated electrons (e_{aq}^-) are produced in lesser amounts shown in Reaction (2.33). Although H^\bullet and hydrated e_{aq}^- play a minor role in the oxidation of organic matter, they are part of the reaction and, therefore, must be included in the oxidation cycle for the final mineralization of the organic carbon.

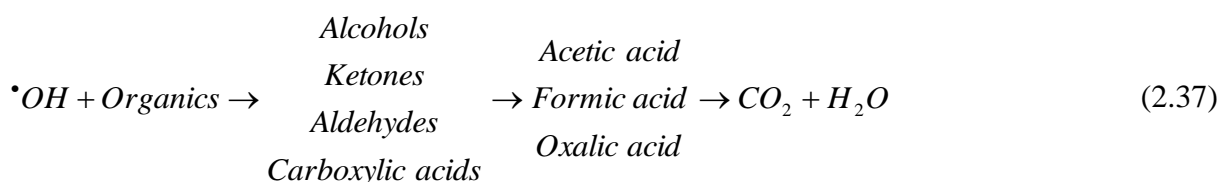
Hydrated electrons (e_{aq}^-) react with dissolved molecular oxygen to form superoxide radical anions ($O_2^{\bullet-}$), whose conjugated acid HO_2^\bullet with a pK_A value of 4.8 implies that ($O_2^{\bullet-}$) is a weak base in water. The hydroperoxyl radicals (HO_2^\bullet) can disproportionate to form molecular oxygen and hydrogen peroxide, which results in a shifted equilibrium to the right of Reaction (2.34), generating an increased basicity of the superoxyl radical ($O_2^{\bullet-}$). Likewise, the hydrogen radicals formed during the VUV/ H_2O_2 process are transformed into HO_2^\bullet by a quick reaction with dissolved molecular oxygen (Reaction 2.36). Therefore, the water molecule (H_2O) can be labeled as an auxiliary oxidant (similar to H_2O_2) because of the participation of e_{aq}^- and H^\bullet as reductive species in the oxidative cycle (Reactions 2.34 to 2.36).



Figure 2.1 describes the general mechanisms by which an organic compound is oxidized and mineralized by different species generated during the VUV photolysis of water. The types of saturated aliphatic or aromatic organic compounds (RH) that can be degraded by the VUV

photolysis of water include trichloromethane, CHCl_3 , or 1,1,1-trichloroethane, $\text{CH}_3\text{-CCl}_3$, while unsaturated organic compounds include trichloroethylene (CH=CCl_2), trichloroethene, ($\text{Cl}_2\text{C=CClH}$), or tetrachloroethene, ($\text{Cl}_2\text{C=CCl}_2$).

A general oxidation pattern of organic matter carried out by VUV and UV/ H_2O_2 photolytic processes are described in Reaction (2.37), where the parent compound is oxidized by $\bullet\text{OH}$ radicals producing intermediate compounds and finally mineralized to carbon dioxide and water. Intermediates include compounds such as alcohols, aldehydes, ketones, and carboxylic acids. After a C-C cleavage, these intermediates are further degraded producing formic, acetic, and oxalic acids before finally being mineralized to CO_2 and H_2O .



Currently, there are different ways to produce VUV radiation: via low pressure (LP) and medium pressure (MP) mercury lamps as well as excimer lamps. LP mercury lamps emit mostly monochromatic radiation at 254 nm, yet some radiation is also emitted at 185 nm. The wavelength of 185 nm can be harnessed by using high purity quartz sleeves (known as suprasil quartz) with a relative VUV output efficiency of about 10% of that of the 254 nm emissions. By contrast, emissions at 254 nm could reach efficiencies of about 60%. Low-pressure mercury lamps are usually limited to less than 300 W of electric input (Barrera et al., 2012).

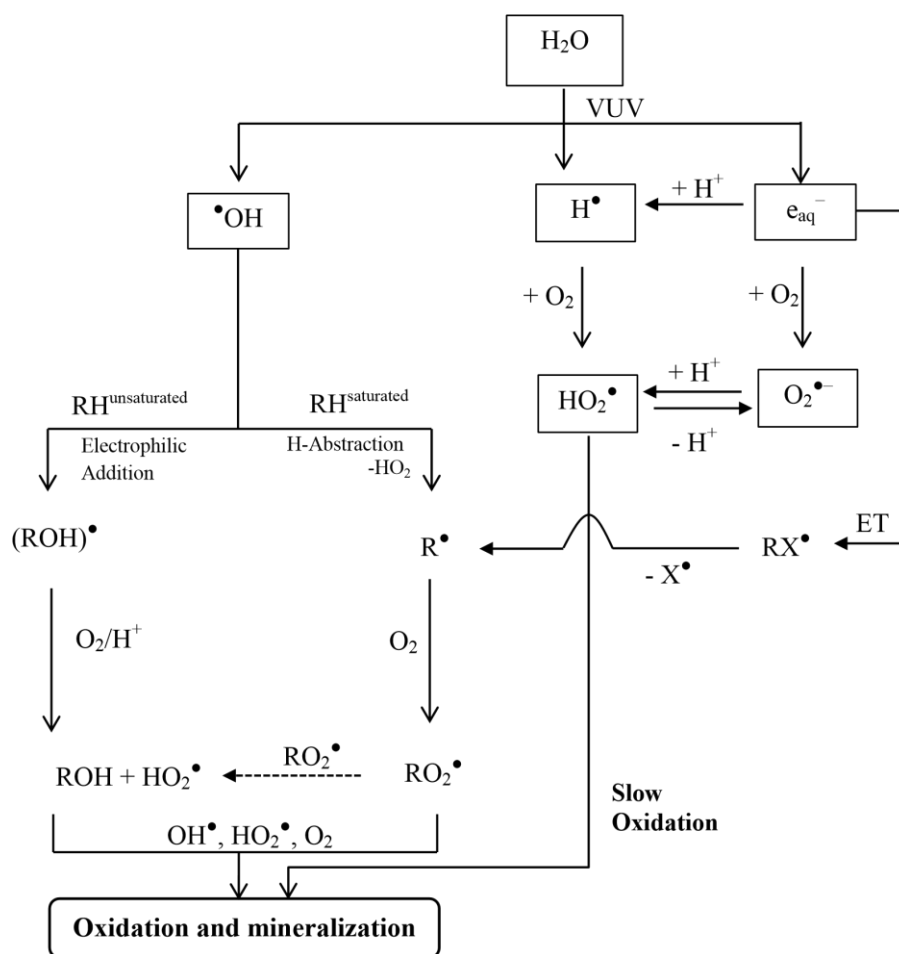


Figure 2.1. Oxidation and mineralization of organic compounds by the VUV photolysis of water. RH: Aliphatic or aromatic hydrocarbons substrate; $\text{X}\cdot$: halogen radical; ET: electron transfer to an acceptor molecule. (Adopted from Oppenländer, 2003)

Another type of lamps is an MP mercury lamp that can emit polychromatic radiation at different emission regions, including UV-C (15-23%), UV-B (6–7 %), UV-A (~ 8%), VIS (~15%), and IR (47–55%). By using a suprasil quartz sleeve, the VUV (185 nm) can be also harnessed obtaining efficiencies of around 20% of that of the UV-C output. Most recently, xenon excimers (Xe_2^*) lamps (i.e. dimers consisting of two atoms of the same structure) have been gaining appeal for VUV production, as they produce VUV at 172 nm, a stronger wavelength, and may reach efficiencies of about 60%. Consequently, xenon excimer lamps are becoming an excellent alternative to the VUV production that is efficient and more powerful wavelength (172 nm) in comparison to LP and MP mercury lamps.

2.5. Need for combined UV-C/H₂O₂/VUV processes for slaughterhouse wastewater treatment

AOPs are becoming more appealing to serve as a complementary treatment in either pre-treatment or post-treatment of biological processes. Additionally, AOPs may inactivate bacteria without adding any additional chemicals to the wastewater in comparison to other techniques such as chlorination or ozonation processes that are commonly used in disinfection of water streams; thus, avoiding the possible formation of hazardous by-products (Barrera et al., 2012). AOPs have been recently used for the elimination and degradation of organics in wastewaters, water reuse and pollution control issues showing excellent overall results (De Sena et al., 2009; Cao and Mehrvar, 2011; Barrera et al., 2012; Bustillo-Lecompte et al., 2013, 2014, 2016).

Considering the most common treatment technologies applied in meat processing plants, the question is whether or not it is justified to complement biological treatment with a pre-treatment or post-treatment process carried out by AOPs. The answer can be directly linked to

factors such as biodegradability, form (colloidal, suspended, or dissolved), and toxicity or inhibitory characteristics of the organic and inorganic constituents unique to each wastewater (Tabrizi and Mehrvar, 2004). A variety of organic compounds toxic to bacteria includes aromatic compounds, halogenated compounds, oils, lipophilic solvents, and anionic surfactants. For instance, aromatic compounds, such as benzene, toluene, and xylenes are also highly toxic to bacteria. Similarly, compounds such as chloroform, trichloromethane, tetrachloromethane, and methylene chloride as halogenated solvents used in manufacturing dyes, pharmaceuticals, and plastics are highly toxic to bacteria used in wastewater treatment (Barrera et al., 2012).

All compounds mentioned above have a common characteristic in that they are non-ionic in charge or structure, thus, causing them to dissolve rapidly into the cell wall exerting toxicity. As a result, undesired effects such as treatment efficiency losses, discharge permit violations, and operational cost increments may arise if these sorts of compounds are not removed before biological treatment. In this case, a pre-treatment process by AOPs should be conducted to eliminate recalcitrant and toxic compounds, maximizing the efficiency of the biological treatment.

Table 2.7 summarizes recent studies carried out on AOPs, namely UV-C/H₂O₂ and VUV, alone and combined with biological treatment and its effectiveness in removing organic compounds from SWW as well as so-called emerging contaminants, such as bisphenol A (BPA), pharmaceutical active compounds (PhACs), personal care products (PCPs), perfluorinated surfactants, and other contaminants from surface waters, whereby AOPs are becoming more appealing to serve as complementary treatment either in a pre or post-treatment stage, to current biological processes. Besides, AOPs inactivate bacteria without adding any additional chemicals to the water, unlike the chlorination or ozonation disinfection processes, thereby avoiding the formation of hazardous by-products (Barrera et al., 2012; Bustillo-Lecompte and Mehrvar, 2015).

Table 2.7. Selected studies on AOPs effectiveness in removing recalcitrant compounds from water and wastewater.

Target Compound	AOP	Analytical parameter	Results	References
Natural organic matter	UV-C/H ₂ O ₂	Substrate by HPLC	Reduction of Non organic material 94%	Goslan et al. (2006)
Trichloroethene	UV-C/H ₂ O ₂	Substrate by HPLC	Complete mineralization in 30 min	Li et al. (2007)
SWW as BOD	Gamma radiation	BOD	Influent BOD of 3860 mg/L. Removal rate (39–86%)	Melo et al. (2008)
Aromatics in SWW	UV-C/H ₂ O ₂	COD and Color	The H ₂ O ₂ /UV treatment was 5.2 times faster than UV alone in removing aromatic compounds >95%	Luiz et al. (2009)
Pharmaceuticals	UV-C/H ₂ O ₂	Substrate	Removal rates between 86–100%	Kim et al. (2009a)
Pharmaceuticals and personal care products	UV-C/H ₂ O ₂	Substrate by HPLC	[H ₂ O ₂] = 8.2 mg/L Removal rates > 90%	Kim et al, (2009b)
Insecticides	UV-C/H ₂ O ₂	Substrate by HPLC	The molar ratio of [H ₂ O ₂]/[TOC] of 220 and pH 2.8. Under these conditions, 97% of the thiacloprid was removed in about 120 min.	Abramović et al. (2010)
Pharmaceuticals	UV-C/ H ₂ O ₂	Substrate by liquid chromatography/mass spectrometry	Removal rates of up to 99%	Rosario et al. (2010)

Target Compound	AOP	Analytical parameter	Results	References
Tetracyclines	UV-C/H ₂ O ₂	Substrate by HPLC and TOC	[H ₂ O ₂] = 0.02–2 mmol/L, 100% removal in 6 min	López-Peñalver et al. (2010)
Neurotoxins	VUV	Substrate by HPLC	[H ₂ O ₂] = 30 mg/L was added to 0.6 mg/L of anatoxin-a >70% degradation	Afzal et al. (2010)
Organics as TOC in Synthetic SWW	Combined Biological–UV-C/H ₂ O ₂	TOC, TN, COD, and BOD	Molar ratio of [H ₂ O ₂]/[TOC] = 3.5; pH neutral; 95% TOC removed	Cao and Mehrvar (2011)
Synthetic SWW	Combined Biological–UV-C/H ₂ O ₂	TOC, TN, COD, and BOD	Removal rates in the range of 5 to 85%	De Nardi et al. (2011)
Synthetic SWW	VUV/H ₂ O ₂	TOC	Up to 58% removal	Barrera et al. (2012)
Synthetic SWW	Combined Biological–UV-C/H ₂ O ₂	TOC, TN, COD, and BOD	Up to 99% removal of TOC and 82% removal of TN	Bustillo-Lecompte et al. (2013)
Synthetic SWW	UV-C/H ₂ O ₂	TOC and TN	Up to 93% TOC removal and 76% TN removal	Khennoussi et al. (2013)
Synthetic SWW	Combined Biological–UV-C/H ₂ O ₂	TOC	Up to 99.9% TOC removal	Bustillo-Lecompte et al. (2014)
Synthetic SWW	UV-C/H ₂ O ₂	COD and BOD	Up to 91% overall removal efficiency	Ozyonar and Karagozoglu (2014)
Actual SWW	UV-C/H ₂ O ₂ with recycle	TOC	Up to 81% TOC removal	Bustillo-Lecompte et al. (2016)

2.6. Concluding remarks

It is evident that conventional wastewater treatment processes, mainly biological processes, are suitable for achieving organic matter removal. However, toxic compounds derived from industrial processes, such as manufacturing of pharmaceuticals, dyes, or plastics are noxious to bacteria used to digest the pollutants and inhibit their ability to properly degrade the target pollutants.

More importantly, conventional processes do not remove trace concentrations of emerging contaminants such as PhACs, BPA, PCPs, trichloroethene, neurotoxins, perfluorinated surfactants, and veterinary pharmaceuticals that might be present in actual SWW. Therefore, the combination of conventional wastewater treatment with other technologies, among which AOPs are gaining momentum, is being strongly considered by policy-makers in regulatory agencies as well as decision-makers in different industry sectors to comply with regulatory standards and enhance wastewater treatment processes, especially in the meat processing industry (U.S EPA, 2004; Environment Canada, 2012; Bustillo-Lecompte and Mehrvar, 2015).

AOPs are a promising technology used in both water and wastewater treatment processes. It has been shown that photochemical processes are one of the most efficient processes among AOPs to produce $\bullet\text{OH}$, which is the most powerful oxidant in the water treatment field. In particular, the vacuum-UV photolysis process is turning into an excellent option to treat wastewater. The many advantages of the VUV process include the production of $\bullet\text{OH}$ from the homolysis of the water molecule without the addition of auxiliary chemicals, which ideally is the main purpose of purification: removing rather than adding more chemicals. The VUV process does not require monitoring of the residual H_2O_2 after treatment or the addition of even more chemicals, such as catalase, to remove it.

Even though producing VUV radiation is more expensive than UV-C radiation, the lighting industry is developing fast and is producing new lamps, which convert electric energy into VUV at higher efficiency rates, thereby reducing the costs (Bustillo-Lecompte et al., 2014; Bustillo-Lecompte and Mehrvar, 2015; Bustillo-Lecompte et al., 2016). Consequently, VUV is becoming one of the outstanding members belonging to the AOPs group, which could produce the coveted $\cdot\text{OH}$ in a simple manner becoming a feasible alternative to UV-C/ H_2O_2 .

AOPs are being used for the oxidation and degradation of the organic and inorganic materials present in SWW through reactions with hydroxyl radicals ($\cdot\text{OH}$). Benefits of their application include not generating highly toxic disinfection by-products (DBPs) during the disinfection stage, unlike other chemical disinfectants such as chlorine, ozone, chloramines, or chlorine dioxide. As shown in the literature review, DBPs pose an extra risk to public health apart from the compounds being targeted by the process itself. Therefore, the VUV process may be used as a complementary stage to the UV-C/ H_2O_2 in order to reduce the H_2O_2 requirements. The VUV occurs within 100 to 200 nm range of the electromagnetic spectrum allowing the direct treatment of the organic matter.

Furthermore, the characterization of this combined system requires the consideration of cross-factor and single-factor effects using the design of experiments (DOE) to identify those factors that influence the multivariable system. Thus, this study aims to fill the gap in the literature on the application of combined UV-C/ H_2O_2 /VUV systems as an alternative to the UV-C/ H_2O_2 photolytic process for the treatment of actual SWW in order to minimize the residual of H_2O_2 and maximize the overall treatment efficiency (Barrera et al., 2012; Bustillo-Lecompte and Mehrvar, 2015; Bustillo-Lecompte et al., 2016).

CHAPTER 3

MATERIALS AND METHODS

3.1. Introduction

This study is focused on determining the performance and the treatment ability of the combined UV-C/H₂O₂/VUV process for the removal of TOC from actual SWW. Experiments were conducted to assess the efficiencies and performance of the combined process. This chapter presents an overall description of the research approach, materials, and procedures.

3.2. Materials

3.2.1. Actual slaughterhouse wastewater

Actual SWW samples were taken from selected provincially licensed meat-processing plants directly from their source in Ontario, Canada, at the time of the study. The actual SWW samples had an average TOC concentration of 800 mg/L. Table 3.1 illustrates overall SWW characteristics from the selected provincially licensed meat processing plants. Distilled water (DW) was used to dilute SWW samples to adjust TOC concentrations for different BBD levels accordingly. A hydrogen peroxide solution (30% w/w) was used.

Table 3.1. Characteristics of the actual slaughterhouse wastewater from selected provincially licensed meat processing plants along with detection limits.

Parameter	Range	Detection limits
BOD (mg/L)	37.950–8,231.0	0.000–10,000
COD (mg/L)	87.230–14,256	0.000–15,000
TN (mg/L)	6.1200–339.20	0.100–25,000
TOC (mg/L)	10.510–1,718.0	0.100–25,000
TP (mg/L)	2.5700–77.310	0.020–125.00
TSS (mg/L)	0.3900–738.00	0.000–750.00
Color (mg/L in the Pt scale)	175.00–400.00	0.000–500.00
Turbidity (Formazine attenuation units – FAU)	200.00–300.00	0.000–1,000.0
pH	6.0–7.1	4.0–10

3.2.2. Experimental setup

As shown in Figures 3.1 and 3.2, a laboratory-scale batch recirculation photoreactor setup including two photoreactors in series providing uniform light distribution was used in this study. Each stainless steel photoreactor (SL-LAB 2, Siemens Inc.) had a working volume of 0.46 L with a length of 305 mm, a diameter of 51 mm and annular space of 13.3 mm. UV-C Low-pressure Hg lamp at 14 W and a VUV LP Hg lamps high output at 14 W (LP4130 and LP4135, Siemens Inc.) were used. UV emission peaks were at 254 nm (UV-C 4 W output) and 185 nm (VUV 3.90 W output).

A quartz sleeve was used to protect the lamps from a fouling formation that may interfere with the UV radiation emission. This particular geometry (slight annular space) and the method of irradiation lead to having a good approximation of an isoactinic condition (uniform light distribution) in the photoreactor (Ghafoori et al., 2015; Bustillo-Lecompte et al., 2016). The total volume of the combined UV-C/H₂O₂/VUV system was 1.6 L, including piping and accessories. A magnetic centrifugal pump (Model RK-72012-10; Cole-Parmer, Tokyo, Japan) with a maximum capacity of 4.6 GPM and a maximum head of 36.1 ft was used.

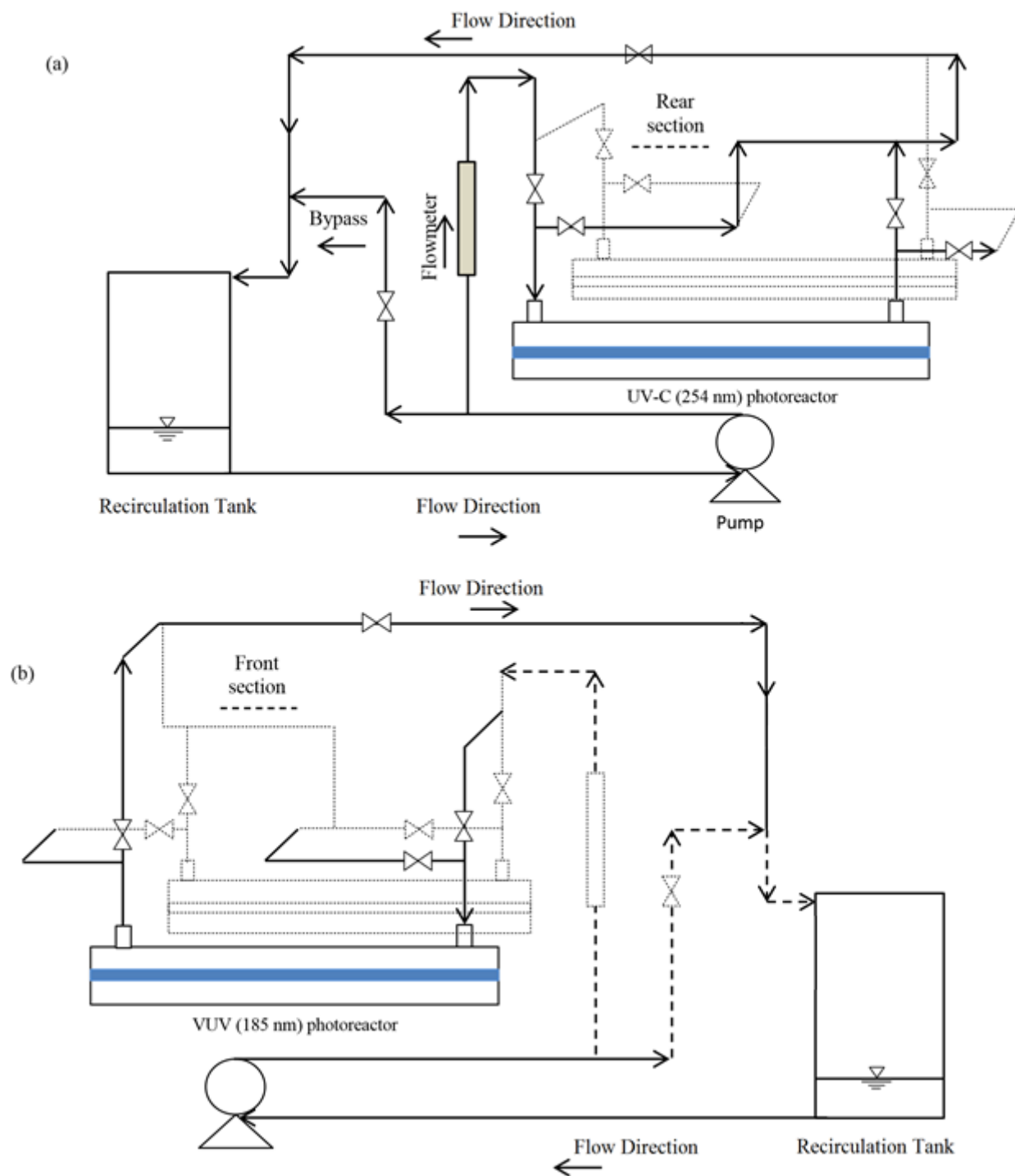


Figure 3.1. Schematic diagram of the experimental setup for the combined UV-C and VUV photochemical processes (a) front view and (b) rear view.

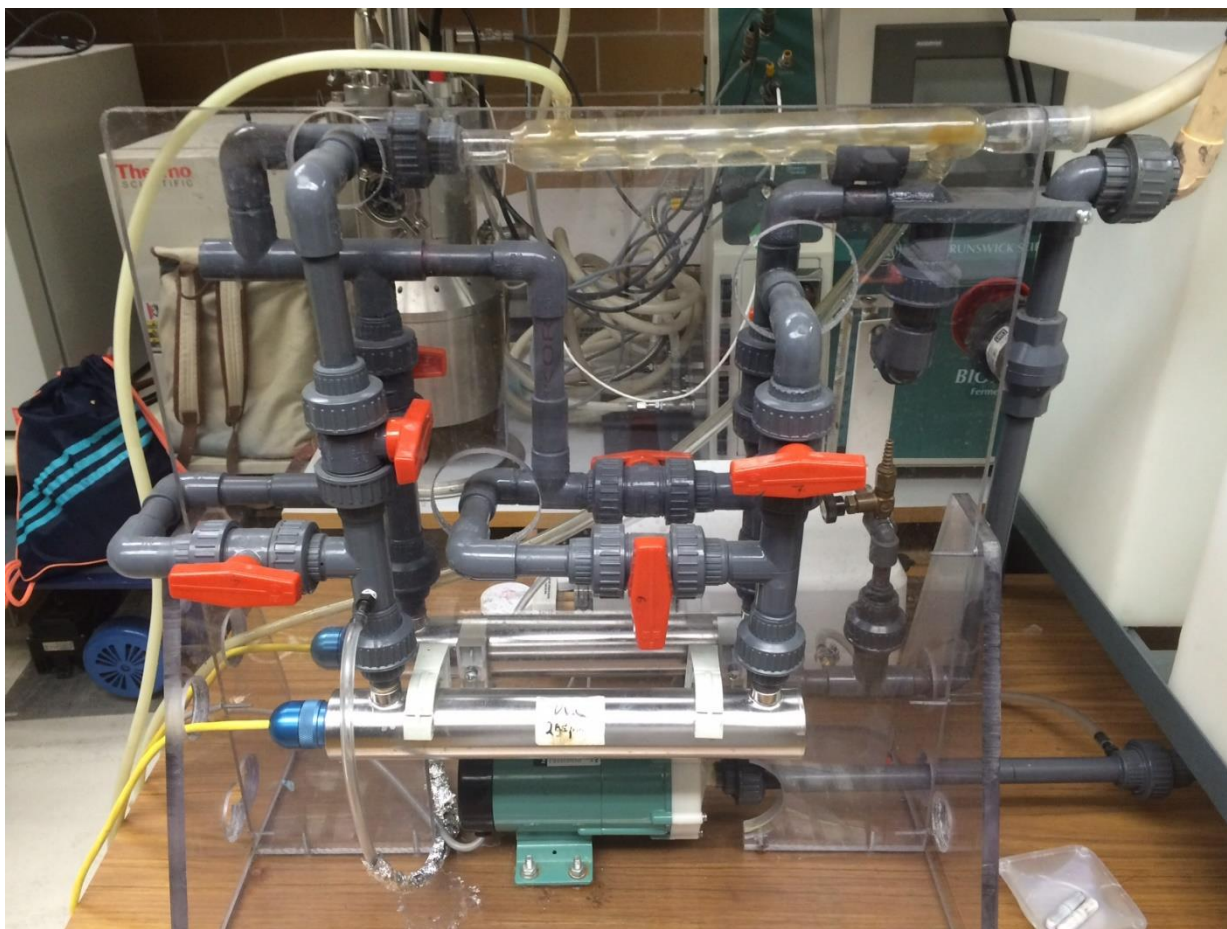


Figure 3.2. Lab view of the experimental setup for the combined UV-C and VUV photochemical processes.

The system was also equipped with a by-pass valve to control the flow-rate and provide the relief to the pump pressure. An in-line acrylic flowmeter with a flow-rate range between 50 and 250 mL/min was used to control the wastewater flow rate during the operation. In addition, the system was supplied with a set of valves that allowed using both processes UV-C and VUV individually as well as the two processes combined.

3.3. Experimental procedure

Experiments with actual SWW were conducted in a batch recirculation operation. The SWW was exposed to the combined UV/VUV/H₂O₂ processes for a total of 2.5 h using H₂O₂ as an oxidant. Furthermore, the following procedure was implemented to carry out each experiment for quality control:

- 1) The UV lamp was switched on for 30 min before starting each experiment to guarantee light intensity stabilization within the photoreactor.
- 2) SWW samples were filtered to separate the liquid portion of the wastewater from the solids.
- 3) Filtered SWW samples were then diluted to reach the desired TOC concentration and guarantee the accuracy of the feed concentration value in a 15 L solution.
- 4) The SWW solution with the desired TOC concentration was recirculated through the magnetic centrifugal pump to the reactors with a maximum capacity of 4.6 GPM.
- 5) A portion of recirculating sample was allowed to pass through the flowmeter to the photoreactors.
- 6) An adequate H₂O₂ concentration was calculated based on the material balance for each experiment and added to the tank.
- 7) Samples were taken at 30-minute intervals until the system reached steady state conditions.

An experiment without UV irradiation, namely dark experiment, was also conducted to evaluate the possible adsorption of organic compounds on the UV photoreactor walls. SWW samples were taken from the combined UV-C/H₂O₂/VUV system. Volumes of 45 mL were collected from each stage to measure TOC, TN, and residual H₂O₂. All experiments were repeated in triplicates, and the average values were reported. Furthermore, three replicates were made for each analytical measurement.

3.4. Analytical techniques

Different parameters, including TOC, TN and residual H₂O₂ were measured according to the *Standard Methods* (APHA, 2012). The details of each analytical technique are explained in the following sections.

3.4.1. Total organic carbon (TOC)

TOC concentrations were measured by a Teledyne Tekmar Apollo 9000 Combustion TOC Analyzer equipped with an automated sampler. Before sample analyses, the TOC analyzer was calibrated, samples were centrifuged at 3,000 rpm for 30 min (Thermo Scientific Heraeus Multifuge X1). Standards were prepared by adding a carbon source to distilled water to achieve determined levels of carbon. The reagent solutions were prepared as follows:

Potassium hydrogen phthalate (KHP) was used as an organic carbon source for TOC calibration. The KHP was dried in an oven at 105°C for 2 h before the preparation of the stock standard solution and stored in a desiccator. For preparation of a 1,000 mg/L of KHP stock standard solution, 2,125 mg of KHP was dissolved in distilled water and diluted to 1 L.

A series of standard solutions, covering the expected range of sample concentrations, (1–400 mg/L), was prepared by accurately diluting the 1,000 mg/L of stock standard solution with distilled water. Through running TOC standard calibration analysis, a TOC calibration curve was obtained (Appendix D.9). Thus, TOC removal efficiency was determined by Equation (3.1).

$$TOC_{rem} = \frac{(TOC_o - TOC)}{TOC_o} \times 100\% \quad (3.1)$$

where,

TOC_o = TOC concentration of initial wastewater sample (mg/L)

TOC = TOC concentration of final wastewater sample (mg/L); and

TOC_{rem} = TOC removal efficiency (%)

3.4.2. Biochemical oxygen demand (BOD)

A respirometer was used to measure the oxygen uptake of the microorganisms in the SWW media. Respirometric experiments were performed using a BI-2000 electrolytic respirometer (Bioscience Inc., Bethlehem, PA) to observe the biodegradability of the untreated and treated wastewater samples while measuring their BOD_5 . The respirometer has eight 1-L bioreactor vessels, prepared according to the standard methods (APHA, 2012).

According to the instrument manual, each respirometer bioreactor loaded with 10 mL of acclimatized activated sludge, 10 mL of the wastewater sample, and filled up to 1 L with distilled water. The bioreactors require continuous aeration to obtain air saturation conditions and continuous agitation. Respirometer tests were carried out for 240 h (10-days), ultimate BOD (BOD_U) was measured, at 25°C and with an oxygen generation rate of 75 mg/L. Cumulative

oxygen uptake data recorded every 0.05 h. The data accessed on a computer screen through the instrument software. Two samples of actual SWW, one treated sample by combined UV-C/H₂O₂/VUV processes, and one distilled water (dw) blank were used.

3.5. Experimental design and optimization studies

A three-factor along with three-level BBD in conjunction with RSM was used to maximize the TOC removal while minimizing the H₂O₂ residual. The initial concentration of TOC (X_1), the initial concentration of H₂O₂ (X_2), and UV irradiation time (X_3), calculated as the exposure time of the actual SWW samples in the photoreactors, were used as independent factors in the DOE. The percent TOC removal (Y_1) and the H₂O₂ residual (Y_2) were considered as the process responses. Thus, each factor was coded at three levels (-1, 0, +1) as shown in Table 3.2. Preliminary experiments were used to determine and select the particular ranges of the factors.

Table 3.2. Independent variables with coded levels based on a three-factor, three-level BBD.

Independent variable	Symbol	Coded levels		
		-1	0	1
TOC ₀ (mg/L)	X_1	50	200	350
H ₂ O _{2,0} (mg/L)	X_2	100	500	900
Irradiation time (min)	X_3	4	8	12

A quadratic model was used to estimate the parametric coefficients by correlating dependent and independent variables using the least-squares regression as shown in Equation (3.2) (Ghafoori et al., 2012, 2014, 2015; Bustillo-Lecompte et al., 2016):

$$Y_i = \beta_o + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^k \beta_{ij} X_i X_j + c \quad (3.2)$$

where $\beta_o, \beta_i, \beta_{ii}$, and β_{ij} are the constant, linear, quadratic, and cross-factor interaction coefficients, respectively; X_i and X_j represent the independent variables; Y_i is the predicted response; and k and c are the number of factors of the model and the residual term, respectively.

The statistical software Design-Expert 9.0.6.2 was employed for the DOE and the estimation of the coefficients for each response function. The significance of each model equation, individual parameters, and factor interactions were evaluated by analysis of variance (ANOVA) at the confidence intervals of 95% ($\alpha = 0.05$).

Two-dimensional (2D) contour plots and three-dimensional (3D) surface responses were obtained in the quadratic models. Additional experimental runs were carried out to validate the quadratic models for maximum percent TOC removal and minimum H_2O_2 residual at the optimal operating conditions, calculated by the software numerical optimization method.

On the other hand, to obtain a simultaneous objective function that represents the geometric mean of all transformed responses, the desirability multiple response method was used to combine the desirable ranges for each response as shown in Equation (3.3) (Myers et al., 2004):

$$D = (d_1 \times d_2 \times d_3 \times d_4 \dots \times d_n)^{1/n} = \left(\prod_{i=1}^n d_i \right)^{1/n} \quad (3.3)$$

where D , d_i , and n are the desirability objective function, each response range, and the number of responses, respectively. For a simultaneous optimization, each response requires low and high values for the optimization. Otherwise, if any response is found outside of its desirability range, the overall desirability becomes equal to zero. In this case, the percent removal of TOC (d_1) is maximized while the H_2O_2 residual (d_2) is minimized.

3.5.1. Box-Behnken design

The Box-Behnken design is a creative methodology for three-level designs to fit second-order response surfaces were developed by Box and Behnken (1960). BBD is based on the construction of balanced incomplete block designs (**Error! Reference source not found.**). For example, a balanced incomplete block design with three treatments and three blocks is presented in Table 3.3.

Table 3.3. Balanced incomplete block design example.

(Adopted from Ghafoori, 2013)

Block number	Treatment		
	1	2	3
Block 1	X	X	
Block 2	X		X
Block 3		X	X

The pairing of Treatments 1 and 2 indicates that the design variables are paired together in a 22 factorial (scaling ± 1) while X3 remains fixed at the centre ($X_3 = 0$). The same applies for Blocks 2 and 3, with a 22 factorial being represented by each pair of treatments while the third factor remains fixed at the centre level.

The BBD could be used as an efficient option in terms of number of experiments. The spherical design and the variable combinations at the center and the midpoints of the edges of the variable space make the BBD unique. The BBD involves all edge points, but the entire cube is not covered. There are no points on the corner of the cube or even a distance from the design center (**Error! Reference source not found.**).

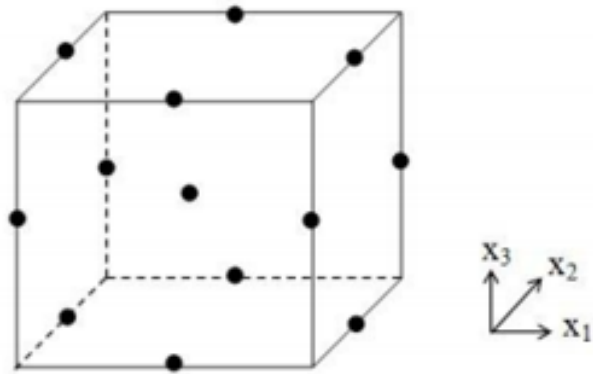


Figure 3.3. Schematic representation of the Box-Behnken design for three factors.

(Adopted from Ghafoori, 2013)

3.5.2. Multiple linear regression

In multiple linear regression problems, certain tests of hypotheses about the model parameters are useful in measuring the effectiveness of the model. The most widely used tests are the Fischer's F-value and p-value tests.

Generally, Fischer's F-value is used to determine the significance of the regression coefficients of the variables while p-value determines the significance of the variable that may indicate the pattern of interaction among variables. The F-value could be determined by the following equation (Myers et al., 2004):

$$F = \frac{MSS_{Model}}{MSS_{Error}} \quad (3.4)$$

where MSS_{Model} is the mean sum of squares due to the model and MSS_{Error} is the mean sum of squares due to error (residuals). The MSS_{Model} and MSS_{Error} values are calculated by the following equations:

$$MSS_{Model} = \frac{SS_{Model}}{df_{Model}} \quad (3.5)$$

$$MSS_{Error} = \frac{SS_{Error}}{df_{Error}} \quad (3.6)$$

where SS_{Model} , SS_{Error} , df_{Model} , and df_{Error} , are the sum of squares of the model, the sum of squares of the residuals, the degrees of freedom for the model, and degree of freedom of the residuals, respectively. The p -values are associated with F -values as they are useful to show whether F -values are large enough to indicate the statistical significance. The significance of the regression could be also verified through the coefficient of determination (R^2), which is defined as follows:

$$R^2 = \frac{SS_{Model}}{SS_{Total}} = 1 - \frac{SS_{Error}}{SS_{Total}} \quad (3.7)$$

where SS_{Total} is the total sum of squares calculated by Equation (3.8):

$$SS_{Total} = SS_{Model} + SS_{Error} \quad (3.8)$$

R^2 is the measure of the amount of the reduction in the variability of a response (y) obtained by using the regression variables X_1, X_2, \dots, X_n in the model. However, a value close to 1 does not necessarily indicates a good regression model.

Adding a variable to the model always increases the R^2 , regardless of whether the additional variable is statistically significant or not. Thus, it is possible for models that have large values of R^2 to yield poor predictions of new estimates of the mean response. Therefore, it is preferred to use an statistic adjusted R^2 given by the following equation (Myers et al., 2004):

$$R^2_{adj} = 1 - \frac{SS_{Error}/(N - p)}{SS_{Total}/(N - 1)} = 1 - \frac{(N - 1)}{(N - p)}(1 - R^2) \quad (3.9)$$

where N and p are the number of independent variables and the coefficients, respectively. The R^2_{adj} , unlike R^2 , is not always increased as variables are added to the model. In fact, if unnecessary terms are added, the value of is often decreased. Therefore, high values of R^2 and R^2_{adj} that are very close to each other imply the significance of the regression.

3.6. Combined UV-C/H₂O₂/VUV treatment of SWW

To evaluate the TOC removal rates achieved the SWW was exposed to the combined processes UV-C/H₂O₂/VUV. The UV-C photolysis consisted of direct absorption of UV radiation at peak maxima of 254 nm by the target pollutants while VUV consisted of the water photolysis (bond cleavage) to produce $\bullet\text{OH}$ and oxidize the pollutants present in the water

sample. The TOC removal from SWW was studied in a batch recirculation mode for four processes.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Introduction

Current research on VUV systems as a complementary treatment to the well-established UV-C/H₂O₂ process have proven the benefits of its application for the treatment of actual SWW. The application of the combined UV-C/H₂O₂/VUV processes maximize the overall treatment efficiency and minimize the residual of H₂O₂ without application of catalase to decompose the H₂O₂ into oxygen and water. In this study, the optimum conditions for maximizing the percent TOC removal were determined using a three-factor three-level BBD combined with the response surface methodology to correlate experimentally obtained data and predicted values. Respirometry assays were also conducted to assess the biodegradability of the actual SWW and the BOD profile before and after the treatment of actual SWW by UV-C/H₂O₂/VUV processes.

4.2. Preliminary experiments

A dark reaction experiment with H₂O₂ in the absence of UV-C and VUV radiation was conducted to determine the extent of TOC removal achieved by this oxidant alone as well as the possible loss of organic matter through adsorption on the walls of the photoreactor or by volatilization. The actual SWW was pumped into the system with the UV lamps off. The TOC removal rate for the dark experiments with no UV radiation by varying H₂O₂ concentration (0, 100, 300, 500, and 900 mg/L) was determined to remain constant with maximum variations of up to 2%.

Thus, it is confirmed that there is no significant organic matter adsorption to the reactor walls or material losses due to volatilization. Subsequently, any degradation can be attributed to the action of the combined UV-C/H₂O₂/VUV process itself.

The total number of experimental trials was seventeen based on three levels and a three-factor experimental design, with three replicates at the centre of the design, to estimate a pure error sum of squares. The independent variables were initial concentrations of TOC mg/L, H₂O₂ concentration mg/L and UV irradiation time that were coded as -1, 0, and +1. The independent variables and their critical experimental levels shown in Table 3.2 were selected based on the preliminary experimental results (Figure 4.1).

As shown in Figure 4.1a, five initial TOC concentrations (50, 150, 250, 350, 450 mg/L) were used. These initial concentrations were selected based on previous studies for the SWW treatment by UV/H₂O₂ (Cao and Mehrvar, 2011; Barrera et al., 2012; Bustillo-Lecompte et al., 2013, 2014, 2015, 2016). It can be observed that as the initial TOC concentration increases, the percent TOC removal decreases. Conversely, the H₂O₂ residual is minimum at an optimum initial TOC concentration value.

Figure 4.1b depicts the influence of the initial H₂O₂ concentration on the TOC removal and the H₂O₂ residual. Five H₂O₂ concentrations (100, 300, 500, 700, and 900 mg/L) were selected and tested based on previous studies (Cao and Mehrvar, 2011; Barrera et al., 2012; Bustillo-Lecompte et al., 2016; Bustillo-Lecompte and Mehrvar, 2015, 2016). Results show that by increasing the H₂O₂ concentration, the H₂O₂ residual also increases whereas there is an optimum H₂O₂ concentration at which percent TOC removal is maximum.

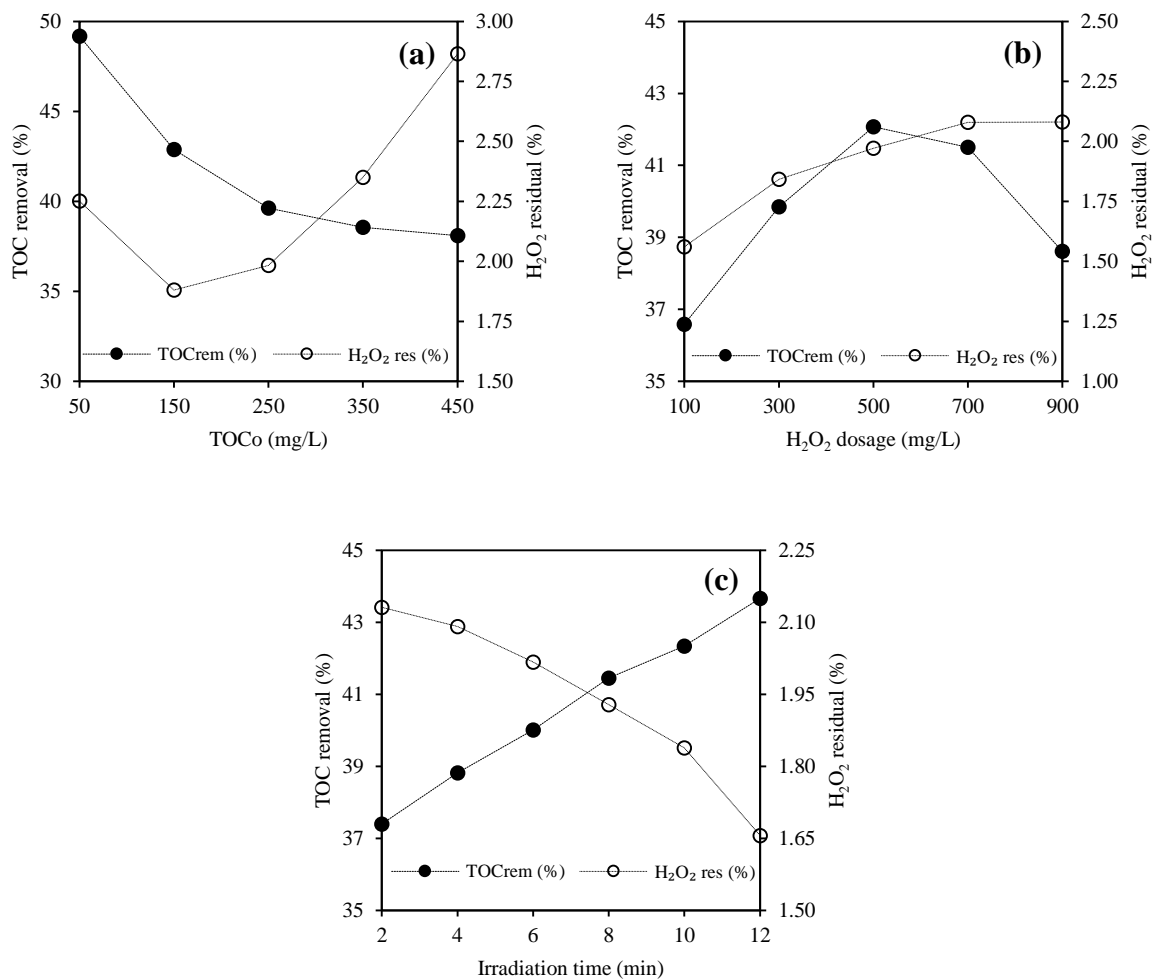


Figure 4.1. Profiles of TOC removal and H_2O_2 residual in a laboratory-scale batch recirculation UV-C/ H_2O_2 /VUV photoreactor for actual SWW treatment under different conditions of (a) initial concentration of TOC, (b) initial H_2O_2 concentration, (c) and irradiation time.

Likewise, Figure 4.1c illustrates the effects of the irradiation time on both the percent TOC removal and the H₂O₂ residual. Up to six irradiation times were examined in the range of 2-14 min. Results demonstrate that the TOC removal is directly proportional to the irradiation time while the H₂O₂ residual is inversely proportional to the irradiation time as established by the profile trends.

4.3. Experimental design and statistical analysis

Table 4.1 portrays the three-factor, three-level BBD with observed and predicted values for both percent TOC removal and H₂O₂ residual by the developed quadratic models related to the UV-C/H₂O₂/VUV processes in a batch recirculating photoreactor for actual SWW treatment.

Table 4.1. Three-factor, three-level BBD for RSM, along with the observed and predicted percent TOC removal and H₂O₂ residual.

Run	Independent variables			TOC removal (%)		H ₂ O ₂ residual (%)	
	X ₁	X ₂	X ₃	Observed	Predicted	Observed	Predicted
1	50	100	8	35.99	35.86	9.43	9.28
2	350	100	8	25.99	26.42	1.87	1.95
3	50	900	8	30.21	29.79	12.6	12.55
4	350	900	8	21.01	21.14	3.16	3.31
5	50	500	4	33.66	34.02	11.5	11.43
6	350	500	4	17.46	17.26	3.71	3.44
7	50	500	12	42.56	42.76	10.1	10.34
8	350	500	12	41.78	41.43	1.73	1.77
9	200	100	4	14.28	14.06	1.12	1.31
10	200	900	4	18.60	18.67	4.70	4.82
11	200	100	12	40.87	40.80	1.23	1.11
12	200	900	12	24.61	24.84	2.43	2.24
13	200	500	8	43.96	44.52	1.22	1.65
14	200	500	8	45.10	44.52	1.51	1.65
15	200	500	8	44.59	44.52	1.84	1.65
16	200	500	8	44.94	44.52	1.84	1.65
17	200	500	8	43.99	44.52	1.84	1.65

RSM was employed for parameter estimation, indicating the relationship between the input factors and the responses, as shown in Equation (3.2). Thus, to predict the response functions for the percent TOC removal (Y_1) and the H_2O_2 residual (Y_2), the following second-order polynomial equations (Equations (4.1) and (4.2), respectively) were developed in terms of the coded factors.

$$Y_1 = 44.52 - 4.52X_1 - 2.84X_2 + 8.23X_3 + 0.20X_1X_2 + 3.85X_1X_3 - 5.14X_2X_3 - 3.47X_1^2 - 12.75X_2^2 - 7.18X_3^2 \quad (4.1)$$

$$Y_2 = 1.65 - 4.14X_1 + 1.16X_2 - 0.69X_3 - 0.48X_1X_2 - 0.14X_1X_3 - 0.59X_2X_3 + 4.75X_1^2 + 0.37X_2^2 + 0.35X_3^2 \quad (4.2)$$

Negative coefficients for the model components, X_1 , X_2 , X_2X_3 , X_1^2 , X_2^2 , and X_3^2 in Y_1 and X_1 , X_3 , X_1X_2 , X_1X_3 , and X_2X_3 in Y_2 , indicate unfavorable effects on the percent TOC removal and the H_2O_2 residual, respectively. While, positive coefficients for X_3 , X_1X_2 , and X_1X_3 in Y_1 and X_2 , X_1^2 , X_2^2 , and X_3^2 in Y_2 indicate favorable effects on the percent TOC removal and the H_2O_2 residual, respectively. Coefficients with values close to zero represent lower relative intensity. Thus, X_1X_2 do not intensely affect the TOC removal while X_1X_3 do not intensely affect H_2O_2 residual. Although this evaluation provides a rapid analysis in terms of the parametrical effect on the response variables, the ANOVA with 95% CI was also applied to evaluate the statistical significance of the developed quadratic models for the percent TOC removal and the H_2O_2 residual as shown in Tables 4.2 and 4.3, respectively.

The statistical significance of each factor coefficient, as shown in Equations (4.1) and (4.2), was determined by the Fisher's (F) exact test, comparing probability (p) values greater than F . As shown in Tables 4.2 and 4.3, the model F -values of 784.87 and 318.01 for TOC removal and H_2O_2 residual, respectively, imply the models are significant. Besides, small probability

values ($p < 0.05$) indicate significant model terms, which confirm the accuracy of the developed models to predict the response functions. On the other hand, p -values > 0.10 indicate the model terms are not significant. In this case, all model parameters are significant with the exception X_1X_2 for TOC removal and X_1X_3 for H_2O_2 residual. The goodness of fit of the model was validated by the determination coefficient (R^2) and the adjusted R^2 that ensures an adequate variation of the quadratic model to the experimental values. The values of R^2 and adjusted R^2 were found to be 0.9990 and 0.9977 for the percent TOC removal and 0.9976 and 0.9944 for the H_2O_2 residual, respectively. Thus, high R^2 and adjusted R^2 values represent a high model significance. The closer the values of R^2 and adjusted R^2 are to one, the better the model prediction is.

Table 4.2. ANOVA for results for prediction of percent TOC removal by quadratic modeling.

Source	Sum of squares	df^a	Mean square	F value ^b	p -value (Prob. $> F$) ^c	Remark
TOC _{removal} model	1968.06	9	218.67	784.87	<0.0001	Significant
X_1	163.62	1	163.62	587.29	<0.0001	Significant
X_2	64.41	1	64.41	231.19	<0.0001	Significant
X_3	541.53	1	541.53	1943.70	<0.0001	Significant
X_1X_2	0.16	1	0.16	0.57	0.4733	Not significant
X_1X_3	59.44	1	59.44	213.36	<0.0001	Significant
X_2X_3	105.88	1	105.88	380.04	<0.0001	Significant
X_1^2	50.71	1	50.71	182.02	<0.0001	Significant
X_2^2	683.99	1	683.99	2455.01	<0.0001	Significant
X_3^2	217.09	1	217.09	779.20	<0.0001	Significant
Residual	1.95	7	0.28			
Lack of Fit	0.84	3	0.28	1.00	0.4773	Not significant
Pure error	1.11	4	0.28			
Corrected total SS ^d	1970.01	16				
R^2	0.9990					
Adjusted R^2	0.9977					
Adequate Precision	75.272					

^a Degrees of freedom (df), ^b Fisher's (F) exact test value, ^c A probability value (p) < 0.05 is considered to be significant, a p -value > 0.10 is considered not significant, ^d Total sum of squares corrected for the mean.

Table 4.3 ANOVA for results for prediction of percent H₂O₂ residual by quadratic modeling.

Source	Sum of squares	df ^a	Mean square	F value ^b	p-value (Prob. > F) ^c	Remark
Model	252.47	9	28.05	318.01	<0.0001	Significant
X ₁	137.20	1	137.20	1555.36	<0.0001	Significant
X ₂	10.74	1	10.74	121.77	<0.0001	Significant
X ₃	3.84	1	3.84	43.49	0.0003	Significant
X ₁ X ₂	0.91	1	0.91	10.34	0.0147	Significant
X ₁ X ₃	0.08	1	0.08	0.95	0.3614	Not significant
X ₂ X ₃	1.42	1	1.42	16.05	0.0051	Significant
X ₁ ²	94.95	1	94.95	1076.40	<0.0001	Significant
X ₂ ²	0.59	1	0.59	6.67	0.0364	Significant
X ₃ ²	0.50	1	0.50	5.72	0.0480	Significant
Residual	0.62	7	0.09			
Lack of Fit	0.30	3	0.10	1.30	0.3900	Not significant
Pure error	0.31	4	0.08			
Corrected total SS ^d	253.09	16				
R ²	0.9976					
Adjusted R ²	0.9944					
Adequate Precision	50.132					

^a Degrees of freedom (df), ^b Fisher's (F) exact test value, ^c A probability value (p) < 0.05 is considered to be significant, a p-value > 0.10 is considered not significant, ^d Total sum of squares corrected for the mean.

Furthermore, the adequate precision of the percent TOC removal and H₂O₂ residual were found to be 75.272 (Table 4.2) and 50.132 (Table 4.3), respectively. Moreover, the lack of fit was calculated to measure how well the model fits the data. The lack of fit p-values of the percent TOC removal and the H₂O₂ residual were found to be 0.4773 (Table 4.2) and 0.3900 (Table 4.3), respectively. An insignificant lack of fit (p > 0.10) is a desirable property because it indicates that the model fits the data well.

On the other hand, the assumption of constant variance was verified by plotting the internally studentized residual versus predicted values (Figures 4.2a and 4.3a). The studentized residuals were found by dividing the residuals by their standard deviations. Figures 4.2a and 4.3a also show randomly scattered points within the outlier detection limits -3 and +3. Therefore,

model predictions, described in Equations (4.1) and (4.2), for both the percent TOC removal and the H_2O_2 residual, respectively, are satisfactory.

Moreover, the normal probability plot of residuals, shown in Figures 4.2b and 4.3b for the TOC removal and the H_2O_2 residual, respectively, showed a straight line pattern followed by the points on the plot, not an S-shaped curve. Consequently, a transformation of the response is not required because of the normal distribution of the residuals (Bustillo-Lecompte et al., 2016).

The correlation between observed and predicted values is presented in Figures 4.2c and 4.3c for the TOC removal and the H_2O_2 residual, respectively. As a result, minor discrepancies are represented by a straight-line trend, which indicates a good agreement between observed and predicted values. Hence, the quadratic model predictions for both the percent TOC removal and the H_2O_2 residual responses are satisfactory.

4.4. Individual effect of model parameters

Since the significance of the models (Tables 4.2 and 4.3) and the accuracy of the model predictions (Figures 4.2 and 4.3) were confirmed, it was required to examine the significance of each model factor. This evaluation was also performed using the F -exact test and p -values for each factor including linear, quadratic, and cross-factor interaction. As presented in Tables 4.2 and 4.3, p -values lower than 0.05 indicate the significance of the model coefficients. Therefore, all three independent variables, the initial TOC concentration (X_1), the initial H_2O_2 concentration (X_2), and the irradiation time (X_3), have significant effect on both responses, the percent TOC removal (Y_1) and the H_2O_2 residual (Y_2), based on their p -value.

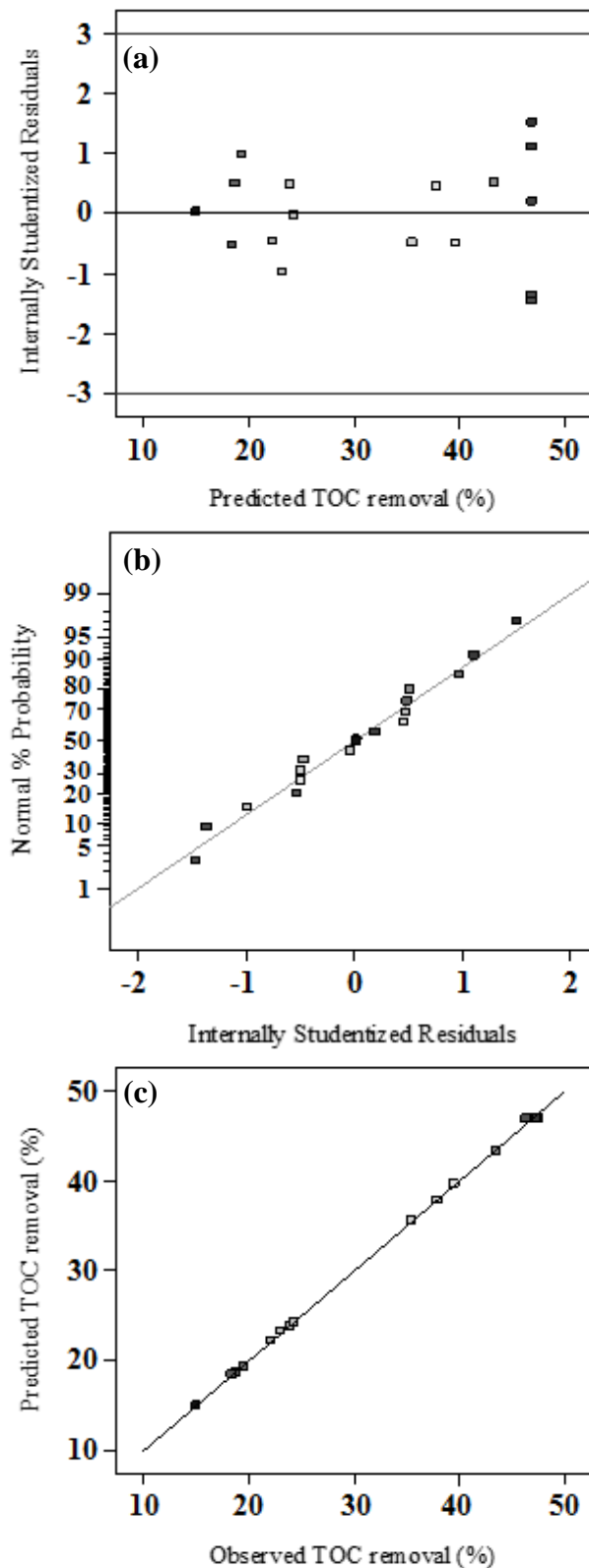


Figure 4.2. Validation of the percent TOC removal model using different plots: (a) internally studentized residuals versus predicted values, (b) normal probability, and (c) observed experimental data versus predicted values.

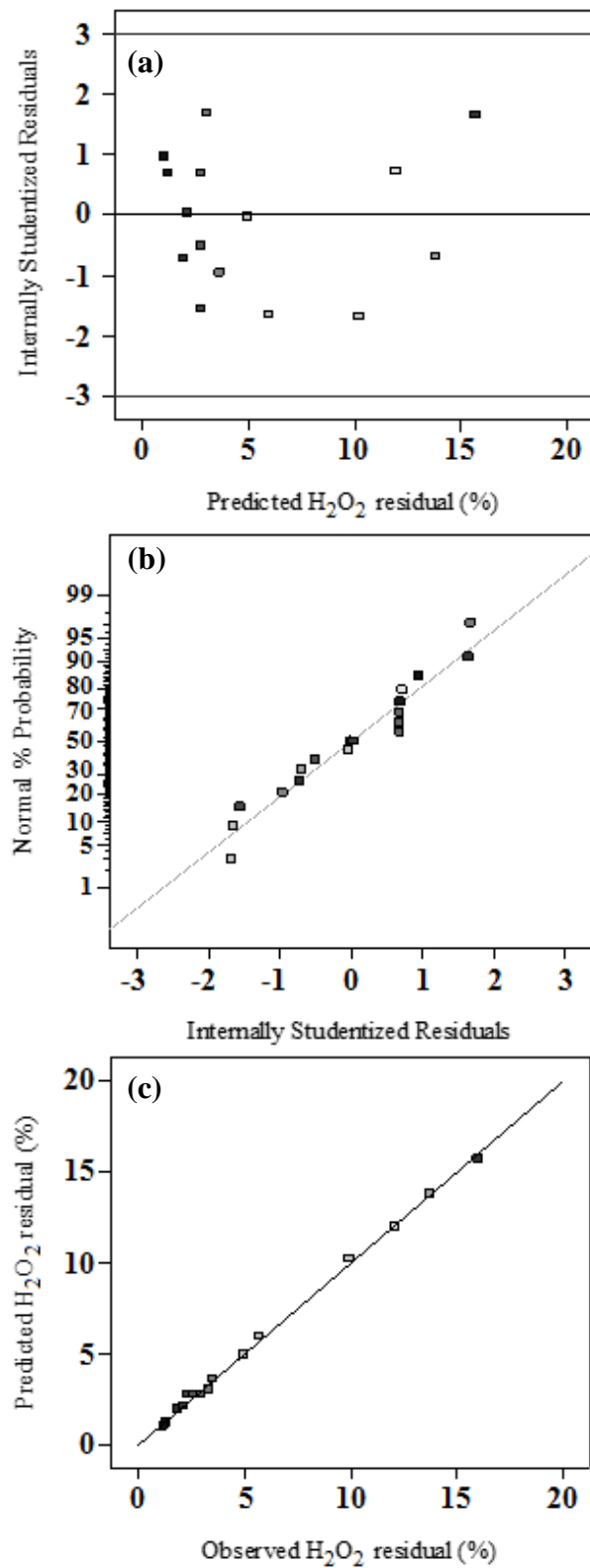


Figure 4.3. Validation of the percent H_2O_2 residual model using different plots: (a) internally studentized residuals versus predicted values, (b) normal probability, and (c) observed experimental data versus predicted values.

Figures 4.4a and 4.5a depict the effect of the initial TOC concentration (X_1) on the TOC removal (Y_1) and the H_2O_2 residual (Y_2), respectively. It can be observed that the initial TOC concentration is inversely proportional to the percent TOC removal, whereas there is an optimum initial TOC concentration at which the H_2O_2 residual is minimum. Thus, this confirms the results obtained in the preliminary experiments as illustrated in Figure 4.1a.

On the other hand, Figures 4.4b and 4.5b illustrate the effect of the initial H_2O_2 concentration (X_2) on the TOC removal (Y_1) and the H_2O_2 residual (Y_2), respectively. The predicted models show that there is an optimum H_2O_2 concentration for a maximum percent TOC removal and a direct relationship between the initial H_2O_2 concentration and the H_2O_2 residual, confirming observed values from the preliminary studies as depicted in Figure 4.1b.

Similarly, Figures 4.4c and 4.5c show the effect of the irradiation time (X_3) on the percent TOC removal (Y_1) and the H_2O_2 residual (Y_2), respectively. The predicted models confirm that the percent TOC removal is directly proportional to the irradiation time and that the H_2O_2 residual is inversely proportional to the irradiation time, as previously shown in Figure 4.1c. The results of the predicted model are in line with the values of the preliminary results, which confirms the accuracy of the predicted model for each parameter.

4.5. Interaction of model parameters, 2D contour plots, and 3D response surface

As shown in Tables 4.2 and 4.3, there was only one interaction of model parameters, between influent TOC and H_2O_2 concentrations (X_1X_2), which did not indicate a significant effect on the percent TOC removal, despite the fact that it was significant on the H_2O_2 residual simultaneously. Thus, it can be stated that individual parameters are clearly influencing the trend for the TOC removal as linear effects.

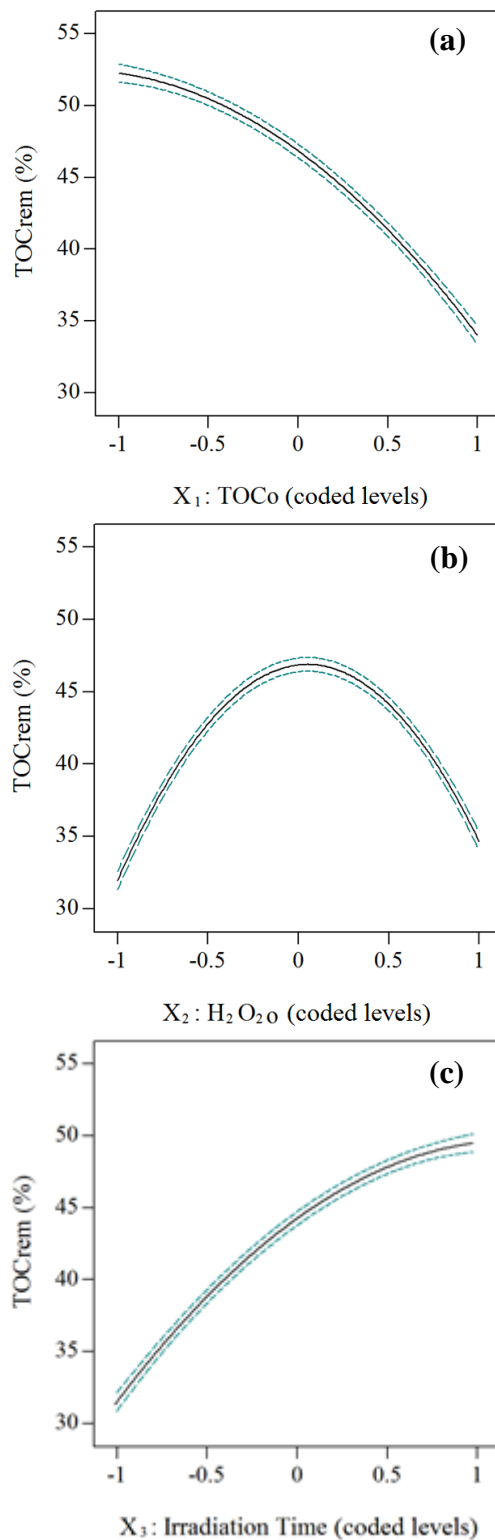


Figure 4.4. The individual effect of model parameters on the percent TOC removal: (a) initial concentration of TOC, (b) initial H_2O_2 concentration, (c) and irradiation time. The continuous lines represent model predicted values, whereas the dashed lines represent the 95% confidence interval bands.

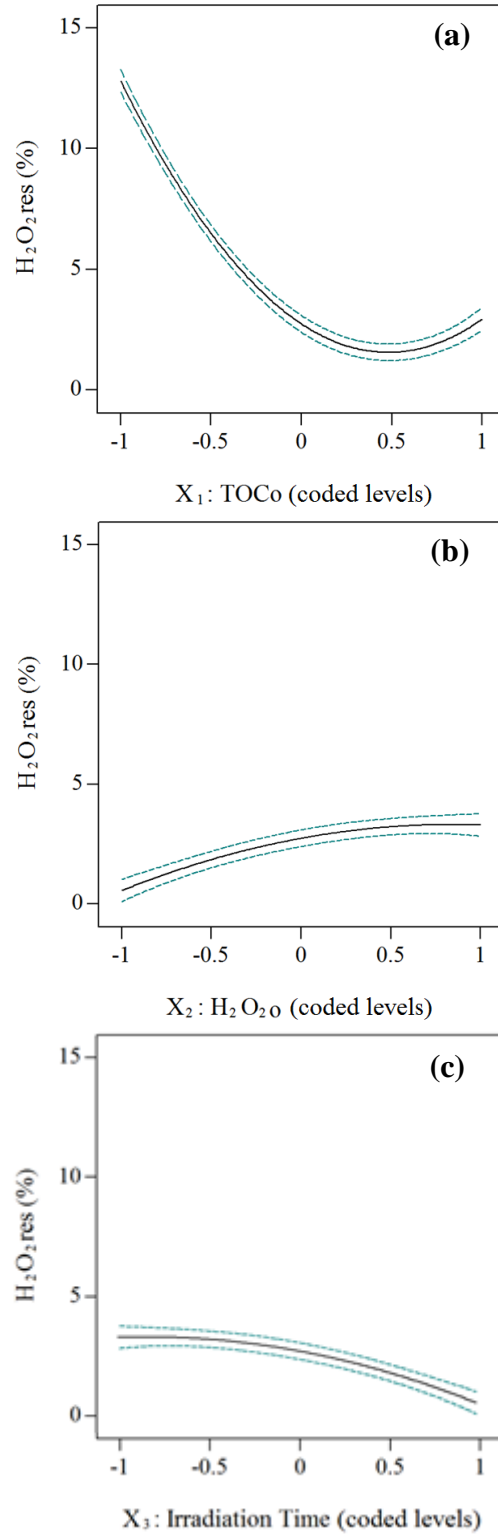


Figure 4.5. The individual effect of model parameters on the H_2O_2 residual: (a) initial concentration of TOC, (b) initial H_2O_2 concentration, (c) and irradiation time. The continuous lines represent model predicted values, whereas the dashed lines represent the 95% confidence interval bands.

The cross-factor interaction effects between independent variables were plotted on the 3D surfaces and 2D contour plots as shown in Figures 4.6 and 4.7 for the TOC removal and the H_2O_2 residual, respectively. These figures are the graphical representations of the regression analysis, where the response functions of two factors are presented while all others are at the fixed levels (Bustillo-Lecompte et al., 2016).

As shown in Figure 4.6a, the percent TOC removal decreases by increasing the initial TOC concentrations within the factor range. The effect of the initial TOC concentration on the percent TOC removal is essentially attributable to the absorption of the UV-C/VUV radiation by organic compounds along with intermediates formed during the photochemical reactions. Hence, the penetrability of the UV-C/VUV light is reduced at higher TOC concentrations. The light absorption by H_2O_2 becomes lower, causing a reduced amount of hydroxyl radicals, major contributor to the TOC reduction, which is also confirmed by the trend in Figures 4.6a and 4.7a.

Therefore, the interaction effect of the TOC concentration and the H_2O_2 (X_1X_2) defines an optimum concentration of the oxidant at a lower initial concentration of the TOC for the maximum TOC removal while generating a minimum H_2O_2 residual at a lower initial H_2O_2 concentration with an optimum initial TOC concentration. By augmenting the H_2O_2 concentration, the percent TOC removal also increases up to an optimum H_2O_2 concentration. After this point, the trend is reversed due to the excess of H_2O_2 recombination (Ghafoori et al., 2012, 2014, 2015). The surface plot of the interaction effect of the initial TOC concentration with the irradiation time (X_1X_3) on TOC removal is similar to that of X_1X_2 for the same response as confirmed by Figure 4.6b.

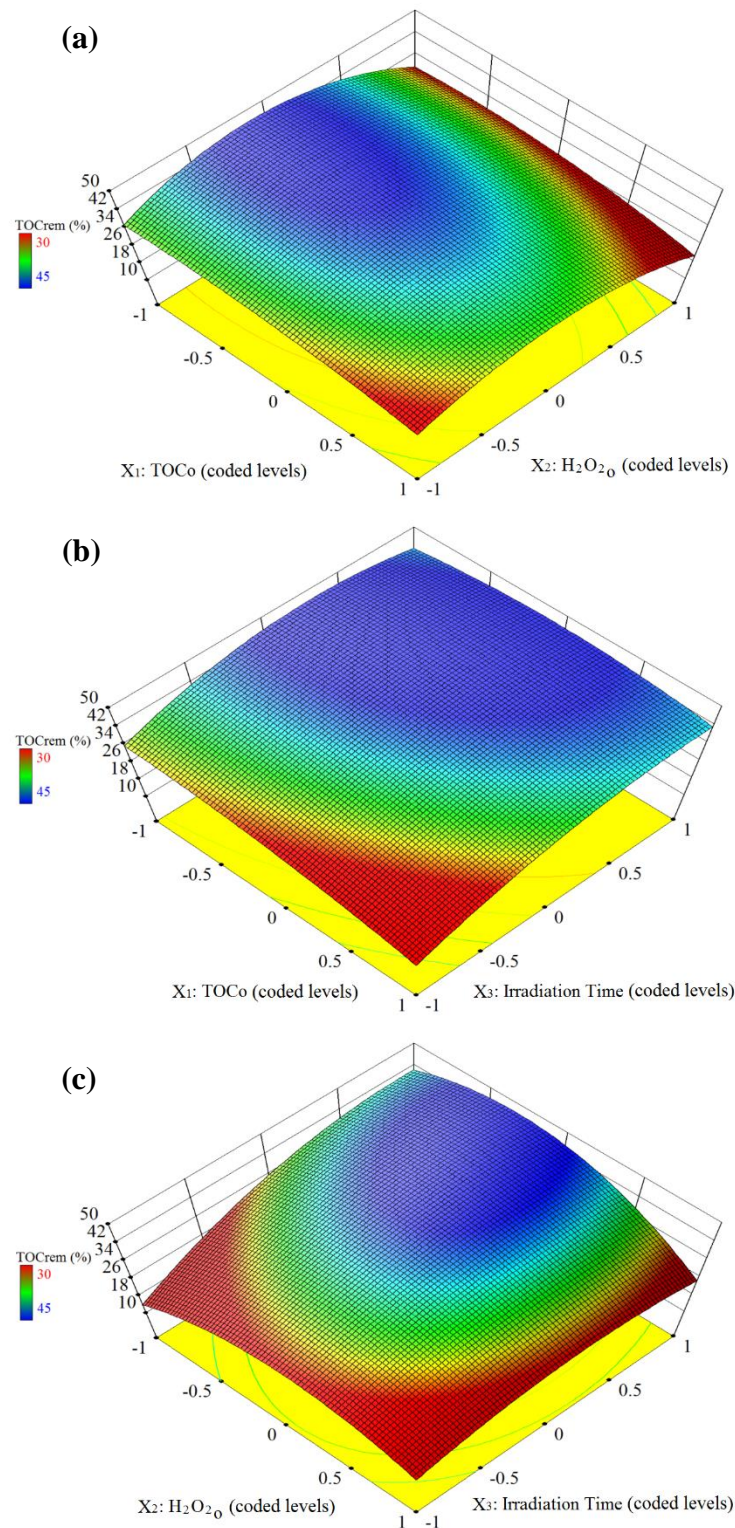


Figure 4.6. Interaction effects of different parameters on the percent TOC removal using 3D response surface and 2D contours: (a) initial concentration of TOC and H_2O_2 (X_1X_2), (b) initial concentration of TOC and irradiation time (X_1X_3), and initial concentration of H_2O_2 and irradiation time (X_2X_3).

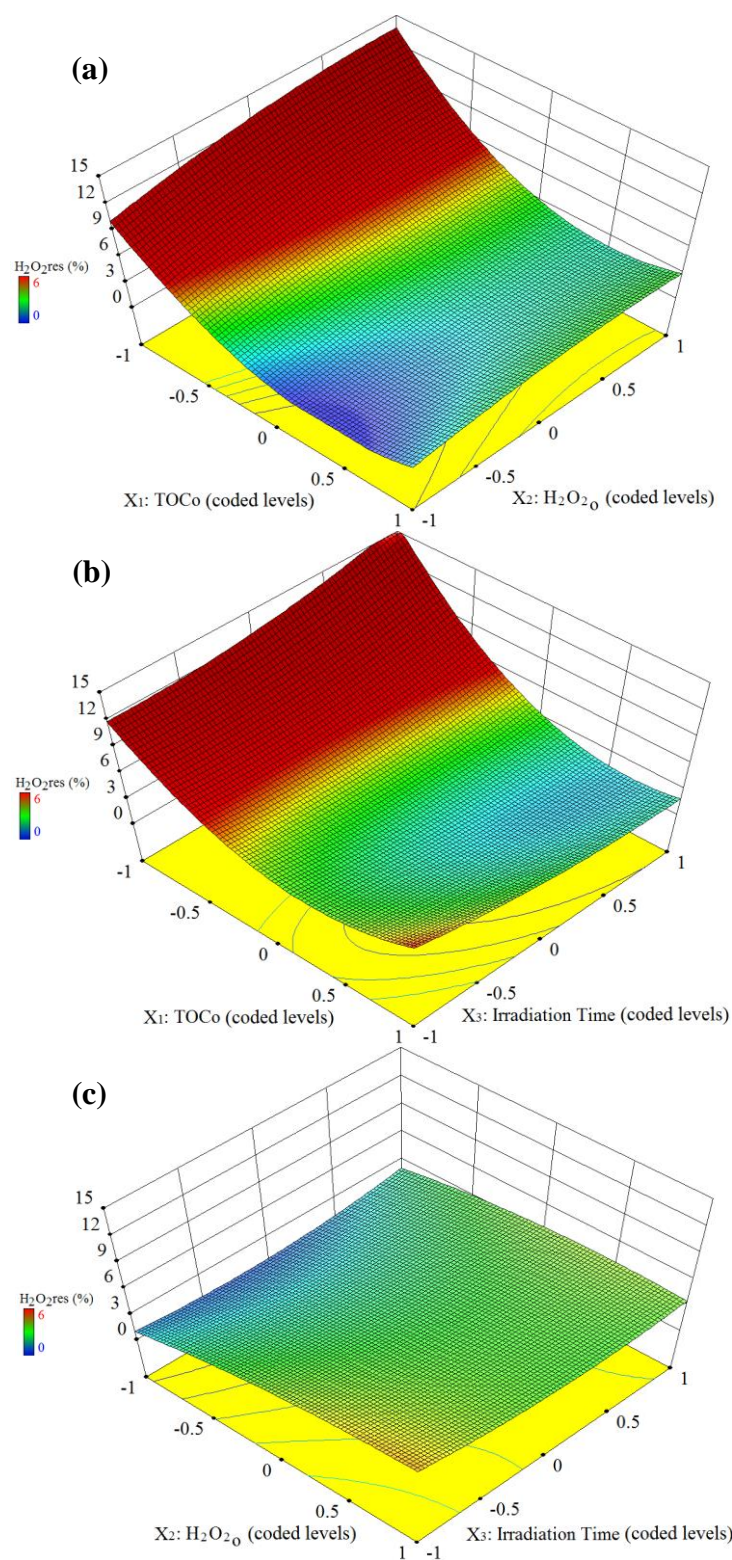
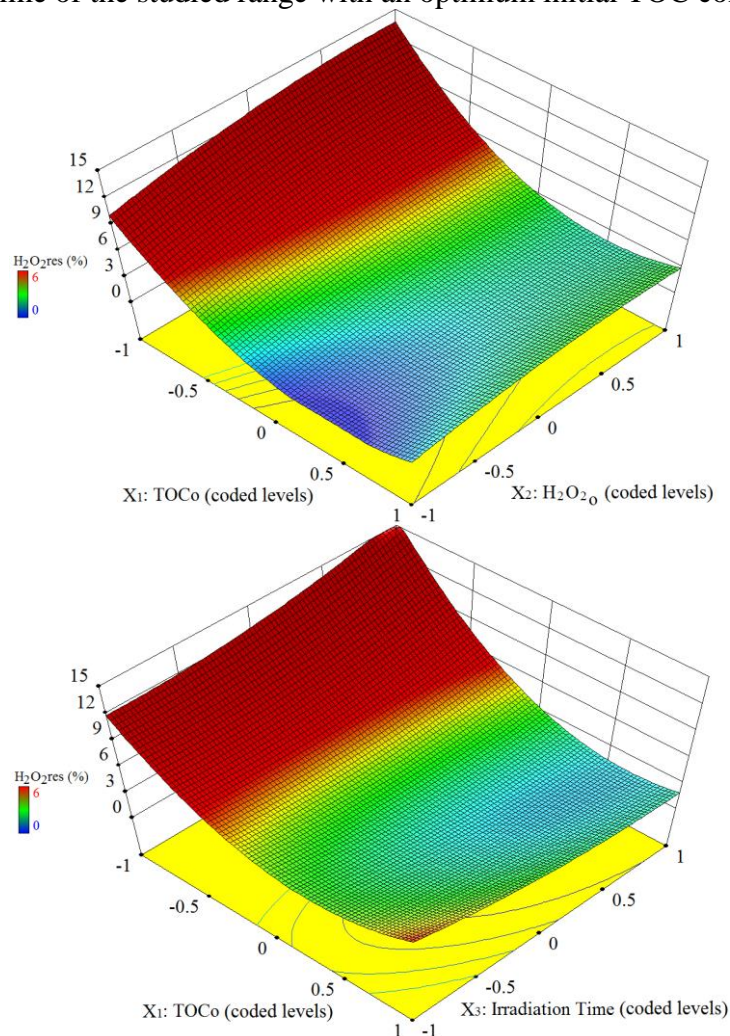


Figure 4.7. Interaction effects of different parameters on the residual H_2O_2 using 3D response surface and 2D contours: (a) initial concentration of TOC and H_2O_2 (X_1X_2), (b) initial concentration of TOC and irradiation time (X_1X_3), and initial concentration of H_2O_2 and irradiation time (X_2X_3).

The 3D plot confirms that the percent TOC removal is inversely proportional to the initial TOC concentration while there is an optimum irradiation time for the maximum TOC removal at which the effect of further irradiation is negative due to the scavenging effect of the hydroxyl radicals (Bustillo-Lecompte et al., 2016). In the case of the X_1X_3 interaction effect on the H_2O_2 residual, the minimum H_2O_2 residual is obtained at an optimum point near the maximum irradiation time of the studied range with an optimum initial TOC concentration (



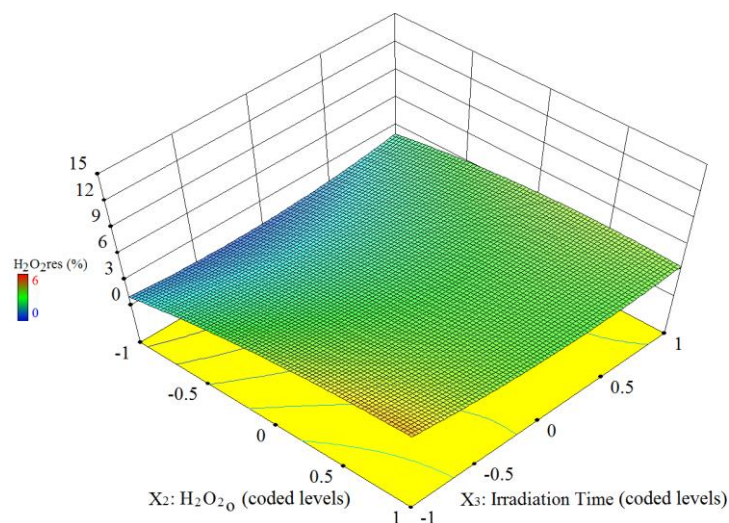
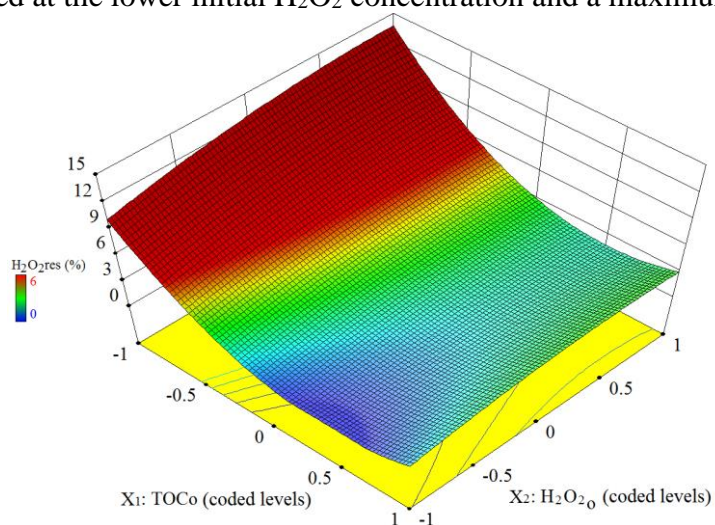


Figure 4.7b).

Lastly, the cross-factor interaction between the initial H_2O_2 concentration and the irradiation time (X_2X_3) shown in Figure 4.6c shows an optimum point at which both factors interact where an optimum initial H_2O_2 concentration with a maximum irradiation time generate the maximum removal of TOC. In the case of the X_2X_3 interaction effect on H_2O_2 residual, the minimum H_2O_2 residual is achieved at the lower initial H_2O_2 concentration and a maximum irradiation time (



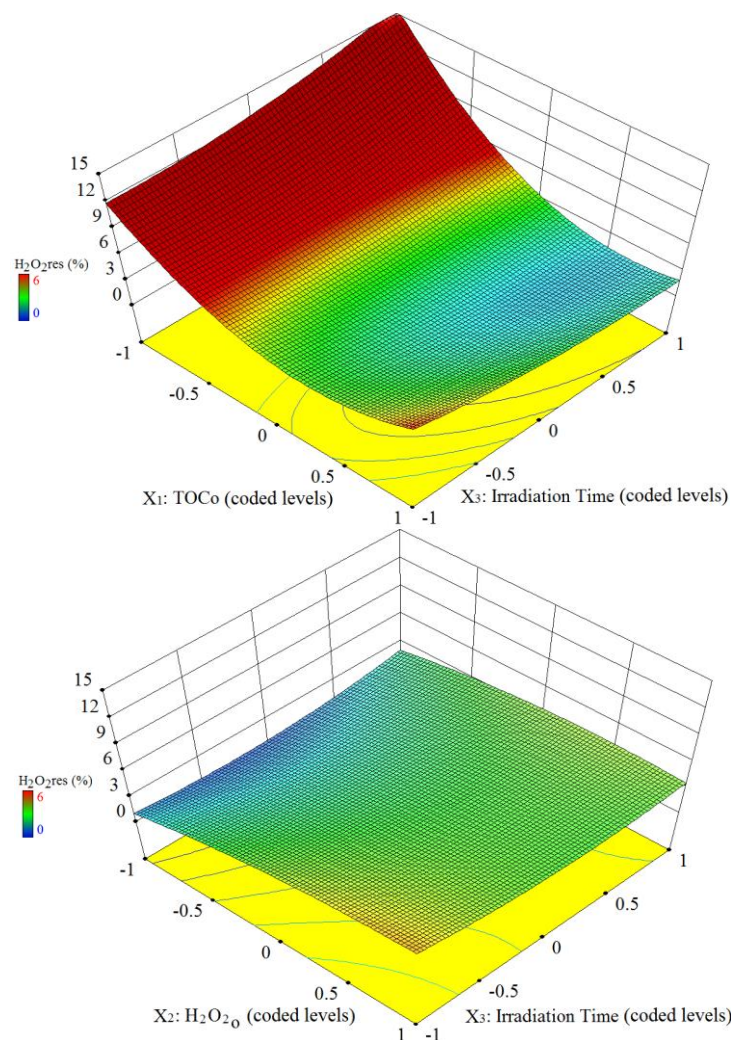


Figure 4.7c).

4.6. Optimization of operating conditions and process parameters

RSM was used to obtain the optimum experimental conditions of the three independent variables, including the initial TOC concentration (X_1), the initial H_2O_2 concentration (X_2), and the irradiation time (X_3) to obtain maximum percent TOC removal and minimum H_2O_2 residual using the numerical optimization method built into the statistical software Design-Expert 9.0.6.2.

Equations (4.1) and (4.2) were defined as objective functions for the percent TOC removal and the H_2O_2 residual, respectively, and the independent factors in their critical range

were used as constraints. The numerical optimization method explores the design space using the developed models to find the optimum factor conditions.

The multiple response approach (Equation 3.3) was used to obtain the desirability 3D response surface (Figure 4.8) by maximizing the percent removal of TOC (d_1) and minimizing the H_2O_2 residual (d_2) at optimum factor settings. Thus, the optimum conditions to achieve the maximum TOC removal of 46.19% and minimum H_2O_2 residual of 1.05% when treating actual SWW were: initial TOC concentration of 213.01 mg/L, initial H_2O_2 concentration of 450.71 mg/L, and irradiation time of 9.06 min.

The obtained optimal operating conditions were tested in another experimental run to validate the predicted values. Thus, a TOC removal of 45.68% and H_2O_2 residual of 1.03% were obtained experimentally, confirming the reliability of the model since they are both between the 95% CI of 43.98–49.82% for TOC removal and 0.16–2.13% for H_2O_2 residual. These results are promising for the application of the combined UV-C/ H_2O_2 /VUV system as a post-treatment method after biological treatment of a high strength actual SWW.

4.7. Comparison between combined UV-C/ H_2O_2 /VUV processes and individual processes

Three individual processes, VUV alone, VUV/ H_2O_2 , and UV-C/ H_2O_2 , were evaluated to compare their performance for the treatment of actual SWW using the optimum parameters obtained in combined UV-C/ H_2O_2 /VUV processes.

Figure 4.9 shows the comparison of all individual and combined processes using an initial TOC concentration of 213.01 mg/L, initial H_2O_2 concentration of 450.71 mg/L (excepting VUV alone), and irradiation time of 9.06 min. Results show that VUV alone have a maximum TOC removal of 39.93% compared to the 41.77% obtained by UV-C/ H_2O_2 alone. Therefore, by adding

the H_2O_2 as an auxiliary component to the VUV treatment is possible to increase its efficiency to 43.62%.

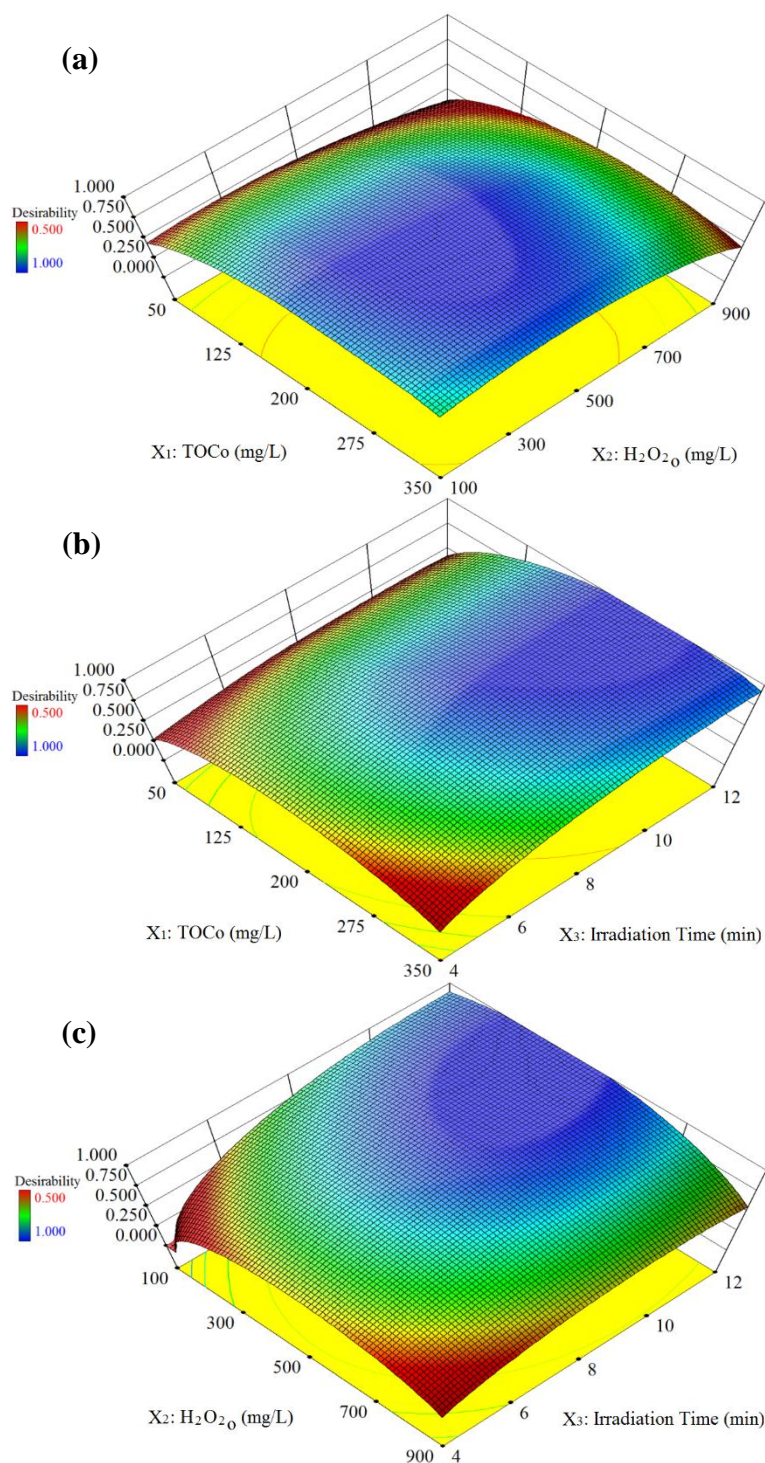


Figure 4.8. Desirability response surface, maximizing the percent removal of TOC and minimizing the H_2O_2 residual at optimum factor settings: (a) initial concentration of TOC and H_2O_2 interaction (X_1X_2) with optimum irradiation time (9.06 min), (b) initial concentration of TOC and irradiation time (X_1X_3) interaction with optimum initial H_2O_2 concentration (450.71 mg/L), and (c) initial concentration of H_2O_2 and irradiation time (X_2X_3) with optimum initial TOC concentration (213.01 mg/L).

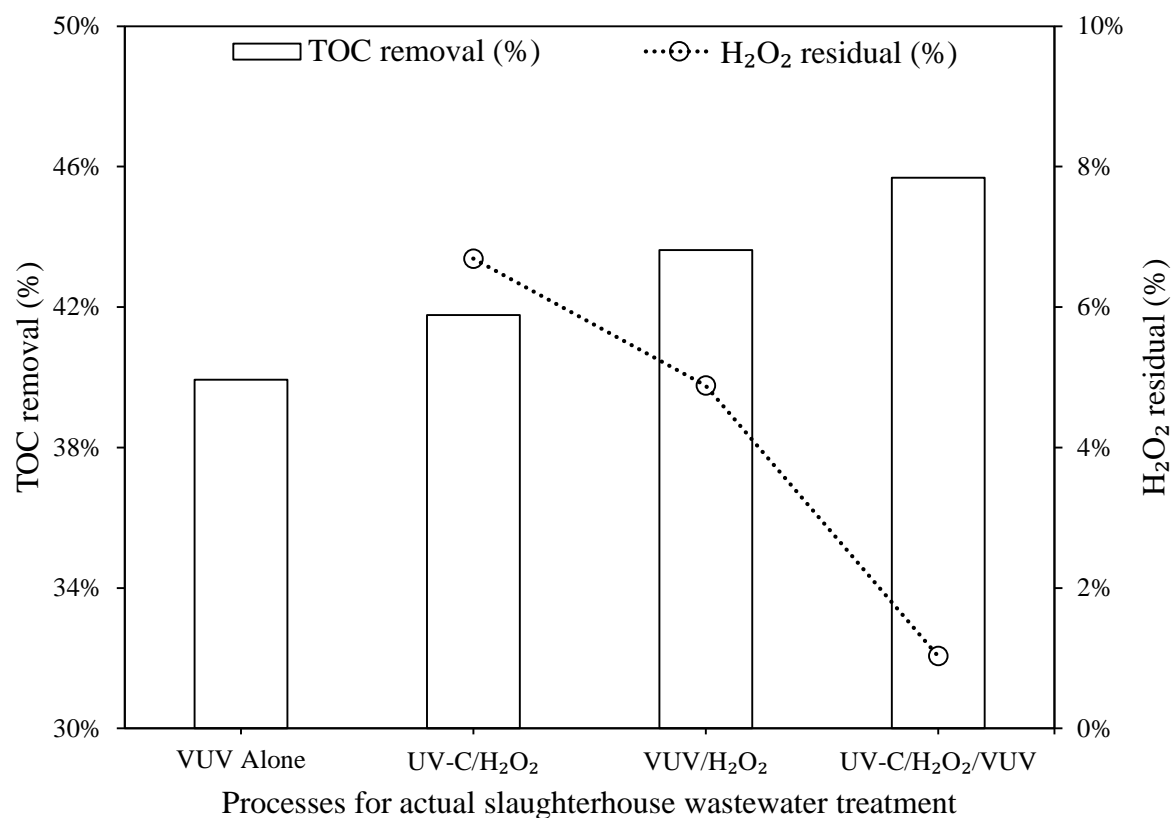


Figure 4.9. Comparison of TOC removal and H₂O₂ residual using different processes for the treatment of actual slaughterhouse wastewater, including VUV alone, VUV/H₂O₂, UV-C/H₂O₂, and combined UV-C/H₂O₂/VUV processes.

Similarly, Figure 4.9 depicts the performance of each treatment process on the H_2O_2 residual. In the UV-C/ H_2O_2 process, the H_2O_2 was measured as 6.69% while in the VUV/ H_2O_2 a 4.88% was obtained. These results confirm that an adequate combination of the UV-C/ H_2O_2 /VUV processes is essential for an optimized TOC removal and H_2O_2 residual.

4.8. Biodegradability of the actual SWW using Respirometry assays

Respirometry analyses were also performed to evaluate the biodegradability of the SWW and the BOD removal efficiency of the combined UV-C/ H_2O_2 /VUV processes. Samples of actual SWW, treated SWW by combined UV-C/ H_2O_2 /VUV process, and a black were evaluated as shown in Figure 4.10. The initial TOC concentration was set at 450 mg/L, the highest level of the initial TOC concentration used for the preliminary studies (Figure 4.1). The BOD_5 was obtained as the oxygen uptake at five days for each sample. Therefore, the BOD_5 concentration of the actual untreated SWW was found to be 493 mg/L as shown in Figure 4.10.

Then, the COD was estimated based on the TOC correlation with COD (Ford et al., 1971). Thus, an industrial effluent with 450 mgTOC/L has an equivalent of 1,400 mgCOD/L. In contrast, the BOD after ten days was found to be 688 mg/L using respirometry assays (Figure 4.10). Consequently, the BOD/COD ratio was calculated to be 0.50, which indicates that the actual SWW is considered to be biodegradable.

Figure 4.10 also illustrates the BOD_5 concentrations in the treated SWW by the combined UV-C/ H_2O_2 /VUV processes to be 189 mg/L, respectively. Thus, the BOD/COD ratio of 0.14 for the treated effluent. The SWW treated effluent becomes less biodegradable since it has already been widely degraded. Therefore, this method is recommended as post-treatment of the SWW.

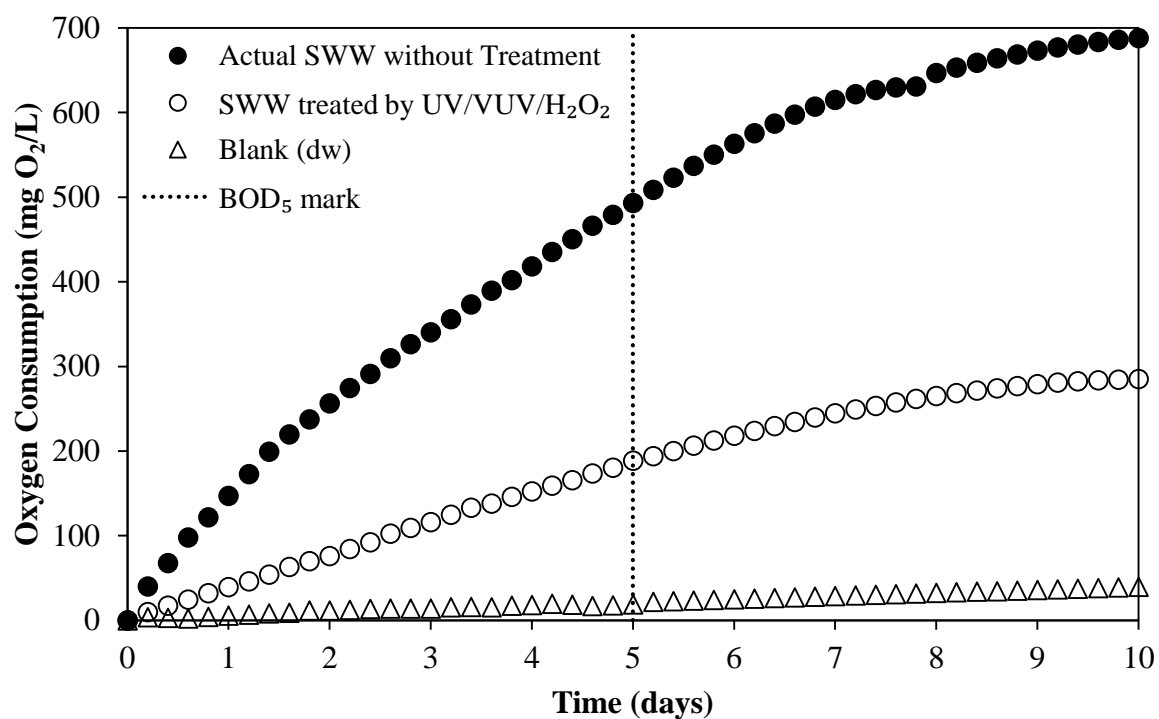


Figure 4.10. Respirometry testing results for different samples of actual SWW, treated SWW by combined UV-C/H₂O₂/VUV processes, and a blank. The initial TOC concentration is 450 mg/L. BOD₅ is obtained as the oxygen uptake at the five-day mark.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

The following conclusions are drawn from this thesis:

- A three-factor Box–Behnken statistical experiment design applied in this study was found to be an appropriate response surface methodology to determine the effects of process parameters on the response functions in the studied range, and results in the treatment of actual slaughterhouse wastewater by UV-C/H₂O₂/VUV process in a batch recirculating photoreactor were reliable. The accuracy of the developed quadratic models was evaluated using analysis of variance.
- Results demonstrated that the initial concentrations of total organic carbon, H₂O₂ and the irradiation time have considerable effect on the total organic carbon removal and the H₂O₂ residual. The interaction between process parameters are different, for instance, the initial concentrations of total organic carbon and H₂O₂ (X_1X_2) did not indicate a significant impact on the total organic carbon removal while being significant on the H₂O₂ residual. Whereas, the initial concentrations of total organic carbon and irradiation time (X_1X_3) did not indicate a significant impact on the H₂O₂ residual while being significant on the total organic carbon removal.
- A maximum total organic carbon removal of 45.68% and minimum H₂O₂ residual of less than 1.03% were found at the optimum operating conditions of 213 mg/L initial

concentration of total organic carbon, 450 mg/L initial H₂O₂ concentration, and 9 min irradiation time.

- The developed mathematical models provided a detailed exploration of the simultaneous cross-factor interactive effects of the independent variables on the responses. Thus, the proposed models explaining the photochemical treatment of actual slaughterhouse wastewater by the continuous UV-C/H₂O₂/VUV photoreactor could be used as a base for future studies on process optimization, photoreactor design, modeling, and scale-up.
- Respirometry analyzes revealed that the SWW treated effluent becomes less biodegradable (BOD/COD ratio of 0.14) since it has already been widely degraded. Therefore, this method is recommended as post-treatment of the actual SWW.
- Actual SWW samples were used in this study to evaluate the accurate performance of the combined UV-C/H₂O₂/VUV system under real conditions, which will permit further studies on kinetics modeling, scale-up, and cost-effectiveness analysis. However, due to the wide range of the actual SWW concentrations, biological treatment must be considered prior to the use of the UV-C/H₂O₂/VUV system, especially at TOC concentrations higher than 350 mg/L.
- Furthermore, primary treatment by storage, DAF, or land application, are the current technologies used in most slaughterhouses in Ontario, where only the large particles, such as solids, feathers, skin, grease, etc., are removed. Therefore, considering the integration of biological treatment and AOPs could be an on-site secondary and tertiary treatment to prevent inadequate discharge of the SWW to water bodies or groundwater, which is detrimental to the environment.

5.2. Recommendations

The following recommendations are suggested for further research on actual SWW treatment:

- Further study should be focused on continuous mode to determine the interaction of process parameters and efficiency in TOC removal and reduction of H₂O₂ residual.
- Further work should be conducted the combination of biological processes with UV/VUV/H₂O₂ as a post-treatment method for cost-effective analysis.
- Further research is suggested by using four factor and four level BBD experimental design using Initial TOC, and H₂O₂ concentrations along with irradiation time and pH considered as process parameters to evaluate a possible optimization in terms of TOC removal and H₂O₂ residual percentage.
- Further research should be also considered the examination of emerging contaminants present in actual SWW, including pharmaceutical compounds used by veterinary physicians, anti-inflammatories, cleaning products, endocrine disruptors, and possible hazardous compounds, which are being discharged without proper treatment, particularly in the livestock farming.
- Further work may be considered the additional investigation of kinetic modeling, optimization of processes, and modeling of the combined UV-C/H₂O₂/VUV processes, as well as the analysis of different intermediates that may be formed during the UV-C/H₂O₂/VUV treatment.

NOMENCLATURE

df_{Error}	degree of freedom of the residuals
df_{Model}	degrees of freedom for the model
dw	distilled water
E	Einstein unit, one mole (6.022×10^{23}) of photons, regardless of their frequency
E^o	standard electrode potential (V)
$h\nu$	quantum of radiation
k	reaction rate constant (1/M.s)
MSS_{Error}	mean sum of squares due to error (residuals)
MSS_{Model}	mean sum of squares due to the model
N	number of independent variables
p	probability value
q_0	incident photon irradiance (E/cm ² .s)
r	nominal radius of the photoreactor (cm)
R^2	coefficient of determination
R^2_{adj}	adjusted coefficient of determination
R_i	inner radius of the photoreactor (cm)
SS_{Error}	sum of squares of the residuals
SS_{Model}	sum of squares of the model
SS_{Total}	total sum of squares
TOC ₀	initial concentration of total organic carbon (mg/L)
V	volume of the sample or reactor (L)

X_i	independent variable i
X_j	independent variable j
y	response
Y_i	predicted response

Greek Letters

α	significance level
α_λ	absorption coefficient (1/cm)
β_o	constant coefficient of the statistical model
β_i	linear coefficients of the statistical model
β_{ii}	quadratic coefficients of the statistical model
β_{ij}	interaction coefficients of the statistical model
ε_λ	molar absorption coefficient of TOC (1/M.cm)
ϕ	quantum yield for TOC removal (mol/E)

Acronyms

2D	two-dimensional
3D	three-dimensional
AOPs	advanced oxidation processes
BBD	Box-Behnken Design
BOCs	biodegradable organic compounds
BOD	biochemical oxygen demand
BOD ₅	5-day biochemical oxygen demand
CEC	Council of the European Communities
COD	chemical oxygen demand
DBPs	disinfection by-products

DO	dissolved oxygen
DOE	design of experiment
ECO	Environmental Commissioner of Ontario
EEA	European Environment Agency
EOP	electrical oxidation potential
KHP	Potassium hydrogen phthalate
LAS	linear alkyl benzene sulfonate
MPP	meat and poultry processing plants
PCP	personal care products
SWW	slaughterhouse wastewater
TN	total nitrogen
TOC	total organic carbon
TSS	total suspended solids
US EPA	United States Environmental Protection Agency
UV	ultraviolet light
UV-C	ultraviolet light of short wave or germicidal; range from 280 nm to 100 nm
VUV	vacuum ultraviolet light; range from 200 nm to 100 nm

APPENDICES

Appendix A. Sample standard deviation

Each experiment in the present work was replicated three times, and the reported results represent the average value of the collected results. Error bars depicted in the figures represent the sample standard deviation (SD), which was used to analyze the accuracy of an experimental measurement for a finite set of experimental data. The SD was calculated as follows.

$$SD = \sqrt{\frac{1}{N-1} \sum_{i=1}^n (\chi_i - \bar{\chi})^2} \quad (\text{A.1})$$

where,

χ_i = observed values of the sample items ($\chi_1, \chi_2, \dots, \chi_n$);

$\bar{\chi}$ = mean value of the sample observations; and

N = sample size.

Appendix B. Relative error analysis

Relative error was used to express an accuracy of an acceptable value of the quantity being measured. The relative error could be positive, negative or zero indicating that the measured value is smaller than, greater than, or equal to the mean of a set of data. The lowest average absolute error was used as a criterion for the optimization of the total electricity costs and reaction time. The relative error can be obtained by Equation (D.2) as shown below.

$$\text{Relative error} = \frac{\bar{\chi} - \chi}{\chi} \cdot 100\% \quad (\text{A.2})$$

where,

χ = accepted value; and

$\bar{\chi}$ = mean of a finite set of data.

The non-linear least square function was used to determine the best-fit criterion, which involves two sets of data are the closest to each other as expressed in Equation (D.3).

$$Z = \sum_{i=1}^n \left[\left(\frac{S_f}{S_0} \right)_{i, \text{experiments}} - \left(\frac{S_f}{S_0} \right)_{i, \text{prediction}} \right]^2 \quad (\text{D.3})$$

Appendix C. Relationship between oxygen and carbon parameters.

(Adopted from Ford et al., 1971)

TABLE II.—Industrial Waste Oxygen Demand and Organic Carbon

Type of Waste	BOD ₅ (mg/l)	COD (mg/l)	TOC (mg/l)	BOD : TOC	COD : TOC
Chemical*	—	4,260	640	—	6.65
Chemical*	—	2,440	370	—	6.60
Chemical*	—	2,690	420	—	6.40
Chemical	—	576	122	—	4.72
Chemical	24,000	41,300	9,500	2.53	4.35
Chemical-refinery	—	580	160	—	3.62
Petrochemical	—	3,340	900	—	3.32
Chemical	850	1,900	580	1.47	3.28
Chemical	700	1,400	450	1.55	3.12
Chemical	8,000	17,500	5,800	1.38	3.02
Chemical	60,700	78,000	26,000	2.34	3.00
Chemical	62,000	143,000	48,140	1.28	2.96
Chemical	—	165,000	58,000	—	2.84
Chemical	9,700	15,000	5,500	1.76	2.72
Nylon polymer	—	23,400	8,800	—	2.70
Petrochemical	—	—	—	—	2.70
Nylon polymer	—	112,600	44,000	—	2.50
Olefin processing	—	321	133	—	2.40
Butadiene processing	—	359	156	—	2.30
Chemical	—	350,000	160,000	—	2.19
Synthetic rubber	—	192	110	—	1.75

* High concentration of sulfides and thiosulfates.

erally range from 0.1 to 0.6 with the COD:TOD ratios ranging from 0.5 to 0.9.

The relative yields of each of the aforementioned parameters (percent of theoretical oxygen demand or carbon concentration) are graphically illustrated in Figure 1.

Recent studies have provided BOD, COD, and TOC data for chemical and

refinery process wastewaters discharged from various plants. These analyses were performed daily for a period of several months. The mean values of the array of organic parameters for each industry are plotted in Figures 2, 3, and 4 and suggest a general correlation within the concentration limits as shown. Then, in order to obtain a more comprehensive pic-

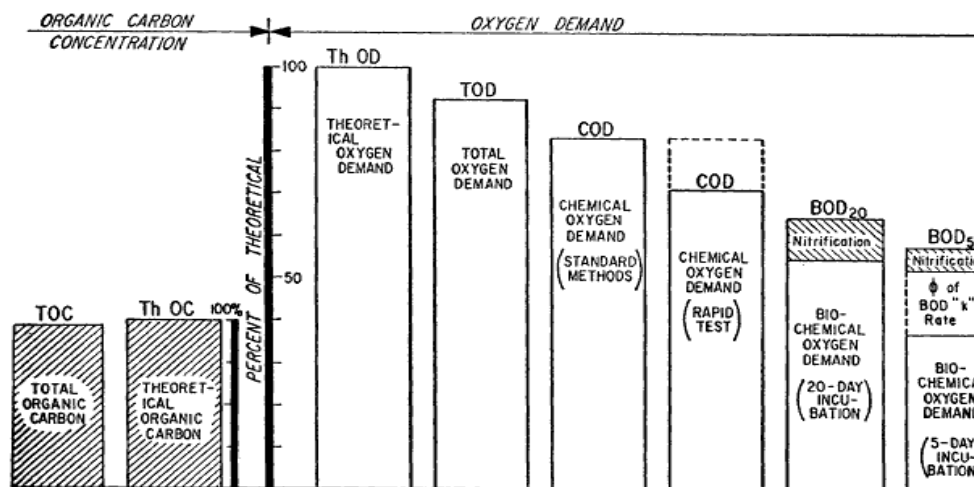


FIGURE 1.—Relationship between oxygen and carbon parameters.

Appendix D. Raw data

Table D.1. Experimental runs for the Box-Behnken Design of Experiments. Every run was repeated in triplicates.

DATE	RUN #	TOC (mg/L)	H2O2 (mg/L)	IRR.TIME (minr)	FLOW (mL/min)
30-Dec-15	1	50	100	8min	115
SAMPLE		RESULTS		MEAN	
	1	86.57			
SWW0	2	85.41		100.00	
	3	84.51			
	1	83.26			
SWW30	2	82.73		82.87	
	3	82.61			
	1	82.39			
SWW60	2	81.57		81.79	
	3	81.42			
	1	71.26			
SWW90	2	67.62		67.96	
	3	64.99			
	1	63.76			
SWW120	2	61.43		62.12	
	3	61.17			
	1				
SWW150	2			0.00	
	3				
H2O2 residual (mg/L)		9.93			

DATE	RUN #	TOC (mg/L)	H2O2 (mg/L)	IRR.TIME (minr)	FLOW (mL/min)
14-Dec-15	2	350	100	8min	115
SAMPLE		RESULTS		MEAN	
	1	312.94			
SWW0	2	297.28		350.00	
	3	294.86			
	1	286.32			
SWW30	2	282.19		278.83	
	3	267.99			
	1	253.9			
SWW60	2	250.9		251.70	
	3	250.3			
	1	246.04			
SWW90	2	244.2		244.33	
	3	242.74			
	1	235.32			
SWW120	2	232.79		232.02	
	3	227.96			
	1	226.19			
SWW150	2	223.27		211.69	
	3 *	185.62			
H2O2 Residual (mg/L)		13.69			

DATE	RUN #	TOC (mg/L)	H2O2 (mg/L)	IRR.TIME (minr)	FLOW (mL/min)
30-Dec-15	3	50	900	8min	115
SAMPLE		RESULTS		MEAN	
	1	69.00			
SWW0	2	68.68		68.18	
	3	66.87			
	1	65.95			
SWW30	2	65.15		65.32	
	3	64.86			
	1	64.83			
SWW60	2	63.86		63.64	
	3	62.23			
	1	61.99			
SWW90	2	60.70		60.75	
	3	59.56			
	1	57.22			
SWW120	2	50.87		52.64	
	3	49.83			
	1				
SWW150	2			0.00	
	3				
H2O2 residual (mg/L)		11.65			

DATE	RUN #	TOC (mg/L)	H2O2 (mg/L)	IRR.TIME (minr)	FLOW (mL/min)
18-Dec-15	4	350	900	8min	115
SAMPLE		RESULTS		MEAN	
	1	404.56			
SWW0	2	397.47		392.68	
	3	376.01			
	1	366.85			
SWW30	2	361.07		362.43	
	3	359.36			
	1	351.76			
SWW60	2	346.45		345.32	
	3	337.74			
	1	333.67			
SWW90	2	333.00		331.13	
	3	326.73			
	1	313.96			
SWW120	2	304.56		305.82	
	3	298.94			
	1				
SWW150	2			0.00	
	3				
H2O2 residual (mg/L)		29.96			

DATE	RUN #	TOC (mg/L)	H2O2 (mg/L)	IRR.TIME (minr)	FLOW (mL/min)
30-Dec-15	5	50	500	4min	230
SAMPLE		RESULTS		MEAN	
	1	61.17			
SWW0	2	60.32		60.36	
	3	59.58			
	1	59.45			
SWW30	2	58.96		58.86	
	3	58.17			
	1	57.86			
SWW60	2	56.77		56.89	
	3	56.05			
	1	55.73			
SWW90	2	53.92		51.29	
	3	44.22			
	1				
SWW120	2			0.00	
	3				
	1				
SWW150	2			0.00	
	3				
H2O2 residual (mg/L)		24.01			

DATE	RUN #	TOC (mg/L)	H2O2 (mg/L)	IRR.TIME (minr)	FLOW (mL/min)
19-Dec-15	6	350	500	4min	230
SAMPLE		RESULTS		MEAN	
	1	309.66			
SWW0	2	308.36		350.00	
	3	306.44			
	1	301.19			
SWW30	2	295.52		296.82	
	3	293.75			
	1	288.66			
SWW60	2	287.26		287.20	
	3	285.67			
	1	280.19			
SWW90	2	279.46		278.99	
	3	277.31			
	1	274.94			
SWW120	2	274.12		274.19	
	3	273.50			
	1	272.38			
SWW150	2	271.54		267.47	
	3	258.49			
H2O2 residual (mg/L)		24.71			

DATE	RUN #	TOC (mg/L)	H2O2 (mg/L)	IRR.TIME (minr)	FLOW (mL/min)
30-Dec-15	7	50	500	12min	75
SAMPLE		RESULTS		MEAN	
	1	61.05			
SWW0	2	58.29		58.64	
	3	56.59			
	1	56.50			
SWW30	2	56.33		56.24	
	3	55.89			
	1	54.18			
SWW60	2	53.55		53.57	
	3	52.97			
	1	52.94			
SWW90	2	52.30		52.01	
	3	50.78			
	1				
SWW120	2			0.00	
	3				
	1				
SWW150	2			0.00	
	3				
H2O2 residual (mg/L)		15.47			

DATE	RUN #	TOC (mg/L)	H2O2 (mg/L)	IRR.TIME (minr)	FLOW (mL/min)
17-Dec-15	8	350	500	12min	75
SAMPLE		RESULTS		MEAN	
	1	385.69			
SWW0	2	376.83		369.61	
	3	346.30			
	1	320.59			
SWW30	2	313.56		314.50	
	3	309.35			
	1	307.05			
SWW60	2	298.19		299.90	
	3	294.46			
	1	291.96			
SWW90	2	288.88		289.38	
	3	287.30			
	1	286.07			
SWW120	2	285.97		284.83	
	3	282.46			
	1	282.02			
SWW150	2	281.97		279.86	
	3	275.60			
H2O2 residual (mg/L)		17.34			

DATE	RUN #	TOC (mg/L)	H2O2 (mg/L)	IRR.TIME (minr)	FLOW (mL/min)
16-Dec-15	9	200	100	4min	230
SAMPLE		RESULTS		MEAN	
	1	164.06			
SWW0	2	163.78		200.00	
	3	152.90			
	1	152.16			
SWW30	2	151.20		151.46	
	3	151.02			
	1	148.72			
SWW60	2	148.46		148.02	
	3	146.89			
	1	145.00			
SWW90	2	144.88		144.78	
	3	144.45			
	1	143.02			
SWW120	2	142.13		141.74	
	3	140.06			
	1	139.06			
SWW150	2	138.78		129.15	
	3	109.62			
H2O2 residual (mg/L)		12.37			

DATE	RUN #	TOC (mg/L)	H2O2 (mg/L)	IRR.TIME (minr)	FLOW (mL/min)
21-Dec-15	10	200	900	4min	230
SAMPLE		RESULTS		MEAN	
	1	224.47			
SWW0	2	224.15		221.30	
	3	215.29			
	1	214.78			
SWW30	2	213.43		212.35	
	3	208.84			
	1	208.38			
SWW60	2	204.54		204.97	
	3	201.98			
	1	199.82			
SWW90	2	199.76		198.52	
	3	195.99			
	1	193.69			
SWW120	2	188.85		189.48	
	3	185.89			
	1				
SWW150	2			0.00	
	3				
H2O2 residual (mg/L)		24.03			

DATE	RUN #	TOC (mg/L)	H2O2 (mg/L)	IRR.TIME (minr)	FLOW (mL/min)
21-Dec-15	11	200	100	12min	75
SAMPLE		RESULTS		MEAN	
	1	131.72			
SWW0	2	124.14		200.00	
	3	123.13			
	1	121.03			
SWW30	2	120.54		119.20	
	3	116.03			
	1	115.82			
SWW60	2	114.43		114.77	
	3	114.07			
	1	109.99			
SWW90	2	108.45		108.76	
	3	107.84			
	1	107.69			
SWW120	2	104.28		105.01	
	3	103.05			
	1	94.34			
SWW150	2	94.05		93.12	
	3	90.96			
H2O2 residual (mg/L)		15.97			

DATE	RUN #	TOC (mg/L)	H2O2 (mg/L)	IRR.TIME (minr)	FLOW (mL/min)
29-Dec-15	12	200	900	12min	75
SAMPLE		RESULTS		MEAN	
	1	169.40			
SWW0	2	167.59		200.00	
	3	164.62			
	1	164.40			
SWW30	2	163.24		163.24	
	3	162.08			
	1	161.14			
SWW60	2	159.89		160.08	
	3	159.20			
	1	157.51			
SWW90	2	156.61		156.44	
	3	155.20			
	1	154.28			
SWW120	2	154.04		152.05	
	3	147.84			
	1				
SWW150	2			0.00	
	3				
H2O2 residual (mg/L)		16.32			

DATE	RUN #	TOC (mg/L)	H2O2 (mg/L)	IRR.TIME (minr)	FLOW (mL/min)
28-Dec-15	13	200	500	8min	115
SAMPLE		RESULTS		MEAN	
	1	150.24			
SWW0	2	148.44		200.00	
	3	146.84			
	1	144.38			
SWW30	2	141.67		142.06	
	3	140.12			
	1	138.66			
SWW60	2	130.45		131.88	
	3	126.53			
	1	123.88			
SWW90	2	122.75		122.10	
	3	119.68			
	1	115.82			
SWW120	2	115.61		115.47	
	3	114.98			
	1				
SWW150	2			0.00	
	3				
H2O2 residual (mg/L)		11.38			

DATE	RUN #	TOC (mg/L)	H2O2 (mg/L)	IRR.TIME (minr)	FLOW (mL/min)
29-Dec-15	14	200	500	8min	115
SAMPLE		RESULTS		MEAN	
	1	176.20			
SWW0	2	175.31		200.00	
	3	172.37			
	1	171.29			
SWW30	2	162.56		164.54	
	3	159.78			
	1	156.06			
SWW60	2	155.35		154.54	
	3	152.20			
	1	151.59			
SWW90	2	149.98		148.83	
	3	144.91			
	1	133.58			
SWW120	2	127.10		126.61	
	3	119.14			
	1				
SWW150	2			0.00	
	3				
H2O2 residual (mg/L)		17.94			

DATE	RUN #	TOC (mg/L)	H2O2 (mg/L)	IRR.TIME (minr)	FLOW (mL/min)
05-Jan-2016	15	200	500	8min	115
SAMPLE		RESULTS		MEAN	
	1	86.57			
SWW0	2	85.41		200.00	
	3	84.51			
	1	83.26			
SWW30	2	82.73		82.87	
	3	82.61			
	1	82.39			
SWW60	2	81.57		81.79	
	3	81.42			
	1	71.26			
SWW90	2	67.62		67.96	
	3	64.99			
	1	63.76			
SWW120	2	61.43		62.12	
	3	61.17			
	1				
SWW150	2			0.00	
	3				
H2O2 residual (mg/L)		14.66			

DATE	RUN #	TOC (mg/L)	H2O2 (mg/L)	IRR.TIME (minr)	FLOW (mL/min)
06-Jan-2016	16	200	500	8min	115
SAMPLE		RESULTS		MEAN	
	1	137.67			
SWW0	2	136.39		200.00	
	3	134.57			
	1	132.98			
SWW30	2	128.99		129.82	
	3	127.50			
	1	125.70			
SWW60	2	122.46		122.74	
	3	120.05			
	1	115.58			
SWW90	2	113.45		112.96	
	3	109.86			
	1	104.39			
SWW120	2	101.38		101.40	
	3	98.43			
	1				
SWW150	2			0.00	
	3				
H2O2 residual (mg/L)		14.66			

DATE	RUN #	TOC (mg/L)	H2O2 (mg/L)	IRR.TIME (minr)	FLOW (mL/min)
07-Jan-2016	17	200	500	8min	115
SAMPLE		RESULTS		MEAN	
	1	137.67			
SWW0	2	136.39		200.00	
	3	134.57			
	1	132.98			
SWW30	2	128.99		129.82	
	3	127.50			
	1	125.70			
SWW60	2	122.46		122.74	
	3	120.05			
	1	115.58			
SWW90	2	113.45		112.96	
	3	109.86			
	1	104.39			
SWW120	2	101.38		101.40	
	3	98.43			
	1				
SWW150	2			0.00	
	3				
H2O2 residual (mg/L)		14.66			

Table D.2. Experimental run tabulation for the Box-Behnken Design of Experiments. Mean and residual values for the TOC removal response.

Run	Mean TOCo (mg/L)	Mean Observed TOC removal (%)	Residuals	Mean TOCrem between blocks
1	50	37.88	-1.19	39.07
3	50	39.52	0.45	
5	50	35.43	-3.64	
7	50	43.44	4.37	
9	200	15.03	-19.86	34.89
10	200	19.58	-15.31	
11	200	22.82	-12.07	
12	200	24.29	-10.60	
13	200	46.27	11.38	
14	200	45.43	10.54	
15	200	46.94	12.05	
16	200	47.31	12.42	
17	200	46.31	11.42	
2	350	18.80	-2.02	20.82
4	350	22.12	1.30	
6	350	18.38	-2.44	
8	350	23.98	3.16	
Run	Mean H ₂ O ₂ O (mg/L)	Mean Observed TOC removal (%)	Residuals	Mean TOCrem between blocks
1	100	37.88	14.25	23.63
2	100	18.80	-4.83	
9	100	15.03	-8.60	
11	100	22.82	-0.81	
5	500	35.43	-3.85	39.28
6	500	18.38	-20.90	
7	500	43.44	4.16	
8	500	23.98	-15.30	
13	500	46.27	6.99	
14	500	45.43	6.15	
15	500	46.94	7.66	
16	500	47.31	8.03	
17	500	46.31	7.03	
3	900	39.52	13.14	26.38
4	900	22.12	-4.26	
10	900	19.58	-6.80	
12	900	24.29	-2.09	

Run	Mean Irradiation Time (min)	Mean Observed TOC removal (%)	Residuals	Mean TOCrem between blocks
5	4.0	35.43	13.33	22.11
6	4.0	18.38	-3.73	
9	4.0	15.03	-7.08	
10	4.0	19.58	-2.53	
1	8.0	37.88	-1.07	38.95
2	8.0	18.80	-20.15	
3	8.0	39.52	0.57	
4	8.0	22.12	-16.83	
13	8.0	46.27	7.32	
14	8.0	45.43	6.48	
15	8.0	46.94	7.99	
16	8.0	47.31	8.36	
17	8.0	46.31	7.36	
7	12.0	43.44	14.81	28.63
8	12.0	23.98	-4.65	
11	12.0	22.82	-5.81	
12	12.0	24.29	-4.34	

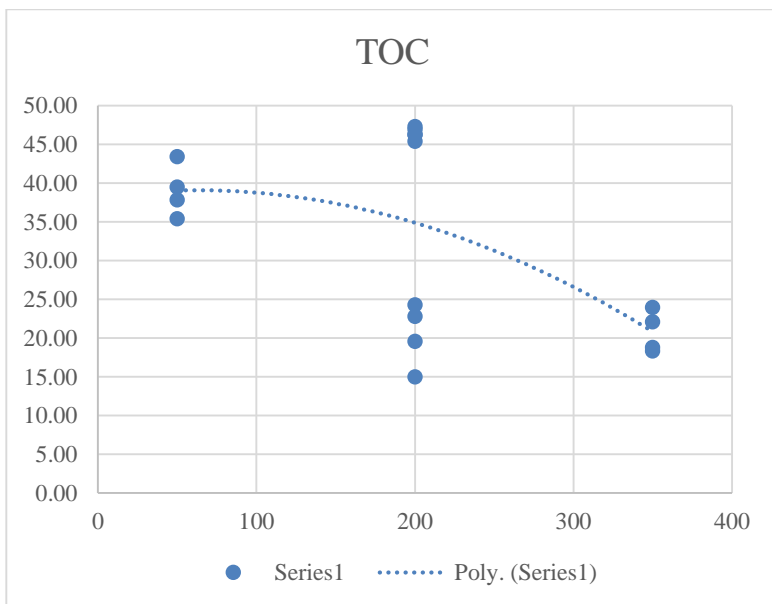


Figure D.1. TOC removal profile in a laboratory-scale batch recirculation UV-C/H₂O₂/VUV photoreactor for actual SWW treatment at different initial concentrations of TOC.

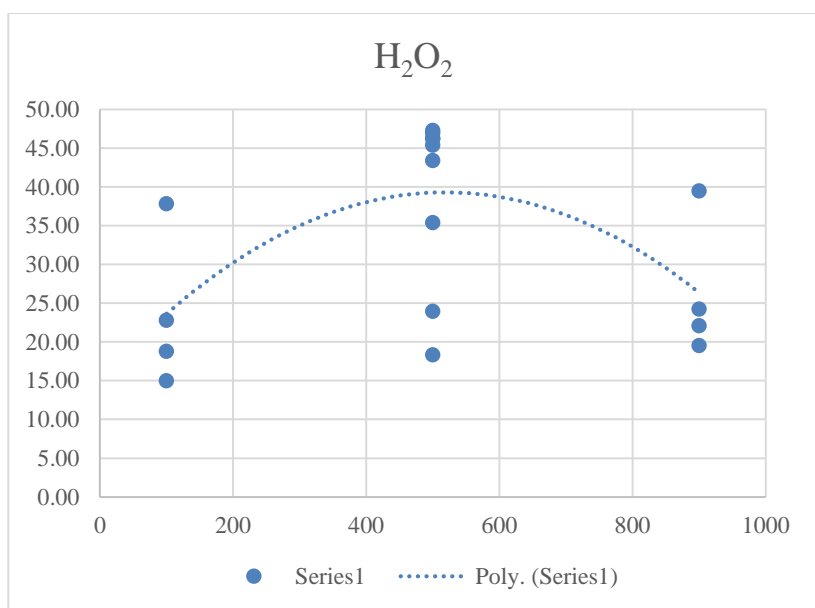


Figure D.2. TOC removal profile in a laboratory-scale batch recirculation UV-C/H₂O₂/VUV photoreactor for actual SWW treatment at different initial H₂O₂ concentrations.

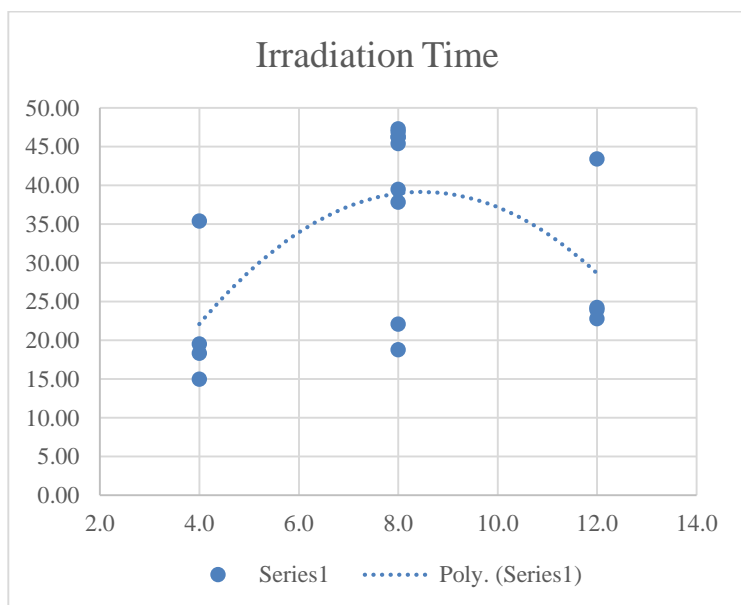


Figure D.3. TOC removal profile in a laboratory-scale batch recirculation UV-C/H₂O₂/VUV photoreactor for actual SWW treatment at different irradiation times.

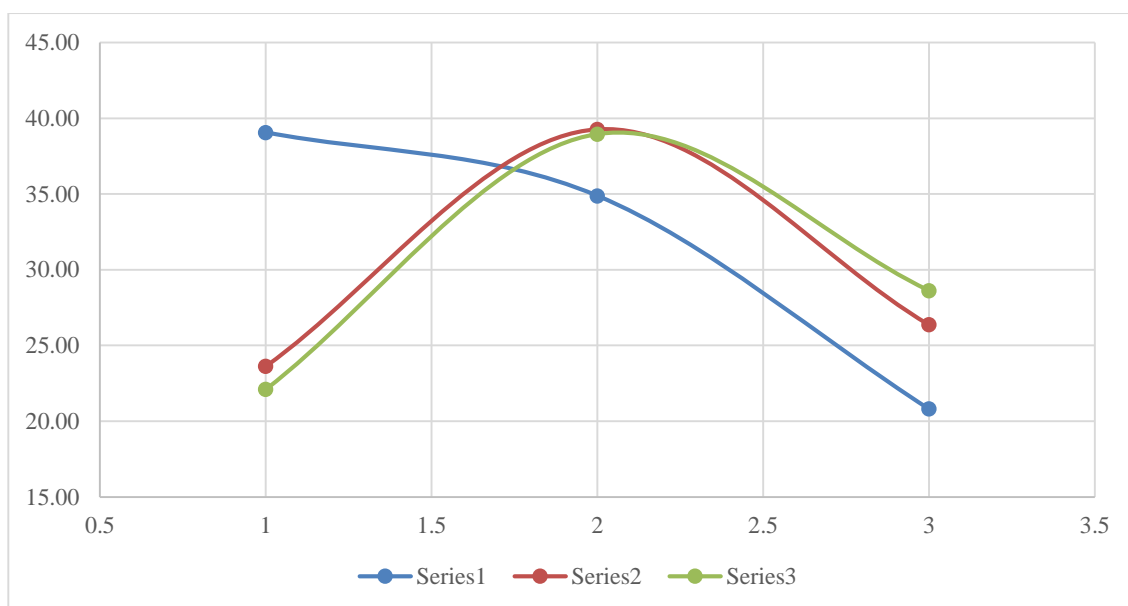


Figure D.4. TOC removal profile in a laboratory-scale batch recirculation UV-C/H₂O₂/VUV photoreactor for actual SWW treatment at different initial concentrations of TOC (Series 1), initial concentrations of H₂O₂ (Series 2), and irradiation times (Series 3).

Table D.3. Experimental run tabulation for the Box-Behnken Design of Experiments. Mean and residual values for the H₂O₂ residual response.

Run	Mean TOCo (mg/L)	Mean Observed H ₂ O ₂ residual (%)	Residuals	Mean H ₂ O ₂ residual between blocks
1	50	9.93	-2.99	12.92
3	50	13.69	0.78	
5	50	12.07	-0.84	
7	50	15.97	3.06	
9	200	1.18	-1.64	2.82
10	200	4.95	2.13	
11	200	2.10	-0.72	
12	200	3.47	0.65	
13	200	2.28	-0.54	
14	200	2.59	-0.23	
15	200	2.94	0.12	
16	200	2.94	0.12	
17	200	2.94	0.12	
2	350	1.30	-1.73	3.03
4	350	3.33	0.30	
6	350	5.67	2.64	
8	350	1.82	-1.21	

Run	Mean [H ₂ O ₂] ₀ (mg/L)	Mean Observed H ₂ O ₂ residual (%)	Residuals	Mean H ₂ O ₂ residual between blocks
1	100	9.93	6.30	3.63
2	100	1.30	-2.33	
9	100	1.18	-2.45	
11	100	2.10	-1.53	
5	500	12.07	6.60	5.47
6	500	5.67	0.20	
7	500	15.97	10.50	
8	500	1.82	-3.65	
13	500	2.28	-3.19	
14	500	2.59	-2.88	
15	500	2.94	-2.53	
16	500	2.94	-2.53	
17	500	2.94	-2.53	
3	900	13.69	7.33	6.36
4	900	3.33	-3.03	
10	900	4.95	-1.41	
12	900	3.47	-2.89	
Run	Mean Irradiation time (min)	Mean Observed H ₂ O ₂ residual (%)	Residuals	Mean H ₂ O ₂ residual between blocks
5	4.0	12.07	6.10	5.97
6	4.0	5.67	-0.30	
9	4.0	1.18	-4.79	
10	4.0	4.95	-1.02	
1	8.0	9.93	5.27	4.66
2	8.0	1.30	-3.36	
3	8.0	13.69	9.03	
4	8.0	3.33	-1.33	
13	8.0	2.28	-2.38	
14	8.0	2.59	-2.07	
15	8.0	2.94	-1.72	
16	8.0	2.94	-1.72	
17	8.0	2.94	-1.72	
7	12.0	15.97	10.13	5.84
8	12.0	1.82	-4.02	
11	12.0	2.10	-3.74	
12	12.0	3.47	-2.37	

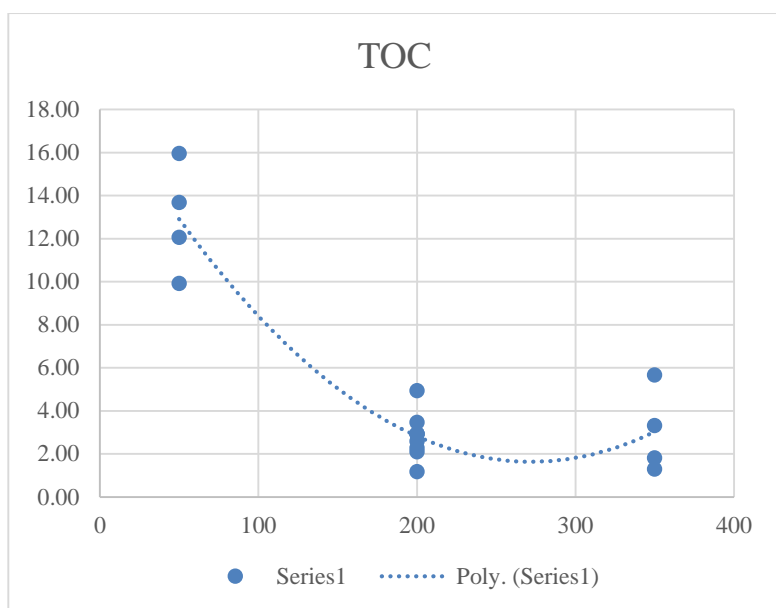


Figure D.5. H_2O_2 residual profile in a laboratory-scale batch recirculation UV-C/ H_2O_2 /VUV photoreactor for actual SWW treatment at different initial concentrations of TOC.

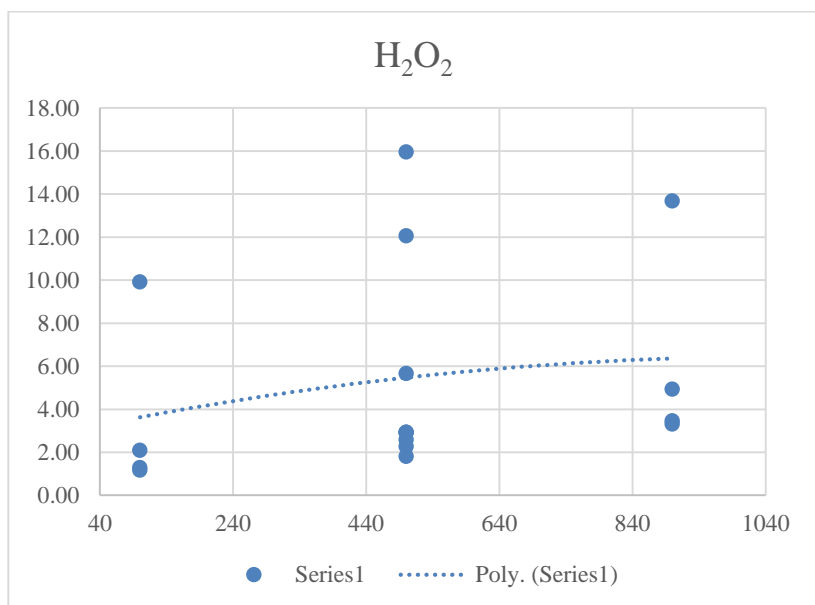


Figure D.6. H_2O_2 residual profile in a laboratory-scale batch recirculation UV-C/ H_2O_2 /VUV photoreactor for actual SWW treatment at different initial concentrations of H_2O_2 .

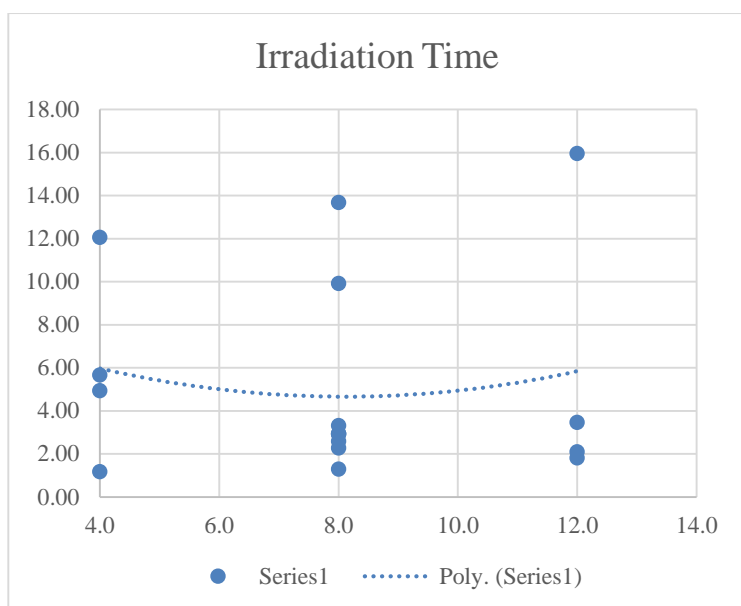


Figure D.7. H₂O₂ residual profile in a laboratory-scale batch recirculation UV-C/H₂O₂/VUV photoreactor for actual SWW treatment at different irradiation times.

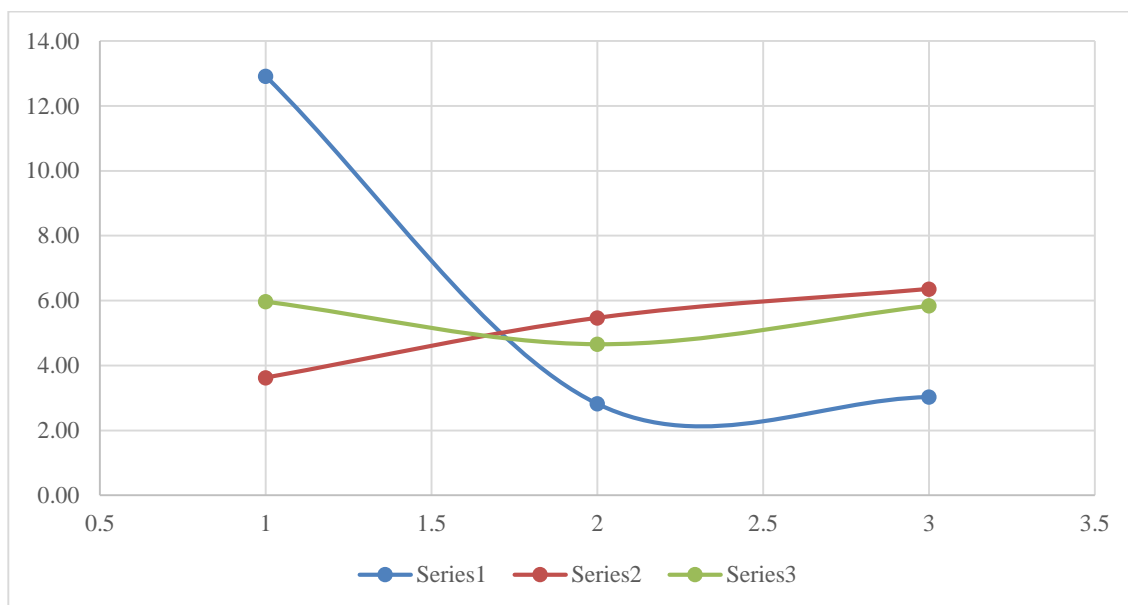


Figure D.8. H₂O₂ residual profile in a laboratory-scale batch recirculation UV-C/H₂O₂/VUV photoreactor for actual SWW treatment at different initial concentrations of TOC (Series 1), initial concentrations of H₂O₂ (Series 2), and irradiation times (Series 3).

Table D.4. Experimental run tabulation for the VUV process alone.

DATE	RUN #	TOC (mg/L)	H2O2 (mg/L)	IRR.TIME (min)	FLOW (ml/min)
05-Apr-16	1	212	0	8.5	55
SAMPLE		RESULTS		MEAN	
	1	199.52			
SWW0	2	212.28		200.74	
	3	190.43			
	1	192.22			
SWW30	2	156.09		179.12	
	3	189.06			
	1	155.31			
SWW60	2	132.30		149.59	
	3	161.15			
	1	143.89			
SWW90	2	123.68		128.58	
	3	118.17			
	1	121.74			
SWW120	2	130.23		127.35	
	3	130.08			
TOC Removal		39.93%			
H2O2 residual		0.00%			

Table D.5. Experimental run tabulation for the VUV/H₂O₂ process alone.

DATE	RUN #	TOC (mg/L)	H2O2 (mg/L)	IRR.TIME (min)	FLOW (ml/min)
05-Apr-16	2	212	473	8.5	55
SAMPLE		RESULTS		MEAN	
	1	146.90			
SWW0	2	158.11		153.95	
	3	156.85			
	1	131.75			
SWW30	2	124.09		131.48	
	3	138.61			
	1	129.16			
SWW60	2	119.78		130.67	
	3	143.06			
	1	131.09			
SWW90	2	125.00		125.16	
	3	119.40			
	1	119.30			
SWW120	2	119.53		119.52	
	3	119.74			
TOC Removal			43.62%		
H2O2 residual		23.10	6.69%		

Table D.6. Experimental run tabulation for the UV-C/H₂O₂ process alone.

DATE	RUN #	TOC (mg/L)	H ₂ O ₂ (mg/L)	IRR.TIME (min)	FLOW (ml/min)
05-Apr-16	3	212	473	8.5	55
SAMPLE		RESULTS		MEAN	
	1	129.40			
SWW0	2	155.32		144.22	
	3	147.95			
	1	155.19			
SWW30	2	124.68		137.38	
	3	132.26			
	1	137.77			
SWW60	2	111.51		121.88	
	3	116.36			
	1	120.44			
SWW90	2	130.98		124.50	
	3	122.08			
	1	123.94			
SWW120	2	115.01		123.44	
	3	131.37			
TOC Removal			41.77%		
H ₂ O ₂ residual		31.65	4.88%		

Table D.7. Comparison between individual and combined UV-C/H₂O₂/VUV processes.

Process	TOC removal (%)	H ₂ O ₂ residual (%)
VUV Alone	39.93%	
UV-C/H ₂ O ₂	41.77%	6.69%
VUV/H ₂ O ₂	43.62%	4.88%
UV-C/H ₂ O ₂ /VUV	45.68%	1.93%

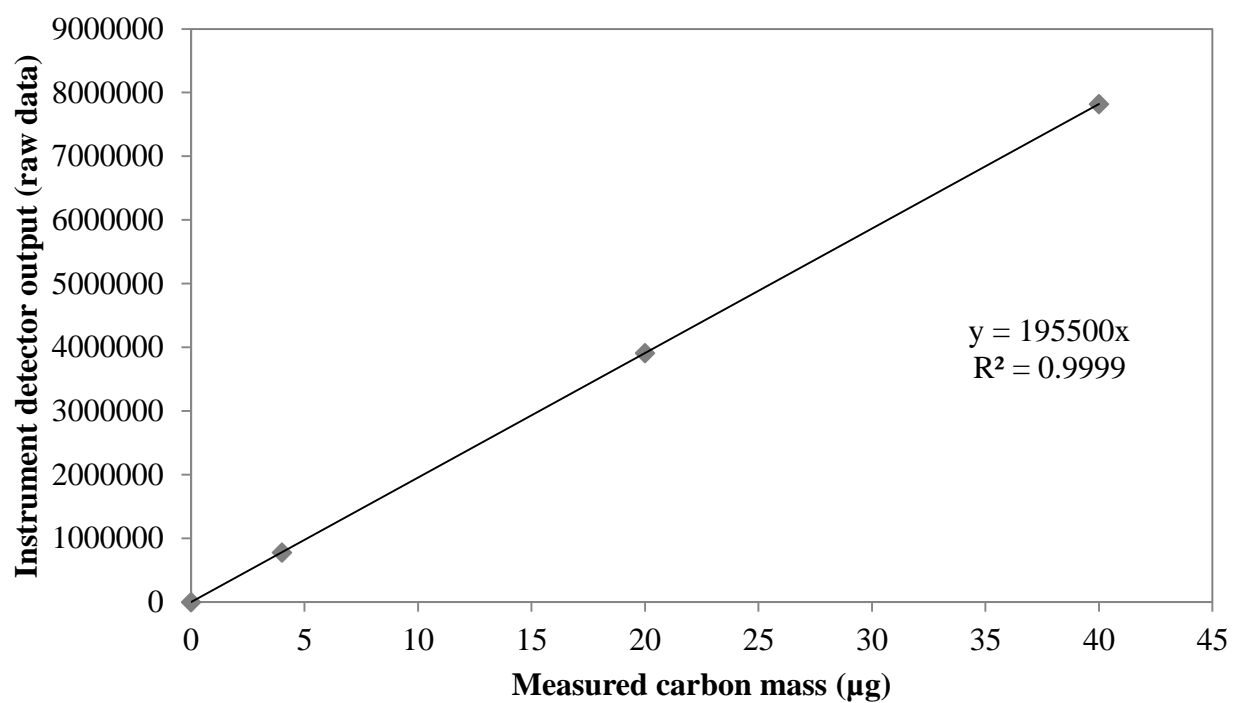


Figure D.9. TOC calibration curve for the range of 1–400 mgTOC/L.

REFERENCES

- Abramović, B., Banić, N., Šojić, D. (2010). Degradation of thiacloprid in aqueous solution by UV and UV/H₂O₂ treatments. *Chemosphere*. 81 (1), 114-119. <http://dx.doi.org/10.1016/j.chemosphere.2010.07.016>
- Adams, C., Spitzer, S., Cowan, R. (1996). Biodegradation of non-ionic surfactants and effects of oxidative pre-treatment. *J. Environ. Eng.* 122 (6), 477-483. [http://dx.doi.org/10.1061/\(ASCE\)0733-9372\(1996\)122:6\(477\)](http://dx.doi.org/10.1061/(ASCE)0733-9372(1996)122:6(477))
- Afzal, A., Oppenländer, T., Bolton, J., El-Din, M. (2010). Anatoxin-a degradation by Advanced Oxidation Processes: Vacuum-UV at 172 nm, photolysis using medium pressure UV and UV/H₂O₂. *Water Res.*, 44 (1), 278-286. <http://dx.doi.org/10.1016/j.watres.2009.09.021>
- Aggelis, G., Gavala, H., Lyberatos, G. (2001). Combined, separate aerobic and anaerobic biotreatment of green olive debittering wastewater. *J. Agr. Eng. Res.* 80 (3), 283-292. <http://dx.doi.org/10.1006/jaer.2001.0732>
- Almandoz, M.C., Pagliero, C.L., Ochoa, N.A., Marchese, J. (2015). Composite ceramic membranes from natural aluminosilicates for microfiltration applications. *Ceram. Int.* 41 (4), 5621-5633. <http://dx.doi.org/10.1016/j.ceramint.2014.12.144>
- Andreozzi, R., Caprio, V., Insola, A., Marotta, R., Sanchirico, R. (2000). Advanced oxidation processes for the treatment of mineral oil-contaminated wastewaters. *Water Res.* 34 (2), 620-628. [http://dx.doi.org/10.1016/S0043-1354\(99\)00169-4](http://dx.doi.org/10.1016/S0043-1354(99)00169-4)
- APHA, 2012. Standard methods for the examination of water and wastewater, 22nd edition, American Public Health Association (APHA), Washington, DC, USA.
- Arvanitoyannis, I.S., Ladas, D. (2008). Meat waste treatment methods and potential uses. *Int. J. Food Sci. Technol.* 43 (3), 543-559. <http://dx.doi.org/10.1111/j.1365-2621.2006.01492.x>
- Aye, T., Mehrvar, M., Anderson, W. (2004). Effects of photocatalysis on the biodegradability of cibacron brilliant yellow 3G-P (reactive yellow 2). *J. Environ. Sci. Heal. A.* 39 (1), 113-126. <http://dx.doi.org/10.1081/ESE-120027372>
- Balcioglu, I.A., Arslan, I., Sacan, M.T. (2001). Homogeneous and heterogeneous advanced oxidation of two commercial reactive dyes. *Environ. Technol.* 22 (7), 813-822. <http://dx.doi.org/10.1080/095933322086180323>

- Barrera, M., Mehrvar, M., Gilbride, K., McCarthy, L., Laursen, A., Bostan, V., Pushchak, R. (2012). Photolytic treatment of organic constituents and bacterial pathogens in secondary effluent of synthetic slaughterhouse wastewater. *Chem. Eng. Res. Des.* 90 (9), 1335-1350. <http://dx.doi.org/10.1016/j.cherd.2011.11.018>
- Belsky, A.J., Matzke, A., Uselman, S. (1999). Survey of livestock influences on stream and riparian ecosystems in the western United States. *J. Soil Water Conserv.* 54 (1), 419-431.
- Beltrán, F.J., Ovejero, G., Acedo, B. (1993). Oxidation of atrazine in water by ultraviolet radiation combined with hydrogen peroxide. *Water Res.* 27 (6), 1013–1021. [http://dx.doi.org/10.1016/0043-1354\(93\)90065-P](http://dx.doi.org/10.1016/0043-1354(93)90065-P)
- Benka-Coker, M.O., Ojior, O.O. (1995). Effect of slaughterhouse wastes on the water quality of Ikpoba River, Nigeria. *Bioresour. Technol.* 52 (1), 5-12. [http://dx.doi.org/10.1016/0960-8524\(94\)00139-R](http://dx.doi.org/10.1016/0960-8524(94)00139-R)
- Bhatkhande, D.S., Pangarkar, V.G., Beenackers, A.A.C.M. (2002). Photocatalytic degradation for environmental applications - A review. *J. Chem. Technol. Biot.* 77 (1), 102-116. <http://dx.doi.org/10.1002/jctb.532>
- Bielski, B. H., Cabelli, D. E., Arudi, R. L., Ross, A. B. (1985). Reactivity of HO_2/O_2^- radicals in aqueous solution. *J. Phys. Chem. Ref. Data.* 14(4), 1041-1100.
- Bolton, J.R., Bircher, K.G., Tumas, W., Tolman, C.A. (2001). Figures-of-merit for the technical development and application of advanced oxidation technologies for both electric- and solar-driven systems. *Pure Appl. Chem.* 73 (4), 627-637.
- Bowers, A., Gaddipati, P., Eckenfelder, J., Monsen, R. (1989). Treatment of toxic or refractory wastewater with hydrogen peroxide. *Water Sci. Technol.* 21, 477–486.
- Box, G.E.P., Behnken, D.W., 1960. Some New Three Level Designs for the Study of Quantitative Variables. *Technometrics*, 2 (4), 455-475. <http://dx.doi.org/10.1080/00401706.1960.10489912>
- Bugallo, P. M., Andrade, L. C., de la Torre, M. A., and López, R. T. (2014). Analysis of the slaughterhouses in Galicia (NW Spain). *Sci. Total Environ.* 481, 656-661. <http://dx.doi.org/10.1016/j.scitotenv.2013.11.079>
- Bull, M.A., Sterritt, R.M., Lester, J.N. (1982). The treatment of wastewaters from the meat industry: A review. *Environ. Technol. Lett.* 3 (3), 117-126. <http://dx.doi.org/10.1080/09593338209384107>
- Bustillo-Lecompte, C.F., Mehrvar, M., Quiñones-Bolaños, E. (2013). Combined anaerobic-aerobic and UV/ H_2O_2 processes for the treatment of synthetic slaughterhouse wastewater. *J. Environ. Sci. Heal. A* 48 (9), 1122-1135. <http://dx.doi.org/10.1080/10934529.2013.774662>

- Bustillo-Lecompte, C.F., Mehrvar, M., Quiñones-Bolaños, E. (2014). Cost-effectiveness analysis of TOC removal from slaughterhouse wastewater using combined anaerobic-aerobic and UV/H₂O₂ processes. *J. Environ. Manage.* 134, 145-152. <http://dx.doi.org/10.1016/j.jenvman.2013.12.035>
- Bustillo-Lecompte, C. F., Knight, M., Mehrvar, M. (2015). Assessing the performance of UV/H₂O₂ as a pretreatment process in TOC removal of an actual petroleum refinery wastewater and its inhibitory effects on activated sludge. *Can. J. Chem. Eng.* 93 (5), 798-807. <http://dx.doi.org/10.1002/cjce.22180>
- Bustillo-Lecompte, C.F., Mehrvar, M. (2015). Slaughterhouse wastewater characteristics, treatment, and management in the meat processing industry: a review on trends and advances. *J. Environ. Manage.* 161, 287-302. <http://dx.doi.org/10.1016/j.jenvman.2015.07.008>
- Bustillo-Lecompte, C.F., Ghafoori, S., Mehrvar, M. (2016). Photochemical degradation of an actual slaughterhouse wastewater by continuous UV/H₂O₂ photoreactor with recycle. *J. Environ. Chem. Eng.* 4 (1), 719-732. <http://dx.doi.org/10.1016/j.jece.2015.12.009>
- Buxton, G.V., Greenstock, C.L., Helman, W.P., Ross, A.B. (1988) Critical Review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($\cdot\text{OH}/\cdot\text{O}-$ in Aqueous Solution. *J. Phys. Chem. Ref. Data* 17 (2), 513-886. <http://dx.doi.org/10.1063/1.555805>
- Cao, W., Mehrvar, M. (2011). Slaughterhouse wastewater treatment by combined anaerobic baffled reactor and UV/H₂O₂ processes. *Chem. Eng. Res. Des.* 89 (7), <http://dx.doi.org/10.1016/j.cherd.2010.12.001>
- CEC. (1991). Urban Wastewater Treatment Directive 91/271/EEC, Council of the European Communities (CEC). *Off. J. Eur. Comm. L* (135), 40-52. <http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:31991L0271&from=EN>
- Chan, Y. J., Chong, M. F., Law, C. L., Hassell, D. (2009). A review on anaerobic-aerobic treatment of industrial and municipal wastewater. *Chem. Eng. J.* 155 (1-2), 1-18. <http://dx.doi.org/10.1016/j.cej.2009.06.041>
- Chelikani, P., Fita, I., Loewen, P.C. (2004). Diversity of structures and properties among catalases. *Cell. Mol. Life Sci.* 61 (2), 192-208. <http://dx.doi.org/10.1007/s00018-003-3206-5>
- Chernicharo, C. (2006). Post-treatment options for the anaerobic treatment of domestic wastewater. *Rev. Environ. Sci. Biotechnol.* 5 (1), 73-92. <http://dx.doi.org/10.1007/s11157-005-5683-5>
- Christensen, H., Sehested, K., Corfitzen, H. (1982). Reactions of hydroxyl radicals with hydrogen peroxide at ambient and elevated temperatures. *J. Phys. Chem.* 86 (9), 1588-1590. <http://dx.doi.org/10.1021/j100206a023>

- Comninellis, C., Kapalka, A., Malato, S., Parsons, S., Poulios, I., Mantzavinos, D. (2008). Advanced oxidation processes for water treatment: Advances and trends for R&D. *J. Chem. Technol. Biot.* 83 (6), 769–776. <http://dx.doi.org/10.1002/jctb.1873>
- Crittenden, J.C., Hu, S., Hand, D.W., Green, S.A. (1999). A kinetic model for H₂O₂/UV process in a completely mixed batch reactor. *Water Res.* 33 (10), 2315-2328. [http://dx.doi.org/10.1016/S0043-1354\(98\)00448-5](http://dx.doi.org/10.1016/S0043-1354(98)00448-5)
- Daigger, G.T. (2009). Evolving urban water and residuals management paradigms: Water reclamation and reuse, decentralization, and resource recovery. *Water Environ. Res.* 81 (8), 809-823. <http://dx.doi.org/10.2175/106143009X425898>
- De Sena, R.F., Tambosi, J.L., Genena, A.K., Moreira, R.d.F.P.M., Schröder, H.Fr., José, H.J. (2009). Treatment of meat industry wastewater using dissolved air flotation and advanced oxidation processes monitored by GC-MS and LC-MS. *Chem. Eng. J.* 152 (1), 151-157. <http://dx.doi.org/10.1016/j.cej.2009.04.021>
- Debik, E., Coskun, T. (2009). Use of the Static Granular Bed Reactor (SGBR) with anaerobic sludge to treat poultry slaughterhouse wastewater and kinetic modeling. *Bioresour. Technol.* 100 (11), 2777-2782. <http://dx.doi.org/10.1016/j.biortech.2008.12.058>
- De Nardi, I. R., Del Nery, V., Amorim, A. K. B., dos Santos, N. G., Chimenes, F. (2011). Performances of SBR, chemical–DAF and UV disinfection for poultry slaughterhouse wastewater reclamation. *Desalination* 269 (1), 184-189. <http://dx.doi.org/10.1016/j.desal.2010.10.060>
- Devipriya, S., Yesodharan, S. (2005). Photocatalytic degradation of pesticide contaminants in water. *Sol. Energ. Mat. Sol. C.* 86 (3), 309-348. <http://dx.doi.org/10.1016/j.solmat.2004.07.013>
- Del Pozo, R., Diez, V. (2005). Integrated anaerobic-aerobic fixed-film reactor for slaughterhouse wastewater treatment. *Water Res.* 39 (6), 1114-1122. <http://dx.doi.org/10.1016/j.watres.2005.01.013>
- Diffey, B.L. (2002). Sources and measurement of ultraviolet radiation. *Methods*, 28 (1), 4-13. [http://dx.doi.org/10.1016/S1046-2023\(02\)00204-9](http://dx.doi.org/10.1016/S1046-2023(02)00204-9)
- ECO. (2010). Sewage Treatment: Not Good Enough. In *Redefining Conservation*, ECO Annual Report 2009/10, Environmental Commissioner of Ontario (ECO), The Queen’s Printer for Ontario: Toronto, Canada, 80–89.
- Edalatmanesh, M., Mehrvar, M., Dhib, R. (2008). Optimization of phenol degradation in a combined photochemical-biological wastewater treatment system. *Chem. Eng. Res. Des.* 86 (11), 1243-1252. <http://dx.doi.org/10.1016/j.cherd.2008.06.001>

- Environment Canada. (2012). Wastewater Systems Effluent Regulations. Fisheries Act. SOR/2012-139. Accessed March 10, 2015. Available online: <http://laws-lois.justice.gc.ca/PDF/SOR-2012-139.pdf>
- Eryuruk, K., Tezcanun, U., Bakir Ogutveren, U. (2014). Electrocoagulation in a plugflow reactor: The treatment of cattle abattoir wastewater by iron rod anodes. *Int. J. Env. Res. Pub. He.* 8 (2), 461-468. http://www.ijer.ir/article_738_36.html
- Feng, H., Hu, L., Mahmood, Q., Fang, C., Qiu, C., Shen, D. (2009). Effects of temperature and feed strength on a carrier anaerobic baffled reactor treating dilute wastewater. *Desalination* 238 (1-3), 111-121. <http://dx.doi.org/10.1016/j.desal.2008.03.011>
- Ford, D.L., Eller, J.M., Gloyna, E.F. (1971). Analytical parameters of petrochemical and refinery wastewaters. *J. Water Pollut. Control Fed.* 43 (8), 1712-1723.
- Franke-Whittle, I.H., Insam, H. (2013). Treatment alternatives of slaughterhouse wastes, and their effect on the inactivation of different pathogens: A review. *Crit. Rev. Microbiol.* 39 (2), 139-151. <http://dx.doi.org/10.3109/1040841X.2012.694410>
- García, M.T., Ribosa, I., Guindulain, T., Sánchez-Leal, J., Vives-Rego, J. (2000). Fate and effect of monoalkyl quaternary ammonium surfactants in the aquatic environment. *Environ. Pollut.* 111 (1), 169-175. [http://dx.doi.org/10.1016/S0269-7491\(99\)00322-X](http://dx.doi.org/10.1016/S0269-7491(99)00322-X)
- Gerbens-Leenes, P.W., Mekonnen, M.M., Hoekstra, A.Y. (2013). The water footprint of poultry, pork and beef: A comparative study in different countries and production systems. *Water Resour. Ind.* 1-2, 25-36. <http://dx.doi.org/10.1016/j.wri.2013.03.001>
- Ghafoori, S., Mehrvar, M., Chan, P.K. (2012). Free-radical-induced degradation of aqueous polyethylene oxide by UV/H₂O₂: Experimental design, reaction mechanisms, and kinetic modeling. *Ind. Eng. Chem. Res.* 51 (46), 14980-14993. <http://dx.doi.org/10.1021/ie3005995>
- Ghafoori, S., Mehrvar, M., and Chan, P.K., 2013. Photoassisted Fenton-like degradation of aqueous poly(acrylic acid): From mechanistic kinetic model to CFD modeling. *Chem. Eng. Res. Des.*, 91 (12), 2617-2629. <http://dx.doi.org/10.1016/j.cherd.2013.05.019>
- Ghafoori, S., Mehrvar, M., Chan, P. (2014). Optimisation of photo-Fenton-like degradation of aqueous polyacrylic acid using Box-Behnken experimental design. *Can. J. Chem. Eng.* 92 (1), 97-108. <http://dx.doi.org/10.1002/cjce.21849>
- Ghafoori, S., Mowla, A., Jahani, R., Mehrvar, M., Chan, P.K. (2015). Sonophotolytic degradation of synthetic pharmaceutical wastewater: Statistical experimental design and modeling. *J. Environ. Manage.* 150, 128-137. <http://dx.doi.org/10.1016/j.jenvman.2014.11.011>

- Glaze, W.H. (1987). Drinking-water treatment with ozone. *Environ. Sci. Technol.* 21 (3), 224–230. <http://dx.doi.org/10.1021/es00157a001>
- Gonze, E., Commenges, N., Gonthier, Y., Bernis, A. (2003). High frequency ultrasound as a pre- or a post-oxidation for paper mill wastewaters and landfill leachate treatment. *Chem. Eng. J.* 92 (1-3), 215-225. [http://dx.doi.org/10.1016/S1385-8947\(02\)00258-9](http://dx.doi.org/10.1016/S1385-8947(02)00258-9)
- Gopala Krishna, G.V.T., Kumar, P., Kumar, P. (2009). Treatment of low-strength soluble wastewater using an anaerobic baffled reactor (ABR). *J. Environ. Manage.* 90 (1), 166-176. <http://dx.doi.org/10.1016/j.jenvman.2007.08.017>
- Goslan, E., Gurses, F., Banks, J., Parsons, S. (2006). An investigation into reservoir NOM reduction by UV photolysis and advanced oxidation processes. *Chemosphere*, 65 (7), 1113-1119. <http://dx.doi.org/10.1016/j.chemosphere.2006.04.041>
- Gray, N. F. (2010). *Water technology: an introduction for environmental scientists and engineers* (No. Ed. 3). IWA Publishing.
- Heijnen, J., Mulder, A., Weltevrede, R., Hols, J., Vanleeuwen, H. (1991). Large-scale anaerobic–aerobic treatment of complex industrial-waste water using biofilm reactors. *Water Sci. Technol.* 23 (7-9), 1427–1436.
- Hirvonen, A., Tuhkanen, T., Ettala, M., Korhonen, S., Kalliokoski, P. (1998). Evaluation of a field-scale UV/H₂O₂-oxidation system for the purification of groundwater contaminated with PCE. *Environ. Technol.* 19 (8), 821-828. <http://dx.doi.org/10.1080/09593330.1998.9618696>
- Hu, S.-T., Yu, Y.-H. (1994). Preozonation of Chlorophenolic Wastewater for Subsequent Biological Treatment. *Ozone-Sci. Eng.* 16 (1), 13-28. <http://dx.doi.org/10.1080/01919519408552377>
- Johns, M. (1995). Developments in wastewater treatment in the meat processing industry: A review. *Bioresour. Technol.* 54, 203-216. [http://dx.doi.org/10.1016/0960-8524\(95\)00140-9](http://dx.doi.org/10.1016/0960-8524(95)00140-9)
- Jones, B.M., Sakaji, R.H., Daughton, C.G. (1985). Effects of ozonation and ultraviolet irradiation on biodegradability of oil shale wastewater organic solutes. *Water Res.* 19 (11), 1421-1428. [http://dx.doi.org/10.1016/0043-1354\(85\)90309-4](http://dx.doi.org/10.1016/0043-1354(85)90309-4)
- Khenoussi, A., Chaouch, M., Chahlaouider, A. (2013). Treatment of the effluent from a red meat slaughterhouse by electrocoagulation flotation with iron electrodes. *Rev. Sci. Eau* 26 (2), 135-150. <http://dx.doi.org/10.7202/1016064ar>
- Kim, I., Yamashita, N., Tanaka, H. (2009a). Performance of UV and UV/H₂O₂ processes for the removal of pharmaceuticals detected in secondary effluent of a sewage treatment plant in Japan. *J. Hazard. Mater.* 166 (2-3), 1134-1140. <http://dx.doi.org/10.1016/j.jhazmat.2008.12.020>

- Kim, I., Yamashita, N., Tanaka, H. (2009b). Photodegradation of pharmaceuticals and personal care products during UV and UV/H₂O₂ treatments. *Chemosphere*. 77 (4), 518-525. <http://dx.doi.org/10.1016/j.chemosphere.2009.07.041>
- Klamerth, N., Rizzo, L., Malato, S., Maldonado, M.I., Agüera, A., Fernández-Alba, A.R. (2010). Degradation of fifteen emerging contaminants at µg L⁻¹ initial concentrations by mild solar photo-Fenton in MWTP effluents. *Water Res.* 44 (2), 545-554. <http://dx.doi.org/10.1016/j.watres.2009.09.059>
- Klavarioti, M., Mantzavinos, D., Kassinos, D. (2009). Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes. *Environ. Int.* 35 (2), 402-417. <http://dx.doi.org/10.1016/j.envint.2008.07.009>
- Koppenol, W.H., Butler, J., Van Leeuwen, J.W. (1978). The Haber-Weiss Cycle. *J. Photochem. Photobiol.* 28, 655–660. <http://dx.doi.org/10.1111/j.1751-1097.1978.tb06989.x>
- Koyama, O., Kamagata, Y., Nakamura, K. (1994). Degradation of chlorinated aromatics by fenton oxidation and methanogenic digester sludge. *Water Res.* 28 (4), 895-899. [http://dx.doi.org/10.1016/0043-1354\(94\)90096-5](http://dx.doi.org/10.1016/0043-1354(94)90096-5)
- Lapertot, M., Pulgarín, C., Fernández-Ibáñez, P., Maldonado, M.I., Pérez-Estrada, L., Oller, I., Gernjak, W., Malato, S. (2006). Enhancing biodegradability of priority substances (pesticides) by solar photo-Fenton. *Water Res.* 40 (5), 1086-1094. <http://dx.doi.org/10.1016/j.watres.2006.01.002>
- Lee, S., Carberry, J. (1992). Biodegradation of PCP enhanced by chemical oxidation pre-treatment. *Water Environ. Res.* 64 (5), 682–690.
- Li, K., Stefan, M., Crittenden, J. (2007). Trichloroethene degradation by UV/H₂O₂ advanced oxidation process: Product study and kinetic modeling. *Environ. Sci. Technol.*, 41 (5), 1696-1703. <http://dx.doi.org/10.1021/es0607638>
- Liu, H., Yang, C., Pu, W., Zhang, J. (2008). Removal of nitrogen from wastewater for reusing to boiler feed-water by an anaerobic/aerobic/membrane bioreactor. *Chem. Eng. J.* 140 (1-3), 122-129. <http://dx.doi.org/10.1016/j.cej.2007.09.048>
- López-Peñalver, J., Sánchez-Polo, M., Gómez-Pacheco, C., Rivera-Utrilla, J. (2010). Photodegradation of tetracyclines in aqueous solution by using UV and UV/H₂O₂ oxidation processes. *J. Chem. Technol. Biotechnol.*, 85 (10), 1325-1333. <http://dx.doi.org/10.1002/jctb.2435>
- Luiz, D.B., Genena, A.K., José, H.J., Moreira, R.F.P.M., Schröder, H.Fr. (2009). Tertiary treatment of slaughterhouse effluent: Degradation kinetics applying UV radiation or H₂O₂/UV. *Water Sci. Technol.* 60 (7), 1869-1874. <http://dx.doi.org/10.2166/wst.2009.583>

- Luiz, D.B., Silva, G.S., Vaz, E.A.C., José, H.J., Moreira, R.F.P.M. (2011). Evaluation of hybrid treatments to produce high quality reuse water. *Water Sci. Technol.* 63 (9), 2046-2051. <http://dx.doi.org/10.2166/wst.2011.468>
- Mehrvar, M., Tabrizi, G.B. (2006). Combined photochemical and biological processes for the treatment of linear alkylbenzene sulfonate in water. *J. Environ. Sci. Heal. A* 41 (4), 581-597. <http://dx.doi.org/10.1080/10934520600572975>
- Melo, R., Cabo Verde, S., Branco, J., Botelho, M.L. (2008). Gamma radiation induced effects on slaughterhouse wastewater treatment. *Radiat. Phys. Chem.* 77 (1), 98-100. <http://dx.doi.org/10.1016/j.radphyschem.2007.03.006>
- Millamena, O.M. (1992). Ozone treatment of slaughterhouse and laboratory wastewaters. *Aquac. Eng.* 11 (1), 23-31. [http://dx.doi.org/10.1016/0144-8609\(92\)90018-S](http://dx.doi.org/10.1016/0144-8609(92)90018-S)
- Miller, R.M. (1988). Sequential degradation of chlorophenols by photolytic and microbial treatment. *Environ. Sci. Technol.* 22 (10), 1215-1219. <http://dx.doi.org/10.1021/es00175a015>
- Mittal, G.S. (2006). Treatment of wastewater from abattoirs before land application - A review. *Bioresour. Technol.* 97 (9), 1119-1135. <http://dx.doi.org/10.1016/j.biortech.2004.11.021>
- Mohajerani, M., Mehrvar, M., Ein-Mozaffari, F. (2012). Photoreactor design and CFD modelling of a UV/H₂O₂ process for distillery wastewater treatment. *Can. J. Chem. Eng.* 90 (3), 719-729. <http://dx.doi.org/10.1002/cjce.20569>
- Mowla, A., Mehrvar, M., Dhib, R. (2014). Combination of sonophotolysis and aerobic activated sludge processes for treatment of synthetic pharmaceutical wastewater. *Chem. Eng. J.* 255, 411-423. <http://dx.doi.org/10.1016/j.cej.2014.06.064>
- Myers, R.H., Montgomery, D.C., Vining, G.G., Borror, C.M., Kowalski, S.M. (2004). Response Surface Methodology: A Retrospective and Literature Survey. *J. Qual. Technol.* 36 (1), 53-77.
- Neyens, E., Baeyens, J. (2003). A review of classic Fenton's peroxidation as an advanced oxidation technique. *J. Hazard. Mater.* 98 (1-3), 33-50. [http://dx.doi.org/10.1016/S0304-3894\(02\)00282-0](http://dx.doi.org/10.1016/S0304-3894(02)00282-0)
- Oppenländer, T. (2003). Photochemical purification of water and air, *Advanced Oxidation Processes (AOPs): Principles, reaction mechanisms, reactor concepts*. Weinheim, Germany: Wiley-VCH.
- Oller, I., Malato, S., Sanchez-Perez, J. (2011). Combination of Advanced Oxidation Processes and biological treatments for wastewater decontamination - A review. *Sci. Total Environ.* 409 (20), 4141-4166. <http://dx.doi.org/10.1016/j.scitotenv.2010.08.061>
- Ozyonar, F., Karagozoglu, B. (2014). Investigation of technical and economic analysis of electrocoagulation process for the treatment of great and small cattle slaughterhouse wastewater. *Desalin. Water Treat.* 52 (1-3), 74-87. <http://dx.doi.org/10.1080/19443994.2013.787373>

- Pera-Titus, M., García-Molina, V., Baños, M.A., Giménez, J., Esplugas, S. (2004). Degradation of chlorophenols by means of advanced oxidation processes: A general review. *Appl. Catal. B-Environ.* 47 (4), 219-256. <http://dx.doi.org/10.1016/j.apcatb.2003.09.010>
- Pignatello, J.J., Oliveros, E., MacKay, A. (2006). Advanced oxidation processes for organic contaminant destruction based on the fenton reaction and related chemistry. *Crit. Rev. Env. Sci. Tec.* 36 (1), 1-84. <http://dx.doi.org/10.1080/10643380500326564>
- Pulgarín, C., Kiwi, J. (1996). Overview on photocatalytic and electrocatalytic pretreatment of industrial non-biodegradable pollutants and pesticides. *Chimia* 50 (3), 50–55.
- Rajakumar, R., T. Meenambal, J. Rajesh Banu, I.T. Yeom. (2011). Treatment of poultry slaughterhouse wastewater in upflow anaerobic filter under low upflow velocity. *Int. J. Environ. Sci. Te.* 8 (1), 149-158. <http://dx.doi.org/10.1007/BF03326204>
- Rosario-Ortiz, F., Wert, E., Snyder, S. (2010). Evaluation of UV/H₂O₂ treatment for the oxidation of pharmaceuticals in wastewater. *Water Res.* 44 (5), 1440-1448. <http://dx.doi.org/10.1016/j.watres.2009.10.031>
- Salminen, E., Rintala, J. (2002). Anaerobic digestion of organic solid poultry slaughterhouse waste - A review. *Bioresour. Technol.* 83 (1), 13-26. [http://dx.doi.org/10.1016/S0960-8524\(01\)00199-7](http://dx.doi.org/10.1016/S0960-8524(01)00199-7)
- Sawyer, C., McCarty, P., Martin, G. (2002). *Chemistry for Environmental Engineering and Science* (5th ed.). New York, NY: McGraw-Hill Science.
- Sehested, K., Rasmussen, O.L., Fricke, H. (1968). Rate constants of OH with HO₂, O₂⁻, and H₂O₂⁺ from hydrogen peroxide formation in pulse-irradiated oxygenated water. *J. Phys. Chem.* 72 (1968) 626-631. <http://dx.doi.org/10.1021/j100848a040>
- Shannon, M.A., Bohn, P.W., Elimelech, M., Georgiadis, J.G., Mariñas, B.J., Mayes, A.M. (2008). Science and technology for water purification in the coming decades. *Nature*, 452 (7185), 301-310. <http://dx.doi.org/10.1038/nature06599>
- Shemer, H., Kunukcu, Y.K., Linden, K.G. (2006). Degradation of the pharmaceutical Metronidazole via UV, Fenton and photo-Fenton processes. *Chemosphere.* 63 (2), 269-276. <http://dx.doi.org/10.1016/j.chemosphere.2005.07.029>
- Shu, H. (2006). Degradation of dyehouse effluent containing C.I. Direct Blue 199 by processes of ozonation, UV/H₂O₂ and in sequence of ozonation with UV/H₂O₂. *J. Hazard. Mater.* 133 (1-3), 92–98. <http://dx.doi.org/10.1016/j.jhazmat.2005.09.056>
- Sigge, G.O., Britz, T.J., Fourie, P.C., Barnardt, C.A., Strydom, R. (2002). Combining UASB technology and advanced oxidation processes (AOP's) to treat food processing wastewaters. *Water Sci. Technol.* 45 (10), 329–334.

- Staehelin, J., Bühler, R.E., Hoigné, J. (1984). Ozone decomposition in water studied by pulse radiolysis. 2. OH and HO₄ as chain intermediates. J. Phys. Chem. 88 (24), 5999-6004. <http://dx.doi.org/10.1021/j150668a051>
- Steber, J., Wierich, P. (1986). Properties of hydroxyethane diphosphonate affecting its environmental fate: Degradability, sludge adsorption, mobility in soils, and bioconcentration. Chemosphere, 15 (7), 929-945. [http://dx.doi.org/10.1016/0045-6535\(86\)90058-5](http://dx.doi.org/10.1016/0045-6535(86)90058-5)
- Tabrizi, G.B., Mehrvar, M. (2004). Integration of advanced oxidation technologies and biological processes: Recent developments, trends, and advances. J. Environ. Sci. Heal. A 39 (11-12), 3029-3081. <http://dx.doi.org/10.1081/LESA-200034939>
- Tarr, M. (2003). Chemical Degradation Methods for Wastes and Pollutants: Environmental and Industrial Applications. New York, NY: Marcel Dekker.
- Torkian, A., Alinejad, K., Hashemian, S.J. (2003). Posttreatment of upflow anaerobic sludge blanket-treated industrial wastewater by a rotating biological contactor. Water Environment Research 75 (3), 232-237. <http://dx.doi.org/10.2175/106143003X141015>
- Tritt, W.P., Schuchardt, F. (1992). Materials flow and possibilities of treating liquid and solid wastes from slaughterhouses in Germany. A review. Bioresour. Technol. 41 (3), 235-245. [http://dx.doi.org/10.1016/0960-8524\(92\)90008-L](http://dx.doi.org/10.1016/0960-8524(92)90008-L)
- US EPA. (2004). Effluent Limitations Guidelines and New Source Performance Standards for the Meat and Poultry Products Point Source Category. Environmental Protection Agency (EPA): Federal Register Vol. 69, No. 173.
- Valta, K., Kosanovic, T., Malamis, D., Moustakas, K., Loizidou, M. (2015). Overview of water usage and wastewater management in the food and beverage industry. Desalin. Water Treat. 53 (12), 3335-3347. <http://dx.doi.org/10.1080/19443994.2014.934100>
- Venhuis, S., Mehrvar, M. (2005). Photolytic treatment of aqueous linear alkyl benzene sulfonate. J. Environ. Sci. Heal. A 40 (9), 1731-1739. <http://dx.doi.org/10.1081/ESE-200068007>
- Vera, M., Aspé, E., Martí, M.C., Roeckel, M. (1999). Optimization of a sequential anaerobic-aerobic treatment of a saline fishing effluent. Process Saf. Environ. 77 (5), 275-290. <http://dx.doi.org/10.1205/095758299530152>
- Verheijen, L., Wiersema, D., Pol, L. H. (1996). Management of Waste from Animal Product Processing. Retrieved February 19, 2016, from Food and Agriculture Organization of the United Nations - FAO Corporate Document Repository - J. De Wit International Agriculture Centre: <http://www.fao.org/wairdocs/lead/x6114e/x6114e00.htm>

- Vymazal, J. (2014). Constructed wetlands for treatment of industrial wastewaters: A review. *Ecol. Eng.* 73, 724-751. <http://dx.doi.org/10.1016/j.ecoleng.2014.09.034>
- Wang, X.-W., Fei, Q.-Z., Xu, Z., Guo, H.-Y., Zhang, S.-T. (2009). Study on treatment of slaughterhouse wastewater with co-coagulation flotation and SBR process. 3rd International Conference on Bioinformatics and Biomedical Engineering iCBBE 2009, art. no. 5163535. <http://dx.doi.org/10.1109/ICBBE.2009.5163535>
- World Bank Group. (2007). Environmental, Health and Safety (EHS) Guidelines for Meat Processing. General EHS Guidelines: Environmental Wastewater and Ambient Water Quality. Accessed March 10, 2015. Available online: <http://www.ifc.org/ehsguidelines>
- Wu, P., Mittal, G. (2011). Characterization of provincially inspected slaughterhouse wastewater in Ontario, Canada. *Can. Biosyst. Eng.* 53, 6.9-6.18. <http://www.csbe-scgab.ca/docs/journal/54/C12062.pdf>
- Zepp, R.G. (1978). Quantum yields for reaction of pollutants in dilute aqueous solution. *Environ. Sci. Technol.* 12 (3), 327-329. <http://dx.doi.org/10.1021/es60139a010>