Development of UVC advanced oxidation photolysis combined with membrane electro - bioreactor for simultaneous removal of emerging contaminants and reduction of by-products

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A Thesis
In the department
of
Building, Civil and Environmental Engineering

Presented in Partial Fulfilment of the Requirements
For the Degree of
Doctor of Philosophy (Civil Engineering)

Concordia University

Montreal, Quebec, Canada

August 2020

CONCORDIA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

This is to certify that the thesis prepared

By: Sasan Fazeli

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Doctor Of Philosophy (Civil Engineering)

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ABSTRACT

Development of UVC advanced oxidation photolysis combined with membrane electro-bioreactor for simultaneous removal for emerging contaminants and reduction of by-products

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The continuous discharge of emerging contaminants (ECs) to the aquatic ecosystem generate concerns due to their unpredictable risks to human and environment. The presence of ECs in source water attributed to the conventional wastewater treatment facilities which are not fundamentally designed to completely eliminate these micropollutants at low concentrations.

The aim of this research was to enhance the wastewater treatment to the level of its potential reuse as a source of water. The investigations were conducted at lab and pilot scale in 8 phases and several stages. Initially, the removal of selected ECs was optimized. Subsequently, the by-product formation and their identification were conducted. Then, the study focused on the by-product removal. In subsequent phases, the optimal technological parameters were verified in natural conditions, at the pilot scale in AOP (advance oxidation process) and AO-MEBR (membrane electro-bioreactor) facilities. Such approach permitted to study the removal of sulfamethoxazole (SMX), 17- alpha ethynyl estradiol (EE2), caffeine (CAF) and paracetamol (PCM) from various aqueous solutions (DI water, river water, effluent after wastewater treatment, and wastewater). A developed model investigated the effect of technological parameters on pharmaceuticals' removal efficiency and on by-product abatement.

The results showed superior removal efficiency (99%) by both UV/H_2O_2 AOP and UV/O_3 AOP of SMX, PCM, CAF and EE2 in comparison to sole UVC photolysis (30-40%). UV/O_3 AOP demonstrated an elevated rate and removal by 10-15% higher than ozonation alone. The target ECs such as SMX, PCM were removed by more than 80% in effluent and more than 90% in river water during 60 minutes. The differences in the ECs and their byproducts removal from various aqueous matrices were discussed from the matrix properties perspectives, particularly non-target constituents (EfOM, NOM and sacavengers) present at different amounts in target matrices. The influence of operational parametrs (oxidant and UV doses, exposure time, pH) was defined, where particular usefulness of Surface Response Methodology was underlined. Overall, the SMX and by-products' abatement (99.99%) in different matrices by AO-MEBR hybrid system was evident.

Four major SMX by-products (BP-99, BP-270, BP-288, BP-172) identified by LC-MS-MS, revealed longer lifetime and stability even after parent SMX ion removal. By applying optimal technological parameters, i.e. pH, oxidant dose and aeration rate, the by-products amounts were successfully controlled. Degradation mechanisms, reaction pathway and evolution of by-products during treatment in various aqueous solutions were conducted. Particular attention was paid on the effect of OH scavenging, the role of non-target constituencies, operation parameters, as well as aeration and superoxide radicals. Furthermore, the toxicity was decreased and energy consumption for target pollutant removal was minimized (20-25%).

The AO-MEBR system not merely improved the quality of effluent with respect to refractory organic pollutants, but also likely promoted by-products and toxicity mitigation as well as saving energy leading to improved potential of water recovery from sewage.

ACKNOWLEDGEMENT

I would like to express my sincere gratitude to my supervisor, Dr. Maria Elektorowicz for her constant support, numerous valuable suggestions, creative guidance, encouragement and inspiring advice through the course of this thesis. Without all her support, I would not be in this situation to finish my PhD.

Indebtedness and appreciation are due to my committee members, Dr. R. Farnood, Dr. V. Titerenko, Dr. J. Hadjinicolaou and Dr. F. Nasiri for accepting the appointment to the dissertation committee, as well as for their suggestions, valuable comments, and support.

I would like to convey my deepest appreciation to Dr. F. Haghighat, Dr. Z. Chen and Dr. L. Yerushalmi for all scientific and financial supports for the UV/O_3 AOP pilot setup designing, manufacturing and developing such a tremendous setup led to achievement of important and valuable results for my thesis.

Special thanks to Mr. Josef Hirib of the Department of Building, Civil & Environmental Engineering at Concordia University for his excellent technical help and his amazing ability to assemble the advanced oxidation pilot plant in the BCEE department.

My very sincere thanks to Dr. Mohammed Farshidi, my friend and classmate, for his valuable technical and scientific advices and priceless support throughout my study.

My very sincere thanks to Dr. Alexandra Furtos, Mass Spectrometry lab manager from Polytechnique Montreal who allowed me to use some of the facilities in the research lab and her valuable analysis works.

DEDICATION

To:

The spirit of my beloved father, Hassan Fazeli

The enormous debt of gratitude to my father for his advices, educational supports starting from primary school, his encouragements and love

My beloved mother, Forough Khorasani

For her unconditional love and support from my birthday and inclusively her role on my education and her deepest warmest spiritual supports in my life

My dearest love, Fariba Zahedi

For her endless love, continuous inspiration to follow my dreams, always being by my side, and her heartfelt assistance throughout all arisen hardships

My amazing son, Mohammad Amin

For his endless love, ongoing encouragement and unconditional supports specially during my Ph.D. studies. I never forgot his words: “Dad! I fully standing at your back to support”

For their supports and unconditional loves, I couldn’t finish this thesis

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Nomenclature

AOP	Advanced Oxidation Process
A.A.	Atomic Absorption
ANOVA	Analysis of Variance
AO / EMBR 1	Hybrid system in effluent matrix without ECs
AO / EMBR 2	Hybrid system in effluent matrix with ECs
AO / EMBR 3	Hybrid system in influent matrix with ECs
AO / MEBR	Advanced Oxidation/ Membrane Electro Bio-Reactor
APCI	Atmospheric Pressure Chemical Ionization
BP-172	By-product 172
BP-270	By-product 270
BP-288	By-product 288
BP-99	By-product 99
BPs	By-products
BPs	By-Products
C_f	Final concentration
C_{in}	Initial concentration
CO_3^{2-}	Carbonate ion
COD	Chemical Oxygen Demand
DBPs	Disinfection By-Products
diss. 1	air dissolution for 5 min in water before treatment @ 1 L/min
diss. 5	air dissolution for 30 min in water before treatment @ 5 L/min
DIW	Deionized Water
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
EBR	Electro Bioreactor
ECs	Emerging Contaminants
EDCs	Endocrine Disrupting Chemicals
EE2	17 –Alpha Ethinyl Estradiol
E_{EO}	Electrical Energy Per Order
Eff	Effluent
EfOM	Effluent Organic Matter
ESI	Electro Spray Ionization
FWHM	Full Width at Half Maximum
GAC	Granular Activated Carbon
H_2O_2	Hydrogen Peroxide
HAAs	Haloacetic Acids
HCO_3^-	Bicarbonate ion
HPLC	High Performance Liquid Chromatography

Ka	Acid dissociation constant
*K*ow	Octanol–water partitioning coefficient
kWh	Kilo Watt Hour
LC-MS-MS	Liquid Chromatography Mass Spectrometer
LC-QTOF-MS	Liquid Chromatography Quadrupole Time of Flight Mass
LP-UV	Low Pressure UV
m/z	Mass to charge ration
MEBR	Electro Membrane Bioreactor
mg/ L	Milligram Per Liter
μγ/Λ	Micro Gram Per Liter
min	Minute
mJ	Millijoule
mM	Millimolar
MP-UV	Medium Pressure UV
mW	Milliwatt
ng/L	Nanogram Per Liter
NIOSH	National Institute of Occupational Health and Safety
NOM	Natural Organic Matter
PCM	Paracetamol
Ph.	Phase
PhACs	Pharmaceutical Active Compounds
Pka	Logarithm of ka
ppb	Part Per Billion
PPCPs	Pharmaceuticals and Personal Care Products
R%	Removal efficiency percentage
ROS	Reactive Oxygen Species
RW	River water
SMX	Sulfamethoxazole
SOM	Synthetic Organic Matter
SPE	Solid Phase Extraction
St.	Stage
SUVA	Specific UV Absorbance
TBA	Tertiary Butyl Alcohol `
THMs	Trihalomethanes
TOC	Total Organic Carbon
TW	Tap Water
US-EPA	United States - Environmental Protection Agency
UV	Ultraviolet
UV-Vis	Ultraviolet -Visible
UVC	Ultraviolet C
UVT	UV Transmittance
VUV	Vacuum UV
W	Watts

W.W.	Wastewater
WWTP	Wastewater Treatment Plant
ε	Molar Absorption Coefficient
μM	Micro Molar
$\boldsymbol{X_1, X_2, X_3}$	X_1 = H_2O_2 dose, X_2= aeration rate, X_3 = pH

1 Introduction

1.1 Background

The widespread detection of emerging contaminants (ECs) in wastewater effluents, rivers and even in drinking water in the range of µg/L to ng/L have been reported in many studies (Fazeli et al. 2019; Luis and Jover 2014; Luo et al. 2014; Terzić et al. 2008; Brion et al. 2004).

Emerging contaminants are a wide range of synthetic chemicals in global use that have recently been monitored by advances in toxicological knowledge, analytical instruments and risk assessments (Zhang et al. 2018; Eriksson et al. 2017). However, ECs were not commonly detected in the past but have potential to enter the environment. A wide range of ECs include hormones, pharmaceuticals and personal care products (PPCPs), endocrine disrupting chemicals (EDCs), pesticides, detergents, flame-retardants, pharmaceutical active compounds (PhACs), and textile chemicals (Yan et al. 2010; Glassmeyer et al. 2017). Only in Europe, 100,000 chemicals are in use, 30% of which are of environmental relevance and the concentration of pollutants in some cases is in the range of mg/L (Cabrera-Rodríguez et al. 2018; Luis et al. 2014). For example, polyfluorinated alkyl substances (PFAS) and perfluorooctanoic acid (PFOA) have been detected and contributed to contamination of drinking water supplies (McCarthy et al. 2017; Lei et al. 2015).

The concentration of these ECs are higher than limit value in several European countries (Buekers et al. 2018; Gavrilescu et al. 2015a). Concentrations of perfluoro-sulfonic acid (PFOS) and perfluoro-octanoic acid (PFOA) in drinking water and even in the blood of European citizens were above the limit value for individuals at more contaminated sites (Dauchy 2019; European Commission 2018; Brack et al. 2017; Buekers et al. 2018).

Accordingly, a large diversity of pollutants is released to the environment (Giannakis et al. 2015; Gregorio et al. 2014). The number and diversity of pollutants in water bodies has increased in comparison to the recent past (Boix et al. 2016). This large increase is due to everyday administrated PPCPs and extensive application of ECs in agriculture, transport and industry (Murnyak et al. 2011; Soberman et al. 2020). Therefore, ECs are daily adding to the environment as nonbiodegradable materials and hazardous wastes (Gavrilescu et al. 2015a). Another main cause of increasing levels of ECs in the environment is limited capabilities of conventional wastewater treatment plants to remove them sufficiently. The occurrence of ECs in water resources have stimulated increasing concerns. Because, a variety of adverse effects on environment and public health have been linked to the presence of ECs in surface and ground waters. Furthermore, the ecotoxicological effect of ECs and their potential hazards raises public concerns due to low biodegradability and frequent detection in the environment (Gong et al. 2018; Catalá et al. 2015).

There is no strong evidence and enough literature to prove or disprove the direct impact of ECs on human health. However, researchers reported the environmental impact of endocrine disrupting chemicals (EDCs) at ng/L concentrations (Luo et al. 2014b; Brian et al. 2007; Kidd et al. 2007; Stewart et al. 2014). The impact had clear toxicity towards certain aquatic organisms (Crane et al. 2006; Santos et al. 2010; Barbosa et al. 2016; Osorio et al. 2016; Bourioug et al. 2018).

The presence of ECs in drinking water (S A Snyder et al. 2007; Leung et al. 2013; Machado et al. 2016; Furlong et al. 2017) and source waters have been proved even at ng/l concentrations (Alder et al. 2010; Kasprzyk-Hordern et al. 2009; S. D. Kim et al. 2007; Teodosiu et al. 2018; Peña-Guzmán et al. 2019).

Sulfamethoxazole (SMX), paracetamol (PCM) and 17- alpha ethynylestradiol (EE2) are amongst ECs that their traces (in ppb to ppt) have been found in surface water (Behera et al. 2011; Roberts et al. 2006; Drillia et al. 2005; Göbel et al. 2005). These pollutants persist in the environment due to insufficient removal at the wastewater treatment plants (WWTPs) (Almuktar et al. 2018; Haiba et al. 2016). Therefore, finding a solution to treat these pharmaceuticals effectively from effluents before discharging into the surface waters is an urgent need.

1.2 Problem statement

Emerging contaminants are widely spread in lakes, rivers, estuaries, reservoirs, marine waters, surface water and wastewater effluents, at a concentration over ng/L (Barbosa Junior et al. 2016; Gavrilescu et al. 2015a; 2015b). This problem comes from insufficient elimination of ECs in current wastewater treatment plants (Deblonde et al. 2011; Rosal et al. 2010; Amin et al. 2014; Bolong et al. 2009).

Researchers reported several pharmaceuticals and ECs in drinking water output treatment facilities amongst 20 water treatment units (Schriks et al. 2010; Jardim et al. 2012; Fawell et al. 2012; Machado et al. 2016; Glassmeyer et al. 2017; Furlong et al. 2017; Riva et al. 2018). One of the main causes of the presence of these pollutants in water bodies is wastewater effluent (EfOM) discharge into the surrounding surface water sources which are treated inefficiently (Naidoo et al. 2013; Lonigro et al. 2016; Chaudhry et al. 2017; Almuktar et al. 2018).

Effluent organic matter (EfOM) mainly consists of a mixture of PhACs and EDCs, proteins, lipids, polysaccharides, humic materials and polyphenols (Almuktar et al. 2018; Chaudhry et al. 2017; Lonigro et al. 2016; Naidoo et al. 2013). This mixture could be named as dissolved organic matter (DOM) (Chefetz et al. 2006; Ilani et al. 2005; Guillossou et al. 2020). The DOM can contribute to forming by-products (BPs) upon a certain treatment condition and can affect water quality (Matilainen et al. 2011; Sun et al. 2019).

Effluent organic matter (EfOM) from WWTPs carry all ECs from industry and other sources of contaminant points. ECs present a slow biodegradability or non-biodegradability behavior in the environment. Therefore, most attention should be paid to increase the removal of dissolved organic carbon (DOC) from wastewater effluent (Gatidou et al. 2019; Arvaniti et al. 2015). Due to the occurrence of ECs in water resources and their impact on the environment, there is an urgent need for investigation and application of new technologies to remove ECs (Sorlini et al. 2014; Gavrilescu et al. 2015a; Bui et al. 2016; Stefan 2017; Khanzada et al. 2020). Many technologies have been examined for the removal of ECs from water streams and surface waters and effluent wastewater. Amongst these technologies, advanced oxidation processes (AOPs), such as UV/H_2O_2 AOP and UV/O_3 AOP, have been identified as an effective technology to decompose recalcitrant ECs (Aoudj et al. 2019; Pesqueira et al. 2020). Although UV oxidation processes present a viable and promising technology to remove micropollutants, there is a rising concern about the potential production of degradation BPs and increasing potential hazard (Richardson et al. 2012; 2007; Richardson 2003; Richardson et al. 2011; Bond et al. 2011). Furthermore, high energy consumption of AOPs is an obstacle of this technology especially when applied for wastewater treatment directly. In addition, a low quantum yield that results from shielding UV irradiation in a high concentration of EfOM, limits direct AOP application for wastewater treatment. In summary, AOPs for the elimination of ECs have faced the following challenges:

1) Reduction of ECs target pollutant's degradation rate due to a high load of EfOM
2) Scavenging of OH radicals by EfOM
3) Excessive energy consumption by AOPs due to a high EfOM load.

4) Production of larger amounts and diversity of by-products.
5) Toxicity elevation because of miscellaneous by-products accumulation.
6) Low quantum yield of AOPs.

Therefore, in order to increase the efficiency of AOPs, a hybrid system including a pre-treatment leading to a minimal DOC output, energy saving, and minimization of BPs formation is required. The AOP system can be used downstream of a pre-treatment setup.

1.3 Objectives

AOP is a viable and robust method targeting ECs removal from aqueous matrix, thus, it might be applied to enhance the quality of water and particularly the effluent generated by wastewater treatment plant. Such successful approach would provide new water resources. However, conducted studies should consider a number of issues which are not always addressed in other works. On account of limitations on AOPs that were discussed in the previous section, the main objective of this research is considered as follows:

- Enhance potential of water reuse by developing an AO-MEBR (advance oxidation/ membrane electro- bioreactor) hybrid system for wastewater treatment, targeting residual organic matter (EfOM), emerging contaminants (ECs) and their by-products removal in accordance with sustainable development principles.

In order to address this objective, the following sub-objectives were comprehensively defined:

- To design and install a reactor to implement UV/H_2O_2 AOP treatment, in order to remove emerging contaminants (ECs) from water and wastewater effluents.
- To design and manufacture an UV/O_3 AOP pilot scale reactor to eliminate ECs.

- To investigate the effectiveness potential of UV/H_2O_2 AOP as water /wastewater remediation technology for elimination of ECs.
- To investigate the effectiveness potential of UV/O_3 AOP pilot as water treatment technology.
- To maximize organic matter (EfOM) removal from effluent, while minimizing by-product formation under best operational conditions.
- To investigate micropollutants removal in both water and effluent matrices (EfOM) by AOP.
- To identify target pollutants by-products generated during AOP oxidation
- To evaluate the persistence of target pollutant (SMX, PCM, CAF, EE2) in different aqueous matrices (DI water, river and effluent)
- To investigate target micropollutants' removal with the application of a hybrid system in the MEBR pilot plant.
- To define an impact of operational conditions, including UV dose, oxidant dose, pH, aeration and scavenger's prohibition, on the removal performance.
- To define optimal operational conditions in order to enhance the performance of a hybrid system at a pilot scale.
- To investigate the target micropollutant's degradation pathway by highlighting the main by-products formation.
- To investigate the effect of operational parameters on parent ion and BPs evolution and potential toxicity.
- To validate AOP photolysis models based on experimental results.

1.4 Research novelty

- Application of a hybrid AO-MEBR system to target simultaneously micropollutants' elimination and effluent organic matter removal following sustainable development principles.

- Application of a hybrid treatment system to simultaneously maximize OH radical reactivity (to an efficient removal of micropollutants) and minimize the BPs formation potential by minimizing BPs precursors.

- Defining the operational conditions impact on target compounds by-products formation and their potential toxicity in water matrix.

- Describing of the operational conditions impact within hybrid AO/MEBR system on by-products formation in a real effluent matrix.

1.5 Thesis structure

The thesis experimental work consists of eight phases and several stages which are described in detail in Chapter 3 and the research outcome in Chapter 4.

Chapter 1 provides introduction, background, problem statement, thesis objective and the novelty of the research. Chapter 2 presents the literature review of advanced oxidation processes and the type of the most viable methods including UV/H_2O_2 AOP and UV/O_3 AOP. The advantages and limitations of the methods are also reviewed. Furthermore, Chapter 2 reviews the previous investigations on pharmaceuticals removal and the mechanism of photolysis, and ozone-based process with focus on ozone based and hydrogen peroxide photolysis. Moreover, in this chapter the by-products formation resulting from AOP methods is discussed. The methodology of this research is provided in Chapter 3. The designing and manufacturing of the experimental setup in both lab scale and pilot scales are discussed. Materials and chemicals for the experiments, target pollutants and the analytical methods are also defined in this chapter. The experimental design and operational parameters are also defined.

In Chapter 4, the major outcome of this research work is discussed. Degradation and elimination of four selected target pollutants by AOPs and then AO-MEBR hybrid system are shown as well. The removal of target micropollutants such as paracetamol (PCM), caffeine (CAF), sulfamethoxazole (SMX) and 17-alpha ethynylestradiol (EE2) is disused with respect to various operation conditions. Evolution of the parent ion and its by-products is monitored and discussed. The effect of technological parameters and the type of aqueous matrix on by-products evolution and their degradation pathways are also discussed in this chapter.

Chapter 5 includes conclusion, contribution, as well as recommendations for future work.

2 Literature review

At the beginning of this chapter most common AOP systems including (H_2O_2/O_3), (O_3/UV) and (H_2O_2 /UV) are introduced as well as the role of ozone and OH radicals to oxidize target pollutants in water samples are described. The priority of selected target pollutants in this review is discussed based on evaluation parameters. Considering research objectives, recent developments of UV based AOPs are reviewed and discussed in section 2.2. Recent studies on AOPs by-product formation are defined in section 2.3, where the background about factors affecting by-products formation and methods of their control are included. Furthermore, it deals with the current gaps and advancements in target topics. The reviewed papers with a summary of their experimental conditions are presented in Tables 2.4 and 2.5.

2.1 Advanced oxidation processes

Removing persistent organic pollutants from water, requires alternative water treatment technologies since conventional water treatment facilities are unable to treat recalcitrant micro pollutants completely. Advanced Oxidation Processes (AOPs) are among promising technologies to degrade high chemically stable and/or low biodegradability emerging contaminants (ECs) due to producing highly reactive OH radicals, which react with most organic pollutants non-selectively (Amor et al. 2019; Jiménez et al. 2018; Krzemińska et al. 2015; Chemlal et al. 2014; Vincenzo Naddeo 2013; Oller et al. 2011).

Applying one of the highly reactive oxidants, i.e. hydroxyl radicals (•OH) to oxidize organic contaminants using the term advanced oxidation processes for these methods. In which

UV light and hydrogen peroxide and /or ozone is utilized and oxidation carried out through a chain of radical reactions (Miklos et al. 2018; Krishnan et al. 2017; Stefan 2017; Y. Lee et al. 2016; Ribeiro et al. 2015a; Luo et al. 2014a; J. L. Wang et al. 2012; Andreozzi et al. 1999).

The most advantages of AOPs in comparison to conventional treatment methods can be described in production of OH radicals as known highly reactive species (Krishnan et al. 2017; Dewil et al. 2017; Tiwari et al. 2017)**.** The OH radicals can destroy non-selectively a wide range of synthetic organic chemicals (SOC) in a short time due to the nature of extremely rapid kinetics of OH radicals (Krishnan et al. 2017; Oturan et al. 2014).

The wide range of SOCs include pesticides, fuels, solvents, PPCPs, endocrine disrupting chemicals (EDCs). Hydroxide radicals destroy high doses of SOC completely compared to other water treatments methods such as air stripping, adsorption, activated carbon and reverse osmosis (Von Sperling 2015; Dewil et al. 2017; Zhou et al. 2001; Gupta et al. 2012).

AOPs advantages are the ability to complete destruction of organic contaminant, non-volatile organics and organics that are not adsorbable and then not needing further treatment for treatment residual (Bui et al. 2016; Bethi et al. 2016; Teodosiu et al. 2018)**.**

Advanced Oxidation Processes (AOPs) are usually expensive due to high electricity consumption for UV and ozone generation in situ. However, AOP technologies have the ability to mineralize recalcitrant organics completely and reduce contaminants concentration from hundreds of mg/L to less than 5ppb (Rein Munter 2001; Oturan et al. 2014)**.** Furthermore, AOPs appeal is for working on near ambient pressure and temperature and not needing high pressure to operate and also not facing fouling and plugging problems (Matilainen et al. 2010a; Lamsal et al. 2011; Sillanpää et al. 2018)**.** However, other methods such as reverse osmosis (RO), nanofiltration (NO), ultrafiltration (UF) and microfiltration (MF) have these limitation (Crittenden et al. 2012b; Davis

2010; Zhou et al. 2001; Paździor et al. 2019). For example activated carbon needs carbon regeneration and this technology can remove hydrophobic non-polar organics with $K_{OW} > 2$ (Huggins et al. 2016; Çeçen et al. 2011; Imai et al. 2002).

2.1.1 Typical AOPs systems

Combinations of ozone with UV and /or hydrogen peroxide are examples of typical AOP systems such as:

- Hydrogen peroxide / Ozone (H_2O_2/O_3)
- Ozone / UV Irradiation (O_3/UV)
- Hydrogen peroxide / UV Irradiation (H_2O_2/UV)

In comparison with the other AOPs, the combination of UV with ozone and/or H_2O_2 have the most oxidation potential (Rein Munter 2001; Esplugas et al. 2002).

The reaction of ozone with hydrogen peroxide in H_2O_2/O_3 system, produce 2 moles of OH^0 radicals (Contreras et al. 2016; Stepnowski et al. 2005).

$$2\,O_3 + H_2O_2 \rightarrow 2OH^0 + 3O_2 \qquad (2.1)$$

Ozone with exposure of UV light produces both hydrogen peroxide and hydroxide radicals.

$$3\,O_3 + H_2O + h\nu \rightarrow 4\,O_2 + 2\,OH^0 \qquad (2.2)$$

In the presence of UV irradiation, hydrogen peroxide dissociates to hydroxide radicals (Esplugas et al. 2002; Contreras et al. 2016).

$$H_2O_2 + h\nu \rightarrow 2\,OH^0 \qquad (2.3)$$

2.1.2 Reactions mechanism and kinetics

Chemical species in water absorb UV light at a specific wavelength and the corresponding absorption (A) is defined by Beer-Lambert law ($A = \varepsilon\ b\ c$). At a specific wavelength, the molar absorption coefficient (ε) defines how strongly a chemical species absorb the light (Babu et al. 2019; Babuponnusami et al. 2012). Ozone and hydrogen peroxide in aqueous solution absorb UV radiations between 200 and 360 nm, with a maximum at 253.7 nm. For ozone, the molar absorption coefficient is : O_3 $\varepsilon_{max} = 3600$ L mol^{-1} cm^{-1} and for hydrogen peroxide is: H_2O_2 $\varepsilon_{max} = 18.6$ L mol^{-1} cm^{-1} (Teodosiu et al. 2018; Mohajerani et al. 2009; Simon Parsons 2004). Since the ε_{max} value of O_3 is much larger than that of H_2O_2 at this wavelength, the ozone photolysis process should be more efficient in this condition ($\lambda = 253.7$ nm) than H_2O_2 photolysis (Simon Parsons 2005; Sivagami et al. 2018). However, there are other factors that should be considered such as the cost of the reactants and end products during the treatment if comparison between ozone and H_2O_2 photolysis is considered. (S. Parsons 2015; Boczkaj et al. 2017; Kanakaraju et al. 2018). In AOP UV/ H_2O_2 system, the oxidation mechanism for destruction of target pollutants could be performed by indirect reaction with hydroxyl radicals and/or direct photolysis with UV irradiation (Movahedyan et al. 2009; Mota et al. 2009). Hydrogen peroxide goes to photolytic dissociation in water by UV light and consequently destruction of organic pollutants occurs by highly reactive OH radicals formed in this process.

$$H_2O_2 + h\nu \rightarrow 2\,{\bullet}OH \qquad (2.3)$$

$$HO_2^- + h\nu \rightarrow {\bullet}OH + O{\bullet}^- \qquad (2.4)$$

$$HO_2^- + O{\bullet}^- \rightarrow O_2{\bullet}^- + OH^- \qquad (2.5)$$

The reaction of ozone with target compounds may be directly by molecular ozone or indirectly by

OH radicals that are produced either by UV irradiation or by ozone under certain conditions (Kanakaraju et al. 2018). Therefore, in ozone reactions, two different reaction pathways lead to different reaction products. Indirect reactions involve ozone dissociation initiated by OH^- anions (Von Gunten 2003a; Gómez-Ramos et al. 2011; Rosal et al. 2010).

$$O_3 + H_2O \rightarrow O_2 + H_2O_2 \quad (2.6)$$

$$2\,O_3 + H_2O_2 \rightarrow 2\,{}^{\bullet}OH + 3\,O_2 \quad (2.7)$$

$$3\,O_3 + OH^- + H^+ \rightarrow 2\,{}^{\bullet}OH + 4\,O_2 \quad (2.8)$$

Ozone in direct reactions oxidizes organic compounds selectively. Unsaturated bonds of molecules such as aromatics and phenols are broken by ozone in aqueous media (Figure 2.1). The reaction rate constant (k) where direct pathway is dominant is typically between 1 to 10^3 M^{-1} s^{-1} (Von Gunten 2003b; Mehrjouei et al. 2015). In some water samples where radical scavenger (carbonate and bicarbonate) concentrations are high, ozone reaction leads to direct oxidation of pollutants. By changing the pH to acidic levels of less than 4, the reaction mechanism tends to fulfill the direct pathway. However, in basic pH values of greater than 10, the reaction proceeds by indirect mechanism (Nakada et al. 2007; Gottschalk et al. 2010).

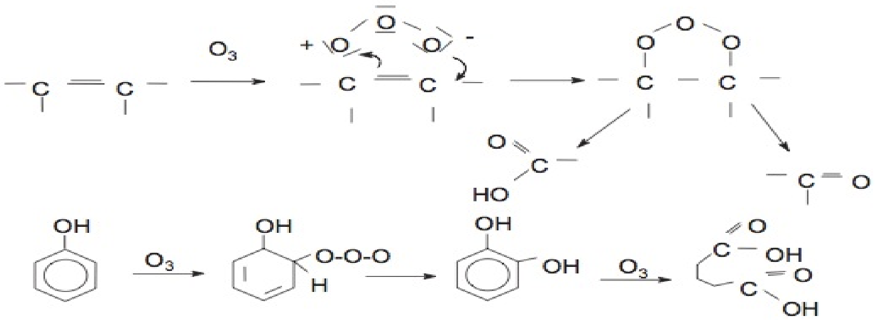


Figure 2.1 Direct reaction of ozone with organic compound (Gottschalk et al. 2010)

By adding hydrogen peroxide or by increasing the pH, the rate of ozone decomposition can be increased significantly (Gottschalk et al. 2009). The pH of water is important because hydroxide ions initiate ozone decomposition (Cai et al. 2016; Acero et al. 2000). Hydroxyl radicals, produced by ozone decomposition in water, are one of the strongest oxidants in water (David Yao et al. 1991).

According to the direct reaction of ozone with dissolved matter (solute), decomposition of ozone, and the subsequent reaction of decomposed ozone with the solutes, it has a complex behaviour in water. On account of dependence of most ozone reactions to pH and its dose, under various treatment conditions, the results would be different (Yao et al. 1991; Gottschalk et al. 2008). By considering the existence of natural organic matter (NOM) in water resources, one of the most problematic issues related to pre-ozonation of surface waters is the formation of DBPs (Wert et al. 2007a; Shane A Snyder et al. 2003; Richardson et al. 2011).

Additional problems occur from the need to remove trace organics and post treatment after oxidation, as well as bacterial regrowth in water distribution systems, etc. Mechanism of ozone reaction in direct oxidation of organics leads to the formation of compounds such as aldehydes, ketones, and aliphatic acids. Ozonation of river water may lead to the production of low molecular weight DBPs (Hammes, Salhi, Köster, Kaiser, Egli, and Von Gunten 2006; Saskia G Zimmermann et al. 2011).

Examples include aldehydes and ketones whose production is controlled by ozonation contact time and residual concentrations and types of precursors. Decomposition of ozone at neutral and basic pH occurs more often than at acidic pH (Saskia G. Zimmermann et al. 2011; Tay et al. 2015). In order to control ozone reactions, the water pH and concentration of dissolved ozone in water should be controlled. Under various controlling parameters and conditions, different types of products may form. To prevent DBPs formation, optimal dosage of ozone should be used which may range between 0.5 - 2 g of ozone per gram of DOC (Cai et al. 2016; Hammes, Salhi, Köster, Kaiser, Egli, and Von Gunten 2006).

2.1.3 Hydroxyl radical and superoxide mechanisms

The main mechanism for destruction of organic pollutants can be described through oxidation of these contaminants by hydroxyl radicals which are generated in advanced oxidation processes (AOPs) (Howe et al. 2013; Crittenden et al. 2012a).

As described earlier, the production of hydroxyl radicals is performed by direct photolysis or indirect oxidation. In order to obtain maximum OH radical formation during AOPs, an optimum oxidant dosage and irradiation is required (Guan et al. 2018; Vaughan et al. 1998).

Table 2.1. Relative oxidation power (after Parsons and Williams 2004; Carey 1992)

Oxidizing agent	Oxidation potential(V)
Fluorine	3.06
Hydroxyl radical	2.80
Oxygen (atom)	2.42
Ozone	2.08
Hypochlorite	1.49
Chlorine	1.36
Hydrogen peroxide	1.31
Chlorine dioxide	1.27
Oxygen (molecule)	1.24
Permanganate	1.23

As it is shown in Table 2.1, the hydroxyl radical is much stronger than other strong oxidants such as chlorine, hydrogen peroxide and ozone. Extremely rapid kinetics of OH radicals in comparison to reaction rate constants of ozone with organic compounds, expected a very fast and short time of treatment for AOPs due to production of OH radicals (Liang et al. 2009).

Table 2.2. Reaction rate constants (k, M^{-1} s^{-1}) of ozone vs. hydroxyl radical (after Munter 2001)

Compound	**O_3**	**$^{\bullet}OH$**
Chlorinated alkenes	10^3-10^4	10^9-10^{11}
Phenols	10^3	10^9-10^{10}
N-containing organics	10-10^2	10^8-10^{11}
Aromatics	1-10^2	10^8-10^{11}
Ketones	1	10^9-10^{10}
Alcohols	10^{-2} - 1	10^8-10^9

The OH radicals attack aggressively to organic contaminants by two types of mechanisms. The first mechanism is hydrogen abstraction from the target compound and the second mechanism is adding OH radical to contaminant. In the mechanism of hydrogen atom abstraction, a chain of radical oxidation initiates (Turchi et al. 1990).

$$^{\bullet}OH + RH \rightarrow {}^{\bullet}R + H_2O \text{ (hydrogen abstraction)} \quad (2.9)$$

$$^{\bullet}R + O_2^{-} \rightarrow {}^{\bullet}RO_2 \quad (2.10)$$

$$RX + {}^{\bullet}OH^{-} \rightarrow {}^{\bullet}RX^{+} + OH^{-} \rightarrow \text{(electron transfer to hydroxyl radical)} \quad (2.11)$$

Reaction of methanol with OH radical in the presence of oxygen is an example of a hydrogen abstraction mechanism which leads to complete mineralization of methanol. The efficiency of water treatment and rate of reactions, which are conducted by OH radical oxidation, depends on contaminant concentration and the nature of organic compound (An et al. 2010).

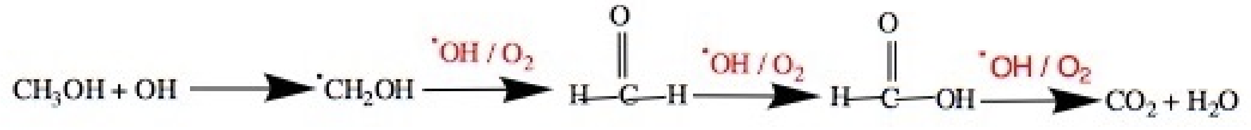


Figure 2.2. Reaction of methanol with OH radical (R. Munter 2001)

The superoxide ion ($O_2^{\bullet -}$) as a highly reactive radical has an important role in the treatment of contaminated soil, groundwater and in the destruction of organic contaminants in both aqueous and non-aqueous phases (Hayyan et al. 2016; Kalyanaraman et al. 2017).

This radical can be produced when oxygen molecule (O_2) is reduced through disproportionation reactions in simultaneous oxidation/reduction mechanisms. The reduction of oxygen (O_2) is performed in chemical and electrochemical methods by adding one electron to the oxygen molecule. In these methods, hydroperoxyl radical species are formed as an intermediate and then by subtracting one hydronium ion, it changes to the superoxide.

$$O_2 + H^+ + e^- \rightarrow HO_2^{\bullet} \qquad (2.12)$$

$$HO_2^{\bullet} \rightarrow H^+ + {}^{\bullet}O_2^- \qquad (2.13)$$

Mechanism for pollutants destruction can be described as nucleophilic substitution of ${}^{\bullet}O_2^-$ to the target contaminant and contribution in the transition state by electron transfer as illustrated in the following equation (Koppenol 1990).

$$O_2^{\bullet -} + AX \quad \rightarrow \quad [O_2^{\bullet -} \cdots A \cdots X \rightleftarrows O_2 \cdots A \cdots X^{-}] \quad \rightarrow AO_2^{\bullet} + X^{-} \qquad (2.14)$$

2.1.4 Target pollutants and their priority to choose

Based on an extensive literature review on the types, concentrations and appearance of ECs and trace pollutants in drinking water, surface water and groundwater, seventy one compounds have been identified to be the most prominent (Murray et al. 2010; Gavrilescu et al. 2015b).

The ECs with the highest priority have been identified to be industrial chemicals, pesticides, pharmaceuticals and personal care products (PPCPs) that have been the subject of regulation and require the highest degree of treatments (Murray et al. 2010). These chemicals are frequently detected in European rivers, U.S. streams and groundwater and Canadian rivers. These pharmaceutical compounds at concentrations similar to those detected elsewhere in North America are distributed in surface waters in Quebec (Yargeau et al. 2007; Atkinson et al. 2012). Yargeau et al (2007) reported that the Yamaska River basin in Quebec is highly polluted by pharmaceuticals with concentrations ranging from 1-578 ng/L. Sulfamethoxazole, paracetamol and carbamazepine were present at concentrations up to 578 ng/L and 106 ng/L, respectively. By considering the acceptable daily intake (ADI) for humans, the priority pollutants that pose a serious risk to human's health include PPCPs, 17alpha-ethinylestradiol (EE2) and carbamazepine (Murray et al. 2010). Three target compounds including acetaminophen, 17alpha-ethinylestradiol (EE2) and sulfamethoxazole were chosen for the present research, based on the following reasons:

A- Frequency of appearance in Canadian water and wastewater

B- Potential health hazard posed by these chemicals

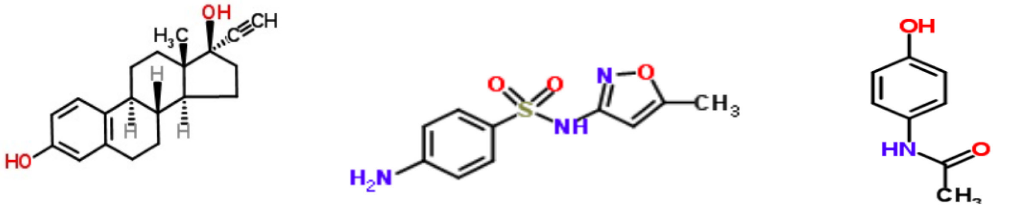
C- Possible detection of these chemicals by available instruments, e.g. LC-MS/MS

Another classification that was considered for these pharmaceuticals is the order of their removal efficiency by conventional activated sludge treatment (Sipma et al. 2010; H. Jones et al. 2005). EE2 is very hard to remove in comparison to sulfamethoxazole (Table 2.3) and paracetamol can be removed more easily in comparison to two other compounds. USEPA and European Union (EU) have recognized these pharmaceuticals as emerging contaminants that require regulation in future, on account of their impact on the ecological environment and their persistence in the water body system (Westerhoff et al. 2005). One further priority consideration for three pharmaceuticals is their chemical structure. EE2 has three aromatic rings, SMX has two and PCM has one aromatic ring, which may have different responses to the molecule breakdown and dissociation products.

Table 2.3. Removal comparison of different classes of pharmaceuticals (after Sipma et al.,2010)

Group	**Pharmaceutical**	**Log *K*ow***	**pKa**	**Therapeutic class**
High removal (>65%)	Paracetamol (PCM)	0.27	9.46	Analgesic
Medium removal (30 ~ 65%)	Sulfamethoxazole (SMX)	0.48	5.5	Antibiotic
Low removal (<30%)	17alpha-ethinylestradiol (EE2)	3.67	10.33	Contraceptive

* *K*ow = Octanol–water partitioning coefficient



EE2 **SMX** **PCM**

Figure 2.3. Target pollutants' structure; The National Center for Biotechnology Information

2.2 Recent developments in UV-based AOPs

AOPs in all water treatment methods benefit oxidant photolysis, which yields highly reactive OH radicals to destroy contaminants. In the corresponding procedures, oxidative degradation of organic pollutants happened by applying photochemical methods in the aquatic media. The following review includes recent developments in which researchers applied either alone or/and combination of UV, H_2O_2 and O_3. In some studies, authors added some catalysts (TiO_2, Fe^{2+}/Fe^{3+}) or make combinations of oxidant and/or catalysts, e.g. Fenton (H_2O_2 / Fe^{2+}/Fe^{3+}) or Photo-Fenton (UV/ H_2O_2 / Fe^{2+}/Fe^{3+}) to their experiments. A summary of data and experiment conditions, results and limitations are listed in Table 2.4.

2.2.1 General developments

The treatment results of different kinds of single organic pollutants, PPCPs, NOM and EDCs by AOPs are shown in Table 2.4 and 2.5. The review of these results and comparing them give an insight to method validation of AOPs. Table 2.4 corresponds to the result of ozone based AOPs, H_2O_2 based AOPs and other photo catalysis AOPs. The studies represent removal efficiency of different types of AOPs and capability of each AOP to remove emerging contaminants. Table 2.5 compares different types of ozone and H_2O_2 based AOPs in order to find the best choice for treatment. Almost in most studies, researches have used synthetic water, including a single or group of emerging contaminants, and their experiments were carried out at bench scale and batch mode and concentrations around mg/L of pollutants. However, emerging contaminants have occurrences in environment water body at concentrations between µg/L to ng/L. According to the information summarized in table 2.4 and other information in the reviewed papers, the researchers have used sole UV and sole ozone methods to remove different types of emerging contaminants and then compared the results to the AOPs in which oxidant/UV were applied simultaneously. The highlighted point in all studies is the dependence of pollutant degradation on the nature of target compounds even by AOPs or UV and sole ozone (I. H. Kim et al. 2008).

Post-ozonation after UV irradiation or pre-ozonation before UV irradiation had no significant effect on TOC removal. For most of the compounds including antibiotics, antiepileptic and anti-inflammatories, removal efficiency obtained more than 80%. However, some organic pollutants such as chlorophenols are more resistant to oxidation and removal from the water in comparison to the above-mentioned compounds. Other researchers used catalyzed based methods including TiO_2 and Fenton treatment. Similar to ozone and H_2O_2 based AOPs, photo catalysis AOPs revealed much higher TOC removal in comparison to using these methods without UV irradiation. In the other word, TOC removal in all non-UV oxidation methods is lower than UV based oxidation processes. In order to reach higher removals, most researchers applied higher UV doses and/or higher oxidant doses and showed satisfactory results according to the destruction of target pollutant(s). However, some of these studies noted higher TOC removal and others did not note about TOC change or noted un-changed TOC.

Another remarkable point is evaluation of emerging contaminant removal by using total organic carbon (TOC) factor in water after each treatment. In most of the studies, researchers did not include data and parameters based on individual contaminant identification and/or removal efficiency. They measured only TOC as a mineralization factor for removal efficiency.

All AOPs have shown more TOC removal in comparison to using UV, ozone, or catalyst alone. However, TOC removal was not high (between 50% to 80%) in comparison to individual pollutant(s) removal, i.e. more than 90% in most cases. This remarkable point shows the existence of organic matter rather than target pollutants after treatment.

A brief review of recent studies about AOPs, which are mostly discussed for TOC removal efficiency, are presented in the following synthesized cases and corresponding remarkable points by highlighted gaps of knowledge are summarized in section 2.4.

Jeirani et al. (2015), studied effectiveness of different AOPs including UV, ozone and O_3/UV to remove manganese and dissolved organic compound (DOC) in a batch bench-scale setup (Jeirani et al. 2015). The sole UV was not an effective method to remove organic compounds, but it was suitable to decrease manganese. The sole Ozone in comparison to ozone/UV was effective to remove manganese even at lower oxidant dose (6.2 mg/L), however ozone/UV should apply the higher dose of oxidant to remove the same amount of manganese. The highest organic matter removal (89%) was obtained by AOP in comparison to ozone alone at higher oxidant dose (15.2 mg/L), but both ozone and AOP showed a similar removal efficiency of DOC with lower ozone concentration (6.2 mg/L).

The removal of 32 pharmaceuticals and endocrine disrupting compounds including caffeine, carbamazepine, ibuprofen and sulfamethoxazole with concentrations in the range of 170-

490 ng/L from water was evaluated through a pilot plant AOP system (Benotti et al. 2009). In this study, different combinations of UV radiation with oxidants, H_2O_2 and TiO_2 were used after microfiltration, and removal efficiency for 29 compounds was higher than 70% and for three of them, it was less than 50%. This result indicates a different response of some persistent pollutants to the same treatment condition. Researchers also calculated the energy consumption for this treatment. The electrical energy per order (E_{EO}) for UV/TiO_2 was higher in comparison to the UV/ H_2O_2 system, but authors did not include any explanation for this different result.

Table 2.4. Recent studies on ECs degradation by UV based AOPs

Reference	Contaminants Matrix	AOP System	Operational condition	Findings	Remarks
Chin and Berube (2005)	NOM/ Natural water mountain	UV/O_3 Lab 6.2L /Batch	LP-UV 9.69 mW/cm2 Ozone 0.29 L/min, 12.4 mg/min	Estimating AOP effectiveness to reduce DBPFP; 50% TOC 70-80%; THM – HAA	Measure BPs only by TOC Inject Chlorine Bleach to measure BPs
Peyton and Glaze (1988)	**THM precursors /in water**	**UV/O_3** **Lab 2L /Batch**	**LP-UV** **4 x1.6W/ 2.8×10^{-5} E/ (L. min)** **Ozone = 3×10^{5} mole/ (L. min)**	**Destruction of THM precursors**	**Lab scale /batch/No BPs measurement**
Benotti et al. (2009)	32 PPCPs /River water	UV/TiO_2 UV/H_2O_2 Continuous flow =24 L/m	LP-UV H_2O_2=10-20 ppm TiO_2 =50 ppm	Destruction of 32 EDCs	Lab scale /batch/No BPs measurement
Bottrel et al. (2015)	**Ethylene thiourea (ETU)/synthetized ETU solution (50 mg/L)**	**O_3/H_2O_2** **Lab 2 L/Batch**	**No UV/** **Ozone 12.1 mg/min** **H2O2 (30 % w/v) at concentrations of 400 and 800 mg/ L** **Ozonation was tested at pH=3.0 and 11.0**	**ozonation and peroxone processes are efficient methods to degrade ETU (50 mg /L) However, only the system with O3 at an alkaline pH (11) showed high mineralization efficiency.** **different byproducts produced in different condition (pH, H_2O_2 conc.)/ ethylene urea,** **2- imidazoline**	**reaction mechanism shows by-products rather than molecule fragments.**
Hernandez et al. (2002)	Acetone (5 PPM) Spiked to distilled water	UV/O_3 UV/H_2O_2 $O3/H_2O_2$ Lab 1L /Batch	LP-UV, 12 W MP-UV, 200 W - Ozone 2.25%w H_2O_2,100ppm	%99 removal for UV/O_3 in 30 min 10 ppm with 2% peroxone achieve %99 removal For UV/H_2O_2 more than 700 ppm has adverse effect on degradation.100 ppm is optimal	Lab scale /batch/No BPs measurement

Reference	**Contaminants Matrix**	**AOP System**	**Operational condition**	**Findings**	**Remarks**
Esplugas et al. (2002)	Phenol (100 ppm) /Spiked to distilled water	O_3/ UV/H_2O_2 > O_3 / H_2O_2 > UV/ H_2O_2 > UV/ O_3 Lab 4.5 L/Batch	MP-UV, 1500 W Ozone 0.2–0.3 g/h Different concentrations of H_2O_2	degradation rate with the UV/ H_2O_2 process was almost five times higher than photocatalysis and UV alone, maximum removal Up to %98	Lab scale /batch/No BPs measurement
Saritha et al. (2007)	**4-chloro-2 nitrophenol (100 ppm) /Spiked to distilled water**	**UV/Fenton > UV/TiO_2 > UV/ H_2O_2> Fenton > H_2O_2 > UV** **Lab 1 L/Batch**	**LP-UV, 16 W/ Different concentrations and ratios of oxidant. More than 200 ppm H_2O_2 has no increase of degradation**	**Degradation of 4C-2- NP was strongly accelerated by the photochemical oxidation processes. The optimum conditions obtained for the best degradation with Photo Fenton were pH 3, initial reactant concentration of 30 mg/l Fe2+ and 100 mg/l H_2O_2** **Up to %90/-**	**Lab scale /batch/No BPs measurement**
Collivignareli and Sorlini (2004)	Metolachlor, 10 μ g/L Geosmin, MIB /THMFP 70 μ g/L bromide =30 μ g/L. Surface water/ Q = 10 L/min	UV/O_3 Pilot / continuous	Two LP-UV intensity was about 25 W/m² / Ozone 10 ppm 8 g O_3/h UV 1400 mJ/cm²	Complete removal for all contaminants with 4–10 mg min/L ozone and UV doses of 4,00–6,00 mJ/cm2 15–30% lower for THMFP 40% lower bromate formation / THM precursors, Bromate	Measured BPs by TOC by inject Chlorine. No direct measurement
Shu and Chang (2005)	**Six azo dyes: Acid Orange 10, Acid Red 14 and 18; Acid Yellow 17; Direct Yellow 4; Acid Black** **Distilled water, wastewater**	**H_2O_2/UV**	**UVC; [H_2O_2] = 240 mg L^{-1}** **pH= 5.3** **[Azo dye]0 = 20.0 mg L–1**	**Color removal = 95% at time = 26–92 min; Consumed energy = 2141 × 10–3–7666 × 10–3 kWh, according to the dye**	**Lab scale /batch/No BPs measurement**

Reference	Contaminants Matrix	AOP System	Operational condition	Findings	Remarks
Wang et al. (2010)	**Dichloro acetic acid (DCAA) and trichloroacetic acid (TCAA), (2 PPM)/ Contaminants spiked to the deionized water**	**UV** **O_3** **UV/ O_3** **UV/H_2O_2** **O_3/H_2O_2** **UV/H_2O_2/ O_3** **Lab 2 L/ semi continuous**	**LP-UV, 15W** **Ozone adding 0.3 mg/min** **H_2O_2 2.5 mg/L**	**O_3 /UV showed to be more suitable for the decomposition of DCAA and TCAA in water among the six methods of oxidation** **add O_3 more than required dose is not effective. HCO_3^- and humic acid are radical scavengers which quench decomposition rate/ HAAs** **(there are no byproducts caused by treatment)**	**Measured BPs are not resulting from contaminants. They injected to** **deionized water**
Amirsardari et al.(2001)	TOC, TOX, THMs Turbidity, color, Coliforms/Raw water	O_3 UV/O_3 Pilot 13L/batch	LP-UV, 20W Ozone 1 lit/min	Precursors of TOX and THMs reduced by %98 and %90 Water quality parameters improved/ (THMs)	Measuring BPs precursors in the range of ug/L
Fdil et al. (2003)	**Five chloro - phenoxy acid herbicides: MCPA, MCPP, 2,4-D, 2,4-DP, 2,4,5-T** **Deionized water** `	**UV/O_3**	**UVC; [H_2O_2] = 170 ppm** **pH= 7.0**	**Total photodegradation time = 20–90 min; Mineralization yield (from COD) = 56–79%,**	**Lab scale /batch/No BPs measurement**
Alaton et al. (2002)	Simulated reactive dyebath effluents Mono-chlorotriazine type reactive dyes	H_2O_2/UV	UVC; [H_2O_2] = 680 mg L^{-1} pH= 3	TOC removal = 30.4%; EE_O = 0.633 kWh m^{-3}	Lab scale /batch/No BPs easurement

Reference	Contaminants Matrix	AOP System	Operational condition	Findings	Remarks
Momani et al. (2004)	2,4-dichlorophenol (DCP) (100 mg/L)	UV,UV/ H_2O_2 UV/Fe(III) Fenton Photo-Fenton/ Lab1.5 L/Batch	black–blue lamp 4 W, emits radiation basically at 350nm/ 75 mg/L H_2O_2 10 mg /L Fe(II)	UV photolysis was less efficient for total DCP degradation than other AOPs. In contrast, photo-Fenton reaction in acidic conditions led to a higher DCP degradation in a short time. Sixty minutes of treatment were sufficient for 100% DCP removal with 75 mg/L H_2O_2 and 10 mg /L Fe(II) initial concentration	Work at higher concentrations batch and lab scale and doesn't measure efficiency with more precise analytical instruments
Cruz et al. **(2012)**	**32 ECs including Acetaminophen, Ibuprofen,** **Caffeine,** **Carbamazepine sulfamethoxazole** **/ Waste water treatment plant effluent**	**UV_{254}** **UV/ H_2O_2** **UV/ $Fe^{2+,3+}$ Fenton** **Photo-Fenton/** **Lab/Batch**	**LP-UV** **55 mW/cm²** **, 1.5 $10^{!6}$ Einstein s^{-1}** **/ H_2O_2** **(10, 25 or 50 mg /L)** **5 mg L^{-1} of Fe^{2+} Pollutants initial concentrations ranged 112-578 ng/L and**	**photo-Fenton, employing UV_{254}, is highly efficient at natural pH.** **Best degradations were obtained as H_2O_2 concentration increased (97% of removal in 30 min for H_2O_2= 50 mg L^{-1} and Fe^{2+}= 5 mg/ L ; UV_{254}** **, Fenton, and photo-Fenton under simulated sunlight gave less promising results with lower percentages of removal**	**Lab scale /batch/No BPs measurement**
Peyton et al. (1987)	Methanol, t-butanol, formic acid/ Ground water	UV/O_3 Lab 10L /semi continuous	LP-UV/ 3 x 940 mW= 1.4 x 10^{-5} E/ (L. min) Ozone = 10^{-5}M/L	Model mass transfer and chemical reaction as function of ozone dose rate, UV intensity	Lab scale /batch/No BPs measurement

Comparison of advanced oxidation processes for decomposition of two halo acetic acids (HAAs), dichloro acetic acid (DCAA) and trichloro acetic acid (TCAA) from water, was studied by Wang, et al. 2009. Amongst UV, O_3, UV/O_3, UV/ H_2O_2, H_2O_2/O_3. UV/H_2O_2/O_3 systems, the UV/O_3 was found to be more effective than other AOPs. However, the UV/H_2O_2 /O_3 rate of reaction is nearly the same as the UV/O_3 system but greater for decomposition of two HAAs (K. Wang et al. 2009). In this study ozone was continuously added to the system but did not have an increased effect on HAA decomposition and it was not consumed more than a special amount. This finding could be more remarkable if the authors found out the ozone concentration interval for the system, but there was not any trace of it. On the other hand, providing information about the dose of other oxidants in the system, could be more applicable for future studies.

The degradation of 32 emerging contaminants including sulfamethoxazole, carbamazepine, and ibuprofen at concentrations in the range of 263-578 ng/l by UV, Fenton and photo- Fenton were studied by De la Cruz, et al. 2012. These investigators used a laboratory-scale operation in batch mode and employed UV_{254} nm irradiation with and without H_2O_2 and $Fe^{2+.}$ By increasing H_2O_2 concentration, the degradation was increased (De la Cruz et al. 2012). The best degradations, (97% and 100% removal in 30 minutes) were obtained at the H_2O_2 concentration of 50 mg/L and Fe^{2+} concentration of 5 mg/L.

Matilainen and Sillanpää (2010), reviewed and assessed recent studies to compare various AOPs for the removal of natural organic matter (NOM) from drinking water which is a source of BPs. They reported that the highest molecular weight NOM can be removed from water by conventional treatment methods and the rest can be removed by AOPs (Matilainen et al. 2010b). They also indicated that the formation and type of the generated BPs are strongly dependent on the nature and concentration of NOMs. They also referred to the works on combination of AOPs to BAC (Biological Activated Carbon), which can easily remove more biodegradable compounds formed during AOPs as well as remove BPs precursors. The authors discussed general developments on AOPs but did not review by-product formation.

Phenol mineralization and degradation was studied through various AOPs (O_3, O_3/H_2O_2, UV/H_2O_2, UV/O_3 and $UV/ H_2O_2/O_3$) by researchers (Kusic et al. 2006). Depending on H_2O_2 concentration and pH range, different phenol removal was achieved. The $UV/H_2O_2/O_3$ system was the most effective process for achieving the highest mineralization extent (58% TOC removal) while UV/O_3 was the fastest reaction for phenol degradation. On the other hand, UV/H_2O_2 was the only system where phenol removal was not complete (99.4%) and phenol by-products formation was greater in comparison to other systems (O_3, UV/ O_3, H_2O_2/O_3 and $UV/ H_2O_2/ O_3$). Authors investigated the dependence of phenol removal and by-product formation to pH change, but they did not investigate the dependence of by-products formation to UV dose and/or ozone concentration. Furthermore, they did not compare H_2O_2 systems in a constant dose to compare the effectiveness of AOP systems.

Esplugas et al. (2017), studied the impact of ozonation alone, as well as other AOPs, for removing endocrine disrupting chemicals (EDCs), and pharmaceuticals and personal care products (PPCPs) at μg/L concentrations from water. They demonstrated that by ozonation treatment, satisfactory removal was obtained. In most cases, some compounds such as antibiotics, pesticides, estrogens, antiepileptics, and anti-inflammatories were removed at efficiency higher than 90% by using an ozone dose in the range of 0.1 to 30 mg/L (Esplugas et al. 2007). Nevertheless, the removal of total organic carbon (TOC) was not significant, implying that in many cases the removal of organic compounds was not complete and resulted in the generation of by-products. However, when using AOPs such as UV/H_2O_2 and titanium dioxide photocatalysis (UV/TiO_2), 98% of the pollutants were removed.

Potential formation reduction of two by-products, trihalomethane and haloacetic acids, with ozone-UV advanced oxidation process was evaluated by Chin and Bérubé (2005). They showed that the ozone-UV process could remove up to 50% of the total organic carbon (TOC) and reduce trihalomethane (THMs) and haloacetic acids (HAAs) formation by about 80% and 70%, respectively (Chin et al. 2005). They measured BPs precursors (TOC amount) and only referred to THMs and HAAs formation potential. This experiment did not follow potential formation of ozonation by-products, dissociation intermediates such as aldehydes and ketones and/or bromate compounds, or oxidant exposure time and UV intensity as factors to contribute to the formation of BPs. In addition, this study only considered the NOM in water, and ignored the potential presence of synthetic organic matter (SOM) that often exists in river water and may contribute to the generation of BPs.

Other researchers compared three types of AOPs, including LP-UV/O_3, MP-UV/H_2O_2 and H_2O_2/O_3 processes for the treatment of acetone-contaminated water in a batch one liter glass reactor (Hernandez et al. 2002). The most efficient system was LP-UV/O_3, which showed 99% removal of contaminant in 30 minutes. The MP-UV/H_2O_2 process, using peroxide (H_2O_2) at concentrations higher than 700 mg/L, had an adverse effect on acetone removal due to the loss of hydroxyl radicals, which were removed by scavengers. This adverse effect was seen in the H_2O_2/O_3 process, where higher concentrations of peroxide (100 mg/L) showed a higher removal of acetone. They did not measure by-product during the treatment.

Degradation of phenol at the concentration of 90-112 mg/L was examined by different AOP systems including O_3, O_3/H_2O_2, UV, UV/O_3, UV/H_2O_2, O_3/UV/ H_2O_2 and Fe^{2+}/H_2O_2. The experiment achieved more than 90% degradation in all processes during 80 minutes' contact time. The authors reported Fenton degradation reaction as the fastest AOPs (Hernandez et al. 2002). However, UV/H_2O_2 had the highest degradation rate (almost five times higher) than photo-catalysis and UV alone. The authors measured TOC change and suggested ozonation as the best scenario because of the low cost of operation amongst all other AOPs. However, AOPs showed faster and higher degradation in comparison to ozone alone.

Different advanced oxidation processes (AOPs), namely UV/Fenton, UV/TiO_2, UV/ H_2O_2, UV, and Fenton reaction, were applied to conduct a bench scale batch experiment to investigate degradation of 4-chloro-2-nitrophenol (4C-2-NP) by Saritha, et al. None of the oxidants alone (i.e. H_2O_2) or UV was effective for the treatment, but when using UV combined with H_2O_2, TiO_2 and Fenton, the reduction of COD increased to 50%, 80% and 90%, respectively (Saritha et al. 2007). Accordingly, the Photo-Fenton process was the most effective method to decrease pollutant concentration as evidenced by both COD reduction and 4C-2-NP mineralization. Therefore, the advanced oxidation processes were found to be a viable method to breakdown recalcitrant compounds such as 4C-2-NP in the environment.

2.2.2 Comparison of various AOPs treatments

Table 2.4 summarizes works which apply combinations of UV, H_2O_2 and O_3 and catalysts (TiO_2, Fe^{2+}/Fe^{3+}) through various experiments. They permit to compare the performance of these combinations for specific contaminant(s) and report the removal efficiency for selected combinations (AOP system). The suitability of a specific AOP in these studies was based on previous results assessment and related removal efficiency as shown in Table 2.5.

Table 2.5. Performance comparison of various AOP systems

Target compound(s)	**AOP methods applied**	**Most efficient AOP**	**Remarks**	**Reference**
2,4-dichlorophenol	UV, UV/ H_2O_2 UV/Fe (III) Fenton/ Photo-Fenton/	photo-Fenton (H_2O_2 /UV/Fe (III))	Initial oxidant and pollutant concentration have major influence on degradation rate.	Momani et al. (2004)
Phenol	Fe^{2+}/ H_2O_2 > O_3 / UV/H_2O_2 > O_3 /H_2O_2 > UV/H_2O_2 > UV/O_3	UV/H_2O_2 Highest degradation rate. Fe^{2+}/H2O2, much removal	By increasing oxidant dose (H_2O_2) to some extent, %removal increased, but not more than optimal amount. Increasing catalyst concentration has no effect	Esplugas et al. (2002)
Acetone	LP-UV/O_3 UV/H_2O_2 O_3 /H_2O_2 MP-UV/H_2O_2	LP-UV/O_3 highest rate and extent of treatment	High Oxidant conc.(700mg/L) has scavenging (adverse effect on %removal) effect in MP-UV/H_2O_2	Hernandez et al. (2002)
4-chloro-2 nitrophenol	UV/Fenton > UV/TiO_2 > UV/ H_2O_2> Fenton > H_2O_2> UV	LP-UV/Fenton	More than 200 mg/L H_2O_2 had no increase of degradation	Saritha et al. (2007)

For example, Al Momani et al. reported H_2O_2 /UV/Fe (III) system as the best choice to remove 2,4-dichlorophenol from water in comparison to other AOP systems (UV, UV/H_2O_2 UV/Fe(III) Fenton/ Photo-Fenton). In their experiments, initial oxidant and pollutant concentration had a major influence on degradation rate (Al Momani et al. 2004). The main reason for higher pollutant degradation was higher OH radical production during photo-Fenton reaction in comparison to other combinations. By slightly increasing the oxidant and catalyst doses, removal efficiency increased. However, in concentrations more than 75mg/L for H_2O_2 and 10 mg/L for Fe (III), there is no further impact on higher efficiency. The study shows independence of higher removal efficiency to higher oxidant/catalyst dose by a specific amount. Other researchers conducted similar work by AOP degradation of different target pollutants.

The most efficient AOPs combination for degradation of phenol, acetone and 4-chloro-2 nitrophenol were Fe^{2+}/H_2O_2, LP-UV/O_3 and LP-UV/Fenton respectively (Esplugas et al. 2007; Saritha et al. 2007; Hernandez et al. 2002; Al Momani et al. 2004).

All above researchers have a similar conclusion about higher removal efficiency by higher oxidant and catalyst doses, but to an optimum level. If more than the optimal oxidant's dose was applied, there is no impact on reaction, neither on efficiency nor on degradation rate.

On the other hand, as it is shown in Table 2.5, for three different organic compounds, three different methods are suggested as more efficient technology. Considering all discussions and supposing dependence of the removal efficiency on treatment condition, it is not possible to select a specific combination of AOPs due to different removal efficiency by various AOPs for different contaminants. The key factor to control the treatment (increasing removal efficiency and decreasing BPs) was oxidant and UV irradiation dose control and applying LP-UV lamps instead of MP-UV lamps.

2.3 AOPs by-products formation and their diversity

More than 600 DBPs have been identified in the literature, but only a limited number of them are recognized for their human health effects and/or quantitative occurrence (Richardson et al. 2011; Stuart W. Krasner 2009; Miklos et al. 2018; Sillanpää et al. 2018). In drinking water treatment processes, the use of a disinfectant, such as a strong oxidant like ozone, produces these new products as disinfection by-products (DBPs). The amounts of DBPs formed in drinking water are between μg/L and ng/L; however, more than 50% of DBPs formed by ozonation and chlorination are considered as non-classified and non-identified DBPs (Sadiq et al. 2004; Hammes, Salhi, Köster, Kaiser, Egli, and von Gunten 2006; Richardson et al. 2011; Bond et al. 2011; Stuart W. Krasner 2009). Due to superior benefits of AOPs in remediation of contaminants from the concentrations as high as mg/L to near ppb level, they might be recognized as the 21st century water treatment systems (Luo et al. 2014a; Jiménez et al. 2018; R. Munter 2001); However, similar to other water treatment methods, the possibility of by- products formation while oxidizing micropollutants is imminent (Saskia Gisela Zimmermann 2011; Weinberg et al. 2002; Huang et al. 2005).

Water bodies commonly contain natural organic matter (NOM) and EfOM discharged to the rivers, which have a complex mixture of amino acids, hydrocarbons, proteins, lipids, humic acids and hydrophilic acids. Water quality is diverse from region to region and season to season; this consequently leads to different reactivity of NOM and EfOM with a strong oxidant and possibility of different by-products formation (Wert et al. 2007b; Michael-Kordatou et al. 2015; Shon et al. 2006). However, there is a lack of adequate information for the formation of ozone and OH radicals' by-products and high molecular weight organic by-products (Sillanpää et al. 2018); (Hammes, Salhi, Köster, Kaiser, Egli, and von Gunten 2006; Richardson et al. 2011). Acetaldehyde, formaldehyde, ketones, carboxylic acids, keto aldehydes, keto acids, alcohols, esters, haloamides, haloacetonitriles, nitrosamines and hydroxyl acids are examples of by-products that are produced by an strong oxidant such as ozone or peroxone, i.e. the combination of ozone and hydrogen peroxide (S W Krasner 2009; S. Krasner et al. 2002; Chu et al. 2012; Von Gunten 2003c). Brominated DBPs and nitrogenous DBPs are other kinds of by-products rather than chlorinated by-products (Chu et al. 2012; Liu et al. 2002; Von Gunten 2003c).

Richardson et al. (2011), reported the elevated concentrations and appearance of many emerging BPs when ozone was applied instead of chlorine. They also classified by-products according to the following categories includes regulated and unregulated DBPs (Richardson et al. 2011). Trihalomethanes (THMs), haloaceticacids (HAAs), iodoacetic acid, bromate, bromoacetic acid, dibromoacetic acid, iodo-acids, iodo-THMs, halofuranes, haloamides, chlorate, N-nitroso dimethylamine (NDMA), aldehydes, formaldehyde and acetaldehyde are these categories.

2.3.1 Factors affecting BPs formation

There are several factors that may affect the formation of by-products (BPs). These factors include oxidant dose, UV dose and the concentration of each compound taking part in the reaction. Hydroxyl radicals' scavengers like bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}), organic matter, pH, contact time, alkalinity and nature of pollutants, water quality, amounts of NOM and EfOM are other contributors to BPs formation. In waters containing bromide ions, when ozonation starts at low pH, brominated organic BPs are formed while under high pH conditions, bromate ions are formed.

Overall, the formation of diverse organic BPs depends on pH, temperature, type and concentration of NOM (Von Gunten 2003c; Sillanpää et al. 2018).

2.3.2 Precursors of BPs

Some of the main organic BPs precursors are NOM and EfOM. Organic acids and aldehydes are products of NOM oxidation by ozone (Miklos et al. 2018; Sillanpää et al. 2018; S W Krasner 2009). Total organic carbon (TOC) and dissolved organic carbon (DOC) are among the criteria for NOM measurement. The specific UV absorbance (SUVA) at 254 nm wavelength (UV-254) divided by DOC is another factor. High SUVA values represent the more hydrophobic nature of organic compounds while low SUVA values mean that organic matter is comprised of more hydrophilic compounds. By increasing the temperature, BPs formation rate is increased and the type of precursors of BPs also changes with the seasons (Alaba et al. 2017; Kleiser et al. 2000). Another BP precursor is bromide ion (which exists in the water body), which by ozonation can react with NOM to form brominated DBPs.

2.3.3 Reduction and control DBPs formation

AOP reactions may contribute to by-product formation. One of the methods to reduce BPs formation is removing BPs precursors. Replacing pre-ozonation with another method is another option to reduce BPs. Minimizing NOM, EfOM and bromide concentration in the source water and effluent may be necessary to reduce the BPs formation potential (Krasner 2009b; Singer 1999). BP precursors can be present in the water in both dissolved and particulate matter. Enhancing coagulation before oxidizing NOM, to ensure most of the dissolved NOM is settled, may remove dissolved precursors. For removing BP precursors, applying other treatment processes may be used before any oxidation such as membrane filtration and GAC adsorption.

Membrane filtration is very effective for removing BP precursors and nanofiltration effectively control precursors in comparing to ultrafiltration (UF) that is not effective for preventing BP precursors (Bond et al. 2012; Chang et al. 2001; Hu et al. 2007; Fu et al. 1994).

2.3.4 Recent studies on by-product formation

Many reports on the use of AOPs systems address the degradation and removal of micropollutants and achievement of relatively high removal efficiency (Table 2.4). However, these reports did not investigate the possible formation of by-products during advanced oxidation processes (Table 2.4). The formation of by-products in response to the use of oxidants, i.e.

hydrogen peroxide and ozone, and oxidants combined with UV lamps are investigated in this section.

IJpelaar, et al. (2007), studied by-products formation during oxidation by UV/H_2O_2 system and disinfection by UV in pre-treated natural water. They reported application of low-pressure UV lamps (LP-UV) and medium pressure UV lamps (MP-UV) in water treatments. In their review, the by-products study was limited to assimilated organic carbon (AOC), nitrite (NO_2^-) and bromate (BrO_3^-) formation without addressing formation of degradation products and individual products from organic micro pollutants or operational condition.

They concluded that using higher UV doses when applying MP-UV instead of LP-UV resulted in higher concentration of by-products. They also concluded higher formation of by-products by using UV/ H_2O_2 in comparison to UV alone. This finding shows higher BPs formation by AOPs in comparison to UV alone which is contradictory to previous findings that reflected lower BP precursors by applying AOPs (Chin et al. 2005; Amirsardari et al. 2001; Collivignarelli et al. 2004). Furthermore, other operation conditions such as pH and target pollutant concentrations and mechanism of reaction were not discussed.

There are some reports about the formation of by-products from micropollutants degradation and by-products resulting from direct photolysis. However, limited data is available for concentration of individual by-products, which generally increases in response to the increase of UV dose and oxidant doses. It should be noted that the lack of available data, experimental conditions, water quality and analytical methods do not permit a thorough comparison of findings (Ijpelaar et al. 2007). It can be concluded from the IJpelaar study that formation of by- products using UV/H_2O_2 for emerging micropollutants treatment is very likely (IJpelaar et al. 2007). The authors implied that the higher dose of oxidant and higher power of UV irradiation lead to more removal efficiency, but BPs formation was increased too. However, there is a high demand to investigate the types and concentrations of BPs.

Kleiser and Frimmel (2000) investigated the potential formation of BPs using a lab-scale UV/H_2O_2 reactor with a 5.6 mg/L oxidant concentration and 15 Watt LP-UV lamps. They assessed the removal of BPs precursors, i.e. dissolved organic carbon. They also measured dissolved organic carbon (DOC) concentration after a short irradiation exposure (Kleiser et al. 2000). They obtained removal of contaminants but also reported increasing trihalomethane (THM) generation up to 20%. The increase of UV irradiation time resulted in up to %75 THM formation. The generation of pollutant dissociation products was not addressed in this study and the individual BPs were not measured.

Toor and Mohseni used H_2O_2/UV oxidation process to treat raw surface water and evaluate BPs (THMs and HAAs (0-23 mg/L)) removal efficiency by a lab-scale reactor by LP-UV irradiation of 0–3500 mJ/cm^2. The duration of each batch experiment was adjusted based on the desired fluence (mJ/cm^2). They found when oxidant concentration and UV irradiation were only 23 mg/L and 1000 mJ/cm^2 respectively, the reduction of BPs was efficient (Toor et al. 2007). The THM was measured by spiking chlorine to combine it with the residual DOC but did not address a possible formation of any other by-products resulting from AOP oxidation.

Ratpukdi (2009) studied the natural organic matter (NOM) removal in lab-scale experiments by ozone-based AOPs. He found an important role of ozone concentration in the production of OH radicals and in mineralizing of ECs (Ratpukdi 2009). Simultaneously, by increasing the ozone dose (from 1 to 4 mg O_3/mg C), the concentration of bromate (BrO_3) increased from 64% to 213%. Higher bromate (BrO_{3-}) concentrations were produced at higher

VUV doses that were used to reduce dissolved organic carbon (DOC). Other types of by-products were not measured in this study and the presence of synthetic organic matter was not considered.

The effect of UV/H_2O_2 reactions on BPs formation was evaluated by Dotson, et al. They applied AOPs on two treated water sample and found that BPs concentration increased by using LP-UV and MP-UV lamps with 1000 mJ/cm^2 intensity (Dotson et al. 2010). The trihalomethane (THM) concentration, with the use of hydrogen peroxide, was 25 mg/mg-C (5 mg- H_2O_2 /L) and 37 mg/mg-C (10 mg- H_2O_2 /L). In the presence of sole LP-UV and MP-UV irradiation, the concentration of THM increased to 4 mg/mg-C and 13 mg/mg-C respectively. In these experiments, post chlorination was applied in the form of sodium hypochlorite (NaOCl) for THM assessment. It can be concluded that by applying higher oxidant doses (H_2O_2), and/or higher UV intensity, the medium will have a higher potential to yield BPs.

Lamsal et al. compared AOPs (O_3/UV, H_2O_2/UV H_2O_2/O_3) to evaluate variations in TOC, THM and HAAs formation potential. They reported that O_3/UV and H_2O_2/UV were most effective to reduce NOM and THM-HAAs formation potential (Lamsal et al. 2011). The O_3/UV system had much higher reduction of THM-HAAs formation in comparison to H_2O_2/UV systems.

2.4 Summary

AOPs are a powerful, robust, and promising technologies to remove and mineralize emerging contaminants. The extent of mineralization and removal efficiency depends on the nature of pollutant, type of water and type of AOP system. In most studies, the researchers applied a bench scale AOP system and noted elevated mineralization of target compounds in comparison to UV and /or ozone alone. This higher mineralization of organic pollutants by AOPs is due to OH radical production, which has stronger oxidation power in comparison to ozone or sole UV.

The researchers also reported higher removal of target compounds when they applied higher oxidant doses. However, in some contradictory studies, the results showed independence of higher removal efficiency to higher oxidant/catalyst doses or in contrast with those observations. Some of the studies reported adverse effects of higher doses on contaminant removal as they behaved such OH radical scavengers or produce more by-products. Hence, there is much more demand to investigate dependence or independence of removal efficiency to oxidant dose.

There are several combinations of AOPs that have been utilized to remove emerging contaminants (ECs) and all of them demonstrated satisfactory removal efficiency. It is not possible to select and suggest a specific combination of AOPs for treatment of target compounds in water. This conclusion is due to the different results in removal efficiency that was achieved by different AOPs. Furthermore, in each different AOP methods, different operational conditions as well as types and concentrations of pollutants were applied. The key factors to control and enhance the treatment, i.e. increasing removal efficiency and decreasing BPs production, are the oxidant and UV irradiation dose control as well as LP-UV lamp application instead of MP-UV lamps.

Although a catalyst based AOP (addition of TiO_2, $FeSO_4$ or $FeCl_3$) seems to be more efficient, it is not recommended due to major drawbacks for the practical applications i.e. subsequent catalyst separation, recovery and reuse during the treatment. Furthermore, the energy consumption in the catalytic system is higher in comparison to UV/H_2O_2 systems. Therefore, a combination of UV, O_3 and/or H_2O_2 may be recommended.

AOPs can reduce and mineralize ECs to a large extent, but due to the AOPs oxidative nature (UV and ozone), these processes may produce BPs. In most dominant studies, TOC is measured as a by-product concentration indicator and in some studies THMFP and HAAPF are monitored and presented as total BPs in the media. In the latter studies, measuring THMFP and HAAFP are performed by injecting chlorine (NaOCl) directly to the sample. However, this method may not be a valid procedure to assess all BPs in the water; Because ozone alters the chemical structure of BPs precursors in water and some of the new products (after ozonation) have no ability to react with chlorine.

By applying ozone-based AOPs for water treatment, like other water treatment methods, it carries over by-products in to the medium during processes. Oxidant dose, UV irradiation dose and exposure time have major roles for enhancing removal efficiency. On the other hand, more oxidant and UV irradiation doses may have an adverse effect on treatment due to the formation of by-products during AOPs application. Hence, it is highly recommended to investigate several operation conditions for increasing the treatment efficiency by controlling oxidant and UV doses, and simultaneously, monitoring and decreasing the formation of BPs.

Another remarkable point is the presence of NOM in surface water and EfOM in wastewater effluent. Researchers noted the possibility of higher concentration of by-products due to higher concentration of NOM and EfOM in both water and wastewater treatment plants outputs. One of the important points to achieve an efficient and sustainable treatment is to mitigate NOM and EfOM in water and wastewater upstream the AOPs.

There are some contradictory results in literature about increasing or decreasing BPs by AOPs systems. Some studies reported a decreasing BPs formation potential when applying AOPs by measuring BPs precursors, i.e. DOC before and after treatment. In contrasts, others studies mentioned an increasing BPs formation potential when applying AOPs by measuring the same method. Therefore, there is a high demand to investigate AOPs individual by-products formation in this field; Because most studies measured BPs only by measuring BPs precursors and did not measure individual BPs. An important demand is detection and identification of by-products formation during AOP treatment in order to assess their potential toxicity in a source of water supply (Ribeiro et al. 2015b).

3 Methodology

3.1 Research and experimental Phases

In order to meet research objectives, investigations were conducted on the micro-pollutants removal by advanced oxidation, which considers hybridization of UV/H_2O_2 system with electro-membrane bioreactor (AO/MEBR). The study consists of eight experimental phases and several stages (Table 3.2). The experimental work started with design and installation of a singular system of AOP, followed by a pilot size system and finalizing with a hybrid AOP/MEBR. In phase 1, preliminary tests were conducted for adequate setup of UV system with respect to UV intensity, oxidants' dose (H_2O_2 and ozone), air flow, ozone flow, nitrogen flow, water flow rate and pH adjustments in aqueous phase.

In phase 2, the DI water (DIW) was spiked by SMX, EE2 and PCM target contaminants (section 3.2.1), which were exposed to sole UV irradiation.

During phase 3, an advanced oxidation (H_2O_2/UV AOP) was applied for model compounds (SMX and PCM) which were dissolved in DIW (without other matrices' interaction). Technological parameters including pH, aeration rate, H_2O_2 dose, TBA as OH scavengers' effect, UVC dose, nitrogen as air sparging in water samples were investigated.

In phase 4, the real effluent (with matrix interaction), taken from the pilot facilities of MEBR, was treated by UV/H_2O_2 AOP (hybrid system) without target pollutant (SMX and PCM). Then, the hybrid system (AO/EMBR) was applied to real effluent spiked by SMX and PCM.

In phase 5, the samples obtained from phase 2 and 3 were analyzed by LC-MS-MS. Degradation and transformation of by-products for model pollutants (SMX) were identified by liquid chromatography coupled with mass spectrometer.

In phase 6, the UV/O_3 AOP pilot plant setup was applied to remove target pollutants including, SMX, PCM and caffeine. UVC, Ozone and UV/O_3 were technologies which were applied discretely and then performance of their treatment were compared to each other.

In phase 7, the same treatment method applied in phase 4 was performed for influent samples where the target compound (PCM) was spiked to the input of wastewater pilot facility. Furthermore, an evaluation for ECs removal in river matrix comparison to ECs removal in effluent matrix was conducted.

In phase 8, the by-products monitoring was performed while technological parameters were applied as well. Technological parameters in all treatment phases consisted of variables such as pH, oxidant dose, UV intensity, aeration rate, as well as various sample concentrations and reaction times.

In bench scale setup, treatments have been performed in the 3-liter reactor using batch mode and semi- continuous operation at room temperature (17-22 ^{o}C), as well as ambient pressure and pH close to neutral (7-7.5). The mean UV intensity during the batch as long as semi-continuous treatment was recorded 10.5 and 10 mW/cm^2, respectively. This mean UV intensity was measured by UV sensor located in center of reactor which was controlled by UV power supply in control panel. The treatments were planned with UVC irradiation alone and H_2O_2/UV at different contact times, different pollutant concentrations and different UV doses.

In pilot plant setup, treatments have been performed in the 70-liter reactor using batch mode and semi continuous operation at room temperature (17-22 ^{o}C), ambient pressure and pH around neutral (7-7.5). The mean UV intensity during the batch and semi continuous treatment were recorded between 20 to 21 mW/cm^2. Treatments were planned with UV irradiation alone, ozone and O_3/UV AOP at different contact times, different pollutant concentrations and different UV doses. Target pollutants included PCM, SMX and CAF.

3.2 Materials and target compounds

3.2.1 Target emerging contaminants

Based on the literature review (chapter 2) about the occurrence of micropollutants, pharmaceuticals and personal care products (PPCPs) and ECs in most rivers, surface waters and ground waters (Snyder, et al. 2007; Murray, et al. 2010; Aris, et al. 2014), and furthermore, investigations performed in Canada and Quebec streams by Metcalfe et al. (2004) and Yargeau et al. (2007), the following pharmaceuticals have been chosen for the scope of this work:

1) Sulfamethoxazole (SMX)
2) Paracetamol (PCM)
3) 17α-ethynylestradiol (EE2)
4) Caffeine (CAF)

Choosing of target compounds was discussed, and the initial experiments were performed with sulfamethoxazole and paracetamol in both bench and pilot scales. Furthermore, extra tests were proceeded with EE2 in bench scale and CAF in pilot. Analytical grade paracetamol (CAT-No. FSSP9741311) was purchased from Fisher Scientific. Several synthetic water samples at different pollutant concentrations (66, 132, 198, 330, 462 μmol L^{-1}) were prepared with deionized water (MilliQ Millipore) and tap water, which was dissolved with methanol/water and/or pure hot water. The paracetamol solution concentrations were verified by spectrophotometer and HPLC before the treatment. Other synthetic waters with SMX and EE2 were prepared by the same method or with the same concentrations or using methanol/water as solvent for EE2. Sulfamethoxazole (CAT-No. S7507) and EE2 (CAT-No. E4876) was purchased from Sigma Aldrich, while analytical grade chemicals (acetonitrile, methanol, acetic acid, methylene chloride, ammonium acetate, formic acid) were provided by Fisher Scientific.

For measuring chemical oxygen demand (COD) and total organic carbon (TOC), the ultra-low COD (TNT 820, part number 2415815, method 8000) and TOC (part number 2760345, method 10129) kits from HACH were used.

3.2.2 Investigated matrix types

Experiments were conducted with different matrices such as DI water, tap water, river water, wastewater treatment plant effluent and influent. Target pollutants were spiked to each matrix.

Effluent samples were collected from the output of MEBR pilot facilities in the City of l'Assomption (Quebec). Furthermore, to verify outcome of designed treatment experiments, some effluent samples were collected from WWTP of the City La Prairie (Quebec).

River water samples were collected from four different locations of Saint-Laurent river, Montreal Quebec (Point Claire, Saint - Anne - de Bellevue, Pine Beach and Lachine) (Figure 3.1). Each river sample was characterized, and then, treated individually, Furthermore, a mix solution of four samples was prepared for treatment. Characteristics of effluent and river water (mix) are shown in Table 3.1.

Figure 3.1. River water sampling sites along with Saint-Laurent river

Table 3.1. Characteristics of wastewater treatment MEBR pilot facilities effluent and St-Laurent river water

Parameter	Unit	Effluent	River
TOC	mg/L	3.3	2.9
Chloride	mg/L	126.72	26.48
Nitrate	mg/L	81.03	1.48
Sulfate	mg/L	130.06	25.72
Phosphate	mg/L	0.78	0.69
Sodium	mg/L	86.73	14.33
Calcium	mg/L	22.99	8.53
Magnesium	mg/L	77.33	32.72
Potassium	mg/L	11.53	1.68
UVA	m^{-1}	0.1	0.045
SUVA	mg / (L. m)	3.52	2.2
pH	-	6.73	7.16
Turbidity	NTU	2.21	1.71
Conductivity	µS/cm	1023	292.6
TDS	mg/L	921.1	238.7
Alkalinity	(mM HCO_3^-)	3	0.2

3.2.3 Sampling and number of runs

For each type of AOP methods and hybrid system, the number of samples were provided in the Table 3.2 with details for each phase of work. For each target compound several sets of runs was conducted based on changing the operational parameters. For each set of runs, 12 samples were taken for analysis. Each set of runs was repeated three times. For each parameter a series of runs were conducted.

For example, for SMX, before changing operational parameter, a UV/H_2O_2 AOP treatment was conduct in 60 minutes. Number of samples was 12 based on 5 minutes interval. The run was repeated two more times for reproducibility. Then a new run was conducted with respect to pH change (from 3 to 10). For pH =3, three set of runs were conducted and the run were continued for pH= 4 to 10 range. For example, at pH =3 (12 samples, three set of runs = 36 sample). Then for pH =4 (12 samples, three set of runs = 36 sample), until pH= 10.

Afterwards, the run was repeated for H_2O_2 dose from 0.5 to 24 mM. Then for aeration from 0.0 to 4 L/min. The similar method was applied for UV/O_3 AOP and then for hybrid system and BPs evolution.

3.3 Experimental setup, configuration and design

The AOP setup was designed to have a possibility to treat the contaminated water and effluent in various conditions including batch, semi-continuous and continuous modes. Figures 3.1, 3.2, 3.3 and 3.4. depicts AOP setup and reactor. The AOP setup was placed downstream of the MEBR unit to configure the hybrid system (Figure 3.7).

3.3.1 UV/H_2O_2 AOP setup design

The experimental setup was made of a stainless steel (316 L) tubular reactor (10 cm Diameter, 45 cm length) equipped with a LP-UVC 40-Watt lamp (Trojan Company validated UV Lamp, 40 cm length, 2.8 cm sleeve OD, Ontario, Canada) located on the center of the reactor. To deliver the water samples to the reactor, a peristaltic pump with a Tygon ELFL (06440-35) tubing was included in the system to deliver the synthetic water and effluent to the reactor which then, could be adjusted to desired flow rates. The semi-continuous mode for experiment with a 4-liter Erlenmeyer flask, allowed the contaminated water samples to receive H_2O_2 dosing, mixing the solution, and desired aeration, nitrogen and oxygen flow.

The AOP setup consists of the following parts, as shown in Figure 3.2: a- Feed water container (1); b- Peristaltic pumps (2); c- Reactor (3); d- UV lamp (4); e- Power supply (5); f- Ozone and pH meter (6) ; g- Ozone generator (7); h- Sampling port (8) ;I- UV sensor (9) ; j- Nitrogen, O_2, air (10-12) k-H_2O_2 reservoir (13) L- Heater stirrer (15)

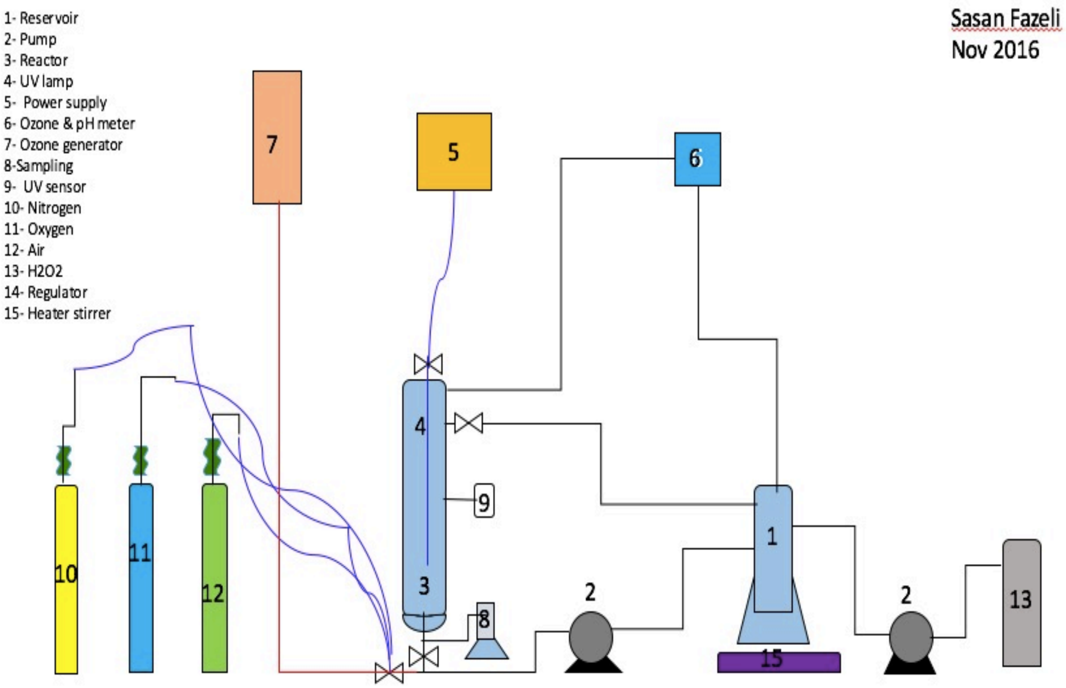


Figure 3.2. UV/H_2O_2 AOP experimental setup

The reactor's picture for advanced oxidation experiments is shown in Figure 3.2. The tubular reactor has a volume of 3.1 Liter. The UV lamp (Figure 3.3 top) was placed in reactor center to provide UV irradiation evenly to the water flow. The reaction chamber consisted of two parts: the body and lamp holder assembly (Figure 3.3). In order to support the reactor body, a vertical stand was designed and made in the Concordia University's workshop. The reaction chamber has four openings for water input, water output, UV sensor and sampling. The UV sensor was mounted within the sensor port to see the UV lamp in the middle of the lamp arc, tangential to reactor body.

UV lamp, power supply and UV sensor (UV Logic sensor Aquafine part no. 793200-001) were provided from Viqua Company (Figure 3.3). The UV/H_2O_2 AOP experimental setup is presented in Fig. 3.4.

Figure 3.3. Reactor chamber and power unit (bottom), LP-UVC lamp assembly (top), Viqua Company

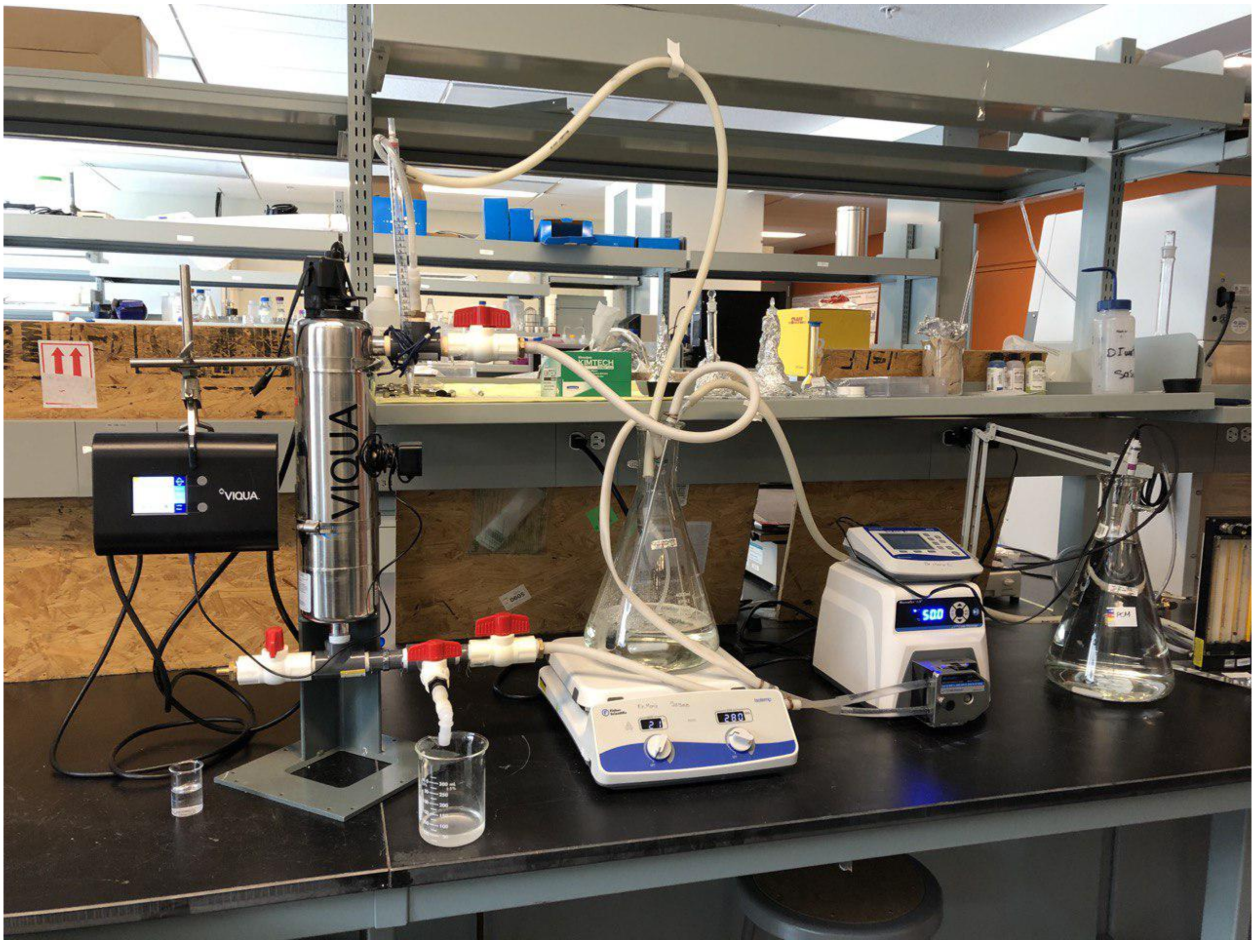


Figure 3.4. UV/H_2O_2 AOP experimental setup

3.3.2 Designe of UV/O_3 -H_2O_2 AOP pilot plant

In order to simulate a realistic water treatment practice, a pilot plant setup was designed for batch, semi-continuous and continuous treatments. To avoid any possible unwanted contamination in the system, all tubing, valves and reactor materials were made of 316 stainless steel. The UV/O_3-H_2O_2 AOP experimental pilot plant setup photo is presented in Fig. 3.6 located in Concordia University, Gina Cody School of Engineering and Computer Science.

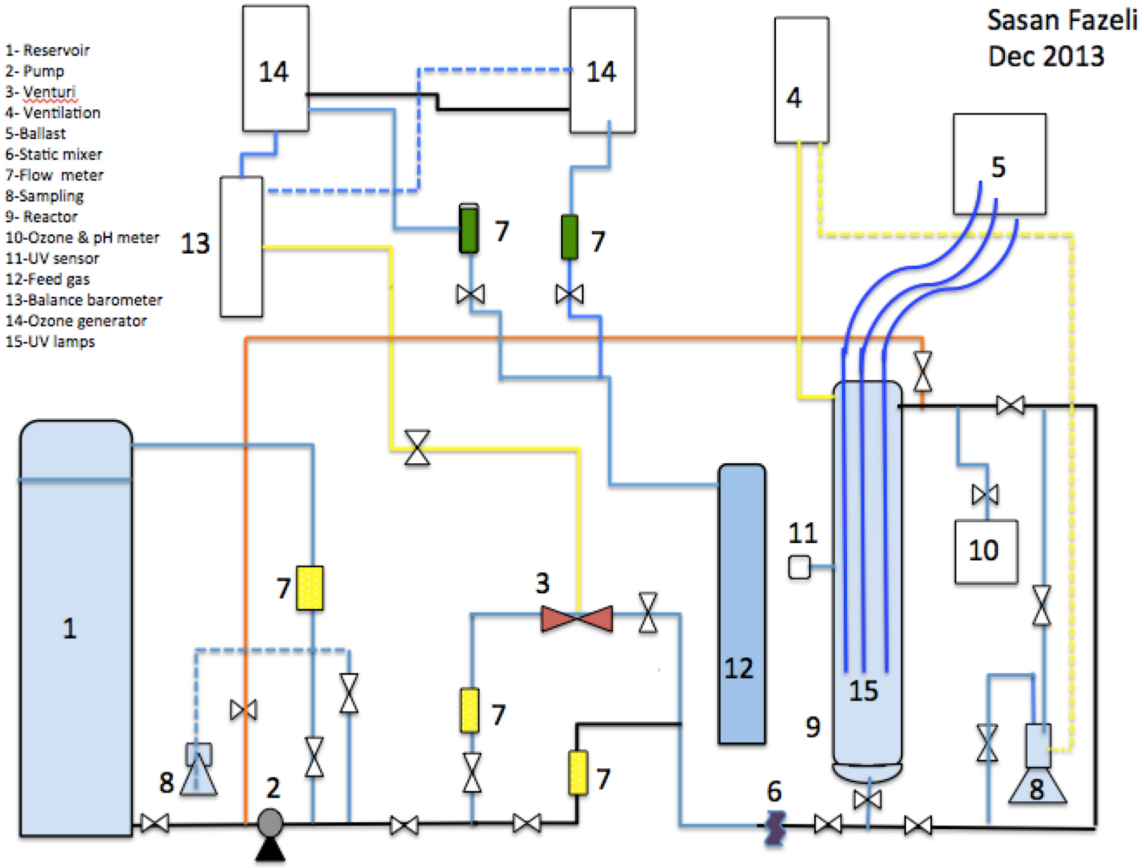


Figure 3.5. Schematic of pilot plant UV/O_3-H_2O_2 AOP setup

3.3.2.1 Experimental pilot plant configuration and components

The pilot setup is designed to deliver different water flow rates (L/min). Proper pump with specific power and its corresponding head loss was selected according to the calculated total head loss in setup including tubing size (3/4"), reactor size and its openings, valves, Venturi device and flow meters in the setup. In order to adjust the desired water flow stream in the setup and ozone dose, two tubing bypasses were designed and included in the setup.

The pilot plant consisted of the following parts (Fig. 3.5): 1- Feed tank, 2- Pump, 3- Venturi, 4- Ventilation, 5- Control panel, 6- Static mixer, 7- Valves and flow meters, 8- Sampling ports, 9-

Reactor, 10- Ozone, pH and temperature detector, 11- UV sensor, 12- Oxygen cylinder, 13- Balance barometer, 14- Ozone generators, 15-UV lamps; Tubing and fittings. In case of air application (instead of pure oxygen) two ozone generators were installed for a sufficient ozone production because one ozone generator didn't produce enough ozone by air flow.

The feed tank (30"D x 56"H, volume = 567-liter capacity) is made of high-density polyethylene. Pump is a chemical resistant 316 stainless steel head, impeller and shaft with seal and O-ring of Viton. The maximum flow rate is 80 L/minute at maximum 12-meter head. The Venturi (Ozone injector) was model 484X Mazzei, PVDF Kynar. For better ozone mixing and dissolution, a perforated plate is mounted at the bottom of the reactor and a static mixer is installed after the Venturi in the water line. The reactor is made of stainless steel 316 L with 52 Liter volume and all other connections and wet parts are 316 stainless steel. The reactor was designed in Concordia University as part of this thesis work and then delivered to Inox Company for manufacturing. Sleeve bolts (Figures A.2 and A.3), UV lamps, lamp sleeve, ballast, UV sensor and other UV spare parts were provided from the Trojan Company (validated UV Lamp AL models, 62", 250w), Quartz Sleeve AL models, 52" Lamp Connectors AL models, UV Logic Sensor. Stainless steel (¾" size) tubing, valves (globe and ball valves) and fittings and flow meters were purchased from McMaster-Carr Co. Two inline ¾" flow meters were applied with a 2 to 20 L/min range in order to control the water flow through the Venturi and reactor. One other flow meter (1", 80 liter/minute range) was mounted to the line to measure total water flow in the system. Ozone detector devices were applied to measure ozone-dissolved concentration in water and air. Ozone detector in water was purchased from ATI company model Q46H/64 with 0-200 mg/L ranges. The pH and temperature can be measured inline, time to time in the setup by mounting a pH sensor in the flow-cell assembly.

The Air ozone detector was purchased from Ozone Solution Company for safety and precaution during work to monitor any ozone leakage in the environment.

Figure 3.6. UV/O_3-H_2O_2 AOP experimental pilot plant setup

3.3.2.2 Design of pilot plant reactor

The reactor shape and dimensions for pilot plant setup were designed to hold high intensity long UV lamps (156 cm), that provide maximum UV exposure to contaminated water flow and supply proper ozone flow to the system. Some other parameters such as UV lamp length and diameter, sleeve bolt UV holder and UV lamps configuration were factors that were considered for reactor shape and dimension calculations. The UV sensor was mounted to see the UV lamps in the middle of lamps and reactor. The reaction chamber consisted of two parts: the body and lamp holder assembly (end-cap). The reactor body had 3 legs to hold the reaction chamber vertically. The reaction chamber had four openings for water input, water output, UV sensor and ozone off-gas exit.

A perforated curved plate with several holes was welded at the reactor bottom for water turbulent flow and better ozone mixing (Appendix 1,2). The reactor had a height of 195 cm with

20 cm diameter. The reaction chamber height was 175 cm and end- cap diameter is 20 cm. The end-cap (lamp holder assembly), which was designed to hold UV lamps, consisted of a plate with 3 holes and lamp sleeve holder rods. Plate holes were placed in the corner of 60-degree triangle with an equal 5 cm distance to the triangle center and reactor wall. Three rods were welded to the end-cap at one side and screwed to another plate on the other side. The lamp holder assembly (end-cap) was fixed by a clamp and sealed with a gasket to avoid any ozone leakage.

3.3.3 AO-MEBR Hybrid system

In order to meet the objectives of the research, a novel hybrid system was proposed. This hybrid system consisted of MEBR (membrane electro-bioreactor) and AOP (advanced oxidation system).

Figure 3.7. Pilot MEBR system in a self-standing cabin (Elektorowicz et al. 2017)
1- Elector bio- reactor 2- Wastewater input 3- Membrane 4- Pump

In this hybrid system, AOP setup is placed downstream of the effluent from MEBR (Figures 3.7, 3.8). A Membrane electro-bioreactor (MEBR) pilot plant, in L'Assomption city, Quebec, had been applied for this study. The MEBR had the capacity of treating 2 m^3/day of municipal wastewater. It was designed to combine biological, electrokinetic and membrane filtration processes (Elektorowicz et al. 2017). By applying an intermittent current at 7 Volt, and SRT of 20 days, the removal of 90-99% of phosphorus, COD, and total nitrogen was achieved. This system permits to create nitrification and denitrifications simultaneously. Furthermore, it removes carbon and almost completely phosphorous from effluent. Additionally, heavy metals, present in wastewater, are deposited on electrodes at a large extend. Due to presence of membranes, bacteria are not passing into effluent, unfortunately, some chemicals pass.

During a period of the time between September to November of 2017, several effluent samples were taken from MEBR and analyzed. The preliminary study of the best operation conditions was conducted. In subsequent stage, the tests were conducted in the pilot plant. According to the COD of effluent, 60 µmole of PCM was spiked to the influent wastewater.

The injection of PCM was repeated for specific periods. Each set of spiking, monitoring and sampling was done once a week. In order to monitor the effect of the PCM concentration on bacteria biomass and its biodegradation, several sets of tests were conducted with different PCM concentrations.

The following test conditions were considered: electro-bioreactor (EBR) chamber effective volume of 830 L; influent and effluent flow = 2 m^3/d; PCM injection rate of 4 L /day; and the PCM desired final concentration in EBR of 20 mg/L. The effluent and supernatant samples were collected from the reactor EBR. During the first twelve hours, the effluent samples were collected every hour, and then, after 12 hours of injection. After 12 hours, the samples were collected in

24th, 48th, 72nd hour, and then, every day for next 7 days. Both PCM and COD changes were recorded during one week (168 hours). The tests were repeated for eight weeks.

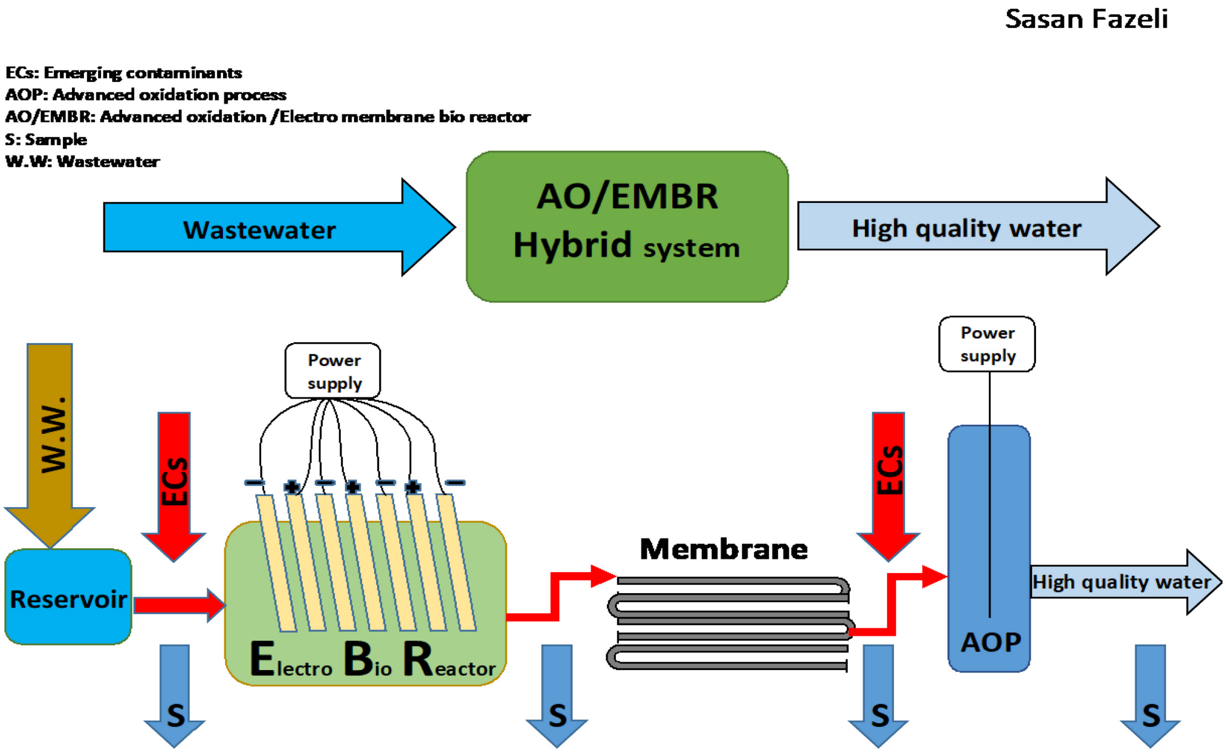


Figure 3.8.The hybrid AO/EMBR system

3.4 UV/ /H_2O_2 AOP experiments for water and wastewater treatment

Experiments were designed for batch and semi - continuous modes. In order to get a clear idea about treatment efficiency, some preliminary tests were performed in advance. These experiments included water flow adjustment, UV lamps intensity measurements, hydrogen peroxide injection, air, nitrogen and oxygen flow rate adjustments. All water treatment experiments were performed in a temperature range of 17-23 ^{0}C and neutral pH 5-7.5, which was monitored by in-line temperature and pH meter.

3.4.1 Feed water preparation

Stock solutions of target compounds were prepared in advance for treatment tests. For bench scale setup, an Erlenmeyer four-liter flask was included in the system as a feed container to deliver the synthetic water and effluents to the system. The synthetic water samples including target compounds with known concentrations were prepared and made ready in order to transfer to the reactor. The target compounds (SMX, PCM, EE2) were dissolved by acetonitrile/water, methanol and /or warm water. For making the standard solutions, acetonitrile/DI water mixture was used. For making synthetic water, paracetamol and sulfamethoxazole were dissolved in water by increasing water temperature gradually and mixing gently. Each water sample and effluent with desired concentration of target compound was prepared in 4-liter Erlenmeyer flask and mixed thoroughly and then transferred to the reactor by pump. The setup was working like a continuous flow stirred tank reactor (CSTR) by stirring the mixture in Erlenmeyer and circulating the water solution by the pump. The concentration of samples was measured with a spectrophotometer and/or HPLC before any runs to verify the desired sample concentration.

3.4.2 UV lamps intensity and dose

In addition to UV application for disinfection purposes, the UV irradiation can also be used for photolysis purposes. By direct UV photolysis at higher irradiation dose more than disinfection dose, i.e. 30-70 mJ.cm^2, organic dissolved matters will be degraded (S A Snyder et al. 2007). Elimination of target pollutants depends on fundamental photolysis parameters. These parameters include UV intensity, scavengers which compete with organics to consume OH radicals, quantum yield and molar absorption coefficient of specific organic (Kang 1997).

For the UV experiments a 43 W low-pressure monochromatic UV lamp (253.7 nm, Trojan Co.) was used as the UVC source. The UV lamp was positioned in reactor vertically and parallel to the water stream. For current experiments, UV intensity was monitored by a UV sensor mounted on the middle of the arc length of the lamp. In batch and continuous operation modes, the mean UV intensity values were recorded between 10 and 10.5 mW/ cm^2. These recordings were measured in a pure tap water without adding any contaminant where UV transmittance equals to UVT =95% @ 254 nm. The UV lamps were warmed up for 3 minutes before initiating each experiment. After 3 minutes, the sample exposure time in the reactor was considered. The UV dose was calculated with exposure time multiplied by UV intensity (Equation 3.1). Exposure time was determined by the reaction time considered for each experiment. Thus, experiments were designed for each phase in Table 3.2.

$$UV\ dose\ (m\ W \cdot s\ /\ cm^2) = UV\ intensity\ (m\ W/cm^2) \times t\ (exposure\ time\ (s)) \qquad (3.1)$$

3.4.3 Semi-continuous treatment and analytical methods

The concentrations of SMX, PCM, EE2 (ECs) and /or COD (chemical oxygen demand) and TOC (total organic carbon) were measured in a solution before and after treatments, as indicators of the experiment performance. The tests were repeated three times for each sample. To verify analysis results, the COD/ TOC tests were conducted on wastewater effluent. For quality control, standard solution with known TOC/COD concentrations (product # 2833249 Hach Co.) was applied. For each test, 4 liters of effluent solution was continuously delivered to the reactor while proper adjustments were applied with respect to the pH value, H_2O_2 dose and aeration rate. The sampling of treated solutions for ECs and/ or COD, TOC analyses was conducted at 5- minute intervals. For measuring COD and TOC, the ultra-low COD (TNT 820, Hach method 8000) and TOC (Hach method 10129) kits were used. For the ECs concentration, spectrophotometer and/or HPLC (described in the previous section) were applied. The removal efficiency (R) was calculated based on equation (3.2), where C_t and C_o are the ECs and/ or COD, TOC concentrations at time t and time zero, respectively.

$$R = (C_0 - C_t)/C_0 \times 100 \qquad (3.2)$$

3.4.4 Design of experiments (DOE) and sampling

3.4.4.1 Standarized experimental approach, local optimization

In a conventional experiment design, when the reactions are affected by operational parameters, each individual variable varying within a range and other variables are held as constant parameters. In such method the optimum value for reaction efficiency will be obtained without considering interaction among other variables (Subramonian et al. 2015). In current research, three parameters including pH, aeration and oxidant (H_2O_2) dose are considered within specified ranges. In this research by applying conventional experiments design and local optimization method, many experiments, more than 3000 experiments, were run. Therefore, eight phases and their related substages were defined in Table 3.2.

At the beginning, the photolysis of target pollutants was performed by applying UV irradiation alone. Then advanced oxidation was applied by combination of hydrogen peroxide and UV irradiation at different doses and intensities. For the UV alone experiments, some series of batch and semi-continuous UV treatment tests were planned with different samples concentrations and different UV exposure times (0 to 180 minutes with 5-minute intervals). For each treatment run, in batch and semi-continuous modes, the reactor was filled with the target compounds (SMX, PCM, EE2) solutions (C_0 = 10, 20, 30, 50, 70 mg/L) and effluents.

Batch treatments (UV alone) were repeated 5 times in order to examine the treatment reproducibility. For each run 12 samples (in a 5- minute interval from 1 to 60 min plus one pre-treatment sample) were taken for analysis. In some cases, treatment continued until 90 minutes or more to achieve high removal efficiency. Hydrogen peroxide/UV runs were performed at different H_2O_2 concentrations from 5 to 530 mg of oxidant per liter. Table 3.2 shows type of pollutants, treatment methods, operational parameters and methods for analysis of treatment efficiency. The treatment runs were planned based on variables indicated in Table 3.2.

Table 3.2. Design of experiments (phases / stages); Operational condition for AOPS' treatments

Phase 1: (9 stages) **Design of experiments, reactor design, setup design**
Phase 1: Design of experiments (DOE); operational condition, treatment runs, sampling
Stage (I) Reactor design of H_2O_2 /UV AOP bench scale setup
Stage (II) Preliminary tests: H_2O_2 /UV AOP Oxidant and UV dosing, pH water air and N_2 flowrate adjustments Number of samples: One sample before each test and then one for each 5min intervals for 30 to 60 minutes of reaction. From 60 to 360 min, one sample for 20 min intervals for AOPs
Stage (III) Experiment design for H_2O_2 /UV AOP bench scale based on: 1- Target pollutants: SMX, PCM, EE2, CAF effluent 2 - Matrix type: DI water, tap water, effluent, municipal wastewater influent 3 - Operational parameters: PH, oxidant dose (H_2O_2), UV dose, contact time, air flow 4 - Ranges: pH = 3 to 10, H_2O_2 = 0.5 to 12 Mm, UV = 5-10 mJ/cm^2, air flow = 0.5 to 5 L/min, N_2= 3 h purge at 1L/min, TBA= 10 times of target pollutant (mole) 5- Number of samples: 12 samples for each run in 60 min. (5min intervals)
Stage (IV) Reactor design of O_3 /UV AOP pilot plant setup
Stage (V) Preliminary tests of O_3 /UV AOP: Oxidant and UV dosing, pH water air and N_2 flowrate adjustments
Stage (VI) Experiment design for O_3 /UV AOP pilot scale based on: 1- Target pollutants: SMX, PCM, EE2, CAF effluent 2 - Matrix type: DI water, tap water, effluent, municipal wastewater influent 3 - Operational parameters: PH, oxidant dose (O_3), UV dose, contact time, air flow 4 - Ranges: pH = 6 -7.5, H_2O_2 = 0.5 to 12 Mm, UV = 20 - 21mJ/cm^2, oxygen flow = 0.5 to 2.5 L/min, ozone rate: 0.25 – 0.8 (mg/L) x min; ozone dose: 2.5 – 14 mg/L 5- Number of samples: 12 samples for each run in 60 min. (5min intervals)
Stage (VII) Design of AO/MEBR system 1- L'Assomption site assessment tests 2- Calculate and acquire data regarding MEBR input and output flow, EBR dimension 3- Dosage calculation regarding PCM spike to MEBR 4- AOP downstream of MEBR; 5- sampling design 6- PCM spike design, etc. 5- Number of samples: 12 samples for each run in 60 min. (5min intervals), From 60 min to 3 days, 12 hours interval for each sample
Stage (VIII) AO/MEBR Preliminary tests: MEBR flow rate test, membrane clogging, sampling of wastewater and effluent, Oxidant and UV dosing, pH and oxygen uptake rate measurements water flowrate adjustments
Stage (IX) Experiment design for AO/MEBR: 1- Target pollutants: SMX, PCM, EfOM, TOC and COD total 2 - Matrix type: Effluent, municipal wastewater influent 3 - Operational parameters: Discharge flow of effluent, retention time

Phase 2: (9 stages)

UV photolysis lab test with water matrix

Phase 2: H_2O_2 /UV AOP bench scale setup

The experiments were planned in both batch and semi continuous modes. Each of target compounds was dissolved in DI water and tap water and tested separately. The pollutant dose was determined to investigate effect of concentration on reactions.
UV intensity = 10 – 10.5 mJ/cm^2
water matrix: DI water, effluent, river water
water flow rate: 0 and 4 L/min
Reactor volume: 3 liters
H_2O_2 dose: 0- 24 mM
Aeration rate: 0- 4 L/min
PH: 3-10

Stages	Experiment condition	Analytical method
Stage (I) Sulfamethoxazole (SMX)	Dose = 20 to 70 mg/L	**Analyses** HPLC, TOC, COD Spectrophotometer LC-MS-MS
Stage (II) Paracetamol (PCM)	Dose = 20 to 70 mg/L	
Stage (III) Ethinyl estradiol (EE2)	Dose = 20 mg/L	
Stage (IV) Adjustment of technological parameters	The pollutant dose for next tests was selected based on COD range of effluent	

Stage (V): O_3 /UV AOP pilot plant setup

The experiments were planned in both batch and semi continuous modes. Each of target compounds was dissolved in DI water and tap water and tested separately. The pollutant dose was determined to investigate effect of concentration on reactions.
UV intensity = 20-21 mJ/cm2
water matrix: DI water
water flow rate: 0 and 50 L/min
Reactor volume: 70 liters
O_3 dose: 0- 20 mg/L
Oxygen rate: 0 - 2.5 L/min
PH: 5-7

Stages	Experiment condition	Analytical method
Stage (VI) Sulfamethoxazole (SMX)	Dose = 20 to 70 mg/L	**Analyses** HPLC, TOC, COD LC-MS-MS Spectrophotometer
Stage (VII) Paracetamol (PCM)	Dose = 20 to 70 mg/L	
Stage (VIII) Caffeine (CAF)	Dose = 20 to 70 mg/L	
Stage (IX) Adjustment of technological parameters	The pollutant dose for next tests was selected based on COD range of effluent	

Phase 3: (9 stages)

H_2O_2 /UV AOP photolysis; DI matrix; lab test

Phase 3: AOP photolysis; Experiment runs in DI water matrix
UV intensity = 5-10 mJ/cm2
water matrix: DI water
water flow rate: 4 L/min
H_2O_2 = 0.5 to 12 Mm, air flow = 0.5 to 5 L/min, pH = 3 to 10

Stages	Experiment condition	Analytical method
Stage (I): EC (SMX) removal without changing of operational condition	In this phase SMX is dissolved in DI water at different doses Dose = 20 to 70 mg/L	HPLC, TOC, COD spectrophotometer
Stage (II): EC (PCM) removal without changing operational condition	In this phase PCM is dissolved in DI water at different doses Dose = 20 to 90 mg/L	HPLC, TOC, COD spectrophotometer
Stage (II): EC (EE2) removal without changing operational condition	In this phase EE2 is dissolved in DI water at different doses Dose = 20 to 90 mg/L	HPLC, TOC, COD spectrophotometer
Stage (III): Study ECs (SMX, PCM) by changing operational condition:	ECs concentration, Oxidant dose effect, pH change, Aeration effect; dosage optimization	HPLC, TOC, COD spectrophotometer
Stage (IV): Study EC (SMX) by changing operational condition;	UV dose effect, nitrogen purge, TBA effect	HPLC, TOC, COD spectrophotometer
Stage (VI): Local optimization of technical parameters	Adjust and find the most efficient condition and apply for maximum removal	
Stage (VII): Response surface methodology (RSM); Design of experiments	Twenty set of experiments were designed by central composite design. Experiments were performed and then compared to the predicted values by RSM	
Stage (VIII): RSM; Optimization	Optimization was performed by polynomial equation Predicted optimum values was compared to adjusted values; ANOVA	
Stage (IX): Electrical energy per order (E_{EO}): Energy consumption evaluation	E_{EO} was calculated based on the energy consumption for 90% of target compound removal in one cubic meter of sample. Oxidant dose effect, pH change, Aeration effect were investigated; Samples: effluent, river water	

Phase 4: (9 stages)

AO/EMBR Hybrid system

Phase 4: AO/EMBR Hybrid system (Effluent removal)
Effluents: effluent1, effluent 2, effluent 3, effluent 4
Matrices: Effluent + SMX, Effluent + PCM
Experimental tests: Effluent matrix
The effluents at different time with deferent COD value were taken from the MEBR

Stages	Experiment condition	Analytical method
Stage (I): Effluent 1, 2 without changing operational condition	Temperature = 17-20 No aeration, PH = 7, H_2O_2 = 12 mM, UV = 10 mJ/cm^2	TOC, COD
Stage (II): Effluent 3,4 without changing operational condition	Temperature = 17-20 No aeration, PH = 7, H_2O_2 = 12 mM, UV = 10 mJ/cm^2	TOC, COD
Stage (III): Effluent 1,2,3,4 by changing operational condition:	Effluent concentration, Oxidant dose effect, pH change, Aeration effect; dosage optimization	TOC, COD
Stage (IV): Effluent 1,2,3,4 by changing operational condition;	UV dose effect, nitrogen purge, TBA effect	TOC, COD
Stage (V): Study effluent 2 + SMX without changing operational conditions	No aeration, pH = 7, H_2O_2 = 12 mM, UV = 10 mJ/cm^2 No pH adjustment	QTOF - MS LC-MS-MS COD, TOC spectrophotometer
Stage (VI): Study effluent 2 +PCM without changing operational conditions:	No aeration, pH = 7, H_2O_2 = 12 mM, UV = 10 mJ/cm^2 No pH adjustment	QTOF - MS LC-MS-MS COD, TOC spectrophotometer
Stage (VII): Study effluent 2+SMX by changing operational conditions:	aeration effect, pH change, Oxidant dosage optimization	QTOF - MS LC-MS-MS COD, TOC spectrophotometer
Stage (VIII): Study effluent 2+ PCM by changing operational conditions:	Aeration effect, pH change, Oxidant dosage optimization	QTOF - MS LC-MS-MS COD, TOC spectrophotometer
Stage (IX) Adjustment / optimization of technological parameters	Find the most efficient condition for maximum COD removal	

Phase 5: (5 stages)

By-products identification, quantification

Phase 5: By-products identification:

Several by-products were identified. Four major by-products were selected based on abundances and stability in the medium

Stages	Experiment condition	Analytical method
Stage (I): Sample preparation using SPE method for concentration	Standard conc. of SMX and PCM Recovery calculation	Spectrophotometer HPLC
Stage (II): Parent ion chromatogram and accurate mass (m/z) and retention time study	SMX and PCM peak detection and retention time study	QTOF - MS LC-MS-MS
Stage (III): Standard method and calibration curve for quantification	SMX and PCM standard conc.	QTOF - MS LC-MS-MS
Stage (IV): Qualification and detection degradation products and transformation products	Standard solutions, BPs identification	QTOF - MS LC-MS-MS
Stage (V): Method development	Apply standard methods (US-EPA method 1694 (2007) and standard method 6810 (2013) and adjust operational analysis based on instrument condition	

Phase 6: (7 stages)

UV/O_3 AOP Pilot plant studies

Phase 6: Pilot plant studies; Advanced oxidation by UV/O_3 AOP method
Matrices: DI water +SMX, PCM, CAF
Reactor volume: 70 Liter,
UV intensity: 20 mJ/cm^2
Water flow rate: 20 L/min
Ozone dose: 2 – 14 mg/L, $O_{2\ flow}$ rate = 0.5 to 2 L/min

Stages	Experiment condition	Analytical method
Stage (I): UVC sole **+ SMX +PCM +CAF** **Mechanism of UV photolysis reaction**	Batch and semi-continuous flow pH = 7, UV = 20 mJ/cm^2	QTOF - MS LC-MS-MS COD, TOC spectrophotometer
Stage (II): Ozone dissolution experiments; Range of oxygen and ozone production; ozone concentration rate adjustment; ozone concentration changes to ECs change	Ozone production based on oxygen flow rate O_2 flow = 0.5 -2.5L/m Dissolved O_3 = 0.25 – 0.8 (mg/L. min)	Ozone flow cell and ozone probe
Stage (III): Ozone sole treatment + SMX **Compare UVC photolysis and ozonation; Mechanism of ozone reaction Compare to other work**	Semi-continuous flow pH = 7, O_3 = 2-14 mg/L,	QTOF - MS LC-MS-MS COD, TOC spectrophotometer
Stage (IV): Ozone sole treatment + PCM **Mechanism of ozone reaction Compare to other work; Compare UVC photolysis and ozonation**	Semi-continuous flow pH = 7, O_3 = 2-14 mg/L,	QTOF - MS LC-MS-MS COD, TOC spectrophotometer
Stage (V): Ozone sole treatment + CAF **Mechanism of ozone reaction Compare to other work; Compare UVC photolysis and ozonation**	Semi-continuous flow pH = 7, O_3 = 2-14 mg/L,	QTOF - MS LC-MS-MS COD, TOC spectrophotometer
Stage (VI): **Pilot application by O_3/UV AOP** **SMX +PCM +CAF** **PCM Comparative treatment: UVC, Ozone, UV/O_3** **Comparative UVC, Ozone, UV/O_3 methods for SMX, PCM, CAF**	Semi-continuous flow pH = 7, O_3 = 2-14 mg/L, UV = 20 mJ/cm^2	QTOF - MS LC-MS-MS COD, TOC spectrophotometer
Stage (VII) Adjustment of technical parameters to find best condition	Find the most efficient condition and apply for maximum removal	

Phase 7: (13 stages)

AO/EMBR Hybrid system

Phase 7: AO/EMBR Hybrid system (Effluent + ECs +River water removal)
Matrix 1: Wastewater +PCM
Matrix 2: Effluent +PCM; Matrix 3: Effluent + SMX; Matrix 4: DI water + SMX
Matrix 5: Effluent + EE2; Matrix 6: River water; Matrix 7: River water + ECs
Experimental conditions: Technological parameters change

Stages	Experiment condition	Analytical method
Stage (I): PCM dosage spike to the EBR compartment; optimization and sampling in different time (wastewater and effluent)	PCM concentration Calculation, sampling plan	COD TOC
Stage (II): Study wastewater +PCM without changing operational condition	PCM spike in to the EBR reactor (20 mg/L)	COD TOC
Stage (III): Study wastewater +PCM by changing operational condition:	Aeration effect, pH change, oxidant dose, dosage optimization	COD TOC
Stage (IV) Study wastewater +PCM by changing operational condition:	UV intensity, nitrogen purge, TBA effect,	COD TOC
Stage (VI): Study effluent +SMX by changing operational condition:	Aeration effect, pH change, oxidant dose, dosage optimization	COD TOC
Stage (VII): Study effluent +SMX by changing operational condition:	UV intensity, nitrogen purge, TBA effect,	COD TOC
Stage (VIII): Study Effluent alone by changing operational condition:	Aeration effect, pH change, oxidant dose, dosage optimization	COD TOC
Stage (IX): Study River water alone by changing operational condition:	Aeration effect, pH change, oxidant dose, dosage optimization	COD TOC
Stage (X): Study River water +SMX by changing operational condition:	Aeration effect, pH change, oxidant dose, dosage optimization	COD TOC
Stage (XI): Study River water +PCM by changing operational condition:	Aeration effect, pH change, oxidant dose, dosage optimization	COD TOC
Stage (XII): Study River water +EE2 by changing operational condition:	Aeration effect, pH change, oxidant dose, dosage optimization	COD TOC
Stage (XIII) Adjustment of Technological parameters for optimization	Find the most efficient condition and apply for maximum removal	

Phase 8: (10 stages)

By-products investigation (effect of operational conditions)

Phase 8: By-products (BPs) investigation
Effect of operational conditions on by-products evolution
Effect of matrix type on by-products evolution

Stages	Experiment condition	Analytical method
Stage (I): BPs selection based on indication method	Select the most persistent and high abundance BPs in solution	QTOF - MS LC-MS-MS
Stage (II): BPs evolution in compare to parent ion	SMX (m/e = 254); BP- 99 BP-172, BP- 270, BP-288	
Stage (III): study the effect of operational conditions on SMX Aeration effect, pH change, oxidant dose, dosage optimization	pH = 3 to 10, H_2O_2 = 0.5 to 12 Mm, UV = 10 mJ/cm^2, air flow = 0.5 to 5 L/min	QTOF - MS LC-MS-MS
Stage (IV): study the effect of operational condition on BP- 99	pH = 3 to 10, H_2O_2 = 0.5 to 12 Mm, UV = 10 mJ/cm^2, air flow = 0.5 to 5 L/min	QTOF - MS LC-MS-MS
Stage (V): study the effect of operational condition on BP- 270	pH = 3 to 10, H_2O_2 = 0.5 to 12 Mm, UV = 10 mJ/cm^2, air flow = 0.5 to 5 L/min	QTOF - MS LC-MS-MS
Stage (VI): **optimization of technical parameters method development**	Find the most efficient condition and apply for maximum EC and BPs removal simultaneously	Apply standard methods and adjust operational analysis based on instrument condition
Stage (VII): study the effect of operational condition on BP- 99	Effluent matrix	QTOF - MS LC-MS-MS
Stage (VIII): study the effect of operational condition on BP- 270	River water matrix	QTOF - MS LC-MS-MS
Stage (IX): study mineralization of SMX and SMX reaction pathway	SMX mineralization end-products: NH_4^+, SO_4^- , NO_3^-	Ion chromatography
Stage (x): study the relation between structure of ECs and toxicity		

Other parameters indicated in Table 3.2 which influence treatment efficiency are considered in all treatment methods. One of the monitoring factors for reaction completion was UV intensity. The UV intensity has an increasing value toward the reaction completion. As the reaction direction goes to products, the UV intensity shows an increasing value. Sample port is located below the reactor. Treated samples were taken on designed time intervals. Treated samples were analyzed after treatment by the spectrophotometer, TOC, COD and HPLC and if further analysis required by LC-MS-MS in next experiments, then, samples were stored in the fridge.

3.4.4.2 Responce surface methodology (RSM) application for DOE

The operational conditions for AOPs, such as oxidant dose, UV dose, reaction time, the nature and concentration of target pollutant and other factors have a very important effect on reaction efficiency. Finding the best condition in such treatment methods that have several variables is very difficult even by conducting numerous experiments to include the effect of all variables. On the other hand, conducting numerous experiments would lead to increased time and cost but not to explore interaction between variables. In order to find the effect of independent variables to the removal efficiency, response surface methodology (RSM) and central composite design (CCD) are found to be effective methods (Myers 2009). In RSM one of the goals is designing the experiments to obtain the minimum number of test runs. In this research the second order polynomial equation is applied, where CCD is one of the most popular classes of second-order designs. CCD evolves using sequential experimentation by two-level factorial to fit a second-order response surface (RSM) to the designed variables. Many researchers have designed the chemical and electrochemical experiments by applying RSM (Li et al. 2010; Zhang Junwei et al.

2010; Sarrai et al. 2016). However, these processes such as catalytic based AOPs and Photo-Fenton using Box-Behnken designs (BBD) or CCD on synthetic samples to remove different pollutants. To our knowledge, there is no report available using CCD focusing on real wastewater effluent where UV/ H_2O_2 AOP targets the removal of micropollutants and EfOM. The main objective of this part of research is using RSM and CCD to optimize operational parameters for degradation of effluent organic matter (EfOM) and SMX by UV/H_2O_2 AOP treatment method. To verify the model, which was developed by RSM, the predicted results were evaluated by actual tests' results. Furthermore, the effects of operational parameters including pH, H_2O_2 dose and aeration on each other and on degradation efficiency were investigated. By applying these three variables, twenty sets of experiments were designed including six central points, six axial points and the rest was fractional factorial points (Fig.3.9).

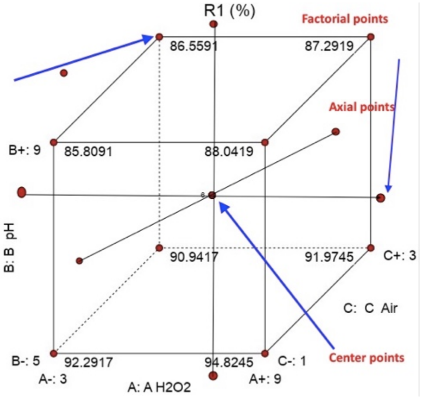


Figure 3.9. Central composite design for pH, H_2O_2 and aeration

Design expert statistical software version 11 was applied to perform regression analysis. The significance fit for the polynomial quadratic equation of predicted model to the experimental values was evaluated by regression analysis of variance, ANOVA. Optimization was planned to find the optimum parameters (pH, aeration rate and H_2O_2 dose) to reach maximum removal of target compounds (SMX, PCM, EE2) and COD, TOC.

3.5 Pilot plant O_3/UV AOP experiments, water treatment method

The pilot plant system (Figure 3.5) was designed and configured to be able to treat emerging contaminants in water with different continuous flow rates (liter/minute). Experiments were designed for batch and semi-continuous modes. In order to get a clear idea about treatment efficiency, some preliminary batch experiments were performed in advance. Before starting experiments, some preliminary water flow tests were conducted where UV lamps intensity and ozone dissolution in the setup were monitored.

3.5.1 Preliminary experiments

The main pilot plant piping, tubing and fittings materials were made of 316L stainless steel. On account of the high cost of stainless-steel materials and damage of stainless-steel ferrules after one-time screwing and fixing, the first pilot plant was assembled with plastic pipes, valves and fittings. The aim of this practice was 1- to simulate, examine and monitor water flow rates input, output, head loss in the system and check the pump head loss and power. 2- to control water flow through the Venturi by control valves, examine the vacuum produced in the ozone line through different water flow rates. 3- to examine the compatibility of piping and valves sizes (3/4”) with reactor opening sizes and water discharge and water recirculation through bypass. 4- to examine and monitor flow meter’s function.

These preliminary tests including compatibility of the size of the Venturi for the designed water flow rates were performed. The compatibility of pipes and valves sizes (3/4”) with reactor size and discharge flow rates on top of the reactor exit was examined. All the tests were confirmed, and water flow rates satisfied setup designed parameters. After successful preliminary tests, the plastic setup was replaced with stainless steel tubing and fittings and a new stainless-steel food grade pump was purchased and installed in the new pilot plant. For better mixing, a static mixer was installed after the Venturi line in the stainless-steel tubing.

After installation of the new setup, dry-air production devices as feed gas sources were replaced by oxygen as a new source of ozone production, due to insufficient ozone production in the system. Ozone and pH detector probes were calibrated and installed. UV lamps and UV detector installation and calibration for the desired functional range were performed.

3.5.2 Feed water preparation

A water container made of high-density polyethylene with a capacity of 150 gallons (576 liter) was prepared to reserve the synthetic water. The synthetic water samples including target compounds with known concentrations were prepared and made ready in order to transfer to the reactor. The water container was washed and cleaned after changing the sample concentration and changing the type of water (tap water or deionized water). The target compounds (PCM, SMX, CAF) were dissolved by methanol and/or hot water. For making the standard solutions, methanol/DI water mixture was used. For making synthetic water, target compounds were dissolved in water by increasing water temperature gradually and mixing gently. Each water sample with the desired concentration of target compound was prepared in 4-liter Erlenmeyer flask and mixed thoroughly and then transferred to 576-liter water container while half of the container was filled with water. Mixing in the container was carried out by recirculating the water solution with the pump. Simultaneously, enough water was adding to the container to reach the desired concentration. The concentration of samples was measured with a spectrophotometer and /or HPLC before any runs to verify the desired sample concentration.

3.5.3 Experimental plan; sole UVC, ozonation, O_3/UV AOP

All water treatment experiments were performed in a temperature range of 17-23 ^{0}C and neutral pH 7-7.5, which was monitored by in-line temperature and pH meter. The effect of temperature change on the results is not in the scope of this research.

In order to address the first objective of the proposal, experiments were planned to perform with UV alone, ozone alone and then a combination of UV and ozone treatment simultaneously. For the UV experiments, some series of batch and semi-continuous UV treatment tests were planned with different sample concentrations (11.3, 25, 52 and 104 mg/L) and different UV exposure times (0 to 60 minutes with five- minute intervals). For performing treatment with ozone alone and O_3/UV, the aforementioned plan was considered with semi-continuous mode.

3.5.4 Experimental design to investigate removal efficiency and by-products reduction

Several factors affect by-products (BPs) formation in a treatment by oxidation. Contact time (exposure time of pollutants to oxidants), pH of water, oxidant dose and the concentration of target compound(s) are the major influencing factors on BPs formation during water treatment (Ijpelaar et al. 2007; Ratpukdi 2009; Dotson et al. 2010). Generally, exposure time has a linear correlation to UV dose and ozone dose.

Some of these factors were applied at different values in order to determine the best operation conditions to minimize by-product formation in UV/O_3 treatment and while keeping maximum removal efficiency of pollutants.

The primary concern in a water treatment plant is a 100% removal efficiency that means elimination of the whole target pollutant from the water, then, a sampling process is important.

The first sample was taken at time zero before the treatment and other samples would be taken in a 5-minute interval and after 100% removal. Then, the concentration of target compounds and pH of synthetic water are other factors that should be taken into accounts.

In current research, a conventional experimental design was applied. Therefore, each individual variable could change within a range but other variables is kept constant. Oxidant dose (ozone), contact time and UV dose were considered as operational parameters.

For oxidant dose, oxygen range between 0.2 and 2.5 L/min and corresponding ozone rates of 0.1 to 0.8 (mg/L). min was considered. For higher ozone rates, the reactions were very fast (based on results in chapter 4) and there was a very limited time for study the reaction. The UV intensities ranging from 4 to 20 mJ/cm^2 were considered for the next stage of work. UV and ozone doses for assigned contact times were fixed. Table 3.2. summarizes the experimental parameter ranges, which were applied to monitor removal efficiency of target pollutants.

Table 3.3. Technological parameters' ranges to perform ozone based AOP experiments

Parameter range	**Minimum**	**Maximum**
O_2 rate	0.2 L/min	2.5 L/min
Ozone rate	0.1 (mg/L). min	0.8 (mg/L). min
UV intensity	5 mJ/cm^2	20 mJ/cm^2
Contact time	0.0 min	60 min

3.5.5 Ozone production and control

Highly pure oxygen (99.99%) was fed to ozone production devices and passed through the discharge electrodes (Corona discharge). By this method, ozone is produced and goes to the Balance barometer. Oxygen was provided from Air-liquid Canada. Ozone generators model VMUS-4 were provided by Azcozone Company. The balance-barometer is another part of the ozone production system, which controls the ozone production flow, volume and safety precautions along with a stainless-steel ozone control 1/4" valve. When ozone is produced, it passes through a Kynar tube and goes to the balance barometer. The balance-barometer was connected to the Venturi by another Kynar tube. When water passes through the Venturi, makes a negative pressure and produces a vacuum through the line connected to the balance-barometer in order to inject the ozone to the water flow.

3.5.6 Ozone /oxygen flow, water flow rate and ozone dissolution

The mixture of oxygen/ozone at adjusted rates (0.5-2.5 L min^{-1}) was passed under the Venturi injector into the solution. Some portion of ozone gas stream was dissolved in water, which is measured by in-line ozone meter, and the residual ozone went to the ventilation system.

The amount of ozone production depends on oxygen flow to the ozone generator. The oxygen flow was controlled by two flow meters to the two ozone generators.

The amount of ozone input to the pilot plant system could be controlled by the oxygen flow rate to the ozone generator, ozone input to the balance-barometer and amount of suction under the Venturi simultaneously. The water flow rate through the Venturi was in the range of 2-2.4 gallon/minute and through the second line to the Venturi was in the range of 1-5 gallon/minute for desired oxygen-ozone mixture rates.

For semi-continuous mode, the Venturi valves should be adjusted for the sufficient vacuum and injection of the desired ozone amount to the water. The amount of suction is adjusted based on water flow, which passes through Venturi and the second water line parallel to the Venturi line. For maximum suction, the maximum water flow (between 20 - 25 L/m) passed through Venturi while the second valve was closed. When lower suction required, the second valve should be opened gradually to reach the desired suction value.

Ozone dissolved concentration was recorded in-line by passing the water flow to the ozone meter flow-cell. Therefore, the water that passed through the flow-cell was returned to the system. Hence it is necessary to adjust vacuum valves again and make the adjustment through all the valves (2 Venturi valves and 3 flow-cell valves).

Ozone was dissolved in water by means of the ozone injector, static mixer and perforated plate. Counter-current water flow contributes to better mixing. Nominal ozone production is approximately 6.5 g/h at 6 L/min of oxygen in each ozone generator according to the ozone device manufacturer document. By considering the nominal amount of ozone production of 6.5 g/h, for oxygen flows of 0.5, 2 and 2.5 L/min, ozone dissolved mass production rates of 9.2, 37 and 44 mg/minute was obtained respectively. Then for the 60-liter system volume, values of 0.15, 0.6 and 0.7 (mg/L). min would be the production rates of ozone dissolved in water, respectively. The nominal and monitored dissolved ozone by the inline ozone detector are represented in Table 3.4.

Table 3.4. Ozone production and ozone dissolved values in liquid film (nominal and monitored)

O_2 flow (L/min)	**O_3 production (Calculated-nominal)**	**Dissolved O_3 (Calculated-nominal)**	**Dissolved O_3 (Monitored)**
	(mg/L). min	(mg/L). min	(mg/L). min
2.5	2.1	0.7	0.8
2	1.8	0.6	0.7
0.5	0.45	0.15	0.25

As it is shown in table 3.4, the dissolved ozone concentration values were greater than nominal values because of engineering design of the system.

3.5.7 UVC irradiation system and control

UVC or Ultraviolet C is short wave UV (100- 280 nm) that is germicidal irradiation which is used for disinfection and inactivation of microorganism (NIOSH, 2020). For this research, higher doses of UVC were applied more than germicidal application.

3.5.7.1 UV lamps configuration and control

Three 250 W low-pressure monochromatic UV lamps (253.7 nm, Trojan Co.) were used as the UVC source in the UV experiments. The UV lamps were positioned in the reactor vertically and parallel to the water stream. They were located in the reactor endplate at a 60-degree triangle with an equal distance from the reactor wall (5 cm from reactor wall and 5 cm from triangle center). This configuration distributes the UV irradiation equally and gives the water stream maximum dose. UV lamps are controlled with a Control Panel (CP). The CP works as an interface to the UV system for local control, monitoring and configuration of the system. The power supplies and ballasts that provide power distribution to the UV lamps and UV sensor are positioned in the CP. The UV sensor records the UV intensity in mW/cm^2, which is displayed on the control panel.

3.5.7.2 The intensity and dose of UV lamps

For current experiments, UV intensity was monitored by a UV sensor mounted in the middle of arc length of the lamp. In batch and continuous operation modes, the mean UV intensity values were recorded as 21.5 and 20-mW/ cm^2, respectively. These recordings were measured in a pure tap water without adding any contaminant where UV transmittance was equal to UVT =95% @ 254 nm.

The UV lamps were warmed up for 3 minutes before initiating each experiment. After 3 minutes, the sample exposure time in the reactor was considered. The UV dose was calculated with exposure time multiplied by UV intensity (equation 3.1).

3.5.8 Treatment and sampling

Treatment runs were planned in batch and semi- continuous operation modes. For each treatment run, in batch and semi-continuous modes, the reactor was filled with the paracetamol solution ($C_{0\text{-PCM}}$ = 72, 165, 344, 688 µmol L^{-1}) or other ECs.

Batch treatments (UV alone) were repeated 5 times for examining treatment's reproducibility. For each run 8 samples plus 3 pre-treatment samples were taken for analysis (total of 55 samples for each UV treatments). Ozone runs were performed in semi-continuous mode with pure water and with synthetic water. Ozone dissolution rate in pure water at different oxygen rates was monitored and recorded. Four ozone runs with different concentrations of synthetic water ($C_{0\text{-PCM}}$ = 72, 165, 344, 688 µmol L^{-1}) were performed and repeated. In each ozone treatment, ozone dissolved concentration was monitored. Ozone treatments were continued until all the paracetamol or ECs were removed from the water and ozone dissolved concentration increased to its highest values. Ozone dissolved concentration was monitored every minute. Ozone concentration in water was 0.0 mg/L at the beginning of treatment and remained constant until most of the paracetamol or ECs were degraded. After ECs were eliminated completely, the ozone value increased gradually. Then, treatment runs continued until the ozone concentration reached the maximum amount in close to pure water before ECs spiking.

For each run, 8 samples plus 3 pre-treatment samples were taken for analysis (total of 44 samples). Ozone-UV runs were operated at the same condition as ozone tests were performed. For ozone-UV runs, the retention time for completion of the reaction was lower in comparison to ozone alone. One of the monitoring factors for reaction completion was UV intensity value in addition to ozone dissolved concentration value. The UV intensity has an increasing value toward the reaction completion. As the reaction direction goes to the products, the UV intensity shows an increasing rate.

Ozone-UV runs were performed for different ECs concentrations. For each run 8 samples plus 3 pre-treatment samples were taken for analysis (total of 33 samples). Sample ports were located after the water tank, before the reactor on the bottom and after the reactor on top of the reactor. Before each treatment, 3 samples were taken from the sample ports to verify the feed water concentrations. Treated samples were taken on designed time intervals and detention times. Treated samples were analyzed after treatment at once by the spectrophotometer and if further analysis required by LC-MS-MS or HPLC, samples were stored in the fridge. The total number of samples including calibration curve samples was more than180 for each treatment.

3.6 Analytical methods

Analyses were carried out by UV-Spectrophotometer, HPLC, COD and TOC vials and LC-MS-MS. For evaluation of treatment performance and quantification at mg/L concentrations, HPLC and two UV-spectrophotometers were applied. The first was a UV-Visible single beam with matched quartz cells (1 cm) model Evolution 201 from Fisher Scientific Co (Appendix 3a). The second was Agilent Cary 8454 UV-Visible with photodiode array (PDA) detector.

For preliminary qualification tests of transformation by-products, LC-MS 6210 QTOF was applied. Ionization sources were ESI+, ESI-. The APCI and mass analyzer was Time of Flight MS-2 with mass range: 40 - 4,000 m/z and a resolution of 10,000 FWHM (full width at half maximum). The FWHM was used to define resolution.

For quantification analysis at ppb levels the Micromass Quattro LC Waters (triple quadrupole) was applied. Its ionization sources were ESI+, ESI- and APCI and mass analyzer was Tandem Quadrupole MS with mass Range: 20 - 4,000 m/z and resolution of 1,000 FWHM. Sample introduction was to the HPLC (Agilent HP 1200) and the column for HPLC was C18 reversed-phase, X-Select HSS T3 XP column purchased from the Waters company with 100Å, 2.5 µm packing size and 3 mm x 50 mm dimensions and, 2 - 8 pH range. The condition of the analyses is described in the next part.

3.6.1 Analytical experiments by spectrophotometer

Standard solution of paracetamol (PCM) and other emerging contaminants with two series of concentrations from 0.1 to 20 and 1 to 70 mg/L were prepared and used for spectrophotometry tests.

Table 3.5 Paracetamol absorption at maximum peak

Name	**Peaks (nm)**	**Abs (AU)**	**Valleys (nm)**	**Abs (AU)**
PCM	243	0.64127	216.0	0.29199

At first step, the solution was scanned in UV spectrophotometer between 200 nm to 350 nm on absorption mode and diluents (DI water) were used as blanks. Table 3.5 shows paracetamol absorption on 0.64127 on maximum wavelength on 243 nm. This 243 nm maximum was selected for making calibration curves and measure removal efficiency of paracetamol (Appendix 4). This analytical method for measuring paracetamol concentration in low mg/L is very simple, accurate and reproducible.

To investigate the reproducibility of the method, another spectrophotometer (Agilent 8454) was applied (Appendix 3.b). A series of PCM solutions, with concentrations from 5 to 90 mg/L, was prepared and scanned from 200 nm to 350 nm (Appendix 6). The maximum absorption for the samples was 243 nm.

3.6.2 Method validation and linearity

Two calibration curves were plotted separately for paracetamol with seven points in a concentration range from 0-90 mg/L and 0-10 mg/L (Table 3.6).

Table 3.6. Paracetamol UV absorbance at different concentrations

Standard name	PCM (mg/L)	Abs < 243 nm >
1	5.00	0.32011
2	10.00	0.64089
3	30.00	1.90900
4	50.00	3.10030
5	70.00	3.75540
6	90.00	4.00000

The response of the equation was found to be linear within the investigation concentration range (0-10 mg/L) where a linear regression equation $Y_1 = 0.064 X + 0.055$ with a correlation coefficient of 0.997 was found. For the concentration range (0-90 mg/L) a linear regression equation $Y_2 = 0.043 X + 0.060$ with correlation coefficient of 0.998 was found as well (Appendix 5). As it is depicted in Appendix 6, Beer Lambert law is not valid for concentrations above 50 mg/L for paracetamol.

3.6.3 COD and TOC analysis for treatment assessment

As it was mentioned in chapter 2, the most popular indicators to assess dissolved organic carbon (DOC) in solution, during emerging contaminants (ECs) and their by-products treatment, are COD and TOC analysis, i.e. chemical oxygen demand and total organic carbon respectively. For these measurements, COD Ultra-low range (0.7-40 mg/L) and TOC low range (0.3-20 mg/L) reagent kits were purchased from HACH company. HACH DRB200 thermostat heating reactor and HACH DR2800 spectrophotometer were used for the tests (Appendix 4). For evaluating the extent of micropollutants mineralization, COD and TOC HACH protocols (method 8000 and method 10129 respectively) were applied respectively. Moreover, for removal efficiency, equation 3.2 and also the following calculations have been applied as follow:

$$R_2 = (COD_o - COD_t) / COD_t \times 100 \qquad (3.3)$$

$$R_3 = (TOC_o - TOC_t) / TOC_o \times 100 \qquad (3.4)$$

Where R_1, R_2 and R_3 are the removal efficiency and Ct and C_o are target compounds concentrations at time t and time zero respectively. COD_o *and* COD_t are COD at time zero respectively and time (t), TOC_o *and* TOC_t are TOC at time zero and time (t) respectively.

3.6.4 Analytical tests by LC-MS-MS

One of the most common methods to identify traces of target compounds is liquid chromatography coupled with mass spectrometry which was used in the current research. Then, protocols for analytical experiments such as US-EPA method 1694 (2007) and standard method 6810 (2013), were developed based on the compound's nature and instrument condition. In the current research, 6210 time of flight LC-MS was applied for qualitative analysis and Waters Quattro micro LC-MS-MS measurements were applied for quantitative analysis (Appendix 5).

3.6.5 Mass chromatogram interpretation

In order to identify unknown by-products resulting from the designed treatment (ozonation and/ or O_3/UV, UV/ H_2O_2), a mass library can be applied. By using a library of mass spectra and comparing with experimental mass spectrum or using software assisted interpretation of mass spectra, the unknown by-products could be identified.

Following the assigned spectrum of interest, the structure of by-products and fragments were assessed. Each spectrum of interest represents the m/z of a compound. For example, the mass of 110.05 may represent the PCM fragment that is hydroquinone ($C_6H_6O_2$). By searching the elemental composition in the applied mass spectrometer (Time of flight) more than 10 matches were found by this instrument with a resolution of 0.020 Dalton. For increasing the resolution of analysis and limit the number of candidate compounds of interest, high Resolution Mass Spectrometry (HRMS) can be used. The HRMS gives the molecular formula of compounds with more resolution up to 0.002 Dalton. Therefore, the number of possible molecular formulas of compounds would be decreased. After this step, by looking at the structure of target compounds and possible fragments or transformation products, the structure of unknown compounds can be proposed.

3.6.6 Solid phase extraction method

Extraction of target compounds was performed by solid phase extraction (SPE) method. Extraction manifold 20-position and SPE cartridge (Oasis HLB 6 cc vacuum cartridge, 500 mg sorbent per cartridge) were prepared from Waters Co. (Figure 3.10). At first step, SPE cartridges were conditioned by rinsing with 3 mL dichloromethane followed by 5 mL methanol and then 7 mL of DI water. After conditioning, an extraction was performed by loading 200 mL sample at a rate of 10 mL/min.

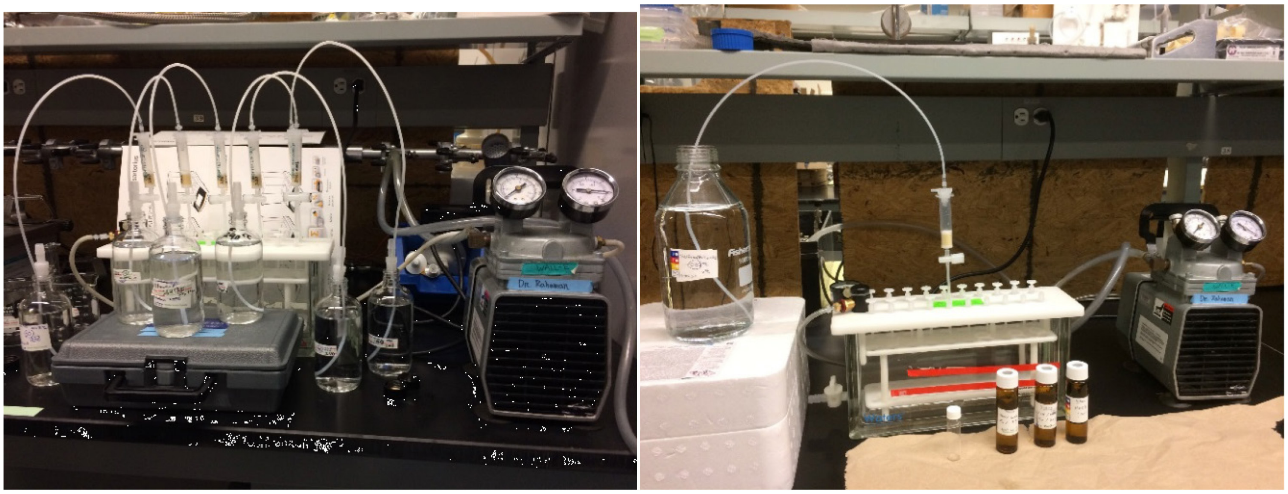


Figure 3.10. Extraction of target pollutants by solid phase extraction (SPE) method

Once loading was completed, SPE cartridges was rinsed with 3.0 mL DI water and then 4.0 mL of the methanol/water (5%) mixture. Then the columns were dried with compressed air for 40 minutes (~12 lb./in^2 or 83 kPa).

The cartridge, then, was eluted with 6.0 mL methanol and the volume of eluent was reduced to less than 1 mL using either zero-grade air or N_2 (Figure 3.11). The value of 1 mL extract was transferred to a 1.5 mL auto sampler vial and finally the vials containing extracts were stored in refrigerator until the time of analysis. The recovery of extraction method was calculated by the standard concentration of target compounds and then applied to the real samples. The developed method is different in operational condition from standard method 6810 with respect to the rate of sample loading, vacuumed for elution, the mixture and type of solvents.

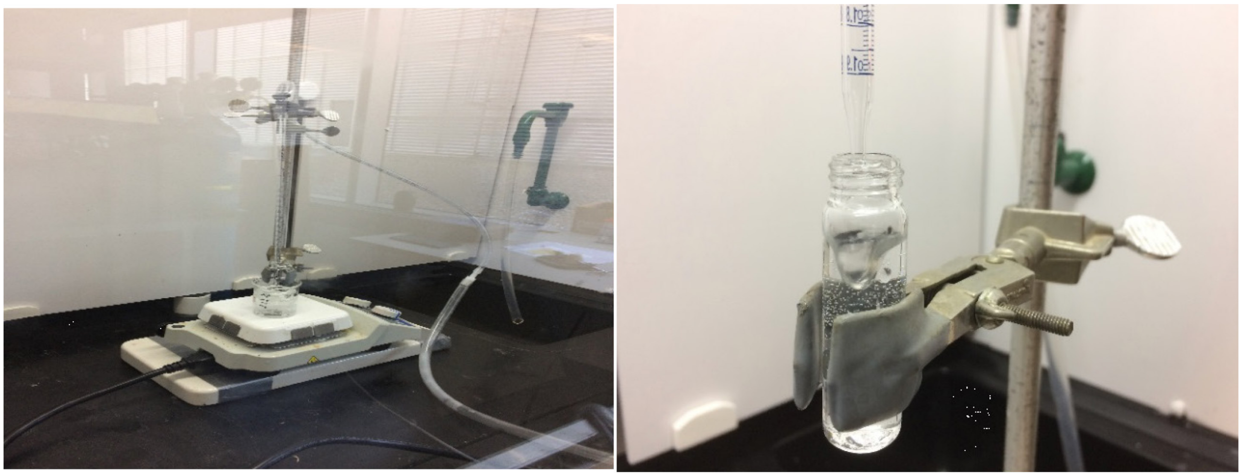


Figure 3.11. Reduction the eluent (extracted target compounds) by nitrogen stream

3.6.7 Analytical method development

The LC-MS experiments were performed and developed on a QTOF 6210 mass spectrometer coupled to a capillary HPLC 1100 series, both from Agilent Technologies and for LC-MS-MS experiments the same HPLC was coupled to Waters Quattro micro LC-MS-MS. For the HPLC method, the chromatographic separation was performed on a SB-C18 RRHD, 1.8 mm, 3.0 x 50 mm column from Agilent, at a flow rate of 0.3 mL/min. A gradient elution was applied to the column in which composition of solvent A was acetonitrile and solvent B was 0.1% formic acid+ H_2O. The mobile phase flow rate was adjusted at 0.25 ml/min and gradient elution was started 7 min for 95% of A and 5% of B and then 8 min for 20% A and 80% B and 9 min back to

95% A and 5% B. Mass analyses were carried out by positive electron spray (API^+) method in which all the ions were protonated. The capillary and cone voltages were operated at 3.5 kV and 25 V, respectively. The temperatures of the electrospray source and nebulizing gas were 80 and 300 ^{O}C, respectively. Nitrogen was used as both the nebulizing gas and dissolution gas at flow rates of 83 and 294 L/h, respectively. Ultra-high-purity argon at a pressure of 3.6 x 10-3 mbar was used as collision gas in the collision cell. The collision energy of 20(eV) was used to generate product ion (152.07) for the target compounds. For ECs analysis other researchers have used the similar method (Yargeau et al. 2007; Carlson et al. 2015). While, for the current research, US-EPA method 1694 (2007) and standard method 6810 (2013) were developed for target compounds based on applied instruments.

3.7 Investigation of electrical energy consumption

The energy requirements as a numerical expression can be used to evaluate the performance of treatment efficiency in UV-based advanced oxidation methods. In advanced oxidation processes (AOPs), the amount of energy which is required to reduce one log (90%) of pollution in one metric cubic of water is defined as electrical energy per order (E_{EO}) (Asaithambi et al. 2015), where the unit of energy is considered in kWh, the volume of pollutant water in liter (L), the time in hour while the C is the concentration of target compound (US.EPA). The E_{EO} unit is kWh/1000 m^3/order of removal (Behnajady et al. 2006).

According to International Union of Pure and Applied Chemistry (IUPAC), the following equation was applied to evaluate the energy consumption for contaminant removal from a water sample (Bolton et al. 2001).

$$E_{EO}\,(kWh/order) = 1000 \times (P \times t) / (V \times \log (C_i / C_f)) \qquad (3.7)$$

where:

P = AOP system power (kW)； V = treated water volume (L); t = required time for treating the water (h); Ci = initial concentration of the target pollutant (mole /L); Cf = final concentration of the target pollutant (mole /L).

4 Outcomes of the study

4.1 Phase 2: Micropollutants' direct photolysis

Application of UV light in water treatment has several advantages either for disinfection purposes or degradation of chemical compounds. Another considerable advantage of UV irradiation in water treatment is its suitability for high water flow rates with short contact time (Gibson et al. 2016).

In phase 2, target pollutants (paracetamol (PCM) and sulfamethoxazole (SMX)) dissolved in deionized water (DIW) were exposed to direct UV light at higher UV doses above 150 mJ/cm^2. This UV dose is higher than doses required for disinfecting purposes, inactivation and 6 log reduction of all forms of microorganisms (Viruses, protozoan, molds, yeasts, bacteria, spore) (Marshall et al. 2003; Light Sources Inc and American Ultraviolet Company 2014; Chevrefils et al. 2006). The following sections discuss the target pollutants' degradation by UV photolysis.

4.1.1 Paracetamol UV Photolysis

Table 4.1 shows PCM removal efficiency (R%) after 60 minutes of UV irradiation in a batch mode treatment. After 60 minutes, the paracetamol solution received 774 mJ/cm^2 energy, which led to paracetamol degradation of 35%-36 % from its initial concentration.

Experiments were repeated at different exposure times, different concentrations, and different types of aqueous medium. The results showed experiment reproducibility with similar removal efficiency (35% - 36%) when PCM receives the same UV dose. During 60 minutes of Ultraviolet irradiation treatment, about one third of the target compound was removed in the medium; which shows the impact of UV on paracetamol destruction that accounts for a considerable molar extinction coefficient (ε =750 M^{-1} cm^{-1}) of PCM.

Table 4.1. Removal efficiency of Paracetamol (C_{in} = 70-80 µmole/L) by sole UV irradiation treatment at different time in a batch mode treatment. UVC = 600 W intensity =21.5 mJ/cm2, solution volume= 70 Liter in reactor of pilot, temperature 18- 20 °C, pH =7, reaction time = 60 min

PCM Sample No.	**Removal%**	**Matrix**	**UV dose (m J/ cm^2)** I = 21.5 mW/cm^2	**Detention time (min)**	**C_{in}(µM)**	**C_f(µM)**
1	35%	TW	774	60	74	48.1
2	35%	TW	774	60	79	51.3
3	36%	DIW	774	60	72	46.1

TW: Tap water; DIW: Deionized water

The tests were repeated for semi-continuous mode. Results for such a UV treatment in semi-continuous mode are demonstrated in Table 4.2. After 60 minutes of treatment in batch and semi-continuous modes, 35.5% and 31% of PCM were removed respectively. However, the latter received less UV dose (Table 4.2).

Table 4.2. Comparison of removal efficiency of paracetamol by UV irradiation treatment in a batch (1) and semi-continuous mode (2), UVC (600 W) intensity =20-21.5 mJ/cm^2, solution volume= 70 Liter reactor in pilot, temperature 18- 20 °C, pH =7, semi-continuous recirculation rate= 25 L/min, time = 60 min

PCM Sample No.	**Removal %**	**UV dose (m J/ cm^2)** I (1) = 21.5 mW/cm^2 I (2) = 20.0 mW/cm^2	**Detention time (min)**	**C $_{in}$(µM)**	**C $_f$ (µM)**
1 (batch mode)	35.5%	774	60	74	47.7
2 (semi-continuous)	31%	720	60	74	51.1

I (1) = UV dose in batch mode; I (2) = UV dose in semi-continuous mode

In this experiment, by considering linear correlation between UV dose and removal percentage, the R% for sample 2 in table 4.2 should be 33.2%, but the result is much lower (31%). The lesser R% could be due to water flow rate (25 L/min) in comparison to batch tests. Indeed, the water flow causes more light scattering, water bubbles, and UV light shielding.

4.1.1 Sulfamethoxazole UV photolysis

During 60 minutes of experiment, SMX in water solution received 387 mJ/cm^2 energy and absorbed UV light efficiently. The experiments were continued for 180 minutes for further degradation. The results showed very fast SMX degradation at early initial time (5 minutes) but after 60 minutes, the degradation rate slowed down (Figure 4.1). This phenomenon may attribute to the formation of SMX by-products that shield UV irradiation and prohibit further degradation.

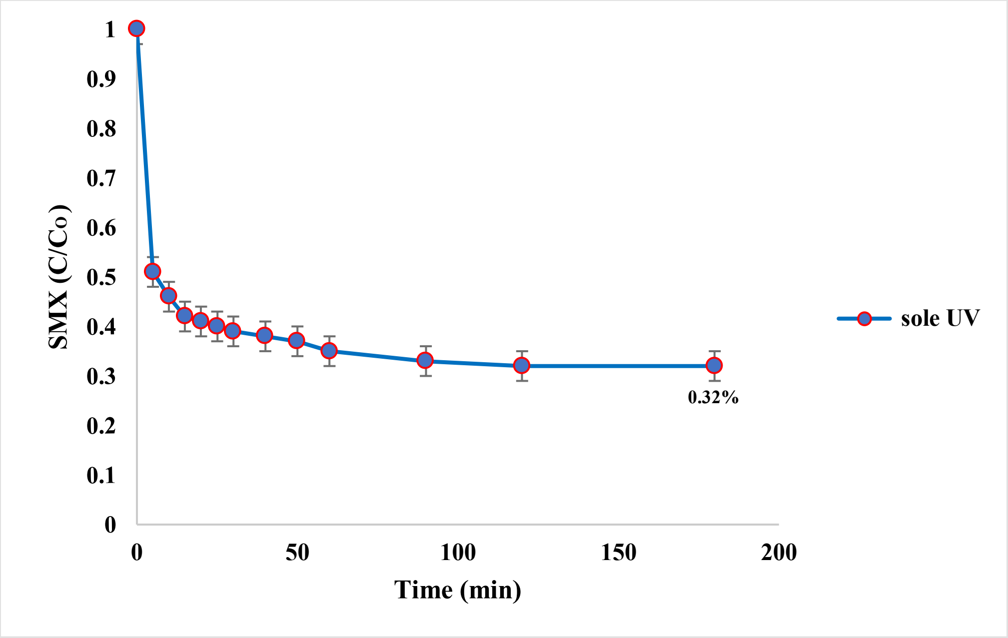


Figure 4.1. SMX removal by UV irradiation alone. Experiment condition: UVC (40 W) intensity =10 mJ/cm^2, reaction time = 60 min, solution volume=3L (irradiated), 4L (total volume), temperature 18- 20 °C, pH = 6, airflow rate= 0 L/min, recirculation rate= 3.2 L/min, reaction time = 180 min

Influence of water media

In order to examine the effect of water medium on treatment efficiency, the comparative tests were carried out on DI water and tap water (TW). Table 4.3 shows the performance results, which are almost the same. The lower value for tap water would be due to hardness of tap water (average 119 mg/L) in Montreal, where carbonates and bicarbonates act as OH radical scavengers (Montreal 2016).

Table 4.3. Removal efficiency of Sulfamethoxazole (C_{in} =55 µmole/L) by UV irradiation treatment in semi continuous mode of treatment. UVC (40 W) intensity =10 mJ/cm^2, reaction time = 60 min, solution volume=3L (irradiated), 4L(total), temperature 18- 20 °C, pH = 6, recirculation rate= 2 L/min

SMX **Sample No.**	**Removal%**	**Matrix**	**UV dose (m J/ cm^2)** **I = 10.5 m W/cm^2**	**Detention time (min)**	**C_{in}(µM)**	**C_f(µM)**
1	64%	DIW	387	60	55	19.8
2	63%	TW	387	60	55	20.4

TW: Tap water; DIW: Deionized water

4.1.2 Photolytic removal comparison between PCM and SMX

According to the information presented in Table 4.4, the removal efficiency by UV photolysis is more than twice higher for SMX compared to PCM. Sulfamethoxazole has molar absorption coefficient (ε)=17527 M $^{-1}$ cm^{-1}(Nelis et al. 1991) while paracetamol has much less molar absorption coefficient (ε) = 750 M $^{-1}$ cm^{-1} (Morelli 1989).

Table 4.4. SMX and PCM molar absorption coefficient (ε), UV dose consumption and removal efficiency Experiment conditions: semi continuous mode of treatment. UVC (40 W) intensity =10 mJ/cm^2, reaction time = 60 min, solution volume=3L (irradiated), 4L(total), temperature 18- 20 °C, pH = 6, recirculation rate= 2 L/min

Sample	**Removal%**	**ε** **M $^{-1}$ cm^{-1}**	**Matrix**	**UV dose (m J/ cm^2)**	**Detention time (min)**	**C_{in}*(μM)***	**C_f*(μM)***
SMX	64%	17527	DIW	387	60	55	19.8
PCM	28%	750	DIW	387	60	55	39.6

DIW: Deionized water

The absorption coefficient (*ε*) can predict a compound's removal efficiency during the treatment with UV irradiation (Kwon et al. 2018a). Higher molar absorption coefficient leads to higher UV absorption and a significant degradation. The organic pollutants (such as PCM) with a low quantum yield or molar absorption coefficient, has a weak degradation under UV treatment (Bolton et al. 2002; Carlson et al. 2015; Kwon et al. 2018b). At low quantum yield the number of PCM molecules degraded per Einstein (N quanta) when light absorbed is low.

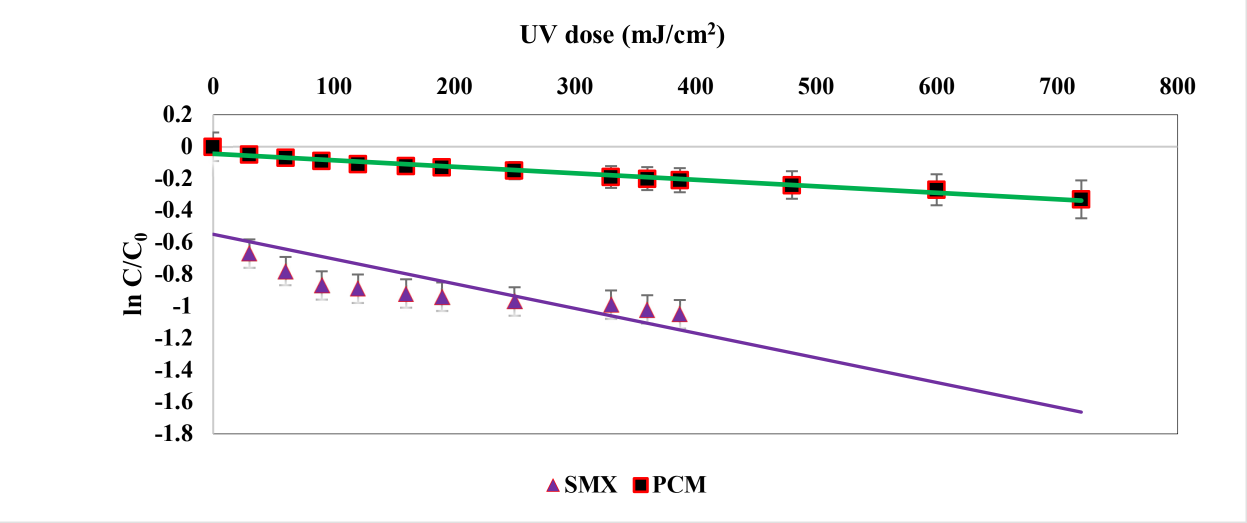


Figure 4.2. Micropollutants (SMX, PCM) degradation by 254 UVC photolysis, Experiment condition: $[SMX]_0$ = 0.55 μM, $[PCM]_0$ = 0.55 μM; UVC (40 W) intensity =10 mJ/cm^2, reaction time = 60 -120 min, solution volume=3L (irradiated) ,4L (total), temperature 18- 20 °C, recirculation rate= 2 L/min

4.1.3 Mechanism of target pollutants degradation by UV light

One of the steps behind the destruction of target pollutants' (SMX and PCM) would be illustrated as a general energy diagram in Figure 4.3. The mechanism of PCM and SMX reaction with UV light can be described as a consequence of energy absorbed by the target compound. The absorption in the UV-C range (253.7 nm) led to breakdown of PCM and SMX structures. UV directly cleaves bonds in PCM and SMX molecules by direct photolysis. Photons emitted by UV have sufficient energy to raise pollutant molecules to the excited electronic states that are unstable in environmental conditions (Figure 4.3).

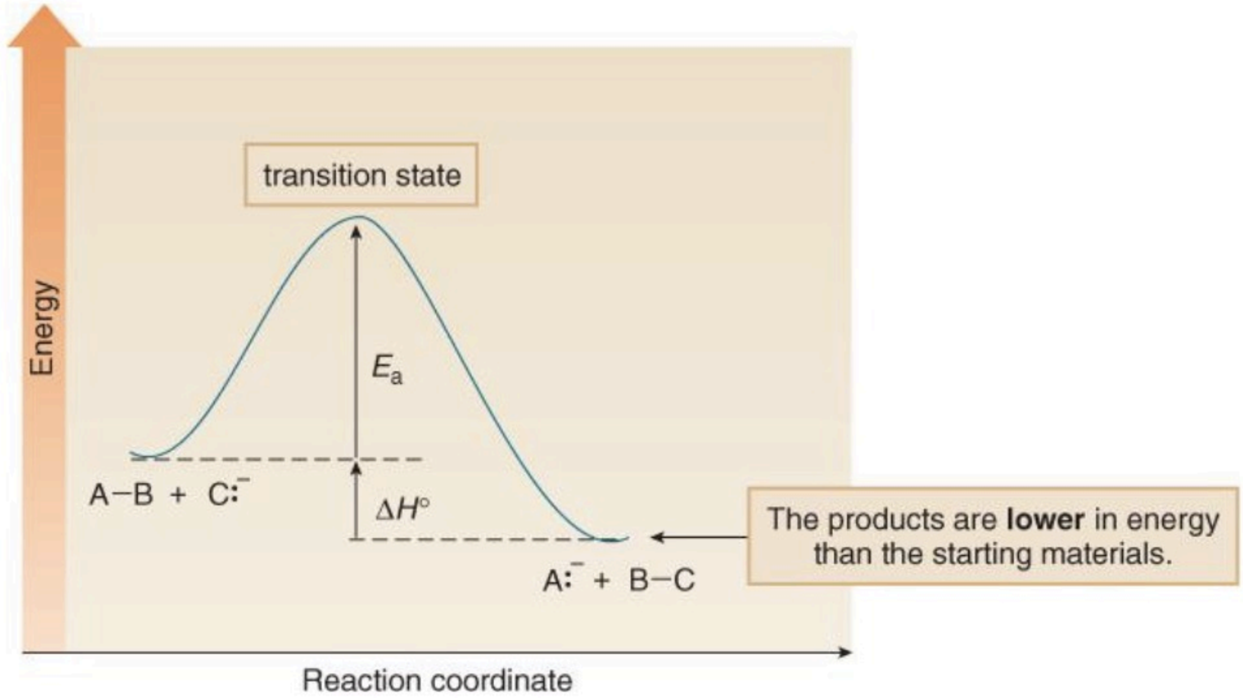


Figure 4.3. Reactants to products energy changes diagram (Samant 2001)

Transferred energy can be returned to the ground state or/and promote chemical reactions. When PCM and SMX go through the chemical reaction, it would be ionized by losing an electron as represented by the following reactions.

$$PCM + h\nu \rightarrow PCM^{+} + e^{-}$$

$$SMX + h\nu \rightarrow SMX^{+} + e^{-}$$

4.1.4 Comparison to other studies

Other studies on degradation of pharmaceutical active compounds (PhACs) by direct UV photolysis are consistent with this research results. Some studies show a negligible degradation by LP-UV (Rosenfeldt et al. 2004; Chin et al. 2005).

However, some other results showed higher removal of target compounds (Kwon et al. 2018b; Thomson et al. 2002). This could be related to the following reasons: The first reason is the nature and chemical structure of pollutants. Some organic pollutants have structures which are hard to break, while some other organic pollutants have structures that are easy to break down. The second reason is molar absorption coefficient and UV light absorption by PhACs. Molar absorption coefficient for PCM is 750 (ε=750 M^{-1} cm^{-1}), which is high in comparison to some other PhACs. On the other hand, the maximum UV light absorption for PCM is 243nm which is in the range of UV irradiation maximum peak of 254nm.

4.2 Phase 3: Advanced oxidation by H_2O_2/UV AOP method for micropollutants removal

4.2.1 Method validation

In order to validate the LC-MS-MS analytical method, a calibration curve was depicted. The calibration curve plotted the peak intensity of a target pollutant and indicates the target compound abundance versus the actual amounts of target pollutants' concentrations ranging from 1μg to 25mg.

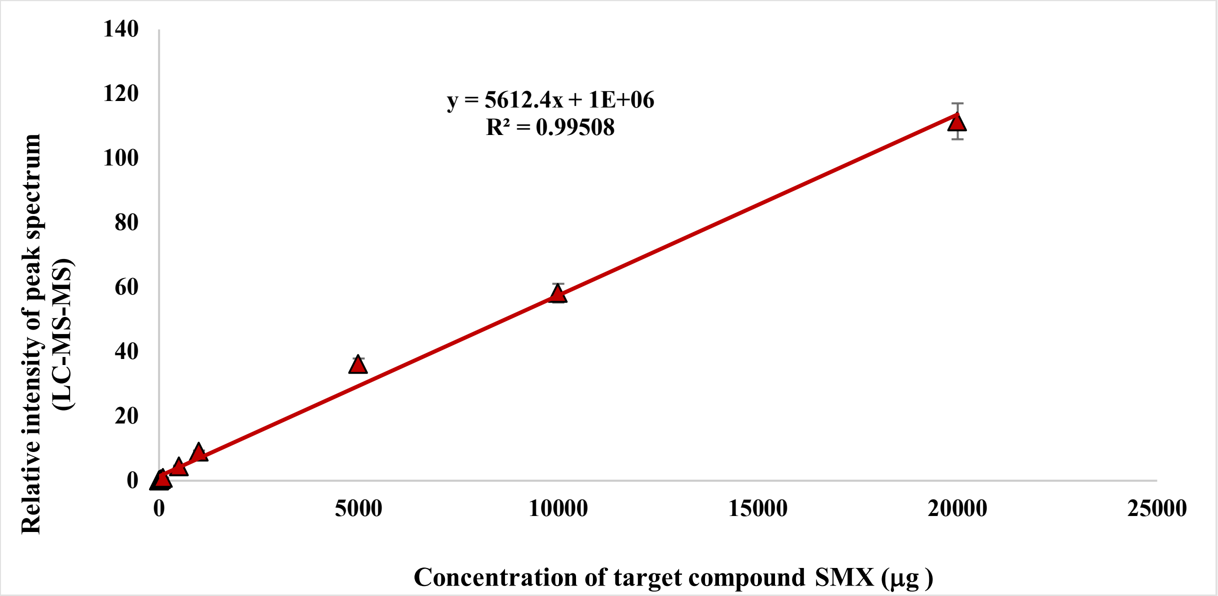


Figure 4.4. Calibration curve for the relative intensity and concentration of SMX target compound

Figure 4.4 shows a linear relationship between the peak intensity and target compound concentration at the range of 1μg to 25mg with the linear regression equation $Y_1 = 5612.4 X + 1E^{+6}$. The linear curve shows a best fit by $R^2 = 0.995$ for this relationship that is an indication of analysis in a validated range.

Figure 4.5 shows a linear relationship between peak intensity and reaction time for 120 min with the linear regression equation $Y_1 = 9001.2\ X + 9951.2$. The linear curve shows a best fit with $R^2 = 0.99984$ for this relationship that is a positive indication of analysis in a validated range.

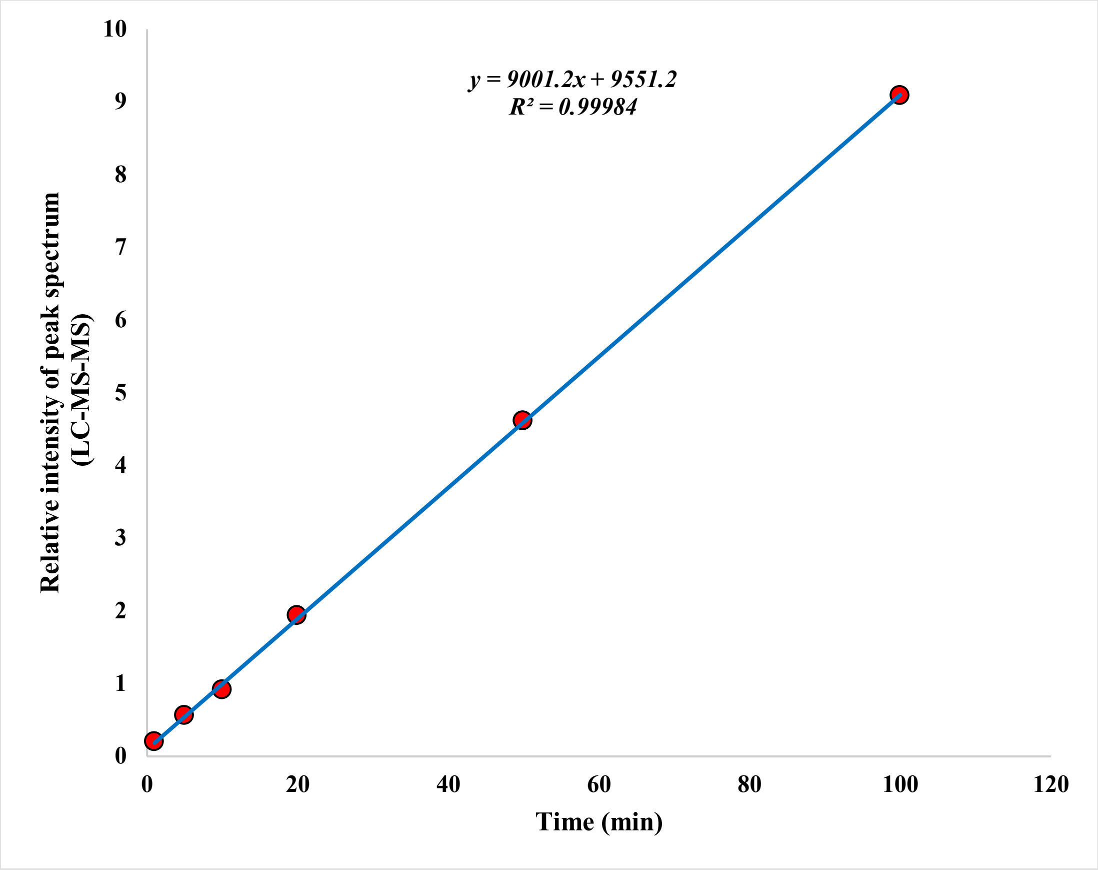


Figure 4.5. Calibration curve for the relative intensity and reaction time of SMX target compound

The next experiment after sole UV treatment, was carried out to add an oxidant in the solution in order to improve the removal efficiency. This oxidant (i.e. H_2O_2 or ozone) can absorb UV light and in reaction with water can produce OH radicals. Considering equation 4.1, by adding H_2O_2 to the solution environment, OH radicals will be formed and attack pollutant structure non-selectively.

$$H_2O_2 \quad + \quad h\nu \quad \rightarrow \quad 2\ HO\bullet \qquad\qquad (4.1)$$

In an advanced oxidation processes, the model pollutant (SMX) is subjected to degradation by both UV irradiation and OH radicals formed during H_2O_2 photolysis which absorbs UV light.

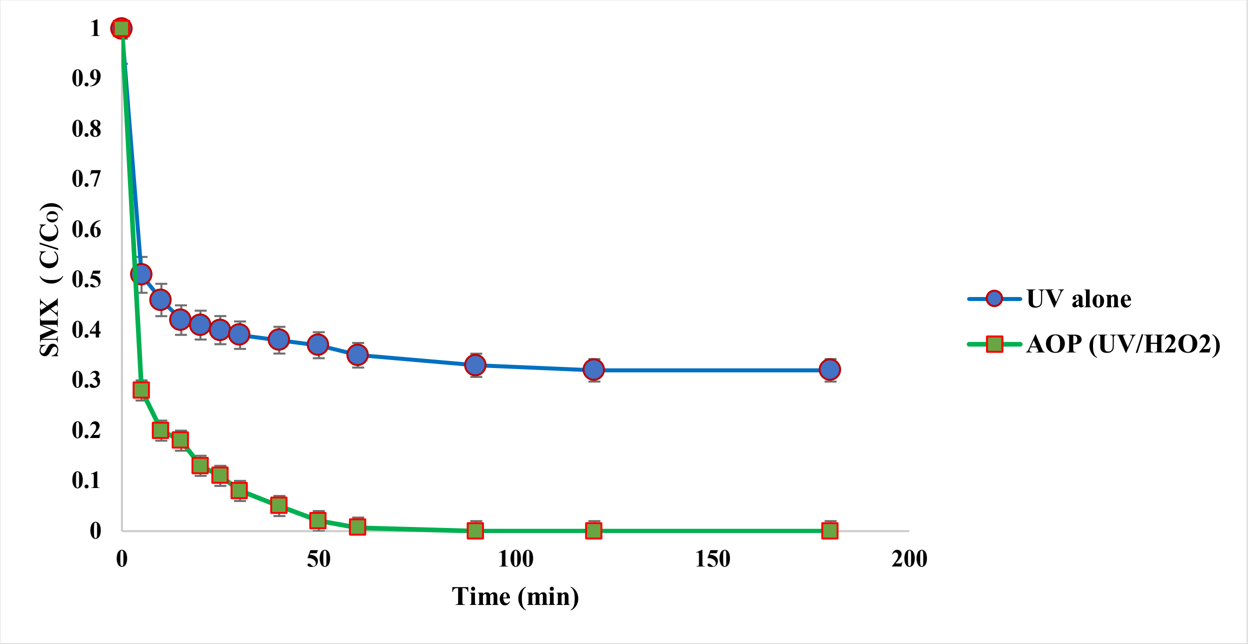


Figure 4.6. Comparison of the SMX degradation rate using UV/H_2O_2 AOP system and UVC photolysis

Figure 4.6 compares SMX reaction rate between sole UV and UV/H_2O_2 AOP. As it is seen in this picture, the rate of reaction in the AOP system is much higher than sole UV. The reaction in this system is almost completed and there is no SMX in the solution after 60 minutes of treatment. However, in sole UV around 60% of SMX is removed and by continuing the reaction till 180 minutes, there is some portion of SMX that is still present in the solution.

4.2.2 Influence of the oxidant concentration (H_2O_2 and OH radicals)

To investigate the effect of operational conditions on the AOP system, several experiments were set to treat water samples containing 0.08 mM SMX, where different H_2O_2 doses were added to the solution. Experiments started with 0.5 mM H_2O_2 and this amount was increased two-three-fold in each individual test. As it is revealed in Figure 4.7, the SMX elimination increased with increasing the concentration of H_2O_2.

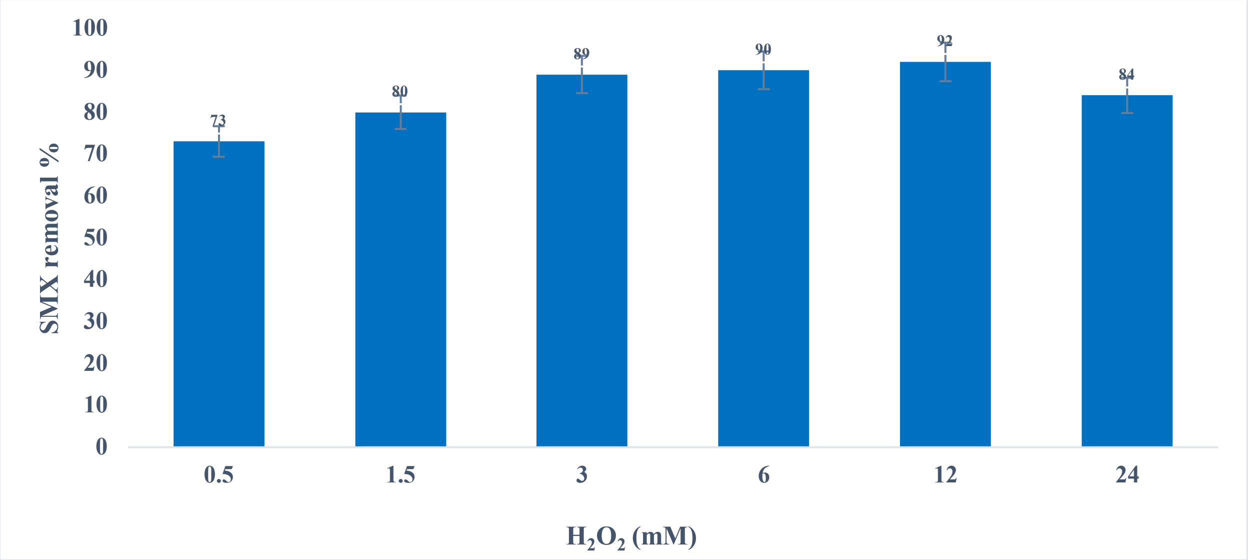


Figure 4.7. Effect of H_2O_2 dose on the SMX removal efficiency
Experiment condition: UVC (40 W) intensity =10 mJ/cm^2, solution volume=3L (irradiated), 4L (total), temperature 18- 20 °C, pH = 7, recirculation rate= 2 L/min, reaction time =10 min

During 10 minutes of reaction, by increasing H_2O_2 concentration from 0.5 to 12 mM, the enhancement of SMX degradation was increased from 73% to 92% (Figure 4.7). However, the excess amount of H_2O_2 (24 mM) resulted in lower removal efficiency and reaction rate in comparison to H_2O_2 doses of 6 mM and 12 mM. This behaviour is due to the scavenging effect of excess H_2O_2.

The following reactions describe this phenomenon clearly:

$$H_2O_2 \quad + \quad h\nu \quad \rightarrow \quad 2\ HO\bullet \qquad (4.1)$$

$$H_2O_2 + HO\bullet \rightarrow HO_2\bullet + H_2O \qquad (4.2)$$

$$H_2O_2 + HO_2\bullet \rightarrow HO\bullet + HO_2 + O_2 \qquad (4.3)$$

$$2\,HO\bullet \rightarrow H_2O_2 \qquad (4.4)$$

$$2\,HO_2\bullet \rightarrow H_2O_2 + O_2 \qquad (4.5)$$

$$HO\bullet + HO_2\bullet \rightarrow HO_2 + O_2 \qquad (4.6)$$

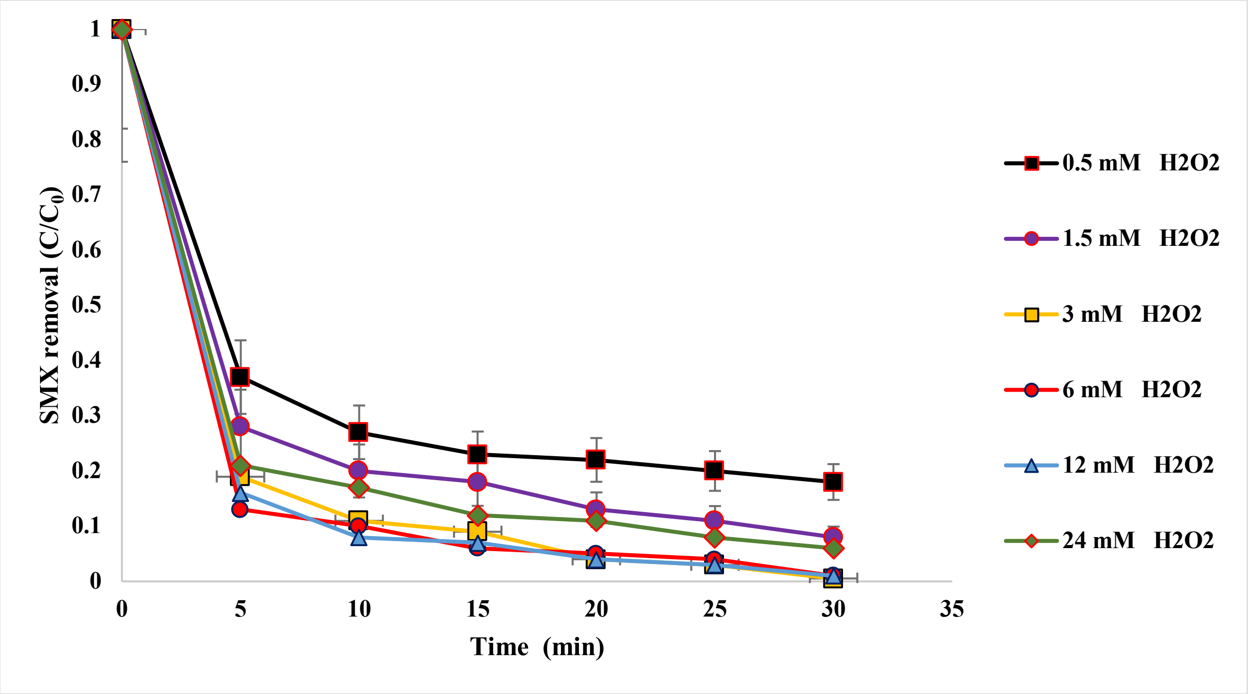


Figure 4.8. SMX degradation rate with respect to change of H_2O_2 dose within UV/H_2O_2 AOP system Experimental condition: UVC (40 W) intensity =10 mJ/cm^2, reaction time = 30 min, solution volume=3L (irradiated),4L (total), temperature 18- 20 °C, pH = 6, recirculation rate= 2 L/min

Increasing the SMX reaction rate would be described by more generation of OH radicals when H_2O_2 concentration was increased. As H_2O_2 concentration was increased, OH radicals' concentrations were increased as well and as a result the possibility of pollutant destruction by radicals would also be increased. Another perspective of SMX degradation can be described when the rate of SMX removal is depicted with time and oxidant dose together. Figure 4.8 could represent the SMX removal versus time by considering different oxidant doses.

Based on the results shown in Figure 4.8, using 3 mM of H_2O_2, a faster reaction rate (close to 6-12 mM of H_2O_2) was shown and the reaction was completed in 30 minutes. However, H_2O_2 doses on 0.5 and 1.5 mM not only showed a lower reaction rate, but also did not complete the reaction in 30 minutes. Hence, 3 mM dose of oxidant would be the best dose for this reaction condition.

As it was discussed earlier in chapter 2, the best operational conditions including the oxidant concentration can play an important role in treatment plants. Therefore, finding the most efficient H_2O_2 dosage is necessary. Hence, this finding can be applied to a bigger size unit as one of the critical operational conditions for water and wastewater treatment plants.

4.2.3 Influence of aeration and superoxide radicals

The air flow can provide oxygen as an electron acceptor for subsequent reactions. Air flow also enhanced mass flow rate by feeding to the sample solution container and causing an increased mixing. As it can be seen in Figure 4.9, aeration can affect treatment efficiency. In AOP UV/ H_2O_2 system during 10 min of reaction, sulfamethoxazole had 70% mitigation without aeration, while with aeration, this number was increased between 72% and 91% when air flow applied to the reactor medium. Further increase of aeration (more than 0.5 L/min) brings a little effect or an adverse effect on the SMX removal. Enhanced treatment by aeration is due to superoxide radicals' generation in a sample solution containing oxygen (Smith et al. 2004; Aliaga et al. 2011). Superoxide radical is highly reactive and can decompose an organic pollutant structure and eliminate it from the water sample (Möller et al. 2012). During photolysis, electrons (e^-) are produced in medium based on the following equations (Hayyan et al. 2016).

$$H_2O + h\nu_{(254nm)} \rightarrow HO\bullet + H^+ + e- \qquad (4.7)$$

$$O_2 + e- \rightarrow O_2\bullet- \qquad (k = 2.0 \times 10^{10} M^{-1} s^{-1}) \qquad (4.8)$$

Another alternative reaction is based on equations 4.9 and 4.10. Hydroperoxyl ($HO_2\bullet$) radicals might be formed as intermediates through the oxygen reduction and also by deprotonation. Then they would be converted to superoxides (Rao et al. 1975; Monteagudo et al. 2011).

When the sample water was saturated with dissolved oxygen (dissolved oxygen concentration from 8.8 to 9.4 mg/L) the amount of superoxide radicals was increased. The result was the treatment improvement by 20% in comparison to no air conditions. (Figure 4.9, diss1& diss5). In this Figure, diss 1 and diss 5 are pre - aeration in sample container by aeration rate of 1 L/min and 5 L/min respectively. Other samples with 0.5 to 4 L/min aeration, had direct aeration by air generator in the reactor.

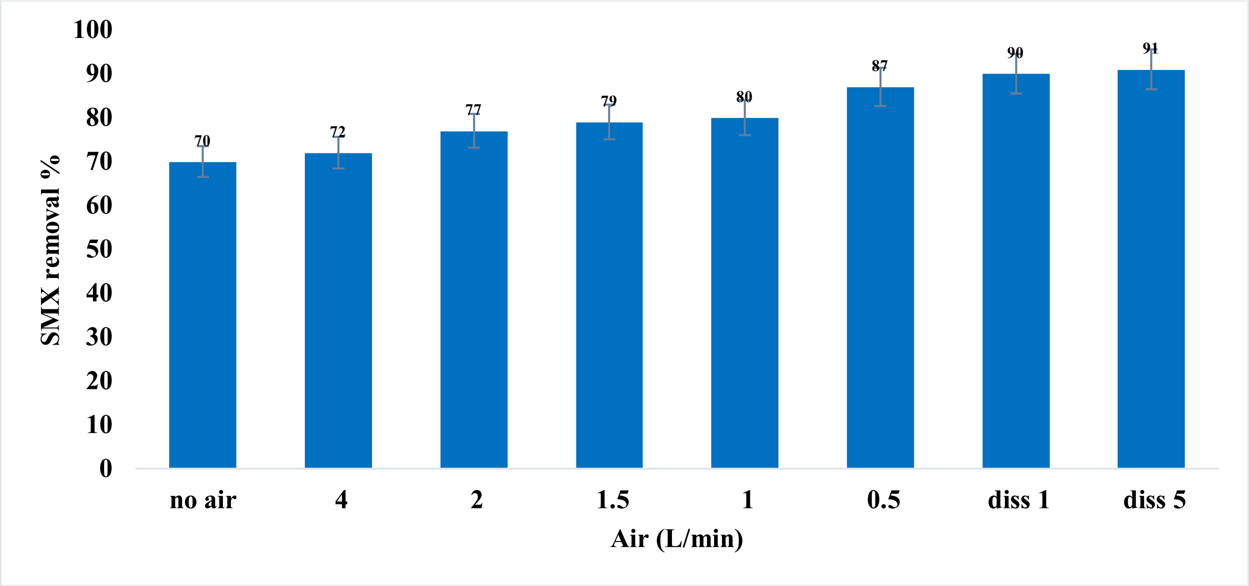


Figure 4.9. Effect of aeration on the SMX elimination by using H_2O_2 AOP system at different air flow rate DO: Dissolved oxygen concentration. Experiment condition: UVC (40 W) intensity =10 mJ/cm^2, reaction time = 10 min, solution volume=3L (irradiated),4L (total), temperature 18- 20 °C, pH = 6, airflow rate=0.5-5 L/min, H_2O_2 = 3 mM

$$O_2 + H^+ + e^- \rightarrow HO_2^\bullet \qquad (4.9)$$

$$HO_2^\bullet \rightarrow H^+ + O_2^{\bullet-} \qquad (4.10)$$

For experimental runs with 1 to 4 L/min air flow, the aeration has lower effect or adverse effect on treatment. This is related to scattering of the UV light by air bubbles and at the same time, the bubbles behavior as UV light barriers. Samples diss1 and diss 5 had airflow rates of 1 L/min and 5 L/min, respectively, where aeration was applied 30 minutes before the reaction started in a 4-liter container separately. In this condition the air bubbles were minimized in the reactor.

4.2.4 Influence of pH change

Another operational parameter which plays an important role in water and wastewater treatment is pH value. The pH of solution can affect simultaneously ionization of a target pollutant and the H_2O_2 decomposition rate (Peng et al. 2016; Buffle et al. 2006; D. Wang et al. 2012). The removal efficiency of some classes of antibiotics such as sulfamethoxazole is pH dependent because it ionizes under certain values below the neutral pH (Verlicchi et al. 2012; Asha et al. 2017). There are two factors, which have a considerable influence on a best pH value for treatment. These two factors work in opposite directions in terms of pH values. The first one works in acidic condition and the other works in basic medium. The acidic pH provides desirable conditions for ionization of target compound, while basic pH is favorable for OH radicals' preservation.

Based on the following reactions, hydroperoxyl anions (HO_2^-) are formed during H_2O_2 photolysis which can be available even more at higher basic conditions (R. Munter 2001).

$$H_2O_2 \rightarrow HO_2^- + H^+ \qquad (4.11)$$

$$HO_2^- + h\nu \rightarrow HO^\bullet + O^{\bullet -} \qquad (4.12)$$

These conditions show pH dependence on reactions that involve hydrogen peroxide as an oxidant in AOPs (Pera-Titus et al. 2004; Villegas-Guzman et al. 2017). On the other hand, the molar absorptivity of hydroperoxyl anions (HO_2^-) is 240 M^{-1} cm^{-1} which is 12 times higher than molar absorption of H_2O_2 that is 20 M^{-1} cm^{-1} (Glaze et al. 1987; Chidambara Raj et al. 2005). In order to find an optimal pH value, a series of tests were conducted at different pH values in both acidic and basic conditions from pH = 3 to pH = 10. As it is shown in Figure 4.10, when pH ranges fall in to acidic conditions (pH=5), the maximum removal of SMX was obtained.

Thus, the conditions for pH around 5 were considered as optimal.

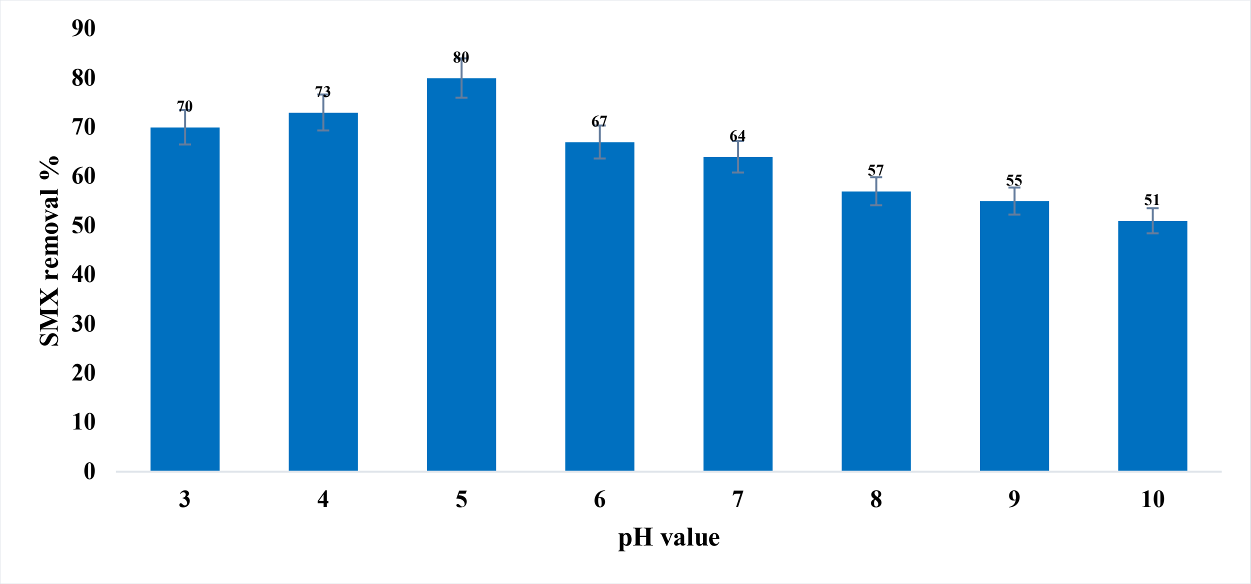


Figure 4.10. Effect of pH change on the SMX removal by using H_2O_2 AOP system
UVC (40 W) intensity =10 mJ/cm^2, reaction time = 10 min, solution volume=3L (irradiated),4L (total), temperature 18- 20 °C, pH =3 to 10, H_2O_2 = 3 mM, recirculation rate= 2 L/min

By increasing the pH value toward the basic conditions, or providing pH less than 5, the elimination of a target pollutant was decreased.

4.2.5 Effect of the UV dose, OH scavenger and Nitrogen

Following the investigations of operational conditions such as pH, aeration and H_2O_2 dose on the SMX degradation rate, other experiment parameters were assessed.

These parameters included UV power, air sparging by nitrogen flow and using tertiary butyl alcohol (TBA) as OH radical scavenger. All the experiment's runs applied UV/H_2O_2 AOP except sole UV. In N_2 -AOP, the solution sample was impacted by nitrogen flow for 30 minutes before the test. In TBA-AOP, the sample solution was spiked by TBA (10 times mole TBA to mole SMX). In UV5-AOP, a UV lamp was applied with the intensity of 5 mJ/cm^2. Figure 4.11 illustrates a comparison between the effects of these parameters on the SMX degradation rate.

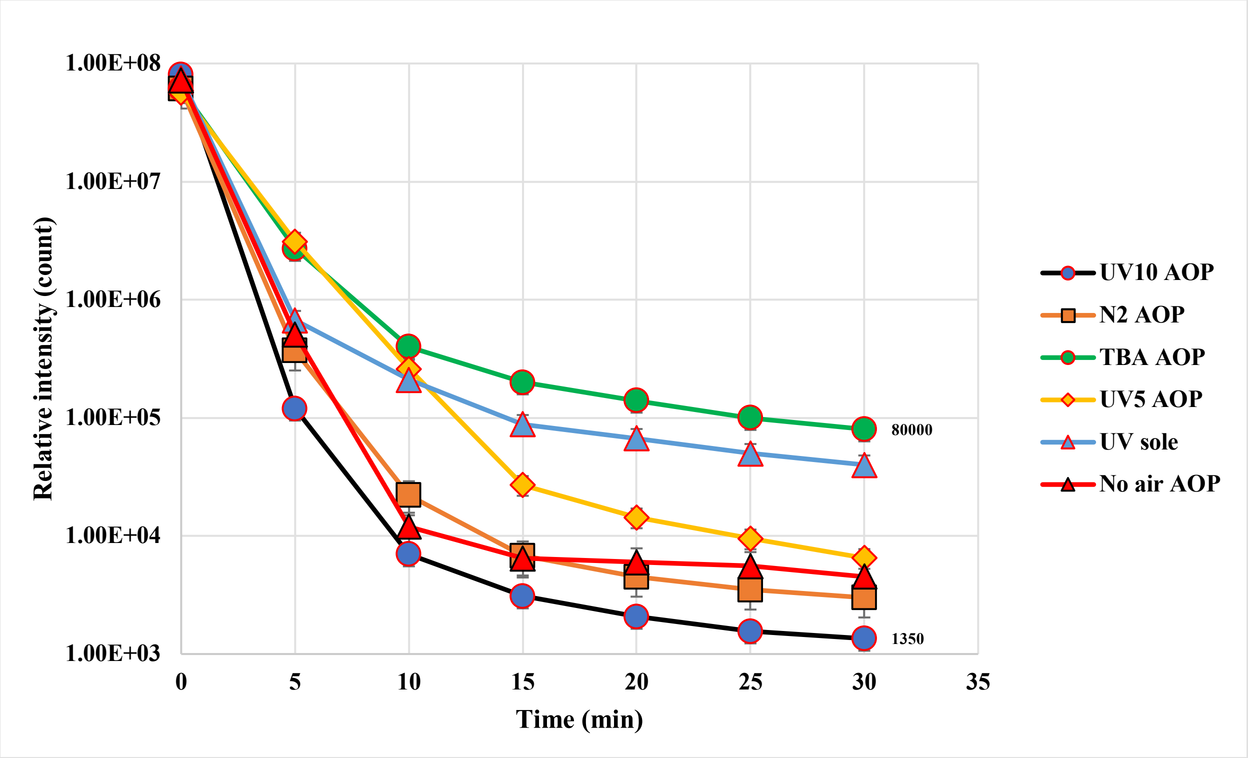


Figure 4.11. Effect of TBA, N_2, UV intensity and air on the SMX removal rate by UV/H_2O_2 AOP; Experiment conditions: UVC (40 W) intensity =5-10 mJ/cm^2, reaction time = 30 min, solution volume=3L (irradiated), 4L (total), temperature 18- 20 °C, airflow rate= 0.0- 0.5 L/min, recirculation rate= 2 L/min, H_2O_2 dose = 6 mM, pH = 5.5

4.2.6 Comparison between air sparging, no air and aeration

Figure 4.11 shows faster degradation rate for an air experiment condition with flow rate of 1.5 L/min. However, two other experiments without air showed lower SMX removal rate than the aeration condition. This behavior may attribute to the superoxide contribution for aeration condition. However, two other samples without air sparging did not benefit from superoxide contribution to the SMX degradation. Two experiments with no air and oxygen discharge by N_2, revealed different behavior for the first 12 minutes of reaction. The sample of pre-nitrogen stream showed lower degradation in comparison with normal condition (no air). This phenomenon may prove the superoxide contribution in normal condition (no air). However, in 15 minutes of reaction, both samples revealed almost similar behavior. At this time (15 minutes) the N_2 sample gained enough oxygen from the atmosphere and showed the similar degradation behavior. The rate of oxygen uptake from the atmosphere was fast and then a sharp degradation increase was recorded between 15 and 20 minutes of reaction. After 20 minutes, both samples played a similar role in the SMX degradation.

4.2.7 Comparison between UV-10, UV-5 and sole UVC

Degradation rate of SMX in UV-10 AOP showed a faster reaction regime in comparison to UV-5 AOP and UVC (Figure 4.11). In UV-5 AOP, the SMX sample received less UV. In return, less OH radical is produced and the SMX species receives less UVC light as well. Accordingly, the rate of degradation in UV-10 AOP is more than UV-5 AOP. Furthermore, the water samples which received only UVC irradiation without H_2O_2 in solution, had lower the SMX removal during the reaction. Because OH radicals were not produced in the solution and SMX molecules only degraded by UVC irradiations.

4.2.8 TBA water samples

In Figure 4.11, the rate of SMX degradation in tertiary butyl alcohol (TBA) samples expressed the slowest reaction in comparison to other samples. In this experiment, TBA competed with SMX species to react with OH radicals. The rate of TBA reaction with OH radicals was much higher than those of SMX. TBA consumed much of the OH radicals in solution and did not allow to react with SMX. Therefore, degradation rate in UV10 AOP sample was much higher than TBA AOP sample. After 30 minutes of reaction, the residual SMX was almost 6 times more in the TBA AOP sample in comparison to UV10 AOP sample. Considering sole UV and TBA AOP, the last samples showed lower SMX degradation. This phenomenon may be attributed to absorption of UVC light by TBA molecules.

Partial conclusion

Figure 4.11 comprehensively illustrated each experiment condition clearly. The following trend in the SMX removal rate was observed.

UV-10 AOP > no-air AOP = N2 AOP > UV-5 AOP > UVC sole > TBA-AOP

4.2.9 Modeling by Response Surface Methodology (RSM)

In section 3.4.4, the experimental design was comprehensively described. Three variables, namely the pH value, H_2O_2 dose and aeration rate, were operational parameters used to investigate organic matter removal efficiency. To design the experiments, the RSM based on fractional factorial, i.e. CCD, method was applied. Twenty experiments defined by CCD method were conducted using the following ranges of three independent variables: 0.0 to 12 mM for H_2O_2 dose, 3 to 11 for pH range, 0.0 to 4 L/m for aeration rate. To virtually understand the behavior of AOP reactions, an empirical second order polynomial model was proposed (eq.4.13). The equation predicts the effect of each independent variable on removal efficiency as well as an interaction between them (Myers 2009).

$$R\ (\%) = A_0 + A_1\,\mathcal{X}_1 + A_2\,\mathcal{X}_2 + A_3\,\mathcal{X}_3 + A_{12}\,\mathcal{X}_1\mathcal{X}_2 + A_{13}\,\mathcal{X}_1\mathcal{X}_3$$

$$+A_{23}\,\mathcal{X}_2\mathcal{X}_3\ + A_{11}\,\mathcal{X}_1^2\ A_{22}\,\mathcal{X}_2^2 + A_{33}\,\mathcal{X}_3^2 \qquad (4.13)$$

In equation (4.13), R is response and $\mathcal{X}$ values representing the operational parameters as independent variables. A_0 is intercept coefficient, A_1, A_2, A_3 are linear coefficients, A_{12}, A_{13}, A_{23} are interaction coefficients between parameters and $\mathrm{A}_{11}, \mathrm{A}_{22}, \mathrm{A}_{33}$ are quadratic terms.

Table 4.5. Independent variables correspond to coded values

Parameter	Symbol	[1]Min	[1]Max	[1]Coded low	[1]Coded high	Mean	[2] SD
H_2O_2 (mM)	$\mathcal{X}_1$	0	12	$-1 \leftrightarrow 3$	$+1 \leftrightarrow 9$	6	2.75
pH	$\mathcal{X}_2$	3	11	$-1 \leftrightarrow 5$	$+1 \leftrightarrow 9$	7	0.84
Air (L/m)	$\mathcal{X}_3$	0	4	$-1 \leftrightarrow 1$	$+1 \leftrightarrow 3$	2	0.9177

[1] Low and high coded values correspond to minimum and maximum experimental values, [2] Standard deviation

The final response (i.e. SMX removal) for each independent variable (pH, H_2O_2, air flow) was an estimated curvature model which can predict the effect of variables on treatment efficiency by UV/ H_2O_2 AOP. Independent variables were coded for low (-1), medium (0) and high (+1) levels as defined in Table 4.5.

These twenty sets of experiments, which were designed by CCD, were included in a matrix with independent variables having different values as presented in Table 4.6. The actual results for each set of experiments is shown along with the predicted responses by CCD. The quadratic terms and coefficients were estimated by analysis of variances. These terms and coefficients are included in the regression equation (Equation 4.14).

Table 4.6. Independent variables and removal efficiency; predicted compared to experimental

Run number	**Variables**			**SMX removal efficiency (R%)**	
	$\mathcal{X}_1$	$\mathcal{X}_2$	$\mathcal{X}_3$	Predicted	Experimental value
1	9	9	3	88.4	87.5
2	3	5	1	90.8	92.1
3	6	3	2	89.7	88.7
4	3	5	3	88.9	90.4
5	6	7	4	91.4	93.3
6	6	7	2	95.9	96.5
7	6	7	2	95.9	96.5
8	6	7	2	95.9	96.5
9	6	7	2	95.9	96.5
10	6	11	2	80.9	83.4
11	12	7	2	88.2	89.6
12	9	5	3	91.8	91.4
13	9	9	1	89.3	88.6
14	6	7	0	94.2	93.7
15	9	5	1	96.1	98.1
16	6	7	2	95.9	96.5
17	6	7	2	95.9	96.5
18	3	9	1	85.4	86.4
19	3	9	3	87.1	85.8
20	0	7	2	81.4	81.9

Equation (4.14), can predict the removal of SMX with respect to independent variables. Furthermore, the interaction between operational parameters, i.e. independent variables and their effect on the SMX removal is expressed by polynomial quadratic equation.

$$R\,(\%) = 55.9943 + 5.1136\ \mathcal{X}_1 + 7.6733\ \mathcal{X}_2 + 0.5909\ \mathcal{X}_3 - 0.0625\ \mathcal{X}_1\mathcal{X}_2 - 0.2083\ \mathcal{X}_1\mathcal{X}_3 + 0.4375\ \mathcal{X}_2\mathcal{X}_3 - 0.3081\ \mathcal{X}_1^2 - 0.6619\ \mathcal{X}_2^2 - 0.7727\ \mathcal{X}_3^2 \qquad (4.14)$$

Table 4.6 shows very close numbers between the predicted removal efficiency and experimental results, which is a strong indicator for the method validation and significance of this model. Furthermore, by plotting the values of experimental results versus predicted values in

Figure 4.12 which was a best fit between these two values, the reliability of model was confirmed by $R^2 = 0.9828$.

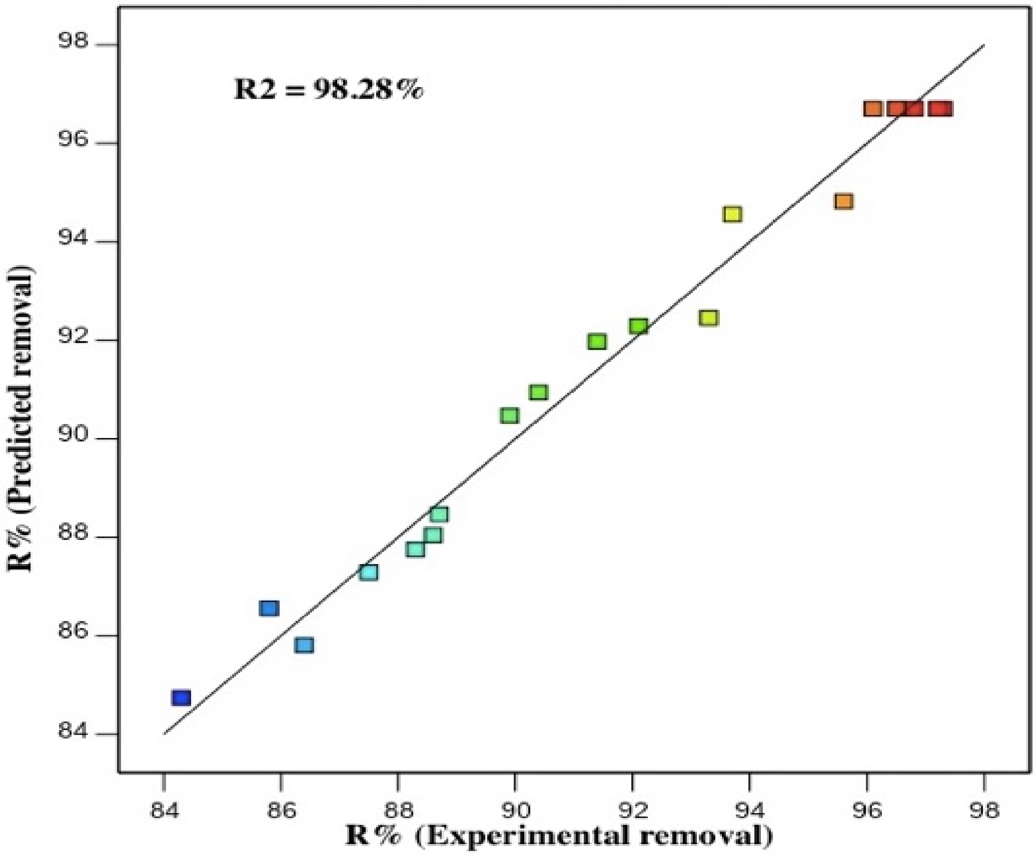


Figure 4.12. SMX removal efficiency; Interrelation between predicted and actual values

Figures 4.13a and 4.14a depicted the counter plots of RSM for SMX removal. In these plots, Figure 4.13.a. includes the effect of aeration rate and pH values, but Figure 4.14.a, presents the effect of pH and H_2O_2 dose.

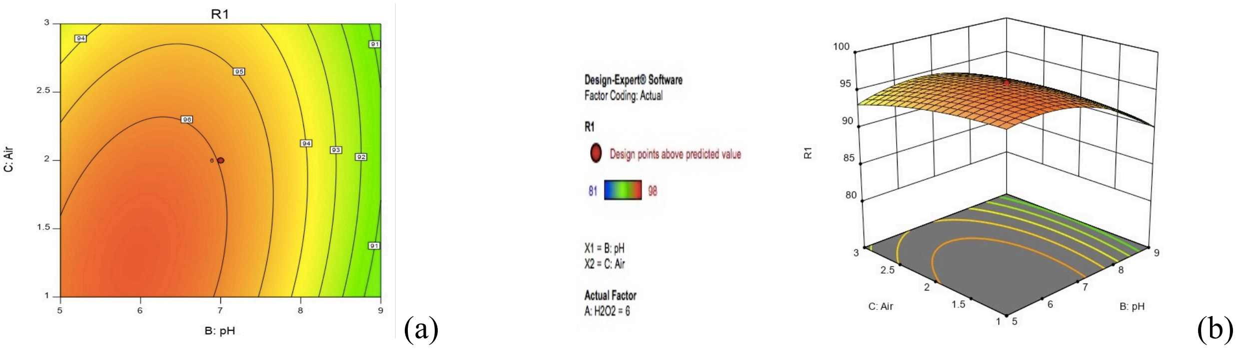
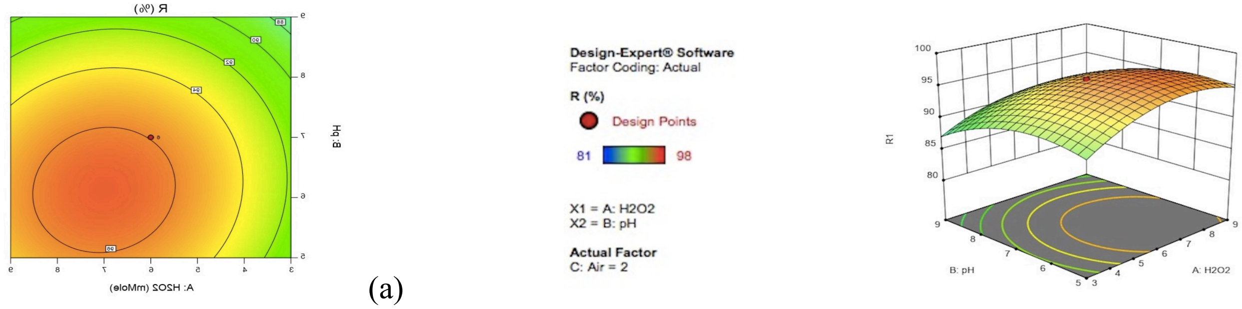


Figure 4.13. Counter plot of SMX removal efficiency (a) pH and aeration interaction 3D surface response (b) pH and aeration interaction

Both variables had significant impact on SMX removal in addition to pH values. In the pH intervals between 4.5 and 7.5, SMX has the highest removal comparing to other ranges. In addition, the maximum removals were fallen between 0 and 2.5 L/min of aeration rates beside the H_2O_2 dose of 4.5 to 8.5 mM.



(a)

(b)

Figure 4.14. Counter plot of SMX removal efficiency (a): pH and H_2O_2 dose 3D surface response (b)): pH and H_2O_2 dose

Table 4.7. Analysis of variances (ANOVA) for SMX removal

Source	Sum of Squares	Degree of freedom	Mean Square	F-value	p-value
Model	445.41	9	49.49	18.62	< 0.0001 significant
A-H_2O_2	45.56	1	45.56	17.14	0.0002
B-pH	76.56	1	76.56	28.8	0.0003
C-Air	7.56	1	7.56	2.84	< 0.0001
AB	1.12	1	1.12	0.4232	0.53
AC	3.12	1	3.12	1.18	0.3037
BC	6.12	1	6.12	2.3	0.16
A^2	193.3	1	193.3	72.71	< 0.0001
B^2	176.26	1	176.26	66.3	< 0.0001
C^2	15.01	1	15.01	5.65	0.0004
Residual	26.59	10	2.66	-	-
Total	472	19	-	-	-

- ***R^2 = 98.28%***

In Table 4.7, the analyses of variance (ANOVA) including *P*-value and *F*-value are provided. The *F*-value of 18.62 implies the model is highly significant. The P-values less than 0.0500 indicate model terms are significant. Therefore, by obtaining the P-value of the model, which was <0.0001, the model shows high significance. These values are in significant agreement with the Fig. 4.12 which represented the relation between predicted and actual results. The experimental results were fitted within a confidence interval of R^2 = 98.6355%. This value has a good agreement with the adjusted R^2 = 96.74 %.

Reaction Optimization

The optimum values as predicted by CCD are highly close to the experimental results (Table 4.8).

Table 4.8. Optimal values and removal efficiency for SMX, predicted versus experimental

H_2O_2	pH	Aeration rate (L/min)	SMX removal (R%)	
			Predicted by model /	Experimental
7.4	5.8	1.1	97.33	98.80

Therefore, there is a significant fit for polynomial quadratic equation model and experimental values. The regression analysis of variance, using ANOVA, with R^2 value of 0.98 confirmed the reliability of predicted quadratic polynomial model which had a good fitness to the experimental values.

Table 4.8. Co-efficient in terms of coded factors and confidence interval

Factor	Co-efficient estimate	DF	Standard error	95% CI low	95% CI high	VIF
Intercept	99.95	1	0.6503	94.51	97.40	
A-H_2O_2	1.69	1	0.4076	0.7793	2.06	1.0000
B-pH	-2.19	1	0.4076	-3.10	-1.28	1.0000
C-Air	-0.6875	1	0.4076	-1.60	0.2207	1.0000
AB	-0.37.50	1	0.5765	-1.66	0.9095	1.0000
AC	-0.6250	1	0.5765	-1.91	0.6595	1.0000
BC	0.8750	1	0.5765	-0.4095	2.16	1.0000
A^2	-2.77	1	0.3252	-3.50	-2.05	1.08
B^2	-2.66	1	0.3252	-3.37	-1.92	1.08
C^2	-.7727	1	0.3252	-1.50	-0.0482	1.08

CI: Confidence interval

Partial conclusion: Technological parameters and RSM

This study showed a significant influence of technological parameters such as pH, H_2O_2 dose and airflow rate, on the SMX removal by using UV/ H_2O_2 advanced oxidation system. It could be concluded that the CCD method in RSM was an adequate approach to investigate optimal reaction parameters, where several variables are involved in the reaction mechanism. The method could be applied to the water treatment and predict reduction of SMX in the water matrix. This model could also be applied to the reduction of EfOM in effluent generated by membrane electro-bioreactor. Elimination of EfOM is an important step to produce reclaim water from sewage.

4.2.10 Electrical energy per order (E_{EO}): Effect of operational condition

As has been mentioned and discussed in previous sections, one of the main limitations of AOPs is high energy demand for these technologies. In AOPs, the major part of the technology is UV lamps which consume a dominant part of electrical energy. The UV irradiation in such AOP oxidation technology is absorbed by organic constituents in the water matrix. Therefore, lower organic matter concentration in the water matrix, results in lower UV irradiation demand and lower electrical energy consumption. In current study, the COD input of domestic wastewater from L'Assomption City was around 150 mg/L. In our hybrid AO/MEBR system, the MEBR device was responsible for the main part of energy saving while an external membrane and the EBR compartment reduced the COD from 150 mg/L to 20-30 mg/L or below. The second scenario for energy saving, was adjusting technological parameters in the AOP setup.

According to the equation (3.7) in chapter 3, the following investigations were performed to evaluate energy consumption of UV/H_2O_2 AOPs in this study. The surveys were based on energy required for the SMX removal from a water sample. The following sections discuss the effect of operational condition on electrical energy consumption per 90% of pollutant removal from a one cubic meter of water sample. Furthermore, the energy consumption for COD removal from river water and effluent samples was discussed.

Effect of aeration on energy consumption

As discussed in the previous sections, the maximum SMX removal was obtained by lowering the rate of aeration (around 1.0 L/m) and maximizing dissolved oxygen in water. Diss. 1 and Diss. 5 samples had the maximum concentration of dissolved oxygen and aeration around 1.00 L/min caused minimum UV scattering effect. As it is revealed in Fig. 4.15, the minimum energy consumption was in Diss.1, Diss. 5 and in 0.5 L/m aeration rate. This finding is compatible with the maximum SMX removal demonstrated in the previous sections. On account of higher removal of SMX in a shorter period of time, the UV energy which is applied for the treatment is then lower than longer reaction treatment.

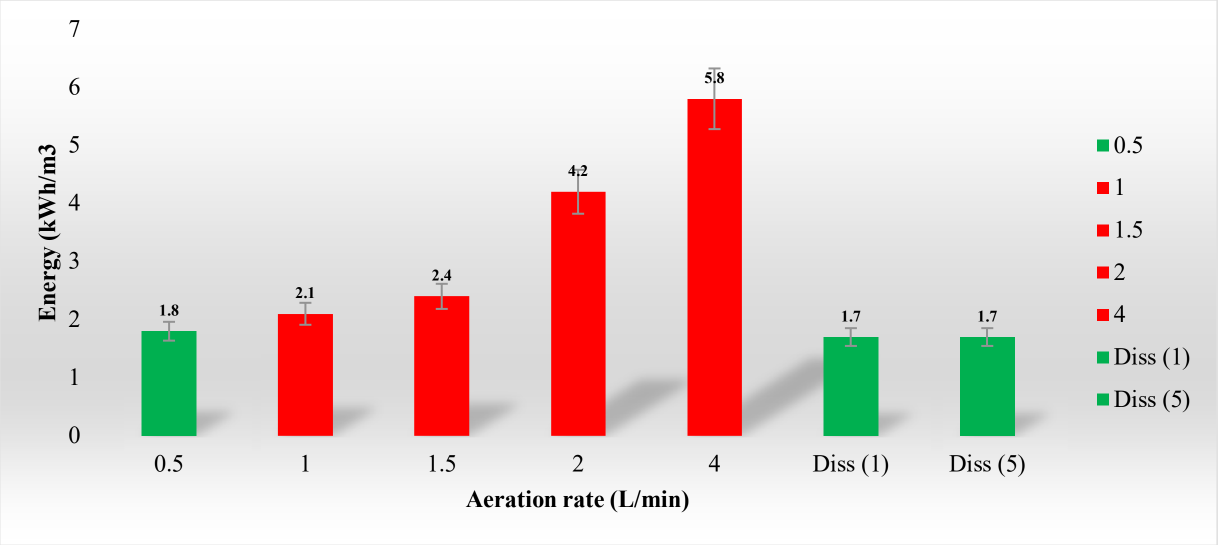


Figure 4.15. Effect of aeration rate on energy consumption
Diss (1) and Diss (5): pre- aeration in sample container by aeration rate of 1L/min and 5 L/min respectively
Other samples with 0.5 to 4 L/min aeration, had direct aeration by air generator in reactor
Experiment conditions: UVC (40 W) intensity =10 mJ/cm^2, reaction time = 30 min, solution volume=3L (irradiated), 4L (total), temperature 18- 20 °C, airflow rate= 0.5- 4 L/min, recirculation rate= 2 L/min, H_2O_2 dose = 6 mM, pH = 5.5

Effect of pH on energy consumption

The maximum energy consumption during the reaction was monitored at more basic condition (Fig. 4.16). However, in acidic pH around 5, the maximum SMX degradation was recorded. Energy consumption is proportional to the reaction time.

The minimum energy was obtained at faster reaction rate and minimum reaction time. Therefore, the minimum energy consumption was recorded at acidic pH around 5. This finding is compatible with the results reported in the SMX removal rate in section 4.2, Fig. 4.10.

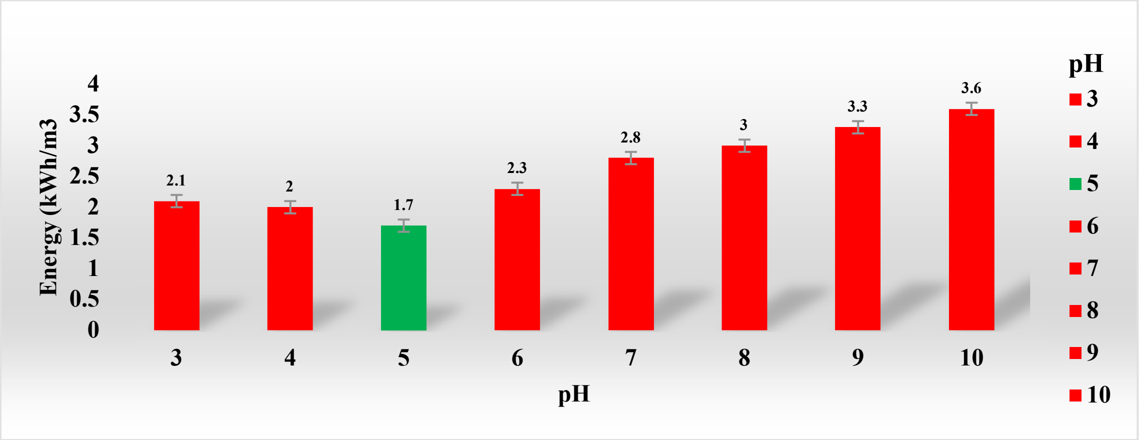


Figure 4.16. Effect of pH changes on energy consumption
Experiment conditions: UVC (40 W) intensity =10 mJ/cm^2*, reaction time = 30 min, solution volume=3L (irradiated),4L (total), temperature 18- 20 °C, airflow rate= 0.5 L/min, recirculation rate= 2 L/min,* H_2O_2 *dose = 6 mM, pH = 3-10*

Effect of H_2O_2 dose on energy consumption

The maximum sulfamethoxazole degradation was reached at higher H_2O_2 doses. However, because of the scavenging effect of H_2O_2 at higher doses more than 12 mM, the SMX degradation demonstrated a reverse behavior in terms of removal rate Fig. 4.8. These findings were compatible with energy consumed for SMX. As it is depicted in Fig. 4.17, the maximum energy consumption reported at 18 mM and higher doses. The minimum energy was acquired at 12 mM and the optimal SMX removal was obtained around 7 mM. Therefore, the minimum energy was not obtained in the H_2O_2 doses where maximum SMX removal acquired. However, in section 4.2.2, Figure 4.8, the curves of H_2O_2 dose of 12mM and 6mM showed SMX removal differences for the first 13 minutes of reaction. After 15 minutes of reaction, both curves revealed similar behaviors. Therefore, the 12mM H_2O_2 dose may be considered for both energy saving and maximum SMX removal.

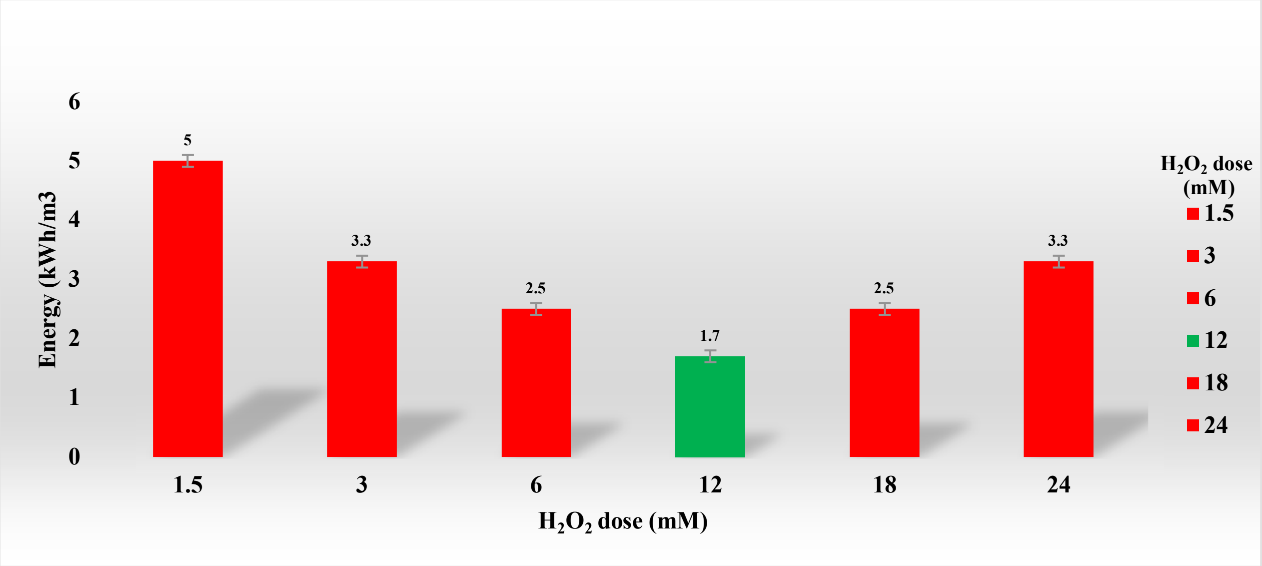


Figure 4.17. Effect of H_2O_2 dose change on energy consumption
Experiment conditions: UVC (40 W) intensity =10 mJ/cm^2, reaction time = 30 min, solution volume=3L (irradiated),4L (total), temperature 18- 20 °C, airflow rate= 0.5 L/min, recirculation rate= 2 L/min, pH = 5.5, H_2O_2 dose = 0.5 - 24 mM

4.2.8. Energy consumption for treatment of river water and effluent

Two samples such as river water and effluent were compared for TOC removal rate. The mean TOC of river water was recorded 2.9 mg/L and for effluent 3.5 mg/L. Figure 4.18 depicts a pareto chart which contains energy as descending value bars and the cumulative total is shown in percentage. The red line shows the increasing rate of energy required for effluent in comparison to the river. The cumulative total represents the energy by percentage. According to the results, 31.6 kwh/m^3 electrical energy is required to remove 90% of TOC of effluent (decrease from 3.5 mg/L to below 1 mg/L), while for river water 20.5 kWh/m^3 was required. Non- target constituents in river and effluent samples, such as carbonate and bicarbonate, scavenged OH radicals and increased reaction time more than for SMX samples in DI water. Therefore, higher energy is required to remove TOC from the river and effluent.

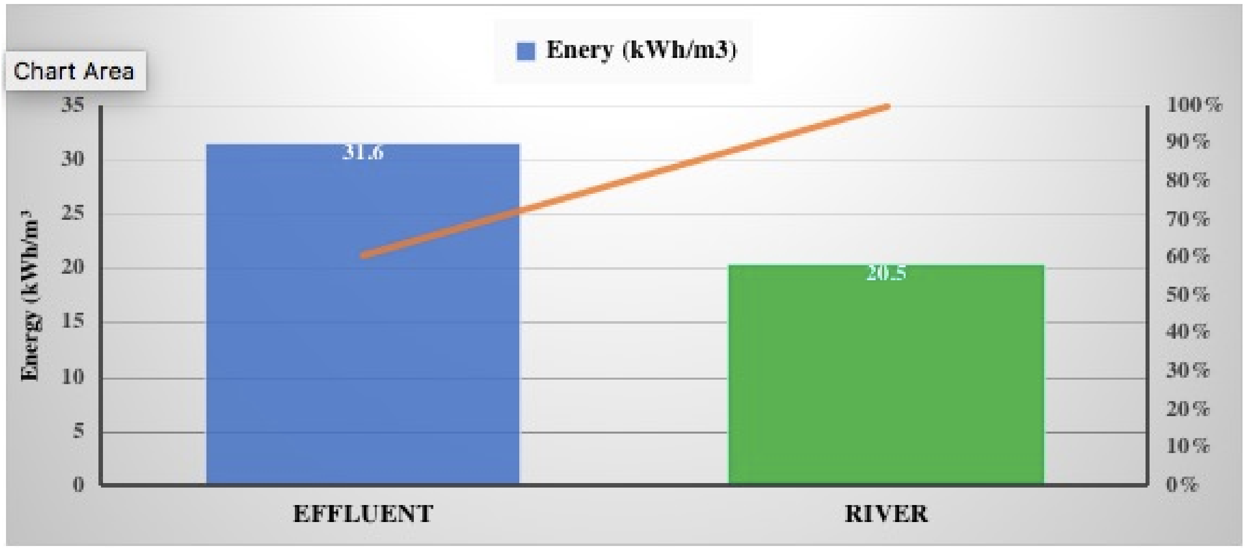


Figure 4.18. Energy consumption for treatment of river water and effluent by UV/H_2O_2 AOP
Experiment conditions: UVC (40 W) intensity =10 mJ/cm^2, reaction time = 123 min (river), 189 min (effluent), solution volume=3L (irradiated), 4L (total), temperature 18- 20 °C, airflow rate= 0.5 L/min, recirculation rate = 2 L/min, pH = 7, H_2O_2 dose = 12 mM

Partial conclusion: Energy consumption

As it is noted in equation 3.7, the rate of reaction affected the energy used for the oxidation process. Furthermore, other parameters such as pH, matrix temperature and reactor shape contributed to the reaction rate (Friedmann et al. 2010). In this study, by adjusting the technological parameters for each experiment, the energy consumption was lowered to a minimum level. Thus, at pH around 5, aeration at minimum rate (0.5 L/min) and H_2O_2 = 12 mM, the minimum energy of 1.7 kWh/m^3 was acquired for SMX removal. The energy consumption for removing 90% of COD from the river and effluent was much higher than the consumption for the SMX alone in DI water samples. This pattern is clear and attributed to the non-target constituents in the river and effluent that scavenged OH radicals. This study revealed that technological parameters had a significant impact on energy used for such an AOP method.

4.3 Phase 4: Hybrid system AO/EMBR; Removal of SMX and PCM in effluent

The concept of developing such a hybrid system has come from the following hypotheses:

A- Reaction efficiency enhancement regarding the ECs removal

Increasing reaction efficiency by reducing the substrate concentration, i.e. DOC, in wastewater influent, would increase OH radical’s reactivity with ECs. as substrates act as OH radical scavengers (Hanasaki et al. 1994; Maezono et al. 2011; Kang 1997). The lower amount of substrate results in a lower amount of OH radical scavengers.

B- Energy saving

By using a pre-treatment unit (such as MEBR) with lower energy consumption, the total energy usage would be reduced.

C- By-products and toxicity reduction in the final water

Wastewater contains large amounts of organic matter and nitrogen compounds undergoing oxidation process. The higher volume of organic matter, i.e. by-product precursor, would result in larger concentration of by-products and its diversity (Dewil et al. 2017). Transformation by-products also behave as OH radical scavengers and reduce reaction performance. As a result, developing such a hybrid system that puts AOP downstream of a pre-treatment unit (MEBR), pushes AOP to be selective in order to target micropollutants removal efficiently, saves the energy, reduces by-product formation and destroys pathogens simultaneously leading to high quality final water matrix.

4.3.1 Effluent removal by AO/MEBR hybrid system

Figure 4.19 depicts the COD removal comparison between different effluents samples which are taken from the EMBR at different times.

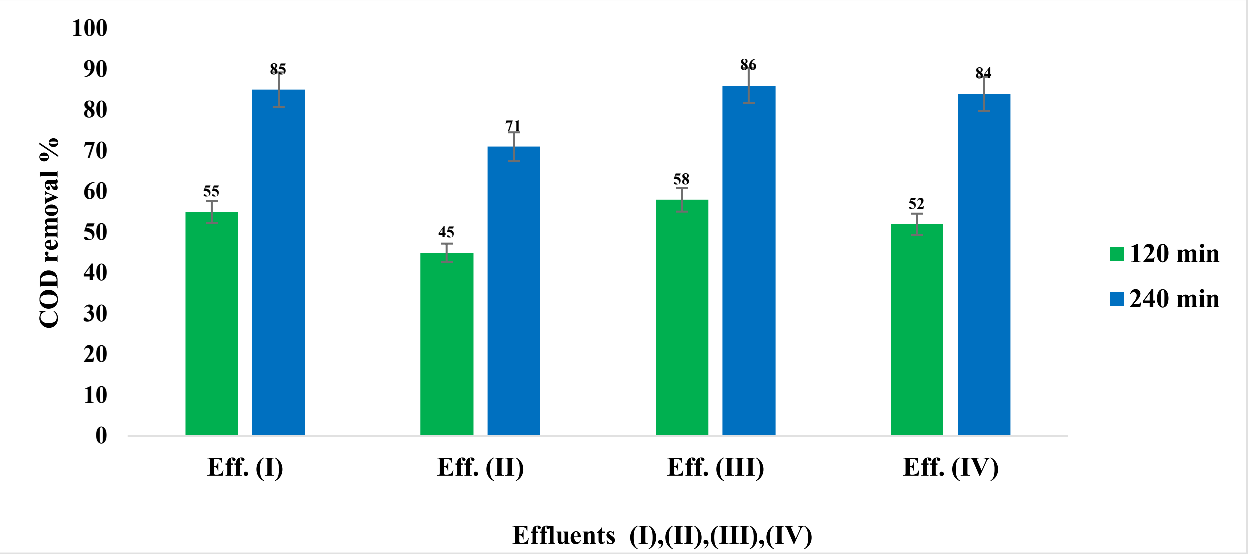


Figure 4.19. Comparison the COD removal by AO/MEBR in different effluents. Samples had different COD concentration at different sampling time; Experimental conditions: Eff(I), (III), (IV): COD = 15, Eff. (II): COD = 20; MEBR: Different effluents, H_2O_2 (3 mM), UV intensity (10 mJ/cm^2), time = 120 and 240 min, no aeration

As it is seen in the Figure 4.19, there are few differences for the COD removal between effluents. This result would be due to the power of the AOP/ H_2O_2 system. The oxidant dose (3mM H_2O_2) for a minimum scavenging effect and the highest power of UV intensity (10 mJ/cm^2) have been applied to treat four effluent samples. In subsequent tests, effluent (II) has been selected for experiments in the hybrid system due to an average COD in effluent (20 mg/L), which was closest to the COD value of the SMX (25 mg/L).

Figure 4.20 shows effluent removal based on different operational conditions: A= no air without adjustment, B = H_2O_2 = 3Mm and aeration = 2.0 L/min (DO = 8.8 mg/L) and C = adjusted condition (adjusted operational condition: H_2O_2 = 12Mm, Air = diss. 1 (DO = 9.4 mg/L). As it is observed in this figure, aeration enhances COD removal, while adjusted condition resulted in higher EfOM removal. Applying aeration would increase the effluent removal by around 7%. Likewise, when adjusted condition applied to the AO/MEBR, the removal efficiency showed an increase about twice.

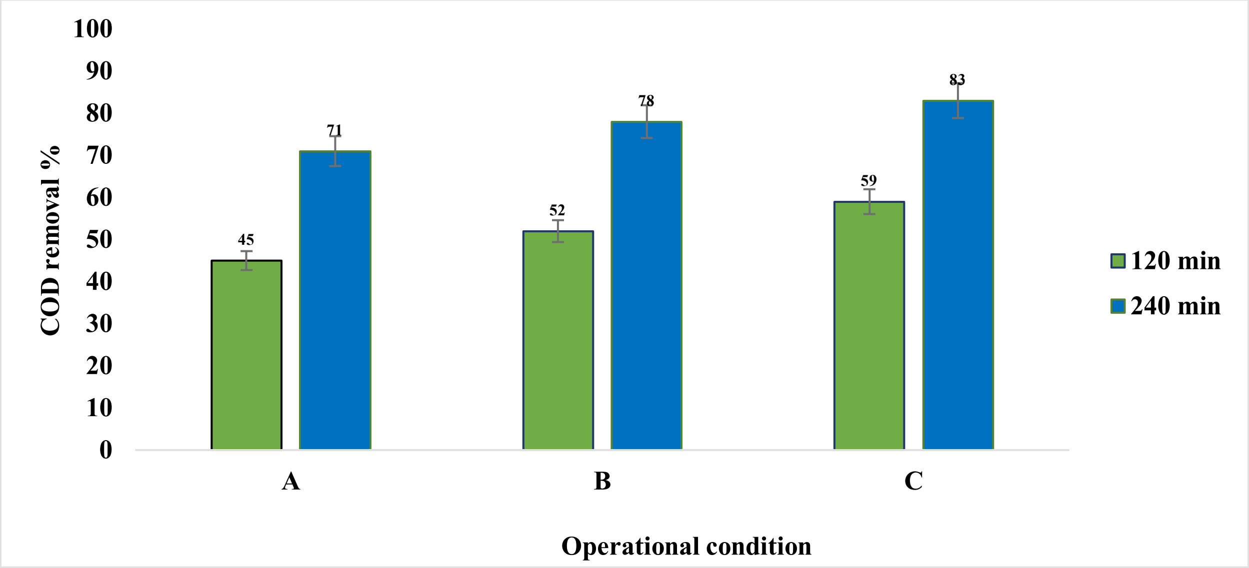


Figure 4.20. Operational condition applied to COD removal in effluent by AO/MEBR
A= no air, without adjustment, B= H_2O_2 = 3Mm and aeration = 2.0 L/min (DO = 8.8 mg/L) C= Adjusted operational condition: H_2O_2 = 12Mm, Air = diss. 1 (DO = 9.4 mg/L)

4.3.2 Effect of water matrix on SMX removal

In order to investigate the potential of AO/MEBR hybrid system to remove micropollutants in wastewater treatment plant effluent, solutions of SMX were spiked to the selected effluent samples (effluent II). Figure 4.21 compares COD removal of different samples. By applying adjusted condition, the sole effluent sample had 83% COD removal in 240 minutes of reaction. This phenomena came from the complex mixture of effluent that contains a wide range of miscellaneous organic matter such as fat and oils, carbohydrates and proteins and other organic micropollutants (Shon et al. 2007; Michael-Kordatou et al. 2015).

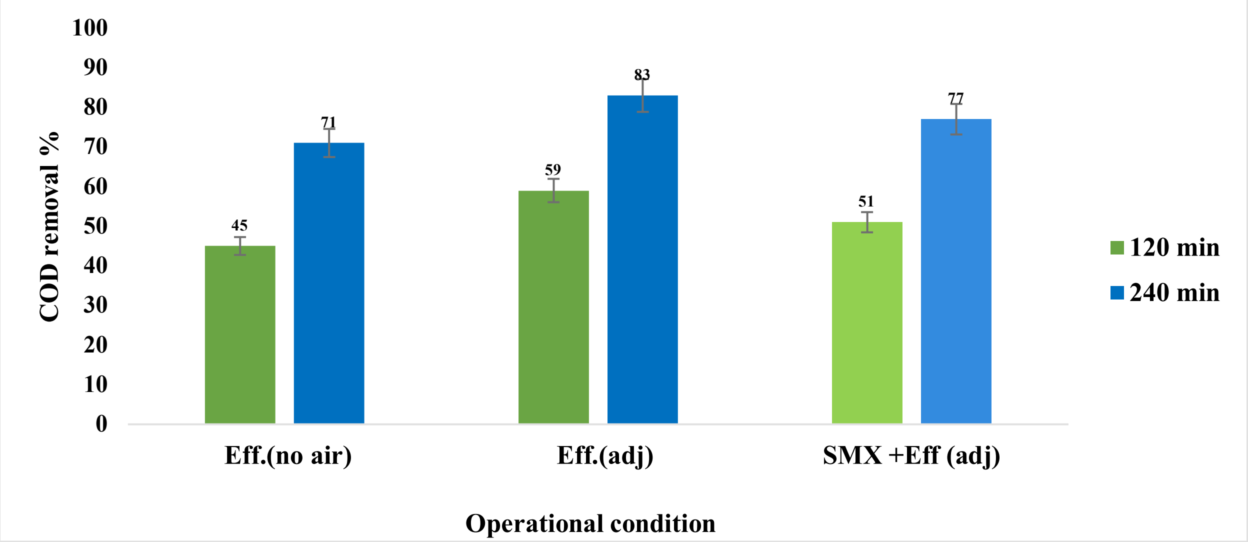


Figure 4.21. COD removal from water and effluent with and without SMX using AO/MEBR Eff. (no air, without adjustment). Adjusted operational condition: H_2O_2 *= 12Mm, Air = diss. 1 (DO = 9.4 mg/L), pH = 6-7, UV intensity (10 mJ/cm*^{2}*), time = 120 min and 240 min.*

The last test was conducted on a sample containing SMX in effluent. The result showed SMX and effluent removal efficiently after 240 minutes. The mixture of SMX + effluent showed the lowest COD removal in mixture (77%,) while sole effluent demonstrated 83% removal. This phenomenon could be attributed to the higher COD of sample and complex mixture of effluents with high refractory compounds and their transformation by-products.

4.4 Phase 5: By-products identification for the target compound (SMX)

4.4.1 Total organic carbon evolution as an indicator of by-product accumulation

Total organic carbon analysis tests confirmed partial mineralization of the target pollutant. Whereas, a high SMX degradation was observed, some by-products accumulation within 40 minutes of reaction were detected (Figure 4.22). The degraded low molecular organic products remained in the medium even after 360 minutes of oxidation reactions. However, almost all SMX species were removed from DI water samples during this period.

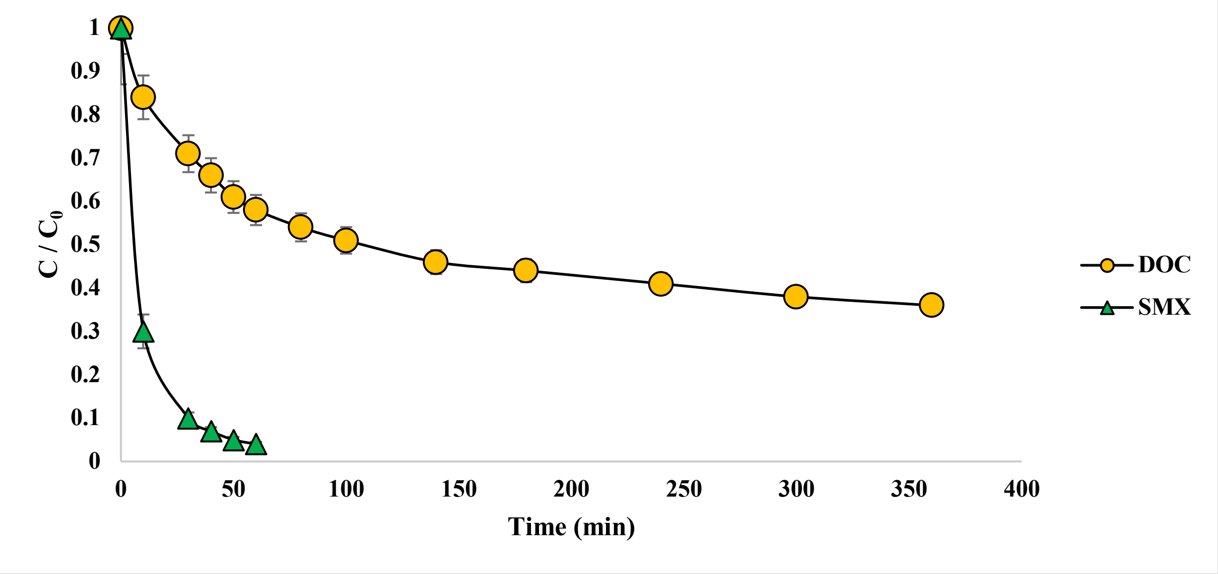


Figure 4.22. Comparison of SMX degradation and DOC abatement as mineralization indicator Experimental conditions: UVC (40 W) intensity =10 mJ/cm^2, reaction time = 360 min, solution volume=3L (irradiated),4L (total), temperature 18- 20 °C, airflow rate= 1.5 L/min, recirculation rate= 2 L/min, pH = 5.5 H_2O_2 dose = 12 mM

4.4.2 SMX chromatogram and its accurate mass spectrum

Sulfamethoxazole selected as a target pollutant. Samples were prepared by dissolving 80 µM of SMX in DI water. AOP treatment of SMX in deionized water (DI) using UV/H_2O_2 system was applied. According to the developed method, described in section 3.5.4, the samples were injected to the LC-QTOF instrument for identification of sulfamethoxazole degradation by-products (BPs) which were formed during the treatment. The importance of this follow-up and characterization of reaction mechanism could be described on account of persistence of intermediates which are formed during the oxidation process even in the situation in which the target pollutant is completely eliminated from the medium (Gómez-Ramos et al. 2011). Therefore, an individual monitoring of target pollutants during the reaction is necessary to obtain an insight to the reaction process.

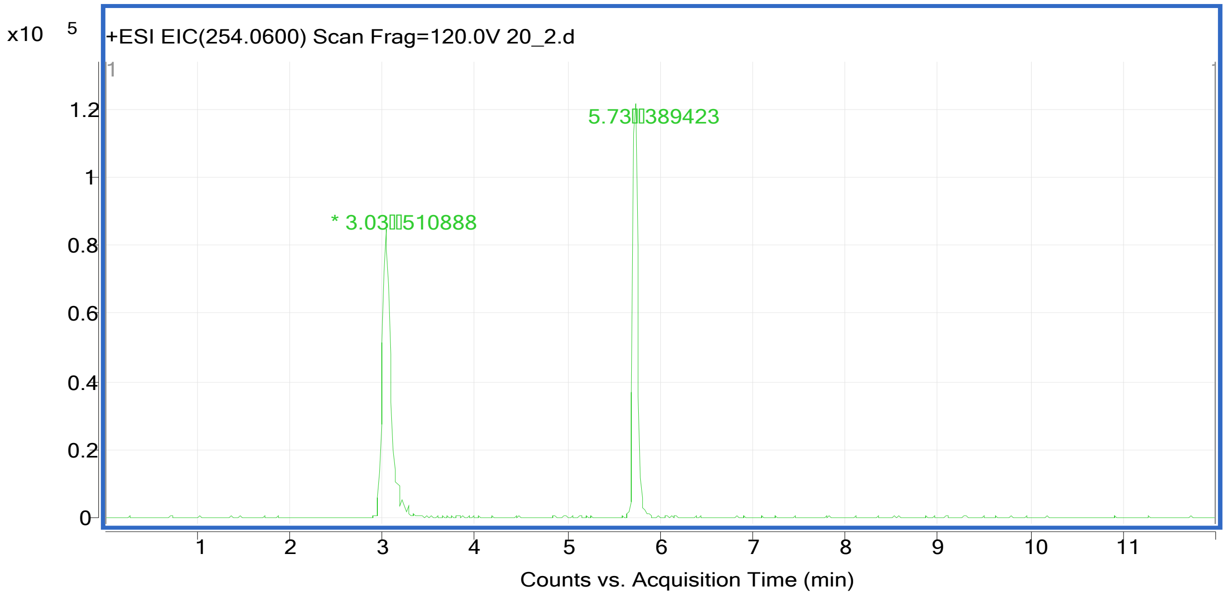


Figure4.23. SMX chromatograms; parent ion (5.73 min) and its isomer (3.03 min)
Y axis (counts): Relative intensity (relative abundance of ion; X axis (m/z): mass to charge ratio
UVC (40 W) intensity =10 mJ/cm^2, reaction time = 30 min, solution volume=3L (irradiated),4L (total), temperature 18- 20 °C, pH = 6-7, airflow rate= 0 L/min, recirculation rate =2 L/min

In order to look at the sulfamethoxazole (SMX) by-products, the initial step is to follow SMX elution in HPLC and its accurate ion mass in LC-MS-MS. Figures 4.23 and 4.24 show the chromatogram and mass to charge ratio of sulfamethoxazole respectively.

In Figure 4.23, the SMX chromatogram and its isomer have retention times of 5.73min and 3.03min, respectively. Sulfamethoxazole protonated molecular ion (parent ion) with a mass to charge ratio (m/z) = 254.0573 is depicted in Figure 4.24.

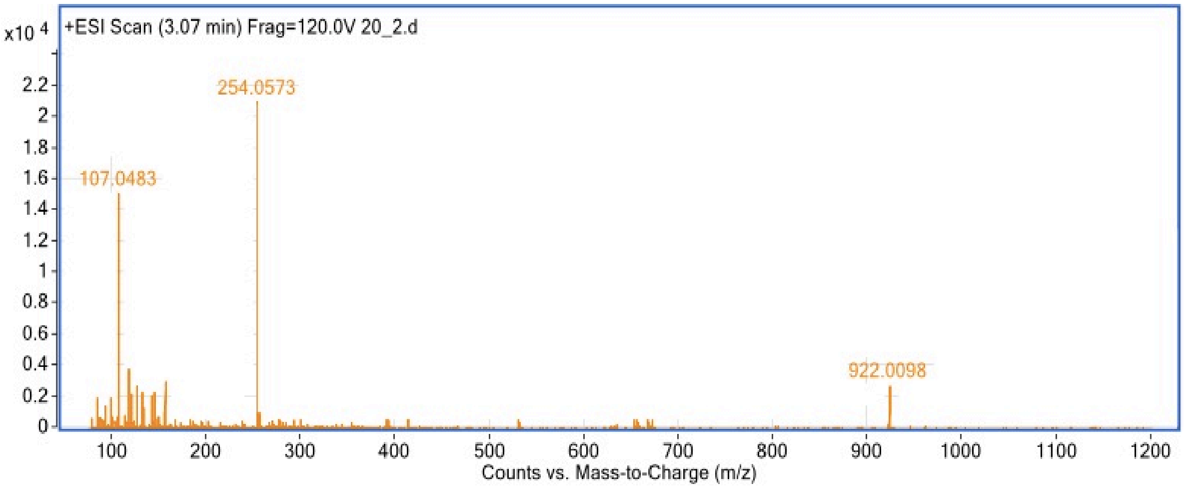


Figure 4.24. Sulfamethoxazole accurate mass spectrum ([M + H] +)
Y axis (counts): Relative intensity (relative abundance of ion; X axis (m/z): mass to charge ratio; UVC (40 W) intensity =10 mJ/cm^2, reaction time = 30 min, solution volume=3L (irradiated),4L (total), temperature 18- 20 °C, pH = 6-7, airflow rate= 0 L/min, recirculation rate = 2 L/min

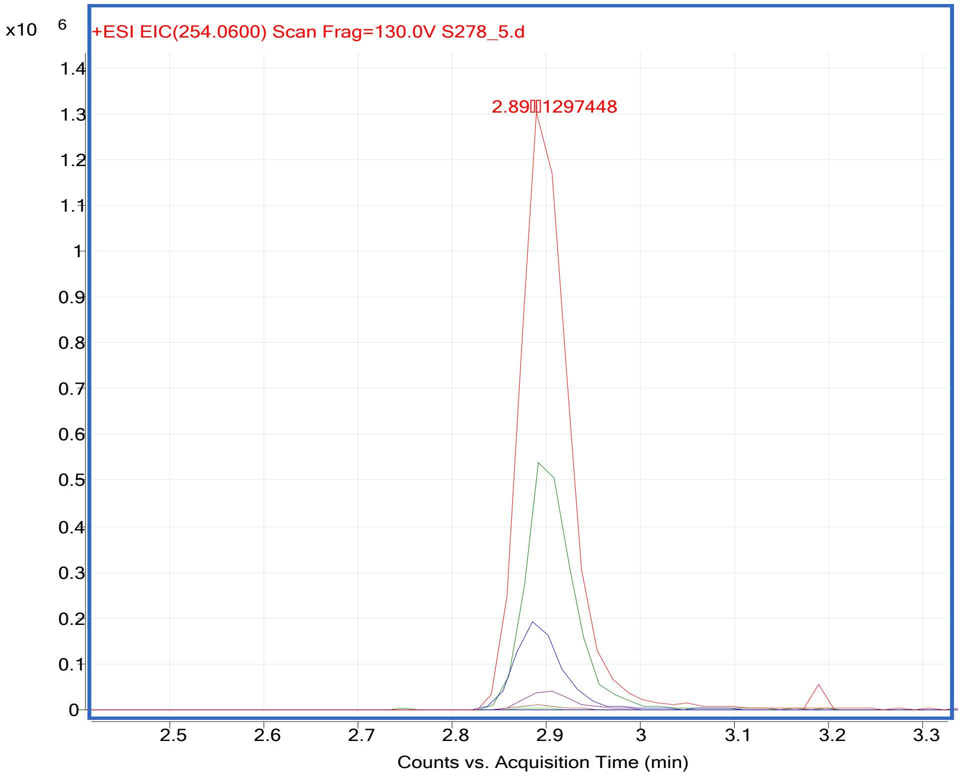


Figure 4.25. SMX elimination through the time by advanced oxidation (UV/H_2O_2)
Y axis (counts): Relative abundance of ion; X axis (min): time UVC (40 W) intensity =10 mJ/cm^2, reaction time = 30 min, solution volume=3L (irradiated),4L (total), temperature 18- 20 °C, pH = 6-7, airflow rate= 0 L/min, recirculation rate=.2 L/min

Figure 4.25 shows the sulfamethoxazole (SMX) removal in the water sample vs. time. The highest peak (highlighted red with intensity of 1.29 * 10 ^{6}) is SMX chromatogram after 5 minutes of reaction. Other peaks show SMX intensity after 10 to 30 minutes of reaction.

4.4.3. Identification of SMX by-products (BP-99, BP-172, BP-270, BP-288)

In preliminary investigation several by-products (BPs) were found during the oxidation process. Some of these BPs had much abundance and more persistence in the water samples, others had higher molecular weight in comparison to small transformation compounds. The intermediate products with lower molecular weight, such as oxalic acid and formic acid were not persistent in the solution, while for the other by-products with higher molecular weight, such as BP-270 and BP-288, leaving the medium was difficult.

Table 4.9. By-products detected by LC-QTOF-MS

	Intermediate products	**(m/z)**
SMX Parent ion accurate mass 254.0573 (m/z)	oxalic acid ($C_2H_2O_4$)	90.034
	glyoxylic acid ($C_2H_2O_3$)	74.0354
	formic acid (CH_2O_2)	46.025
	glyoxal ($C_2H_2O_2$)	58.036
By-products (m/z): 523, 518, 502, 397, 299, 288, 287, 283, 270, 271, 269, 262, 257, 237, 222, 203, 197, 190, 177, 172, 115, 139, 133, 100.11 152.08, 156.01, 164.08, ,171.076, 99.0552		

Table 4.9 shows these BPs resulted from sulfamethoxazole degradation during oxidation by UV/H_2O_2 AOP.

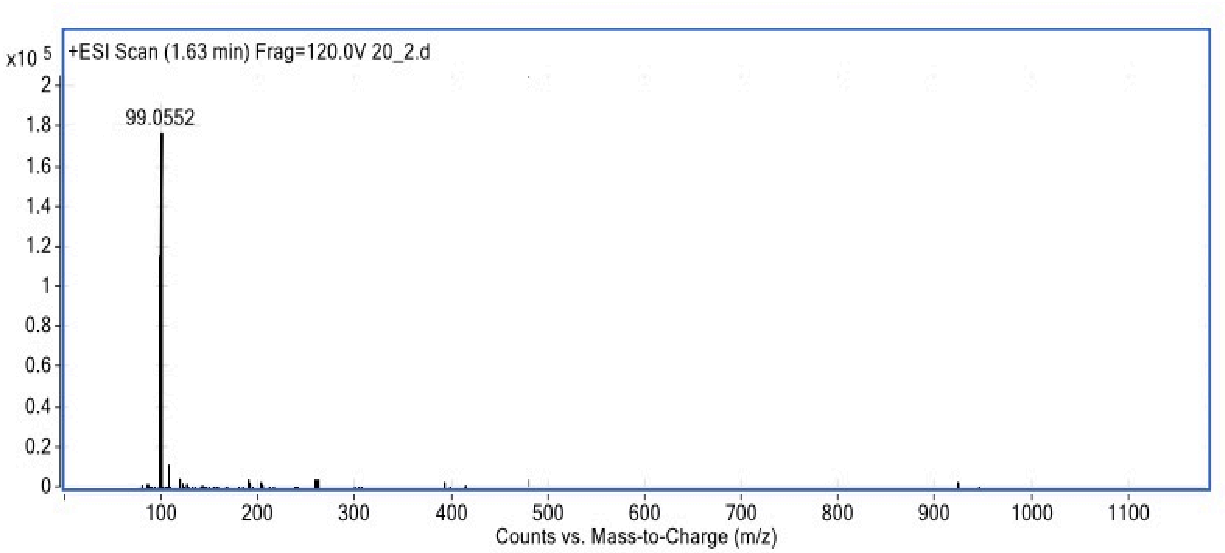


Figure 4.26. Sulfamethoxazole BP-99 with accurate mass = 99.0552
Y axis (counts): Relative intensity (relative abundance of ion; X axis (m/z): mass to charge ratio
UVC (40 W) intensity =10 mJ/cm^2, reaction time = 30 min, solution volume=3L (irradiated),4L (total), temperature 18- 20 °C, pH = 5-6, airflow rate= 0 L/min, recirculation rate= 2 L/min

4.4.3 Identified SMX by-product; BP-99 accurate mass

BP-99 from the list in table 4.9 is depicted by its accurate mass in figure 4.26 and its chromatogram in Figure 4.27. This by-product had the highest concentration in comparison to other BPs and also was more persistent in the solution, thus, it could not be removed easily during the treatment. Other by-products (BPs) which were more stable in the solution and had longer lifetime were BP-270, BP-172 and BP-288. The appearance of these BPs was resulted from hydroxylation of SMX parent ion for m/e = 270, and di hydroxylation of SMX for m/e = 288, split of the SMX molecule in N-C bound for m/e = 99 and N-S bound for m/e = 172.

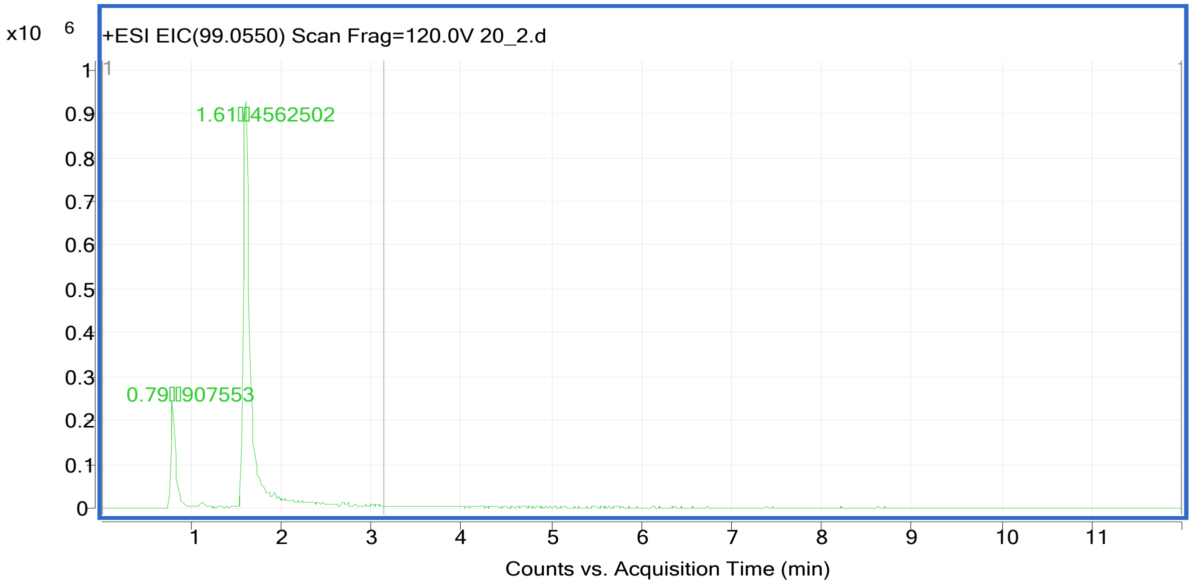


Figure 4.27. Sulfamethoxazole by-product (BP-99) chromatogram (retention times 1.61 parent ion, 0.79 isomer) Y axis (counts): Relative intensity (relative abundance of ion; X axis (m/z)
UVC (40 W) intensity =10 mJ/cm^2, reaction time = 30 min, solution volume=3L (irradiated),4L (total), temperature 18- 20 °C, pH = 5-6, airflow rate= 0 L/min, recirculation rate= 2 L/min

4.4.4 Identified SMX by-product; BP-270 accurate mass

Figure 4.28 shows chromatogram and Figure 4.29 depicts spectrum of BP-270.

In Fig. 4.28, BP-270 two peaks with retention times of 5.49min and 2.30min are demonstrated. The first peak with much abundance was eluted in retention time (RT) = 5.49min. The isomer of BP-270 was eluted at time 2.30.

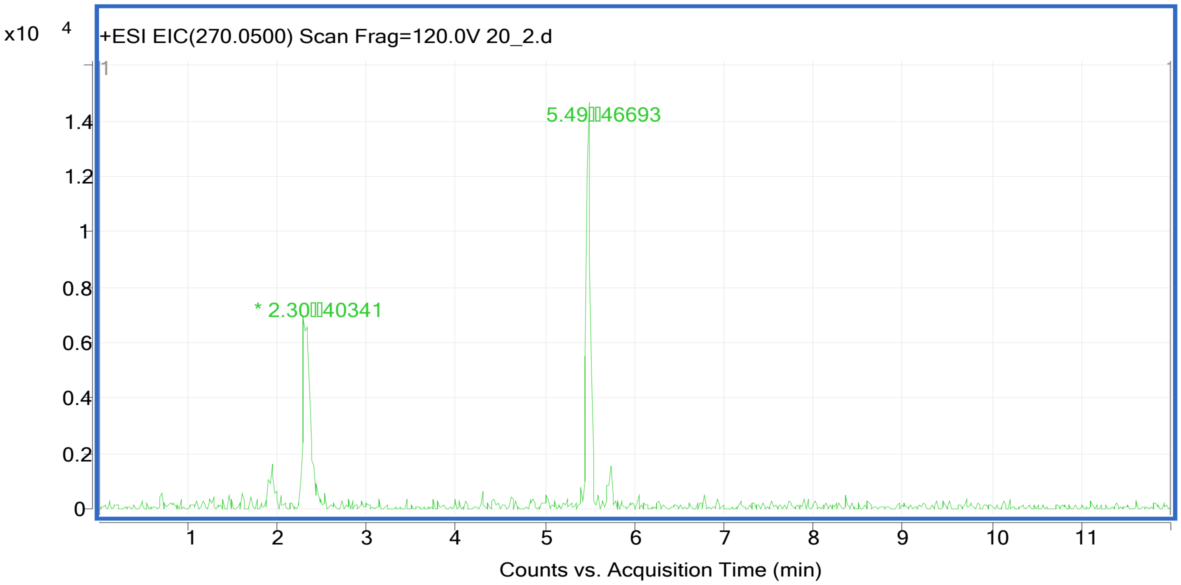


Figure 4.28. BP-270 chromatogram and its isomer with retention times of 5.49 and 2.30; Experimental conditions: UV intensity = 10 mW/cm^2, H_2O_2 dose = 6 mM, Aeration rate= 2 L/min, pH = 5-6, recirculation rate = 2 L/min

In Figure 4.29, the of BP-270 accurate mass spectrum is 270.0530. The accurate mass can help to monitor each by-product precisely.

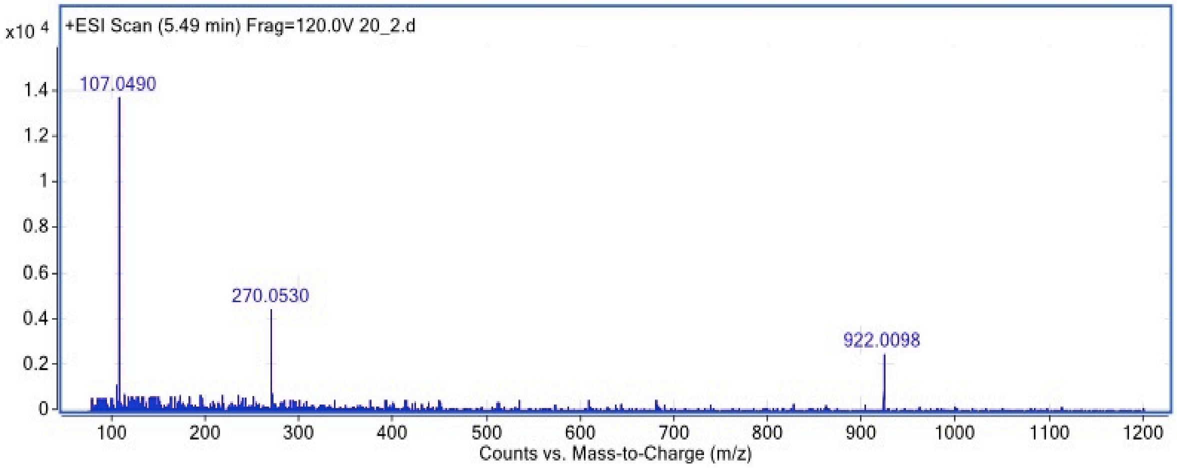


Figure 4.29. BP-270 spectrum with its accurate mass of 270.0530; Experimental condition: UV intensity = 10 mW/cm2, H_2O_2 dose = 6 mM, Aeration rate= 2 L/min, pH = 5-6, recirculation rate = 2 L/min

Figure 4.30 (a) shows the abundance change of BP-270.0550 during five- minute interval. The highest chromatogram is for the first 5 minutes and then decreased after each 5 minutes.

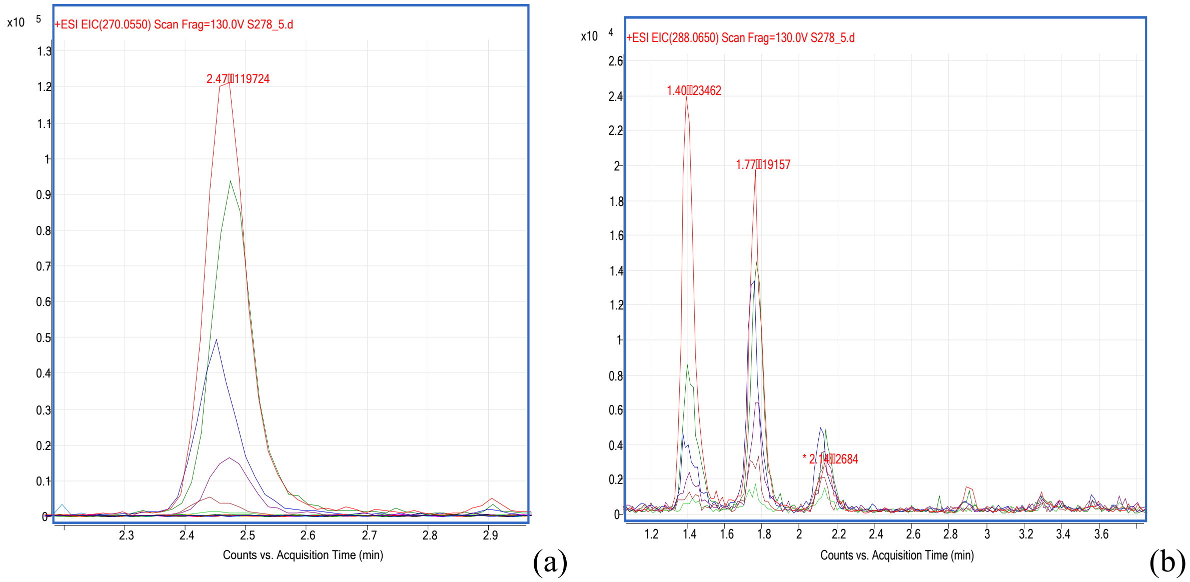


Figure 4.30. Abundance of BPs changes (a) BP-270, (b) of BP-288
Experimental conditions: UV intensity = 10 mW/cm2, H2O2 dose = 6 mM, Aeration rate= 2 L/min, pH = 5-6 recirculation rate = 2 L/min, 30 minutes of reaction

4.4.5 Identified SMX by-product; BP-288 accurate mass

Figure 4.30 (b) depicts BP-288 and its isomers. The main peak eluted at time 1.40 minutes and its isotopes were eluted at times 1.77 and 2.14 minutes. The abundance of the BP-288 main chromatogram at 1.40 retention time was higher than other isomers. The evolution of BP-288 transformation by-products as a function of time and relative ions abundance depicts in Figure 4.31. As it is seen in this Figure, the BP- 288 removed more rapidly than its isomers in 10 minutes. However, BP 288-1 and BP 288-2 showed lower removal rates.

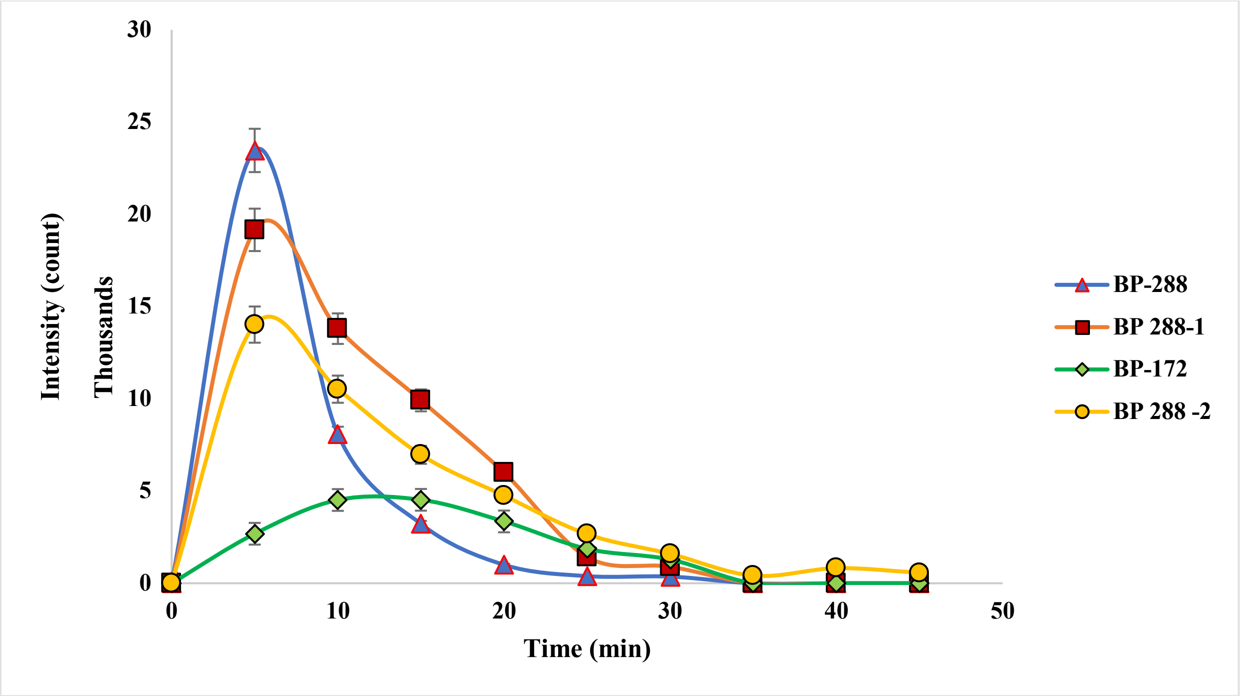


Figure 4.31. Evolution of by-product 288, its isomers and BP-172 over time
Experimental conditions: UV intensity = 10 mW/cm2, H_2O_2 dose = 6 mM, Aeration rate= 2 L/min, pH = 5-6 recirculation rate = 2 L/min, 30 minutes of reaction

However, after 30 minutes of reaction, the concentration of all BPs decreased or almost disappeared. In Fig. 4.31, the evolution of another major SMX by-products, i.e. B9-172 is depicted. BP- 172 has less abundance in comparison to other SMX BPs.

4.5 Phase 6: Pilot plant studies; Ozonation and advanced oxidation by O_3/UV

Operational condition:

A series of treatments have been carried out in the 52-liter reactor using batch mode and semi-continuous operation mode, at room temperature (17-22^{oC}), ambient pressure and around neutral pH (7-7.5). The C_{in} and C_f, corresponding to initial and final concentrations, were measured for target paracetamol (PCM), sulfamethoxazole (SMX) and caffeine (CAF) solutions before and after treatment. The mean UV intensity during the batch treatment was recorded as 21.5 mW/cm^2 while a mean value of 20 mW/cm^2 was in a semi-continuous mode.

Treatments were planned using UV irradiation, ozonation and an advanced oxidation (UV/O_3) at different contact times, different PCM, SMX, CAF concentrations and different UV and ozone doses. The following results represent the removal efficiency for each treatment run conditions. On account of a large volume of tests results, most of the results concern PCM. Comparative results for ozone and AOP UV/O_3 applied to SMX, CAF and PCM removal were shown at the end of this section. The results of each run were presented in an individual table (4.12 to 4-16) and then compared to other treatment runs.

4.5.1 UV results for AOP pilot plant

UV irradiation at 40 mJ.cm^2 dose, is widely used for disinfection purposes against the wide range of water borne pathogens (Luo et al. 2014a; S A Snyder et al. 2007). UV as disinfectant, would lead to reduce the chlorine demand for final disinfection and therefore reduce disinfection by-products (DBP) formation resulting from chlorination. In addition to UV application for disinfection purposes, it can also be used for photolysis purposes. By direct UV photolysis at higher irradiation dose (more than disinfection dose), i.e. 40 mJ.cm^2, organic dissolved matters can be degraded (Y. Lee et al. 2016). In this study PCM, CAF and SMX dissolved samples were treated by direct UV light at higher UV doses (more than 40 mJ/cm^2). Table 4.10 shows the PCM removal efficiency (R%) after 60 minutes of UV irradiation. After 60 minutes, the paracetamol solution received 77.4 J/m^2 energy, which led to paracetamol decomposition by 36.5%-37 % from its initial concentration.

Table 4.10. Removal efficiency of paracetamol (C_{in} =10.57,11.20,12.09 mg/L) by UV irradiation treatment at different times in a batch mode treatment

Sample No.	**Run No.**	**Water type**	**UV dose (J/cm^2) I = 21.5 mW/cm^2**	**Detention time (min)**	**C_{in} (mg/L)**	**C_f (mg/L)**	**R%**
1(3 Nov. 2015)	1	Tap water	77.4	60	11.20	7.23	36.5%
2 (10 Nov. 2015)	2	Tap water	77.4	60	12.09	7.82	36.5%
3 (11 Nov. 2015)	3	DI water	77.4	60	10.57	6.73	37%

UV practices were repeated at different times, different concentrations and different types of water. The results show the experiment reproducibility with similar removal efficiency (36.5%-37 %) under the same UV dose.

Table 4.11. Comparison of removal efficiency of paracetamol by UV irradiation treatment in a batch and semi-continuous mode treatment

Sample No.	**Run No**	**Water type**	**UV dose (Ws/ cm^2) I (1) = 21.5 mW/cm^2 I (2) = 20.0 mW/cm^2**	**Detention time (min)**	**C_{in} (mg/L)**	**C_f (mg/L)**	***R%***
Batch	1	Tap water	77.4	60	11.20	7.23	36.5%
Semi-Continuous	2	Tap water	72.0	60	11.30	8.2	29 %

During 60 minutes of ultraviolet irradiation, about a third of the target compound was removed in the medium. It shows a considerable impact of UV on paracetamol destruction on account of high molar extinction coefficient (ε =750 M^{-1} cm^{-1}). Ozone treatments carried out at semi-continuous modes for a combination of ozone and UV exposure, thus UV was in the same treatment conditions (semi-continuous). Results for such UV treatment in semi-continuous mode are shown in Table 4.11 and Figure 4.32. After 60 minutes of treatment in batch and semi-continuous modes, 36.5 and 29 percent of PCM were removed, respectively; however, the latter received less UV dose because of water samples properties related to flow rate of 20 L/min (Table (4.11) and Figure (4.13)). The rate of PCM elimination for both batch and semi-continuous mode are similar. Still, in semi-continuous mode, less PCM removal is observed due to UV light scattering by water flow rate (Figure 4.32).

Table 4.12. Removal efficiency of paracetamol (C_{in} =11.3 mg/L) by UV irradiation treatment at 5-minute interval in a semi-continuous mode treatment

t (min)	**I_{UV} = (20mJ/cm^2)**	**Removal efficiency**
0	C_0 = 11.3 mg/L C_t (mg/L)	(%)
5	10.5	7
10	10.2	10
15	9.9	12
20	9.7	14
25	9.5	16
30	9.3	18
60	8.2	29

4.5.2 Mechanism of UV photolysis reaction:

The mechanism of PCM reaction with UV light can be elucidated as a consequence of energy absorbed by the target compound. The absorption in the UV-C range (254.5 nm) was led to breakdown of PCM structure. UV directly cleaves bonds in PCM molecules by direct photolysis. Photons emitted by UV have sufficient energy to raise PCM molecules to excited electronic states that are unstable in environmental conditions. Transferred energy can be returned to the ground state or promotes chemical reactions. When PCM goes to the chemical reaction, it would be ionized by losing electron as it is represented by the following reaction: PCM +*hv* → $PCM^+ + e^-$

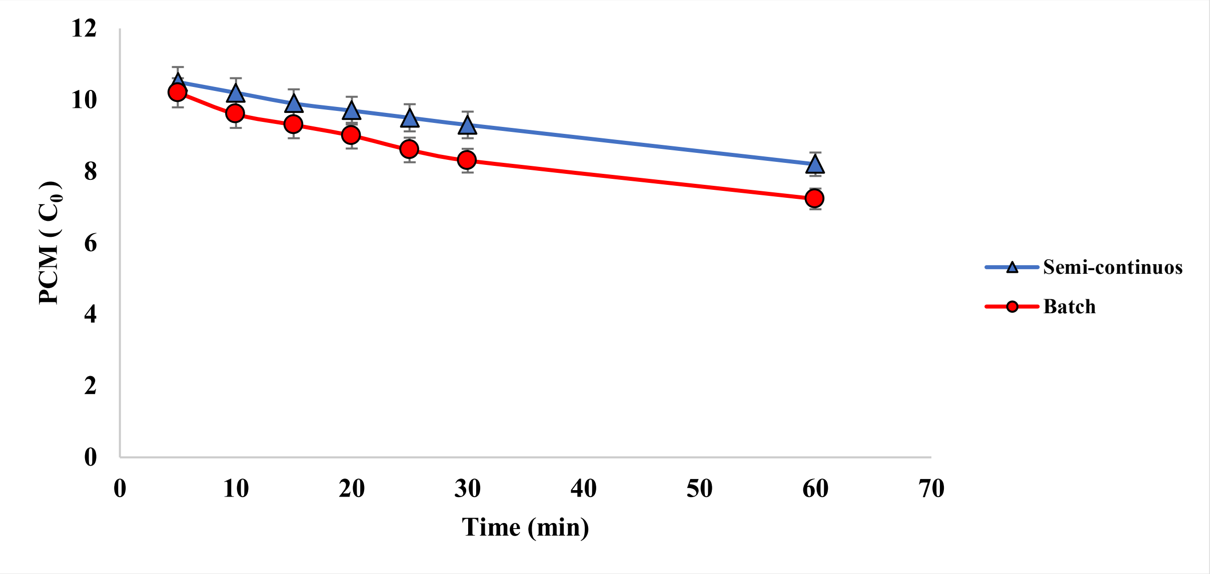


Figure 4.32. UVC photolysis of paracetamol (PCM): Batch versus semi- continuous mode

Experimental conditions: Paracetamol (Co = 11.3 mg/L); UV dose = 77.4 (Ws/ cm²), mean water flow rate: 20 L/min, reactor volume = 70 Liter

Comparison to previous studies

Other studies on degradation of pharmaceutical active compounds (PhACs) by direct UV photolysis are consistent with the outcomes of this research. Some results show negligible degradation by LP-UV (Chin and Berube, 2005; Rosenfeldt and Linden, 2004) and other results show higher removal of target compounds (Thomson et al, 2002; Adams et al. 2002; Snyder et al, 2007). This can be attributed to: i) nature and the chemical structure of pollutants; which are hard or easy to destroy; ii) molar absorption coefficient and UV light absorption by PhACs. Molar absorption coefficient for PCM is 750 (ε=750 M^{-1} cm^{-1}), is high in comparison to other PhACs. On the other hand, the maximum UV light absorption for PCM is 243nm which is in the range of UV irradiation maximum peak of 254nm.

4.5.3 Pilot ozone oxidation applied for micropollutants' removal

A series of tests with ozone were conducted at various treatment conditions. Based on the amount of oxygen flow rate, the dissolved ozone concentration was monitored and recorded by an inline ozone probe.

Table 4.13. Ozone production and ozone dissolved rate (calculated from chapter 3)

Ozonation time (min)	**Ozone production (mg/L)**	**Ozone production (mg/L)**	**Ozone production (mg/L)**
	O_2 flow = 0.5 L/min	O_2 flow = 2.0 L/min	O_2 flow = 2.5 L/min
	Dissolved O_3 = 0.25 (mg/L). min	Dissolved O_3 = 0.7 (mg/L). min	Dissolved O_3 = 0.8 (mg/L). min
5	1.25	3.5	4
10	2.5	7	8
15	3.25	10.5	12
20	5	14	16
25	6.25	17.5	20
30	7.5	21	24
35	8.75	24.5	28

The values of ozone production as a function of oxygen feeding time are listed in Table 4.13. During the 20 minutes ozonation at an ozone dose's rate of 0.25 mg/L. min., almost all (99.5%) of the paracetamol (11.3 mg/L) was decomposed in the reactor. Table 4.14 and Figure 4.33 show ozonation removal efficiency. The C_0 and C_t correspond to the concentration of target compound at times zero and time t, respectively. After 20 minutes, the amount of target compound was reduced to lower than 0. 5% of its initial concentration (11.3 mg/L).

Table 4.14. Removal efficiency of paracetamol by ozonation at 5-minute intervals

At t_0 → C_0=11.3 mg/L	**Ozonation** **$[O_3]$ = 2.5 mg/L**	**Removal efficiency**
t (min)	C_t	(%)
5	7.9	30
10	4.4	61
15	1.2	89
20	0.06	99.5

Ozonation experiments were continued for the target compound at concentrations of 52 mg/L and 104 mg/L, in which ozone dose rates were increased to 0.7 and 0.8 mg/L. min, respectively. There was a little increase of PCM decomposition when the oxidant dose increased from 12 to 14 mg/L for PCM concentration of 52 mg/L (Table 4.15 and Figure 4.34). However, for both doses of oxidant after 25 minutes of reaction the residual concentration of PCM in solution was close to each other without a sharp removal.

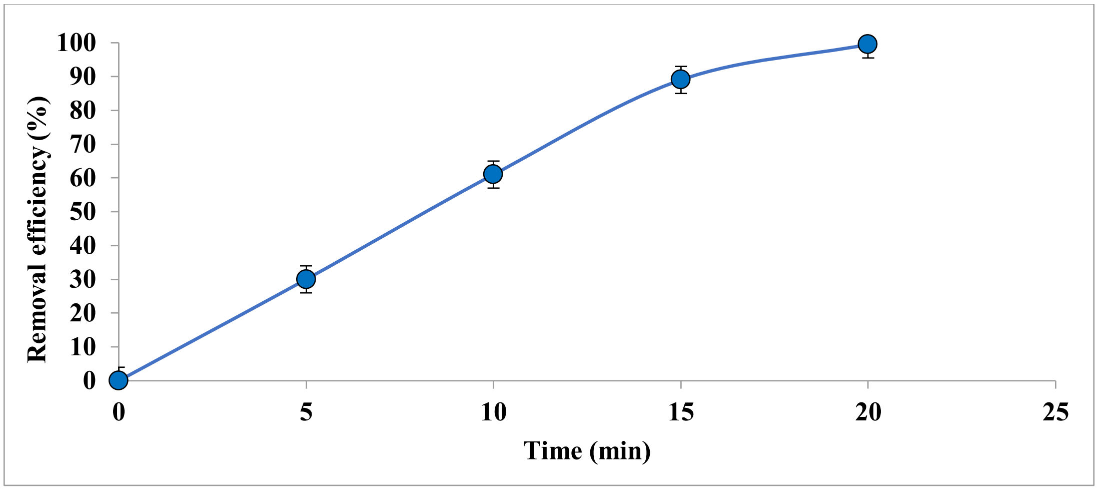


Figure 4.33. Removal efficiency of Paracetamol by Ozonation.
Experimental conditions: $[O_3]$ = 2.5 mg/L, Paracetamol (Co= 11.3 mg/L), UV dose = 0.00 (mWs/ cm^2), mean water flow rate: 20 L/min, reactor volume = 70 Liter

4.5.3.1 Effect of ozone dose on the micropollutant's removal

The experiments were conducted to evaluate an effect of ozone dose change and the target compound concentration change. Accordingly, an increase of PCM from 11.3 mg/L to 52 mg/L and ozone dose from 2.5 mg/L to 12 mg/L were implemented.

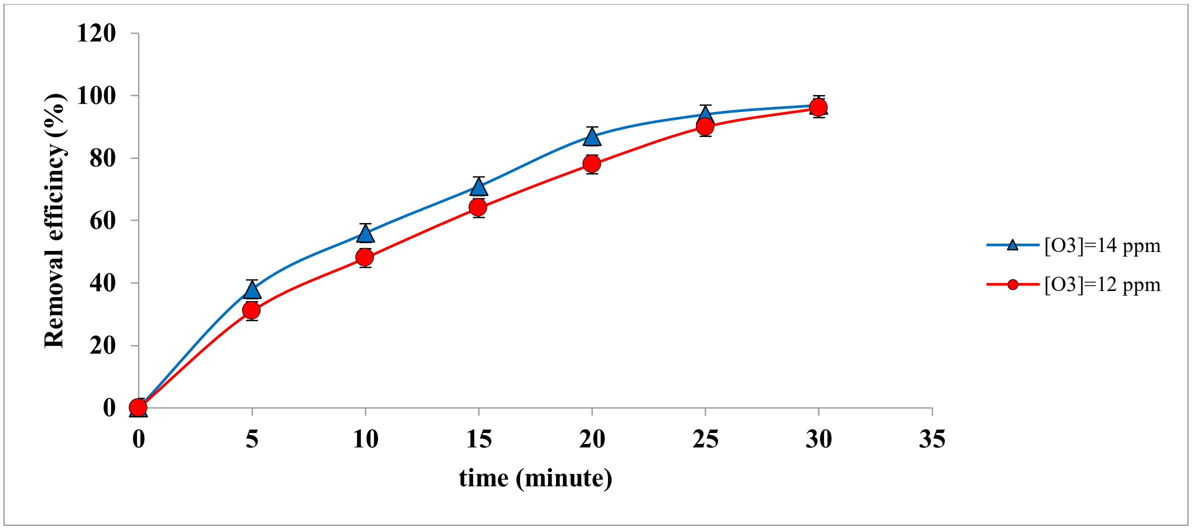


Figure 4.34. Ozonation of paracetamol PCM; Comparison between different ozone dose Experimental condition: Paracetamol (C_0= 52 mg/L); [O_3] =12,14 mg/L, UV dose = 0.00 (mWs/ cm^2), mean water flow rate: 20 L/min, reactor volume = 70 Liter

The results presented in Table 4.15 show that the concentrations of both samples (PCM = 11.3 and PCM = 52) were decreased as a function of the oxidant dose and treatment time. However, the RE3 sample (PCM =11.3 mg/L) shows a rapid decrease in comparison to the RE2 sample (PCM =52 mg/L), while the ozone doses for RE3 sample and RE2 sample were 2.5 mg/L and 12 mg/L, respectively (Table 4.15). This result shows dependence of the target compound removal to its concentration which is not linear. As it is revealed in Table 4.15, with higher concentration of the target compound, more time is required for treatment. Interestingly, by comparing RE2 and RE3 at 20 minutes of reaction time, all target compounds removed from the medium in RE3, however, RE2 needs 15 minutes more time for complete removal of PCM.

Considering five times the linear increase of the ozone and PCM doses as shown in runs RE3 and RE2, the removal efficiency does not have linear relationship either to dose of oxidant or to the contaminant concentration (equations 4.15, 4.16, 4.17).

$$OZ2_{C_0} / OZ3_{C_0} = 52 / 11.3 = 4.6 \quad (4.15)$$

$$OZ2_{[O_3]} / OZ3_{[O_3]} = 12 / 2.5 = 4.8 \quad (4.16)$$

$$RE2\ (15\ \text{min}) / RE3\ (15\ \text{min}) = 64/89 = 0.7 \quad (4.17)$$

Table 4.15. Comparison of removal efficiency (R.E) of Paracetamol at different concentrations (C_0 = 52, 11.3 mg/L) by Ozonation and different ozone concentrations at 5- minute interval

Time (min)	**Ozonation1 OZ1**	**RE1**	**Ozonation2 OZ2**	**RE2**	**Ozonation3 OZ3**	**RE3**
	C_0=52 mg/L		C_0=52 mg/L		C_0 = 11.3	
	$[O_3]$ = 14 mg/L		$[O_3]$ = 12 mg/L		$[O_3]$ = 2.5 mg/L	
5	33.1	36%	35.4	31%	7.9	30%
10	23	56%	26.9	48%	4.4	61%
15	14.7	71%	18.8	64%	1.2	89%
20	6.8	87%	11.2	78%	0.06	99.50%
25	2.9	94%	5.2	90%	0	100%
30	1.5	97%	2.1	96%	0	100%
35	1.1	98%	1.3	97%	0	100%

OZ1: Ozonation 1 (C_0 = 52 mg/L, $[O_3]$ = 14 mg/L); OZ2: Ozonation 2 (C_0 = 52 mg/L, $[O_3]$ = 12 mg/L); OZ3: Ozonation3 (C_0 = 11.3 mg/L, $[O_3]$ = 2.5 mg/L); RE: Removal efficiency; RE1: Removal efficiency for sample OZ1; RE2: Removal efficiency for sample OZ2; RE3: Removal efficiency for sample OZ3.

4.5.4 Comparison the efficiency of UVC photolysis and ozonation

Figure 4.35 shows the reaction rate of PCM elimination which elucidates target compound abatement for UVC photolysis and ozonation method. Both methods obey a pseudo first order reaction. However, ozonation depicted a very fast reaction rate in comparison to UVC photolysis.

Almost all PCM constituents were eliminated from the medium by ozone streams. Regardless, after 60 minutes of reaction, PCM was still present in the medium where UVC was applied.

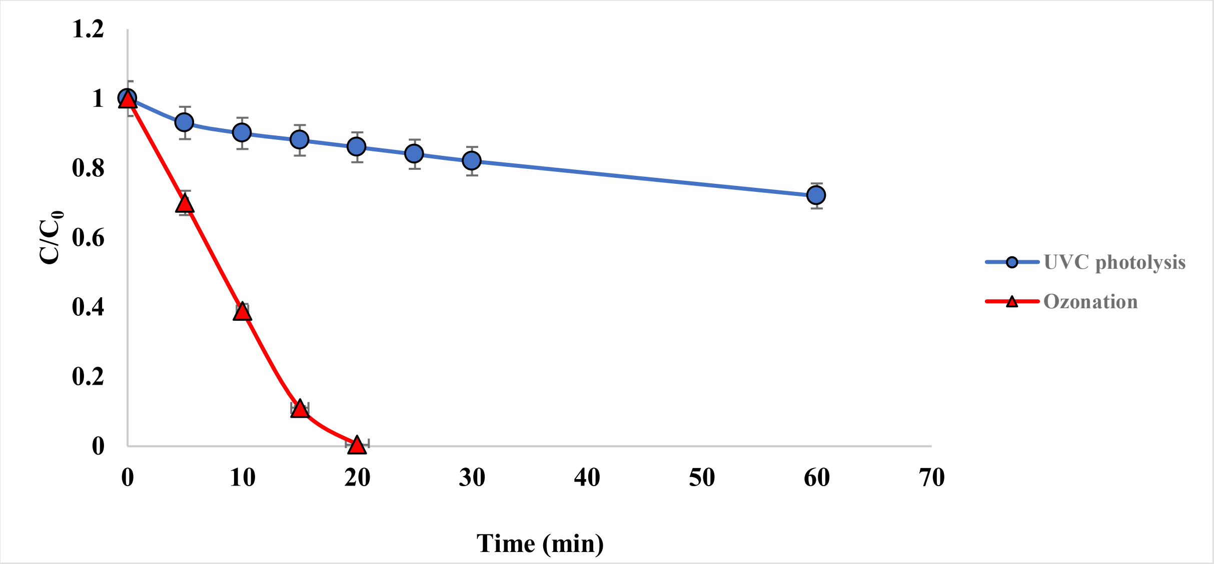


Figure 4.35. Reaction rate of PCM: comparison between PCM photolysis and PCM ozonation. Experimental condition: [O3] = 2.5 MG/L; Paracetamol (Co= 11.3 mg/L); UV dose = 77.4 (Ws/ cm^2), mean water flow rate: 20 L/min, reactor volume = 70 Liter

4.5.5 Mechanism of ozone reaction; comparison to previous works

Reactions of ozone during water treatment are very complex and specific. On account of ozone dipolar structure, this molecule has the ability to attract the target compound as a nucleophile or electrophile agent (Jim Eagleton, 2000). Ozone in two different pathways (directly and indirectly) reacts in water with organic matter. Different types of kinetics, control oxidation by-products of these two reaction pathways. In this section of work, direct reaction of ozone with organic pollutants is slow at the range of 1 - 10^3 M^{-1} s^{-1} (PCM + $O_3^- \rightarrow$ PCM oxide). When an organic contaminant with unsaturated double bond is present in water, dissolved ozone molecules split the bond due to dipolar structure of ozone (Gottschalk et al. 2010). The mechanism of ozone reaction with an organic can be described by the following: (Figure 4.36).

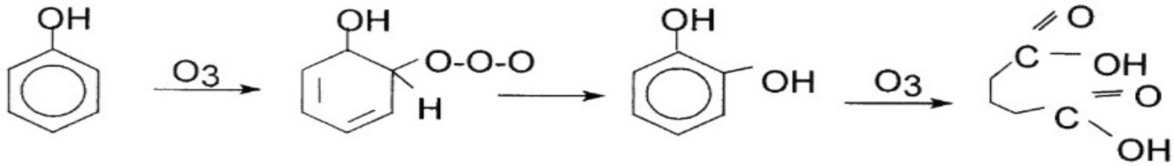


Figure 4.36. Mechanism of phenol ozonation resulting organic structure destruction (Gottschalk et al., 2010)

The same pathway may be suggested for PCM degradation. However, the investigation of PCM by-products should confirm this hypothesis.

Comparison with other studies

The current results are consistent with other studies (Mcdowell et al. 2005; Vogna et al. 2004; Bourgin et al. 2018; Saskia Gisela Zimmermann 2011). In these studies, a wide range of organic matter including PPCPs, pesticides, antibiotics and PhACs were oxidized by ozonation at different solute concentrations and ozone rate (Huber et al., 2004; Andreozzi et al, 2005; Maldonado et al, 2006; Shemer et al, 2006; Carballa et al, 2007; Soo Oh et al, 2007). The authors noted that most of the target pollutants in water were completely removed. However, TOC removal was achieved to some extent and this is an indicator for by-products formation in the medium.

A possible ozonation by-products are currently unknown. The TOC accumulation in the media, is a proof of existence of these by- products. Furthermore, ozone consumption in water samples after complete removal of PCM is another BPs indicator.

4.5.6 Pilot application for micropollutants’ removal by O_3/UV AOP

The AOP (O_3/UV) experiments have been performed for a series of ozone doses, UV irradiation contact times and the paracetamol concentrations (11.3 mg/L and 52 mg/L). Table 4.16 shows the removal efficiency for 5-minute interval experiments during 20 minutes, with 20 mJ/cm^2 of UV intensity and ozone dose rate of 0.25 (mg/L. min). The O_3/UV treatment method could easily remove all PCM in 20 minutes (Table 4.16).

Table 4.16. Removal efficiency of Paracetamol by Ozone/UV at 5- minute interval

At t_0 → C_0 =11.3 mg/L **I_{UV} = (20mJ/cm^2)**	**O_3/UV** **[O_3] = 2.5 mg/L**	**Removal efficiency**
t (min)	C_0 =11.3 C_t	(%)
5	6.2	45
10	2.8	75
15	0.27	98
20	0.0	100

In comparison to ozonation of the same sample (PCM 11.3 mg/L), O_3/UV treatment method showed an increased removal for a mean value of 10% for each 5 minutes. The oxidation removal efficiency by ozone alone and O_3/UV system is illustrated in Figure 4.37.

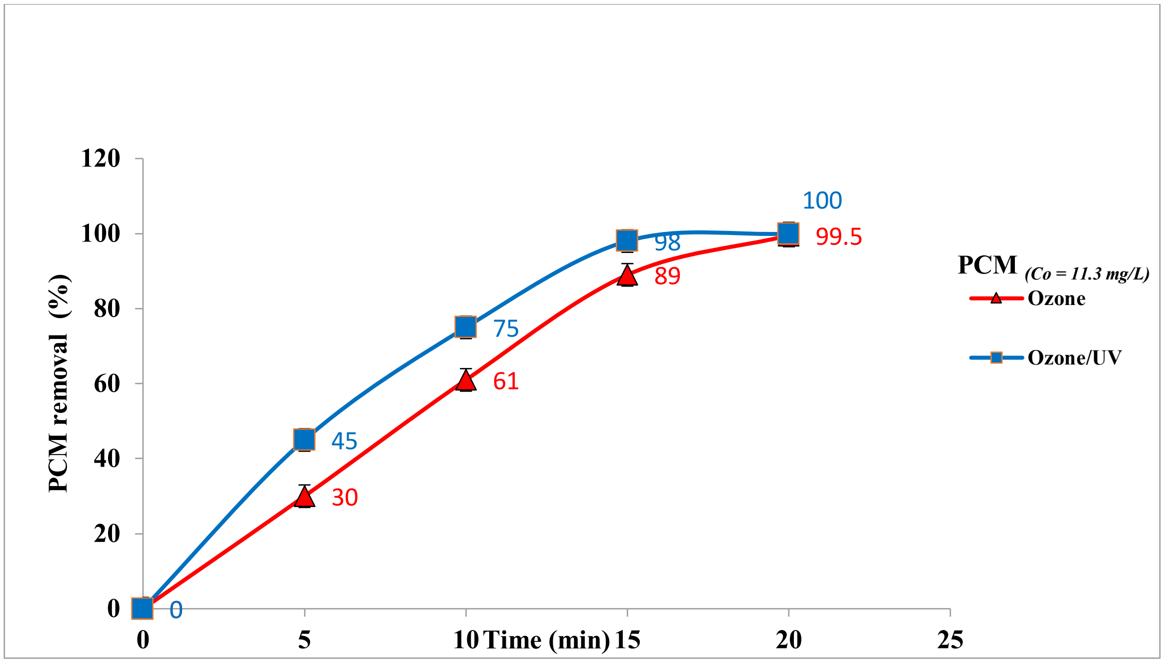


Figure 4.37. Paracetamol (C_0 = 11.3 mg/L) removal efficiency: Comparison of ozone alone and O_3/UV treatment; Experiment condition: Paracetamol (Co = 11.3 mg/L); [O_3] = 2.5 mg/L, UV intensity = 20 mJ/cm^2; UV dose = 77.4 (Ws/ cm^2), mean water flow rate: 20 L/min, reactor volume = 70 Liter

As it is shown in this Figure, in the AOP curve, after 15 minutes of reaction, the PCM is eliminated in the medium and reaction is almost completed, but as it is clear in the ozone curve, PCM was still in the medium until 20 minutes of treatment. Ozone and AOP curves were met at 20 minutes of treatment, however, when the concentration of PCM was more than 11.3 mg/L, the curves did not meet at this point.

4.5.7 Effect of ozone dose, PCM concentration on micropollutant's removal by O_3/UV

Following the effect of PCM concentration, which was discussed in the previous section, the effect of ozone dose also investigated. Therefore, the ozone /UV test was repeated for paracetamol at C_0 = 52 mg/L concentration. The results are shown in Figure 4.38 that illustrates elevated removal efficiency for ozone/UV systems in comparison to ozone alone.

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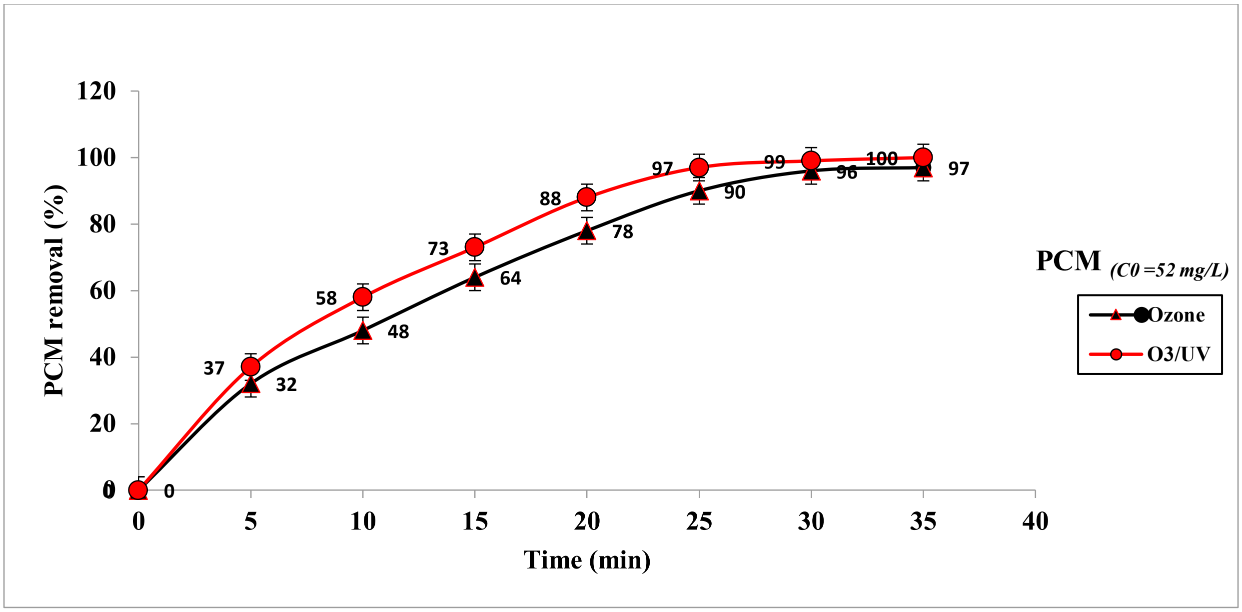

Figure 4.38. Paracetamol (C_0 =52 mg/L) removal efficiency: Comparison of ozone alone and O_3/UV treatment by different ozone concentrations at 5- minute interval; Experiment condition: Paracetamol (C_0 =52 mg/L); [O_3] = 12 mg/L, UV intensity = 20 mJ/cm^2,); UV dose = 77.4 (Ws/ cm^2), mean water flow rate: 20 L/min, reactor volume = 70 Liter

During the first 20 minutes of treatment of PCM (52 mg/L), an increasing of the removal rate (10%) was observed; the result was close to the PCM (11.3 mg/L) removal. Furthermore, Fig. 4.38 presents a reproducibility of experiments that are carried by ozone alone and O_3/UV methods. Accordingly, the oxidation behavior for two methods are similar for low and higher values of the pollutant concentration, oxidant dose and contact time.

Discussion

Combination of ozone and UV as an advanced oxidation process (AOP) produces hydroxyl radicals (OH). Since the oxidation capacity is enhanced primarily by AOP, OH radicals have capability to oxidize refractory organic pollutants (Gottschalk et al, 2000, Ternes et al, 2003). In AOP, the generation of hydroxyl radicals is performed by ozone decomposition through several radical chain reactions. Accordingly, the OH radicals, generated through AOP, are more powerful than ozone alone reactions. Oxidation power of OH radical is 2.8 eV while oxidation power of ozone is 1.5 eV (table 2.1). The oxidation rate of organic matter by AOP is much higher than the reaction rate with ozone alone under the same operation condition. The reaction rate constants between ozone and organic matter are typically between 1-10^3 M^{-1} s^{-1}, while the reaction rate constants between OH radicals and organic pollutants ranges between 10^8–10^{11} M^{-1} s^{-1} (Parsons, 2004, Snyder et al,.2007; Gottschalk et al,.2000; Esplugas et al, 2007).

Another important difference between ozone alone treatment and UV/O_3 AOP is the possibility of lower BPs formation by AOP due to higher oxidation power and higher mineralization of organic compounds in water. Several investigations showed mineralization of AOPs comparable to oxidation by ozone alone, however they did not measure by-products directly (Chin and Beruue, 2005; Alsheyab and Muñoz, 2006; Sarathy and Mohseni, 2007; Mosteo et al, 2009).

In all these studies mineralization of total organic compound was much higher by AOPs in comparison to ozonation alone. Based on the results obtained in this study, two indicators, i.e. ozone dissolved concentration and UV intensity, showed incomplete mineralization of PCM. These indicators, in addition to TOC results, confirmed the existence of by-products in the solution even after PCM is completely removed by both ozone alone and AOP. However, to justify existence and type of by-products, a complementary analysis was necessary. The ozone concentration in water at the beginning of ozonation and after complete PCM removal recorded zero by online ozone detector. This phenomenon elucidates complete ozone consumption by PCM. The ozone dissolved value in water samples after PCM complete elimination had a low increasing trend but to some extent that was not enough in comparison to the ozone concentration in pure water. This phenomenon clearly revealed the accumulation of BPs in the medium.

Like ozonation, in AOP treatment, the ozone concentration was not high enough in comparison to ozone concentration in pure water. Another indicator was UV intensity. UV intensity in PCM solution before AOP treatment was 1.4 mJ/cm^2 due to PCM UV absorption. This amount started to increase when PCM was removed from solution. However due to UV light absorption by other possible by-products in solution, it was not increased until a certain amount of time, i.e. 20 minutes after PCM complete removal.

Oxidation of PCM by direct (ozone molecules) or indirect (OH radicals) pathways was led to formation of by-products and finally to mineralization ($CO_2 + H_2O$). The extent of mineralization and by-products formation depended on the oxidative power of each oxidant (O_3 and OH) and nature of pollutant and type of water and pH value. The reaction pathway of PCM by direct ozonation or by indirect oxidation can be described by double bond cleavage or addition of OH to the aromatic ring (Figure 4.39).

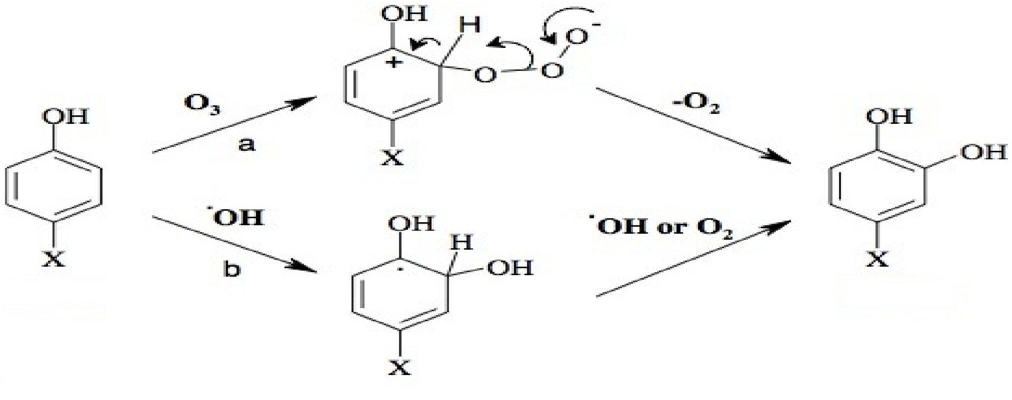

Figure 4.39. Phenolic compound degradation by direct ozonation and indirect pathway
(Mvula et al. 2003)

The combination O_3/UV led only to an increased (not significant) of the PCM removal. However, the most important point that discriminated oxidation by ozone alone and AOP was much higher TOC removal, mitigating the possibility of by-products formation, faster reaction rate, non-selective degradation of target compound and ability of AOP to break down recalcitrant compounds.

4.5.8 Comparative pilot scale study on ozone reactions for SMX, PCM, CAF removal

Each of three target pollutants in DI water was exposed to ozone by means of a constant stream of dissolved ozone. The effect of ozone concentration on removal efficiency is shown in Figure 4.40. After 15 minutes of ozonation with an ozone dose rate of 0.25 mg/L. min, the major part of all target compounds was degraded in the reactor. However, SMX was degraded faster in comparison to PCM and CAF at the same experimental condition. The results revealed an enhancement of reaction efficiency for the three PhACs, when ozone dose was increased in the solution.

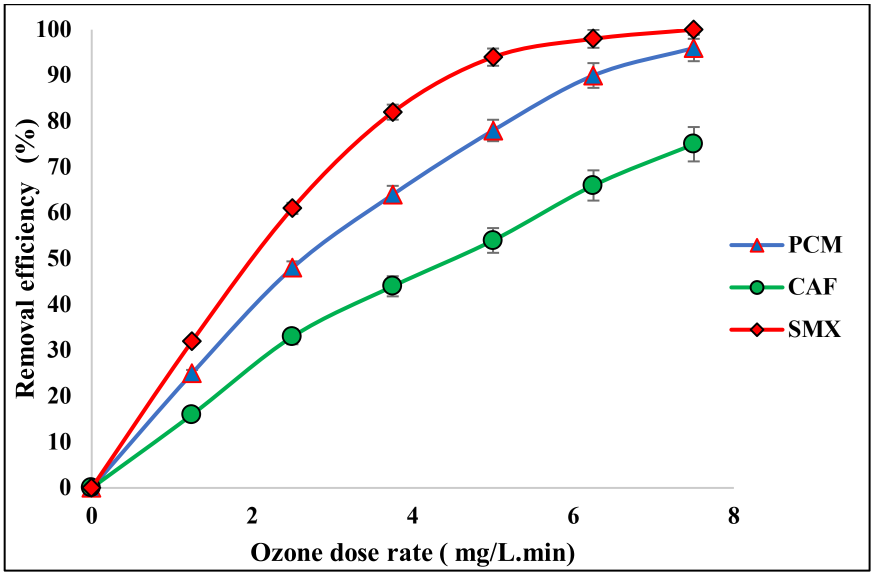

Figure 4.40. ECs degradation with dosage of ozone rate; Sulfamethoxazole (SMX), paracetamol (PCM) caffeine (CAF) removal rate with respect to ozone dose, Experimental condition: Ozone rate = 0.25 (mg/L). min; reaction time: 30 minutes, $[EC_S]_0$= 60 µM; ECs: PCM, SMX, CAF; UV dose = 77.4 (Ws/ cm^2), mean water flow rate: 25 L/min, reactor volume = 70 Liter

After 30 minutes of reaction, by increasing ozone dose to 2.5 mg/L, almost all the target compounds were eliminated completely. CAF was appeared to be hardly degrade by ozone. This is due to higher refractory character of CAF, which led to lower reaction rate of this compound comparing with other compounds. The results confirmed that the ozone concentration has a direct effect on degradation efficiency of all three ECs. Ozone in two different pathways (directly and indirectly) reacts with target pollutants in water (Gómez-Pacheco et al. 2011). Different types of kinetics control the oxidation by-products on ozonation pathways. In this study section, a direct reaction of ozone with organic pollutants is suggested, which is slow and at the range of 1- 10^3 $M^{-1} s^{-1}$ (Von Gunten 2003b; Mehrjouei et al. 2015). The following reaction mechanism is proposed for oxidation of target compounds by ozone.

$$PCM + O_3 \rightarrow PCM\ oxide$$

$$SMX + O_3 \rightarrow SMX\ oxide$$

$$CAF + O_3 \rightarrow CAF\ oxide$$

4.5.9 Evolution of ECs with respect to ozone dose change

Figure 4.41 shows various ratios of O_3 consumed to ECs decomposed by O_3/UV AOP. The AOP reactions were performed in a semi-continuous flow with ozone adding velocity of 0.25 (mg/L) min. It was found that after O_3 addition to the solution, the ozone consumption per mg of ECs decomposed, was almost constant over time until 12 to 14 minutes.

It meant that effective utilization rate of ozone for ECs decomposition had a constant rate with a continuous ozone addition. Therefore, in the semi-continuous mode it is advisable to add O_3 continuously into the system until certain time for saving energy (based on ECs characteristics) to improve the treatment by O_3/UV AOP.

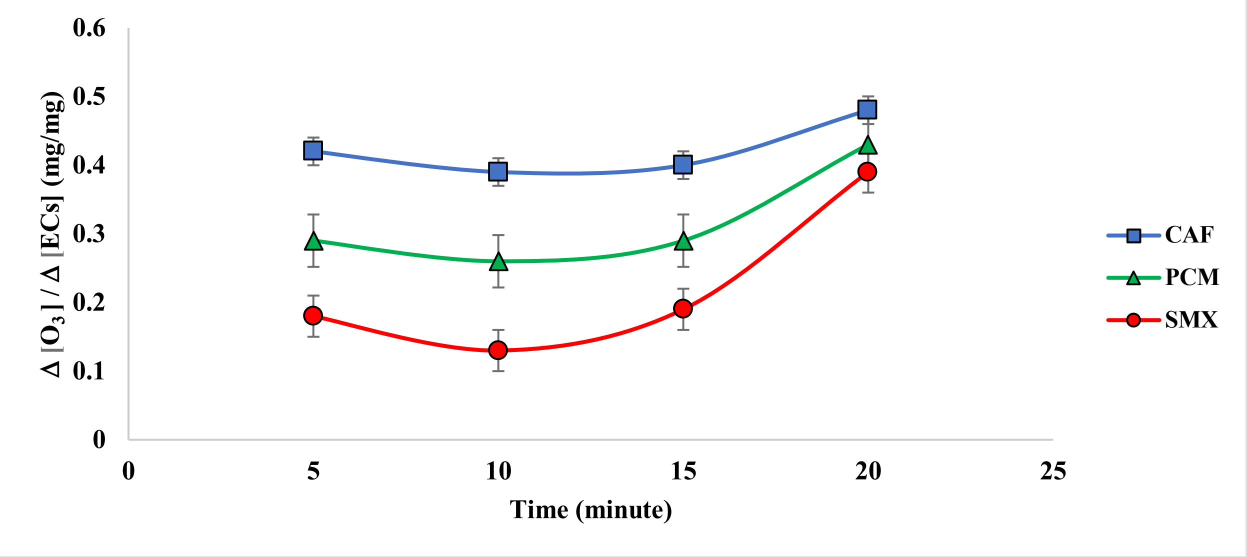

Figure 4.41. Δ [O_3] / Δ [ECs] (mg/mg): Ratios of O_3 consumed to ECs decomposed by O_3/UV AOP Experimental condition Ozone rate = 0.25- 0.5 (mg/L). min; $[EC_S]_0$= 60 µM; ECs: PCM, SMX, CAF; UV dose = 77.4 (Ws/ cm^2), mean water flow rate=25 L/min, reactor volume = 70 Liter

After 15 minutes of reactions, all three ECs were removed around 90% from the medium. However, the ozone consumption showed different values. The ratios of ozone to ECs for CAF was 0.4 and for PCM was 0.3. However, the ratio of SMX consumption was lower in comparison to other compounds. It means that SMX needs less ozone for its structure breakdown at initial time of reaction. After 15 minutes of reaction, the ozone residuals in solution for the SMX curve were higher than in case of CAF and PCM. It means that the SMX degradation products were eliminated faster than PCM and CAF.

4.5.10 Mechanism of ozone reactions for SMX, PCM, CAF

Defining of the ozone reaction mechanism is strategic for a successful oxidation process. Comparing the pKa of three target compounds (SMX, PCM, CAF), SMX has lowest and CAF has highest pKa.

$$pKa_{\text{CAF}} = 14 > pKa_{\text{PCM}} = 10.5 > pKa_{\text{SMX}} = 4.5$$

The larger the pKa, the weaker the acid, and therefore, the lower H abstraction from the molecule, which means that proton is held tightly in the molecule. Therefore, SMX is willing to dissociate easier than CAF and needs less ozone for destruction. The three target contaminants, (SMX, PCM, CAF), are present in water with their unsaturated double bond in aromatic rings. Dissolved ozone molecules with its dipolar structure, split the double bond of target pollutants by its electrophilic attack. The mechanism of ozone reaction can be described by H abstraction from the molecule and/ or ozone addition to the organic molecule. The same pathway may be suggested for degradation of three target compounds. However, the investigation of their by-products should confirm this hypothesis.

4.5.11 Comparative treatment methods for PCM: UVC, Ozone, UV/O_3 AOP

Figure 4.42 summarizes and compares the results of treatment by UV alone, ozone alone and ozone based advanced oxidation system (O_3/UV).

The AOP system (O_3/UV) shows the strongest oxidation of PCM in comparison to UVC photolysis and ozonation. After 15 minutes of reaction, almost all PCM was degraded by O_3/UV AOP. However, in this period, only 12% of PCM was removed by sole UVC and 89% by sole ozone.

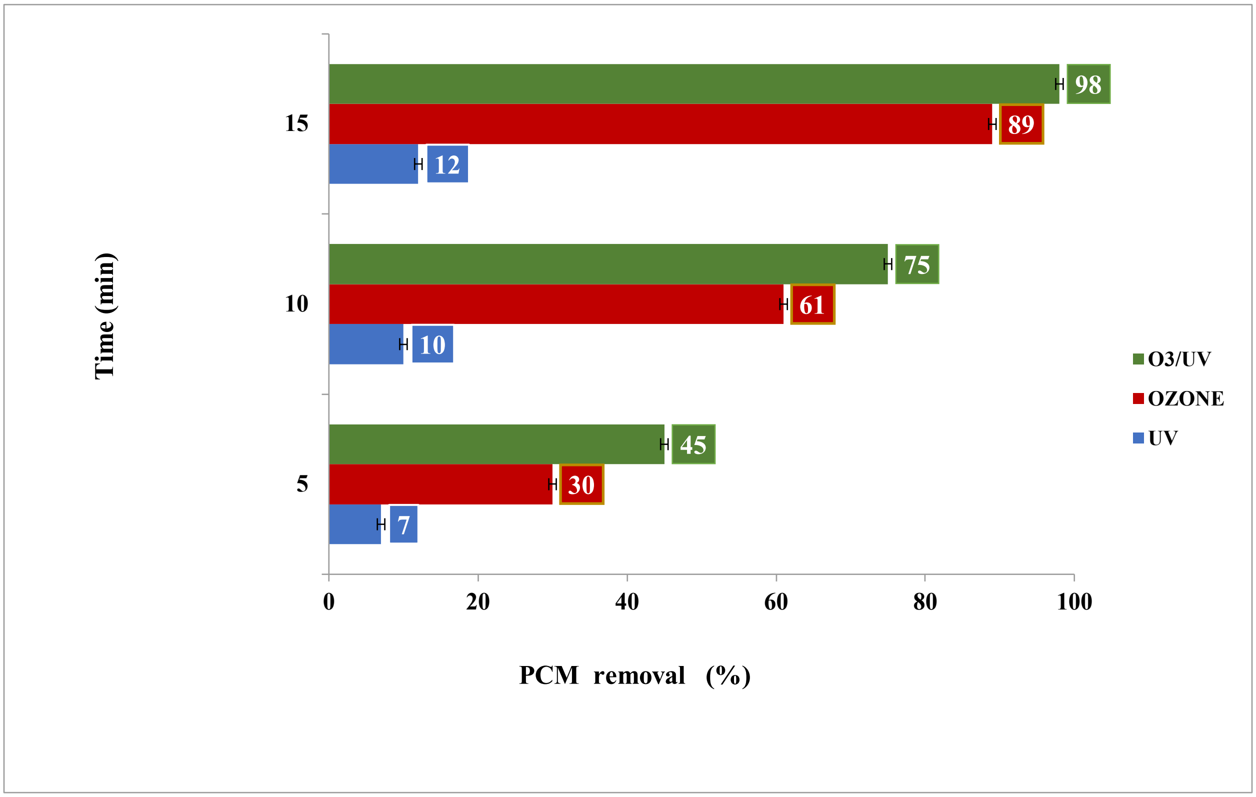

Figure 4.42. Comparison between different PCM removal techniques: UV, Ozone, UV/O_3 AOP
Experimental conditions: PCM =11.3 mg/L, Ozone rate = 0.25 (mg/L). min, UV dose = 20mJ/cm^2, Reactor volume= 70-liter, water flow rate = 25 L/min

4.5.12 Evaluation the effectiveness of UVC, Ozone, UV/O_3 methods for the SMX, PCM, and CAF removal

Figure 4.43 compared three different oxidation methods for three target pollutants. All three oxidation methods depicted a similar removal regime for three different target compounds. The UVC photolysis for all three had the lowest effect in comparison to ozonation and AOP. The following trend was observed for SMX, PCM, and CAF.

UVC **(CAF < PCM < SMX)** < *Ozonation* **(CAF < PCM < SMX)** < *AOP* **(CAF < PCM < SMX)**

Caffeine (CAF) demonstrated the lowest removal in comparison to PCM and SMX. The following trend was applicable for removal of target compounds with respect to oxidation methods.

$$CAF\ \textbf{(UVC, Ozone, AOP)} < PCM\ \textbf{(UVC, Ozone, AOP)} < SMX\ \textbf{(UVC, Ozone, AOP)}$$

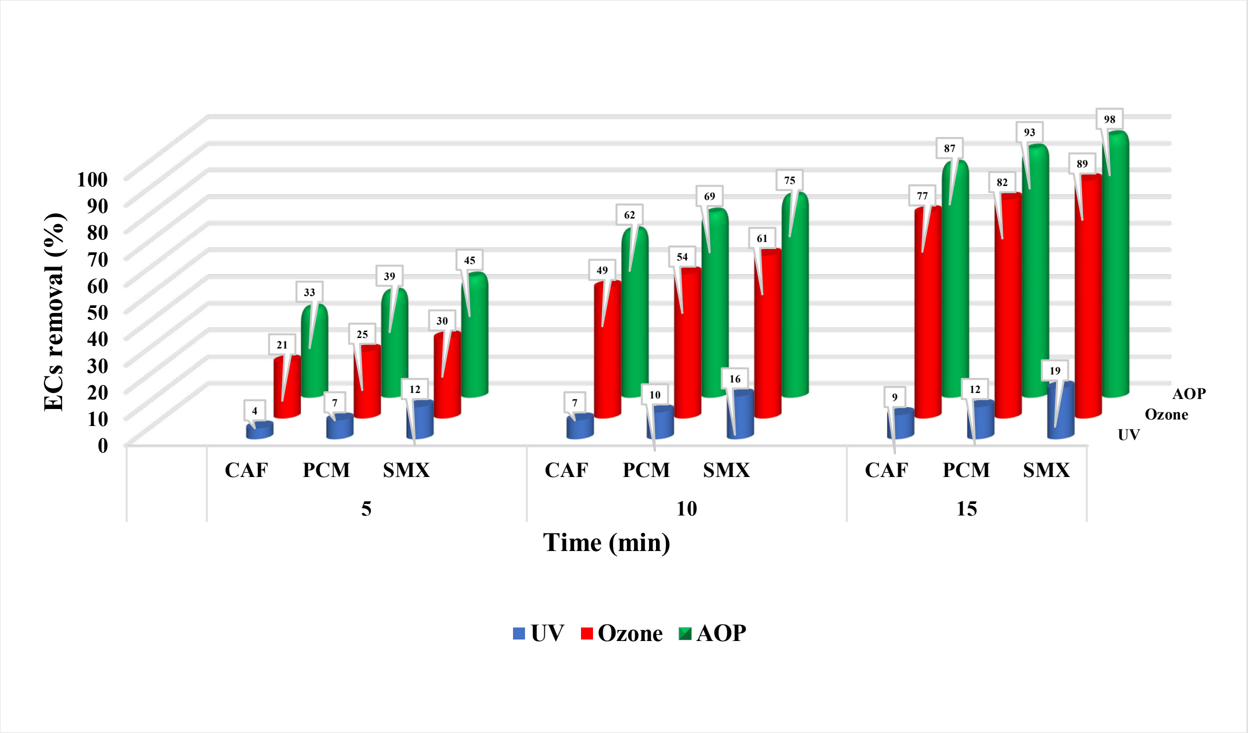

Figure 4.43. Comparison of UV, ozone and UV/O_3 AOP for the ECs removal
Experimental conditions: Ozone rate = 0.25 (mg/L). min; $[EC_S]_0$= 60 µM; ECs: PCM, SMX, CAF
UV dose = 77.4(Ws/ cm^2), mean water flow rate: 25 L/min, reactor volume = 70 Liter

These results confirmed the feasibility and validated the application of various methods for target ECs in aqueous solution.

4.5.13 By-products monitoring

LC-MS-MS instrument was applied to detect paracetamol degradation by-products during oxidation treatment. Several samples have been taken and made ready to investigate by-products formation during treatment. These samples have been taken before and after ozone treatment with a primary concentration of 10 mg/L paracetamol. At the first step, a standard solution of paracetamol 5 mg/L, was injected directly to the mass spectrometer in order to make a parent ion at its molecular weight (152.06) by electrospray positive mode in the mass spectrometer (Figure 4.43).

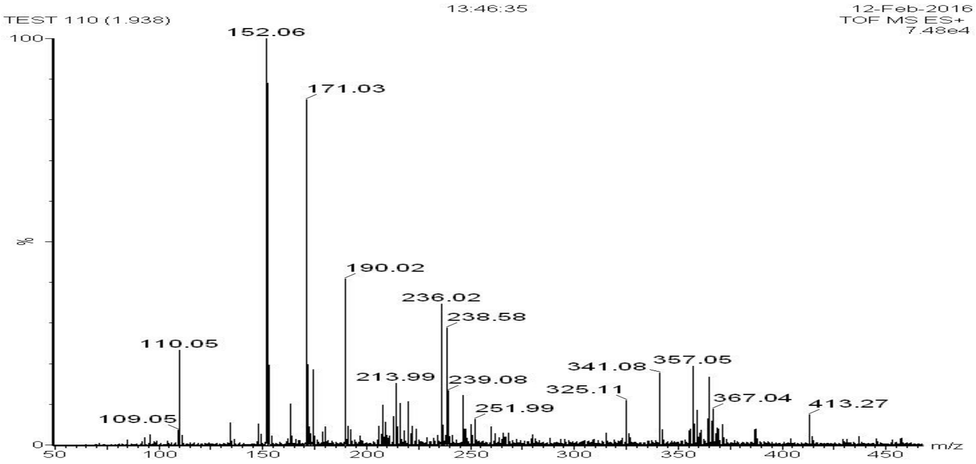

Figure 4.44. Mass spectrum of PCM (5 mg/L)

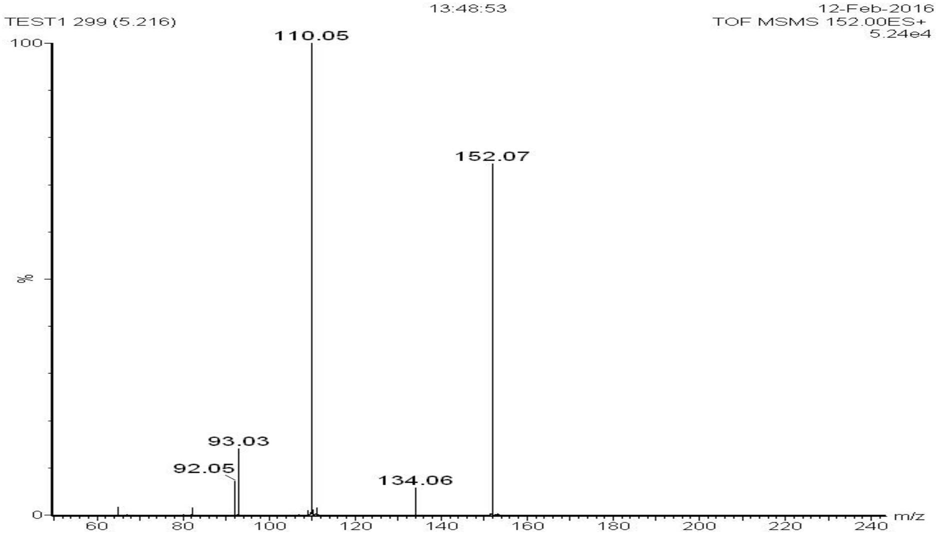

Figure 4.45. Paracetamol daughter (s) and parent ions spectrum

As it is shown in Figure 4.43, a very good peak was obtained at m/z = 152.06. Then other spectra were filtered and just 152.06 allowed to pass through the channel. The parent ion then passed through the second quadruple in order to find the daughter ion(s). Figure 4.44 illustrates the parent ion and daughter ions together.

4.5.14 Conclusions and remarks for Phase 6

Degradation and elimination of three target emerging contaminants (ECs) using a pilot-scale advanced oxidation techniques (AOPs) have been successfully investigated. The ECs, including sulfamethoxazole (SMX), paracetamol (PCM) and caffeine (CAF), spiked in DI water samples, were subjected to UV-C irradiation, ozone based advanced oxidation techniques (AOPs) including sole ozone. By developing an engineered multiple ozone dissolution approach, the pilot benefited higher ozone concentration in liquid film more than nominal values. In return, by adding the fixed ozone rate of 0.25 (mg/L). min to the reactor, the ozone was consumed completely without any off-gas monitoring in the ozone flow-cell of the reactor. To investigate reaction efficiency, UV-Vis spectrophotometer HPLC and LC-MS-MS analysis were applied. In addition, total organic carbon (TOC) and chemical oxygen demand (COD) were used as indicator parameters for a mineralization degree and by-products accumulation. The effect of operational parameters such as UV dose, ozone dose, reaction time and contaminants' concentration were evaluated for rate of reaction and treatment efficiency. The target pollutants achieved deficient degradation by sole UV-C fluence, while enhanced degradation was acquired by ozone treatment and UV/O_3 (Figure 4.43).

Ozone treatment methods rapidly reduced the Paracetamol concentration in water and O_3/UV system played a similar role but faster than ozone, but UV treatment methods were not able to remove the target contaminant as fast as ozone and O_3/UV systems. Furthermore, ozone based AOPs demonstrated an elevated rate and removal (10% more) in comparison to ozonation alone due to contribution of highly reactive OH radicals. As a consequence, the water samples confronted the significant abatement of TOC for all ECs. The effective rate of ozone consumption was constant during 25 minutes of reaction resulting in more than 90% of degradation for SMX, PCM and CAF. All three ECs were eliminated substantially, while SMX demonstrated the highest removal rate (Figure 4.43). To elucidate rate of reactions, the concentration of each pollutant was analyzed individually in 5 min intervals. A pseudo-first order rate constant was proposed for the kinetics of UV/O_3 AOP degradation process.

This study revealed the feasibility of an AOP pilot system to remediate recalcitrant organic contaminants from water samples effectively, to fully recover the water with compliance with drinking water regulations. This pilot plant setup displayed a high potential for application of UV and ozone for removal of micropollutants from water.

4.6 Phase 7: Investigation of ECs destruction by AO/MEBR in different matrices: Influent of wastewater, effluent, river

In the wastewater treatment industry, the membrane electro-bioreactor (MEBR) attracted a significant amount of interest for achieving superior quality of the effluent. Concordia University designed and manufactured an MEBR pilot plant which benefited simultaneous processes of carbon, nitrogen and phosphorous removal in one vessel. The pilot MEBR system consisted of an electrobiorector (EBR) and an external ultrafiltration (UF) membrane module. Thus, an interaction of membrane filtration, activated sludge process, and electrokinetics controlling nitrification and as well as denitrification were found to be the effective technology which could remove phosphorous, ammonia, nitrates, COD at elevated levels. Furthermore, an ultrafiltration membrane prevents bacteria presence in the effluent. Generally, activated sludge wastewater treatment is a combination of biological processes which create conditions for microbial availability to remove nutrients and organic pollutants. However, pharmaceuticals might bring an adverse effect on microbial activity, when for example, antibiotics are present in sewage. The microbial community activity changes for organic pollutants removal could be represented by oxygen uptake rate (OUR) as an indicator.

In the context of MEBR research, this study is unique to evaluate the impact of pharmaceutical organic load to the microbial activity by measuring oxygen uptake rate (OUR) as an indicator. The objective of this part of research was primarily to investigate the effect of paracetamol load as an emerging contaminant to the organic matter removal efficiency by monitoring activated sludge OUR.

4.6.1 Oxygen uptake rate (OUR) in EBR pilot as microbial activity indicator

The results revealed that both COD and PCM concentrations were increased up to the first 12 hours of injection and then almost had a slight reduction between 12 hours mark and day 3 in which the PCM was injected at a constant rate of 4 L/min. After day 3, PCM injection was cut and then both COD and PCM concentration dropped to the initial levels (Fig. 4.45). The removal of PCM and COD showed to be 7% and 1%, respectively. Therefore, there is no high change to the COD and PCM. Indeed, PCM had an adverse effect on biomass and deactivated it for further pharmaceutical removal (Fig. 4.45).

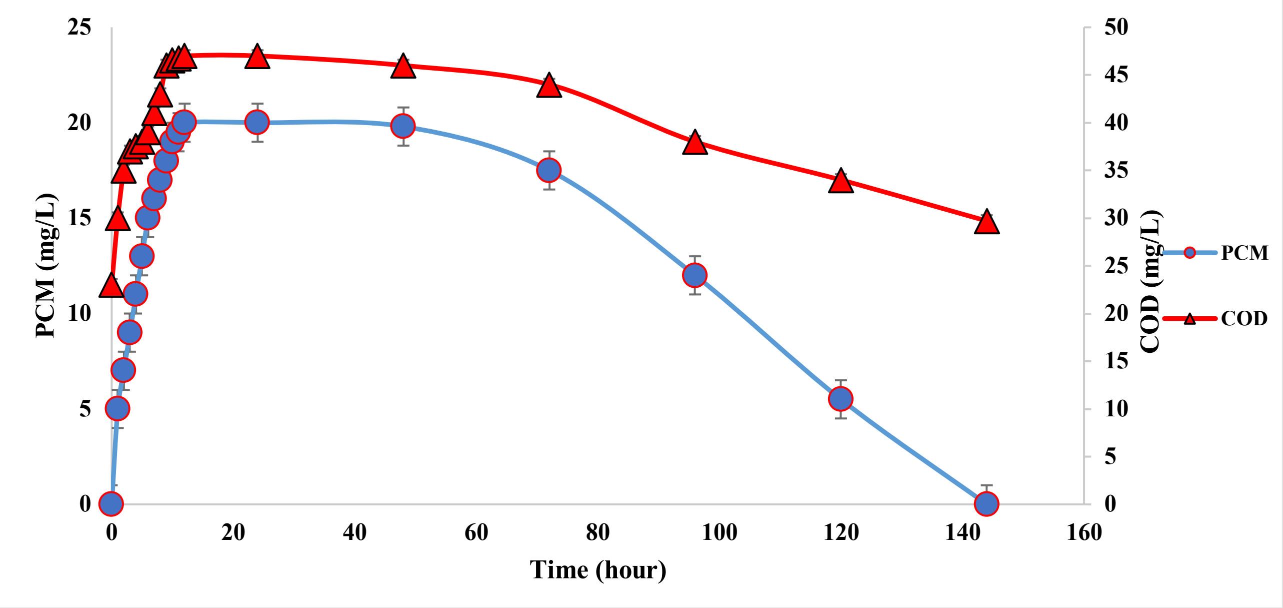

Figure 4.45. PCM and COD changes in MEBR pilot reactor during one week
Experiment condition: PCM injection rate: 4 L/m, Initial COD$_I$= 47 mg/L, COD$_F$ (COD Final after 3 days) = 44 mg/L, PCM$_I$ (PCM Initial) = 20 mg/L, PCM$_F$ (PCM Final after 3 days) = 17.6 mg/L

Removal efficiency (COD) = [(COD$_I$ - COD$_F$) / COD$_I$] x 100 = (47 - 44/47) x100 = 1 %

Removal efficiency (PCM) = [(PCM$_I$ – PCM$_F$) / PCM$_I$] x 100 = (20 -17.6/20) x100 = 7 %

It was also shown that PCM species in wastewater severely inhibited oxygen uptake by microorganisms as compared to the uptake in control samples without PCM. (Fig. 4.46).

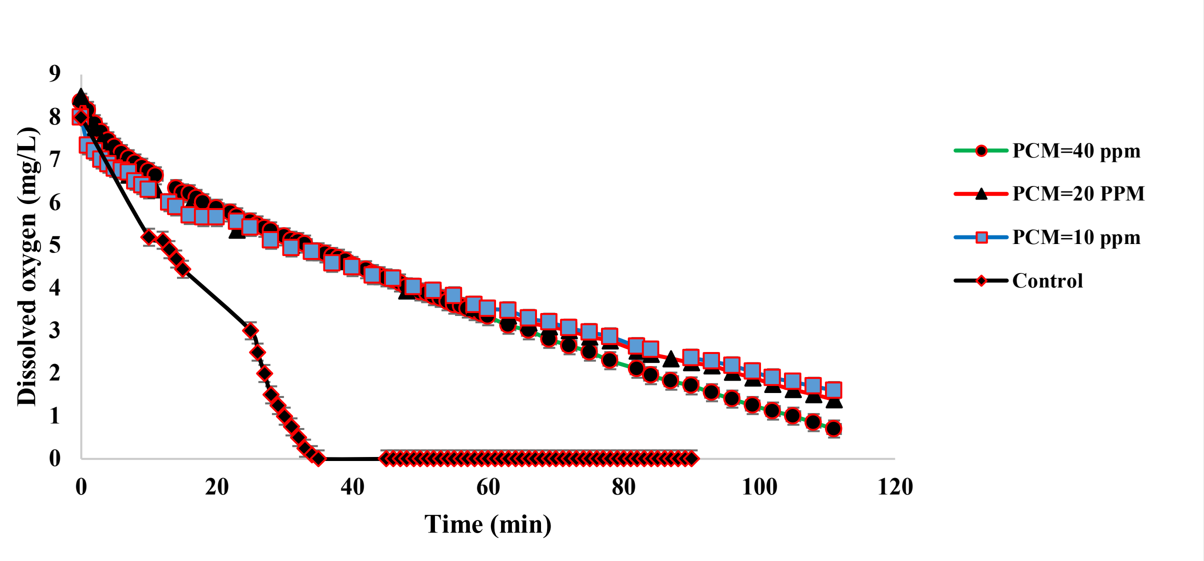

Figure 4.46. Oxygen uptake rate (OUR) comparison between different PCM concentration in AS Experimental conditions: PCM different concentration (PCM) =10, 20, 40mg/L, Control sample: Activated sludge (AS), Wastewater (WW), (without PCM)

The results indicate an independence of PCM low concentration change on microbial activity in activated sludge process. As it is revealed in the Fig. 4.46, the OUR of the control sample have a faster reduction rate in comparison to the samples which were spiked by PCM. The three PCM samples with different concentrations (10, 20 and 40 mg/L) had shown a close OUR descendent. It means that PCM higher concentration did not affect the PCM removal. Paracetamol adversely affected the biological activity of bacteria in the bioreactor pilot system in terms of PCM removal and COD. However, the overall COD of effluent was not changed. Furthermore, the ultrafiltration membrane was not able to inhibit PCM species as emerging micropollutants.

4.6.2 Mechanism of PCM destruction and degradation in wastewater matrix

Generally, removal of pharmaceutical active compounds (PhACs) in activated sludge are performed by two mechanisms. Therefore, it can be proposed that elimination of PCM in MEBR was carried out through these mechanisms as well. The first mechanism was fulfilled by biodegradation process and then later by sorption to the sludge and microorganism. The hydrophobic characteristic of PCM has an important role for sorption that determines interaction between aromatic and/aliphatic portions of PCM to the organism cell and lipid molecules in sludge. K_{OW} of PCM, as an indicator for PCM tendency to adsorb to the sludge or bacteria, is 1.08. It means that the relative tendency of PCM to the sludge or to the bacteria is very low. Researchers reported PhACs removal in wastewater by MBR and conventional activated sludge (CAS) through biodegradation. They also reported no or very small PhACs removal by sorption. Therefore, the only pathway suggested for PCM elimination is through degradation by bacteria.

Partial conclusion

The load of PCM solutions had low impact on biological activity, however, there was not significant reduction of PCM and COD of effluent. The ultrafiltration membrane was not able to inhibit PCM species as emerging micropollutant. The findings of this research enhanced the clarity of our understanding of an EMBR unit ability to remove COD and nutrients when it was affected by a moderate load of PhACs.

4.6.3 Abatement of PCM in different matrices by AO/MEBR hybrid system

Figure 4.47 depicts PCM degradation by the hybrid AO/MEBR system. Different PCM samples were affected by best AOP condition to investigate its degradation rate. Four samples including Sample 1: Wastewater (W.W.) influent from EBR (electro-bioreactor) Pilot, Sample 2: Effluent from EBR pilot output, Sample 3: River water and Sample 4: DI water. All samples including influent, effluent, river water and DI water, spiked by PCM. Sample 1 was taken from inside of the EBR pilot which PCM spiked in to the EBR compartment before treatment, but it was affected by the MEBR process. As it is seen in the Fig. 4.47, PCM degradation showed almost the same behavior rate for both samples 1 and 2 in W.W. influent and effluent. The only difference was for initial PCM concentration in two samples, where, in effluent PCM was lower (18.2 mg/L) due to preliminary its degradation in MBER pilot.

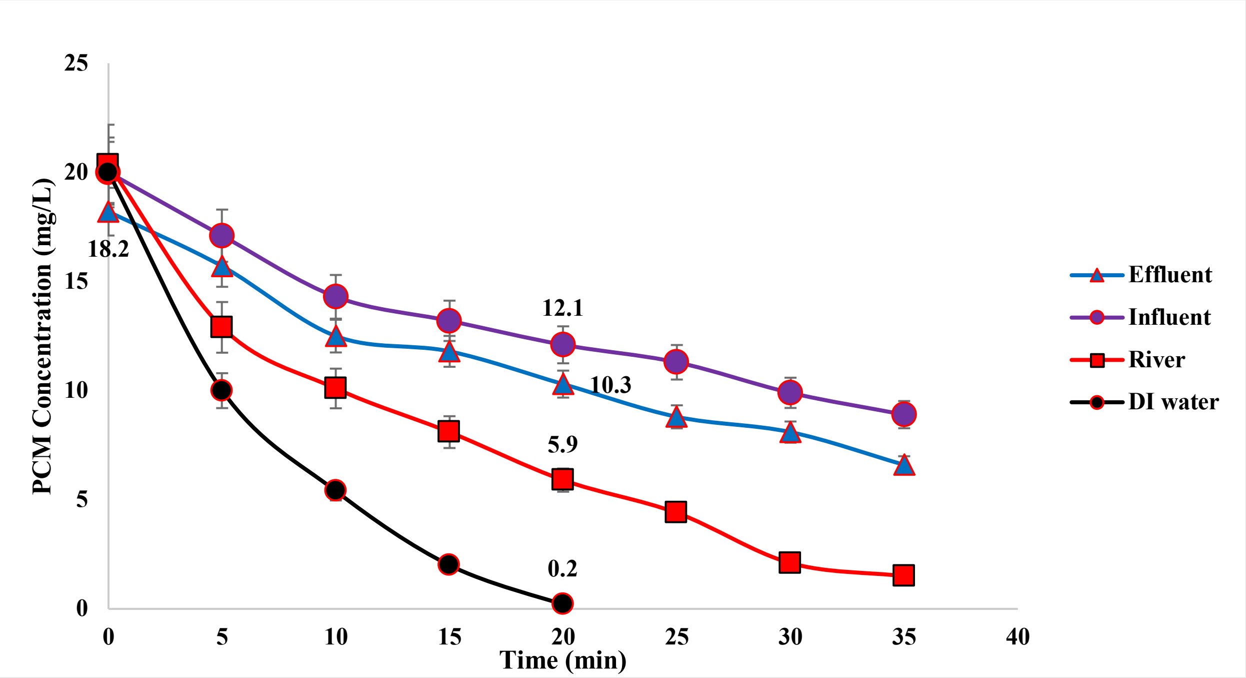

Figure 4.47. PCM degradation in different matrices; Wastewater, Effluent, River and DI water Experimental conditions: UVC (40 W) intensity =10 mJ/cm^2, reaction time = 35 min, solution volume=3L (irradiated),4L (total), temperature 18- 20 °C, pH = 5-7, airflow rate= 0.5 L/min, recirculation rate= 2 L/min, H_2O_2 dose = 6mM, Initial PCM concentration: 20 mg/L for DI water, influent and river water, 18.2 mg/L for effluent

Sample 3, the river water, depicted a faster degradation rate in comparison to effluent and W.W. influent samples. This difference is attributed to the matrix characteristics in river water, W.W. influent and effluent (Table 3.1). As discussed in the by-products section, W.W. influent, effluent and river contain bicarbonate ions and other ions that could scavenge OH radical in AOPs process and influence the treatment efficiency. The level of scavenging effect depends on concentration of non-target constituents. In W.W. influent and effluent samples, the concentration of non-target constituents was much higher (three times more) than river water samples (Table 3.1). Therefore, inhibition of OH radicals in W.W. influent and effluent was more extensive in comparison to river matrix. In conclusion, during 20 minutes of reaction, the degree of PCM degradation in river water samples was almost 2 times more than effluent and W.W. samples (39% in effluent, 71% in river). In this context, DI water samples showed the highest PCM degradation (99%) in comparison to all other samples.

The following is the trend of PCM degradation rates for different water matrices.

DI water > river water > effluent = influent

4.6.4 Effect of non-target constituents present in effluent and river on SMX degradation rate

The presence of effluent organic matter (EfOM) and natural organic matter (NOM) in receiving water resources may affect the extent of SMX removal by AOPs. River water samples were collected from St-Laurent (Quebec) and effluent of treated wastewater (EfW) from WWTP in the City of La Prairie (Quebec). The river and effluent samples were spiked by the target pharmaceutical, SMX. The spiked samples were subjected to the AOP UV/H_2O_2 under best operational conditions. Non-target constituents present in EfOM and NOM contain bicarbonates and other ions which may behave as OH radical scavengers and affect the SMX degradation. The aim of this part of study was to evaluate degradation and elimination of SMX in three water samples. The water samples include river water (RW) containing NOM and wastewater effluent containing EfOM from wastewater treatment plant (WWTP). The level of scavenging effect depends on concentration of non-target constituents. Carbonate and bicarbonate scavenge OH radical based on the following equation. However, in comparison to OH radicals, the reaction of organic compounds in water with carbonate and bicarbonate are very slow.

$$CO_3 + HO^0 \rightarrow {}^{-0}CO_3 + HO^- \quad (4.15)$$

$$HCO_3^- + HO^0 \rightarrow {}^{-}CO_3 + H_2O^0 \quad (4.16)$$

Two water matrices have considerable amounts of bicarbonate and other ions which can behave as OH radical scavengers (Table 3.1). Then, an effect of bicarbonate was investigated in river water and effluent. In effluent there are relatively high concentrations of bicarbonates and other reactive species in comparison to river water samples which is around three times less.

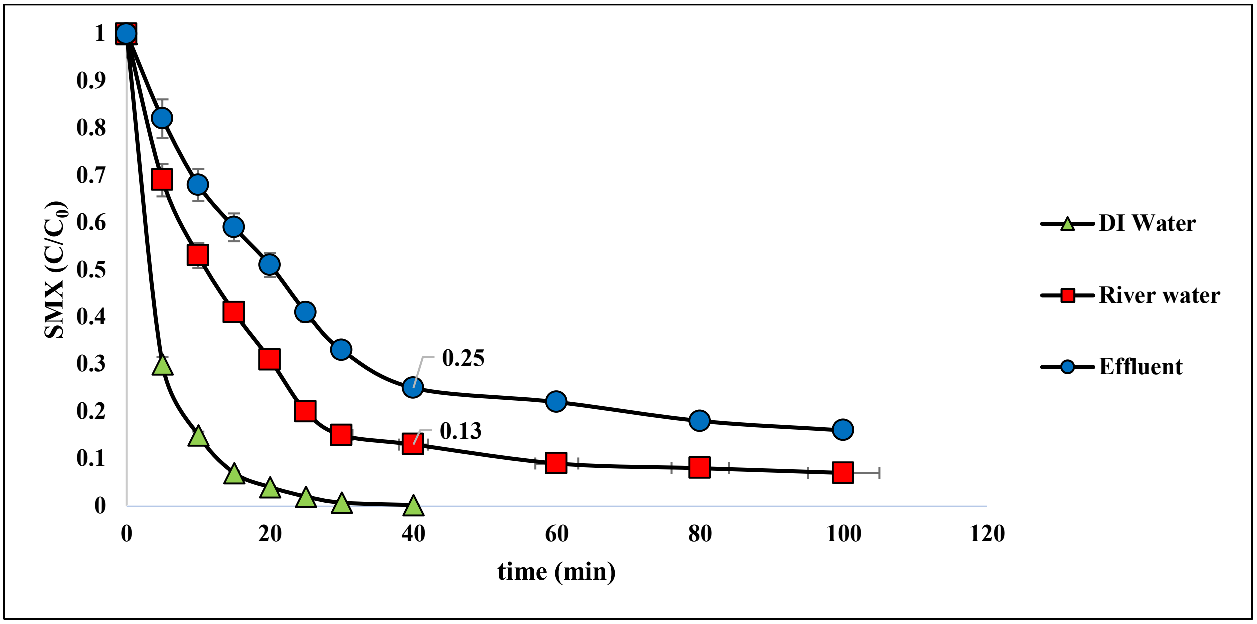

Figure 4.48. Sulfamethoxazole (SMX) degradation rate in different matrices; DIW> RW > Effluent Experiment condition: UVC (40 W) intensity =10 mJ/cm^2, reaction time = 40-120 min, solution volume=3L (irradiated),4L (total), temperature 18- 20 °C, pH = 5-7, airflow rate= 0.5 L/min, recirculation rate= 2 L/min

The results showed a different SMX elimination in three water samples during 40-120 minutes of treatment by AOP. River water samples demonstrated lower degradation (87%) of SMX in comparison to DIW samples (99.99%) because of OH radical scavenger effects by NOM. However, in comparison to EfW samples, RW samples revealed higher (by 12%) elimination of SMX because of substantial presence of bicarbonate and other ions in EfW acting as OH radical scavenger (Fig. 4.48). The following trend with respect to elimination of SMX by AOP has been found: ***DIW> RW > EfW.***

The study showed that the water matrix characteristic had significant effects on pharmaceutical degradation during water treatment by advanced oxidation. This research has important data to be applied for water / wastewater treatment plants considering potential toxicity of target compounds.

4.7 Phase 8: Effect of technological parameters on BPs evolution

Phase 8 follows the results of Phase 5, in which, four major SMX by-products were identified. In this Phase, the effect of technological parameters (pH, aeration and H_2O_2 dose) on BPs evolution, was investigated. The study was conducted in DI water samples and real water samples including river water and effluent wastewater. Mineralization, end-products evolution and reaction pathway are the subjects of interest investigated in this Phase.

4.7.1 Effect of aeration on BPs evolution

As discussed in section 2.1.3, the air flow can provide oxygen as an electron receiver for subsequent reaction and produce superoxide radicals (O_2^{0-}). Superoxide radicals are highly reactive and can decompose organic pollutant structure and eliminate it from water samples (Equation 4.8). During advanced oxidation of target compounds, SMX by-products were affected by aeration of water samples. The by-products behaved the same pattern of SMX parent ions. Fig. 4.49 and Fig. 4.50 depicted the evolution of BP-99 and BP-270 by-products. Both BPs have the minimum abundance when the rate of aeration was between 0.5 to 1.5 L/m. This means that superoxide contributed to the by-product's removal. However, by increasing the air flow rate from 1.5 to 4 L/m, the aeration has lesser effect or an adverse effect on treatment. This can be described by scattering the UV light by air bubbles and at the same time, the bubbles behave as UV light barriers. By decreasing the UV light, the OH radical's concentration decreased and BPs revealed a lower destruction rate.

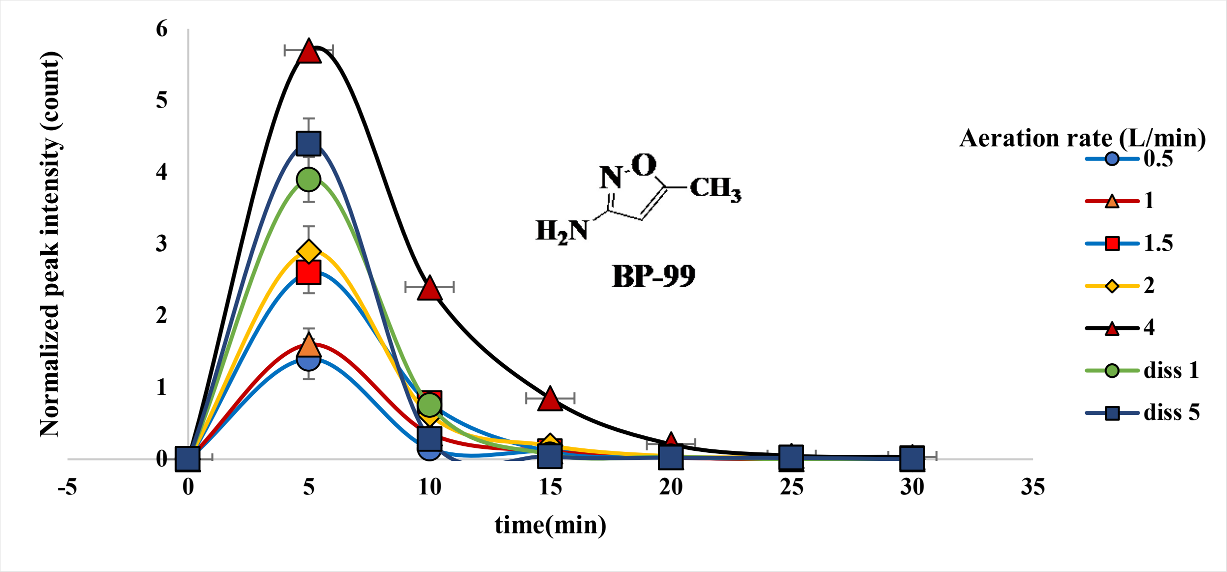

Figure 4.49. The effect of aeration rate (L/min) on BP-99 evolution;
Experimental conditions: UVC (40 W) intensity =10 mJ/cm^2, reaction time = 30 min, solution volume=3L (irradiated),4L (total), temperature 18- 20 °C, airflow rate= 0.5- 4 L/min, water recirculation rate= 2 L/min, H_2O_2 dose = 6 mM, pH = 5.5

The worth point in this study is a difference between behavior of BP-99 and BP-270 to the water sample aeration. In lower aeration rate between 0.5 to 1.5 L/m, the abundance of BP- 99 is by about 10% more in comparison to BP- 270. This can be attributed to the contribution of superoxide to cleavage of S-N bound of SMX. In aeration of the sample more than 2 L/m, the concentration of OH radical decreased in the medium while superoxide could be increased. Therefore, hydroxylation of the aromatic ring of SMX for production of BP- 270 decreased that led to 20% lower abundance of BP-270 in comparison to BP-99.

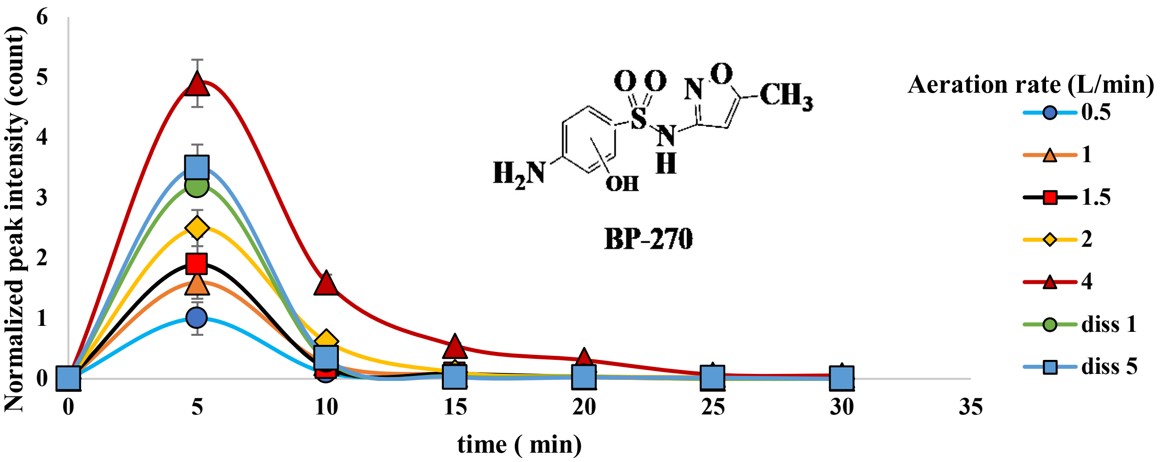

Figure 4.50. The effect of aeration rate (L/min) on BP-270 evolution;
Experimental conditions: UVC (40 W) intensity =10 mJ/cm^2, reaction time = 30 min, solution volume=3L (irradiated), 4L (total), temperature 18- 20 °C, airflow rate= 0.5- 4 L/min, water recirculation rate= 2 L/min, H_2O_2 *dose = 6 mM, pH = 5.5*

4.7.2 Effect of pH on BPs evolution

As discussed previously, the pH change has a significant effect on SMX degradation and removal rate. In acidic condition, i.e. from 3 to 5, there is more degradation and a slight increase of degradation from 3 to 5. However, under basic conditions (pH 7-10), the degradation rate highly decreased. These findings are compatible with previous studies for SMX degradation by other researches (Alharbi et al. 2017; S. H. Lee et al. 2019; T. H. Kim et al. 2012). The phenomena could be elucidated by the following equations, in which hydroperoxyl radical is generated.

$$HO_2^- + OH^\bullet \rightarrow HO_2^\bullet + OH^- \quad (4.17)$$

$$H_2O_2 + HO_2^- \rightarrow H_2O + O_2 + OH^- \quad (4.18)$$

Hydroperoxyl radical is a strong OH radical scavenger and can lead to lower SMX degradation rate. The more alkaline the condition, the more hydroperoxyl radical generated resulting in lower degradation.

4.7.2.1 BP-99 evolution with a pH change

The evolution of BP-99 during oxidation of SMX was investigated with respect to pH change (Figure 4.51). In acidic conditions, there was more by-products' formation; however, when pH shifted from 3 to higher basic condition, the abundance of BP- 99 slightly decreased. Evolution of BP-99 with respect to pH change can be described by the SMX degradation rate.

It is suggested that formation of BP-99 is the effect of the cleavage of sulfonamide (S-N) bound in SMX molecules which has the most abundance during oxidation reaction of SMX. In acidic conditions, the OH radical's concentration is not favored. However, cleavage of S-N bound is more likely at higher pH values. From pH = 3 to 5, there was an increase of the OH radical's concentration, which led to an increasing the rate of BP-99 formation, and simultaneously, degradation of the parent SMX compound. Therefore, in pH 3 and 4 there was less BP-99 because of a lower number of OH radicals than at pH 5 (Figure 4.51).

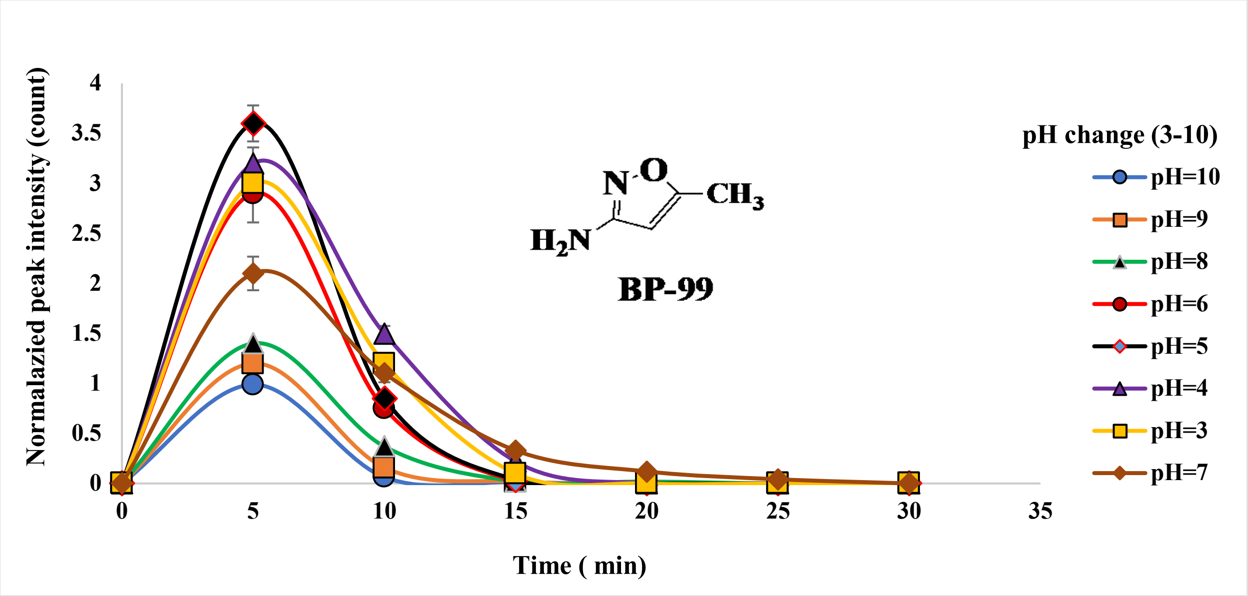

Figure 4.51. The effect of pH changes on BP-99 evolution;
Experimental conditions: UVC (40 W) intensity =10 mJ/cm^2, reaction time = 30 min, solution volume=3L (irradiated), 4L (total), temperature 18- 20 °C, airflow rate= 0.5 L/min, water recirculation rate= 2 L/min, H_2O_2 dose = 6 mM, pH = 3-10

The most probably at pH = 5, there was a balance between OH radicals' formation and its abatement on acidic condition. So, BP-99 concentration at pH= 5 was maximum. From pH 5 to 10, the concentration of OH radicals increased; However, it is not favored for the SMX degradation. Therefore, a reduction of BP-99 from pH 5 to 10 was seen.

Thus, at pH=5, a higher rate of reduction was observed between 5 min to 15 min of reaction time. Contrary at other pH values, the BP-99 reduction rate was slower. An abundance trend of the BP-99 with respect to pH is as follows:

BP-99 abundance: *pH 5 > pH 4> pH 3 > pH 6 > pH 7> pH 8 > pH 9 > pH 10*

Therefore, in pH between 6 -7 there is a moderate BP-99.

4.7.2.2 BP-270 evolution with a pH change

Formation of BP-270 is probably the effect of attacking the aromatic benzene ring by OH radical. In alkaline condition, the abundance of OH radicals are higher than at acidic pH values. Therefore, from pH 3 to 5, there is an increase of BP-270 values (Figure 4.52). From pH 5 to 6, there is a substantial increase of the BP-270 concentration due to higher dose of OH radicals. In basic conditions (from 7 to 10), there is a reverse behavior of BP-270 in terms of its abundance. At pH = 8, BP-270 had the highest concentration. However, from pH 8 to 10, there is a reverse behavior in which the by-product abundance decreases as pH increases because of the scavenging effect of higher dose of OH radicals. The following abundance trend of BP- 270 formation in function of pH was observed:

BP-270 abundance: ***pH 3< pH 4 < pH 6 < pH 5 < pH 10 > pH 9> pH 8 > pH 7***

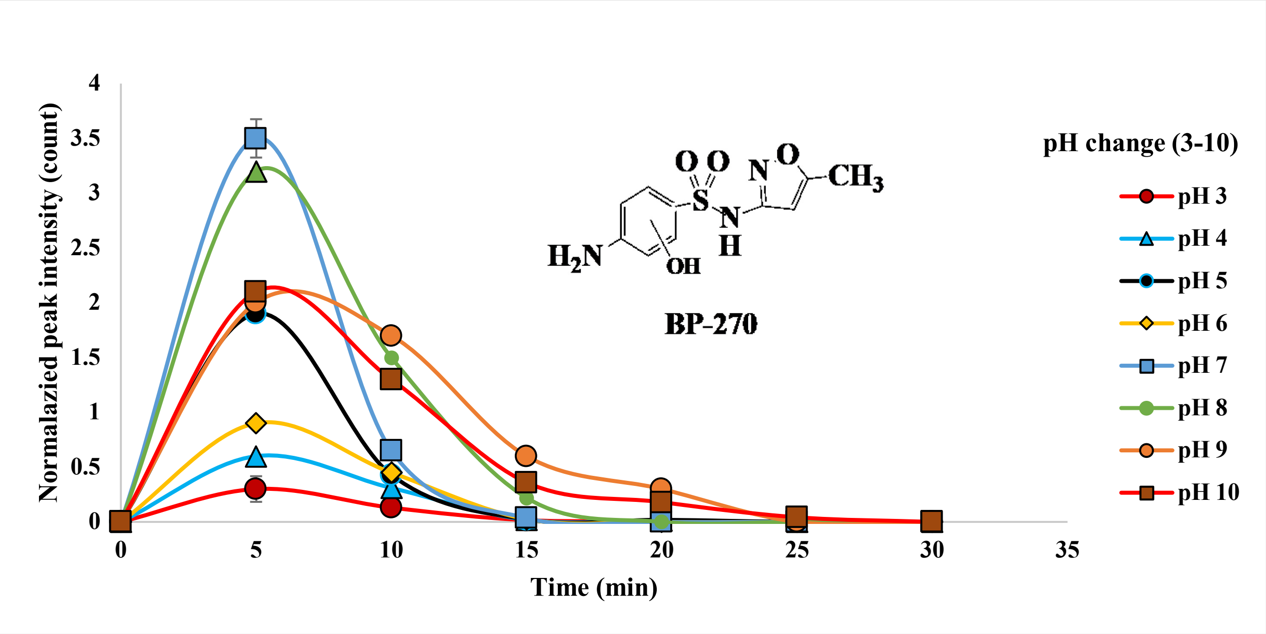

Figure 4.52. The effect of pH changes on BP-270 evolution;
Experiment condition: UVC (40 W) intensity =10 mJ/cm^2, reaction time = 30 min, solution volume=3L (irradiated), 4L (total), temperature 18- 20 °C, airflow rate= 0.5 L/min, water recirculation rate= 2 L/min, H_2O_2 dose = 6 mM, pH = 3-10

Moreover, in best pH value (around 5) there was much less BP-270 formation compared to higher pH values. Furthermore, at this pH, a maximum amount of BP-99 was formed, but a faster removal rate in comparison to other pH values was observed. Therefore, at the best pH value of 5 for SMX ion removal, much less by-product 270 was formed and higher rate removal of BP-99 was observed.

Partial conclusions (pH effect):

Total organic carbon analysis tests confirmed partial mineralization of target pollutants. Furthermore, Fig. 4.58 showed high concentration of degradation by-products during the UV/H_2O_2 oxidation of the parent compound. The high concentrations of BP-270 and BP-99 were present even after an entire removal of SMX. A high abundance of degradation products might bring a potential hazard to the water resources. However, optimal operational conditions can lead to minimization of the by-product formation. At pH 5 for SMX parent ion removal, much less by-product 270 was generated, in addition to the higher removal rate of BP-99, which was the most persistent by-product. Moreover, a moderate abundance for both BPs recorded at pH=6. This study showed a significant influence of pH on water treatment by using UV/H_2O_2 advanced oxidation systems. Furthermore, simultaneous elimination of persistent PhACs along with controlling and minimizing major long-lasting BPs was discovered.

4.7.3 Effect of H_2O_2 dose on BPs evolution

One of the most important parameters which affect BPs formation and destruction during AOPs is the oxidant dose. As discussed in section 4.2.2, as oxidant dose was increased from 0.5 to 12mM, the rate of the SMX degradation was increased but to a limited value of 12 mM. After

12 mM, the excess oxidant dose behaves as OH radical scavenger. Therefore, SMX degradation rate was decreased by more H_2O_2 dose.

4.7.3.1 BP-99 evolution with H_2O_2 dose

As discussed in the pH effect section, BP-99 formation rate is faster than its degradation rate. In fact, (S-N) bond cleavage, which is required for the BP-99 formation, needs 300 kJ/mole. However, benzene ring dissociation energy, for the BP-99 degradation, requires around 3200 kJ/mole energy. At low H_2O_2 dose (between 0.5 to 1.5 mM) there is maximum BP 99 abundance, in comparison to higher doses (Fig.4.53). However, for 1.5 mM dose, the highest BP values was recorded because its faster formation rate rather than lower degradation rate. Between 3 to 6 mM H_2O_2 dose, the lowest concentration of BP-99 was observed. This finding may attribute to the balance between formation and destruction rate of BP-99. At this oxidant dose, there are much higher concentration of OH radicals for degradation of BP-99. Between 12 and 24 mM, the H_2O_2 behaves as OH radical’s scavenger; Therefore, there are not enough OH radicals to destroy the BP-99 aromatic ring (Fig.4.53).

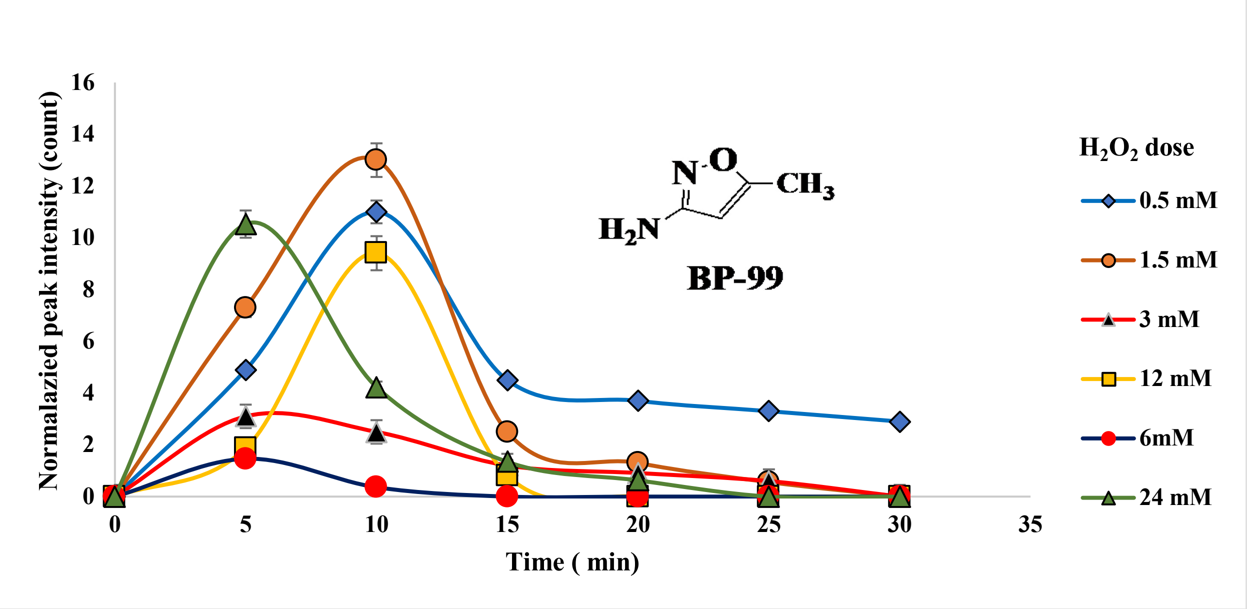

Figure 4.53. The effect of H_2O_2 dose change on BP-99 evolution;
Experimental conditions: UVC (40 W) intensity =10 mJ/cm^2, reaction time = 30 min, solution volume=3L (irradiated),4L (total), temperature 18- 20 °C, airflow rate= 0.5 L/min, water recirculation rate= 2 L/min, pH = 5.5
H_2O_2 dose = 0.5 - 24 mM

It is worthy to note that the H_2O_2 dose range between 3 to 6 mM was the best dose for minimum BP-99 abundance. Furthermore, H_2O_2 dose = 6 mM, was the best dose for SMX removal.

4.7.3.2 BP-270 evolution with H_2O_2 dose

For BP-270, the evolution pattern is much different than BP-99. Based on data depicted in Figure 4.54, the lowest BP-270 abundance was reported for 6 to 12 mM dosage and the highest for 24 mM. This behavior may be attributed to the simultaneous formation and degradation pattern of BP-270 as discussed in the pH section of this chapter. Formation of BP-270 is much faster than degradation of molecules. At a high oxidant dosage around 12 mM, formation of this molecule was maximal.

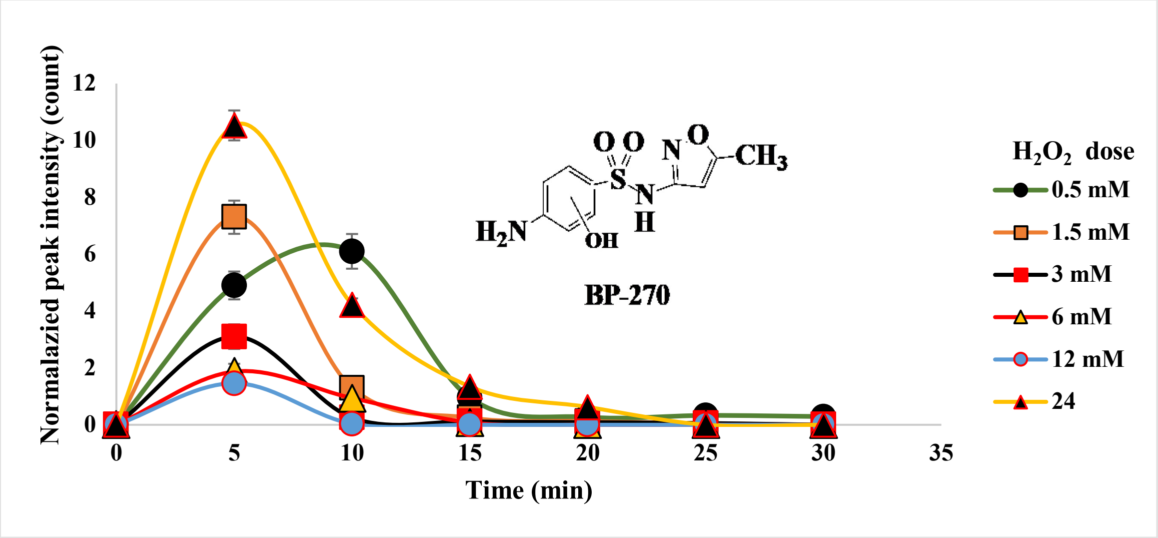

Figure 4.54. The effect of H_2O_2 dose change on BP-270 evolution;
Experimental conditions: UVC (40 W) intensity =10 mJ/cm^2, reaction time = 30 min, solution volume=3L (irradiated), 4L (total), temperature 18- 20 °C, airflow rate= 0.5 L/min, water recirculation rate= 2 L/min, pH = 5.5, H_2O_2 dose = 0.5- 24 mM

However, the destruction rate was recorded at a maximum level either. Therefore, the minimum concentration of BP-270 was observed around 12 mM H_2O_2 dosage. On the other hand, in 24 mM, the scavenging effect for this value is the highest. Therefore, BP-270 molecules do not have a chance for destruction but much more possibility for formation at initial time of reaction. For lower H_2O_2 doses between 0.5 to 1.5 mM, the same pattern of BP-99 observed for BP-270. Relatively, the abundance of BP-270 between 0.5 to 1.5 mM was much higher than H_2O_2 doses between 3 to 12 mM. This behavior may be attributed to the faster formation of BP-270 than its degradation rate. This is worth to note that in the dose ranges between 6 to 12 mM, BP-270 showed the minimum abundance; however, H_2O_2 dose of 6 mM was the best for the maximum SMX removal.

Partial conclusion (technological parameters effects)

At pH = 5 lower concentration of BP-270 and faster degradation of BP-99 was observed. However, at pH = 6, moderate abundance of both BPs was recorded. At aeration between 0.5 to 1.5, the minimum concentrations of BPs were obtained. At H_2O_2 dose = 6 mM both BPs were controlled and minimized. Therefore, the best value ranges for controlling and minimizing the BPs were obtained as following. The H_2O_2 dose = 6 mM, aeration 0.5 to 1.5 L/min, pH = 6. These ranges were close to the maximum degradation of SMX parent ion which was obtained in sections 4.2.2 to 4.2.4.

4.7.4 Effect non-target constituents in effluent and river on by-products evolution

Regularly, EfOM and NOM are present in wastewater effluent and natural waters streams. In addition to organic pollutants, some other non-target constituents such as carbonates, bicarbonates and other mineral ions are present in effluent and river matrices (Table 3.1). These non-target constituents can interfere with degradation of the target contaminants. Bicarbonate ions and other ions in the river and effluent can scavenge OH radicals in AOPs and influence the treatment efficiency. The level of scavenging effect depends on the concentration of non-target constituents. Carbonates and bicarbonate scavenge OH radical based on equations 4.15 and 4.16. However, in comparison to OH radicals, the reaction of organic compounds in water with carbonate and bicarbonate are very slow (Babuponnusami et al. 2012).

4.7.4.1 Effect of non-target constituents on BP-99 evolution

For BP- 99 two reactions might happen simultaneously: formation and degradation. Two water matrices contain a considerable amount of bicarbonates and other ions which can behave as the OH radical scavengers (Table 3.1). The effect of bicarbonate was investigated in river water and effluent. In effluent there are relatively high concentrations (about three times) of reactive species that scavenged OH radicals, in comparison to river water samples. As it is seen in the Figure 4.55, at 60 minutes of reaction, the relative BP-99 residual in river water is 33%, while, in effluent is 91%. The higher abundance of BP-99 in the effluent is attributed to the presence of bicarbonates or other ions, which scavenged OH radicals much more. While in the DI water sample solution, the degradation of SMX by UV/H_2O_2 was not inhibited.

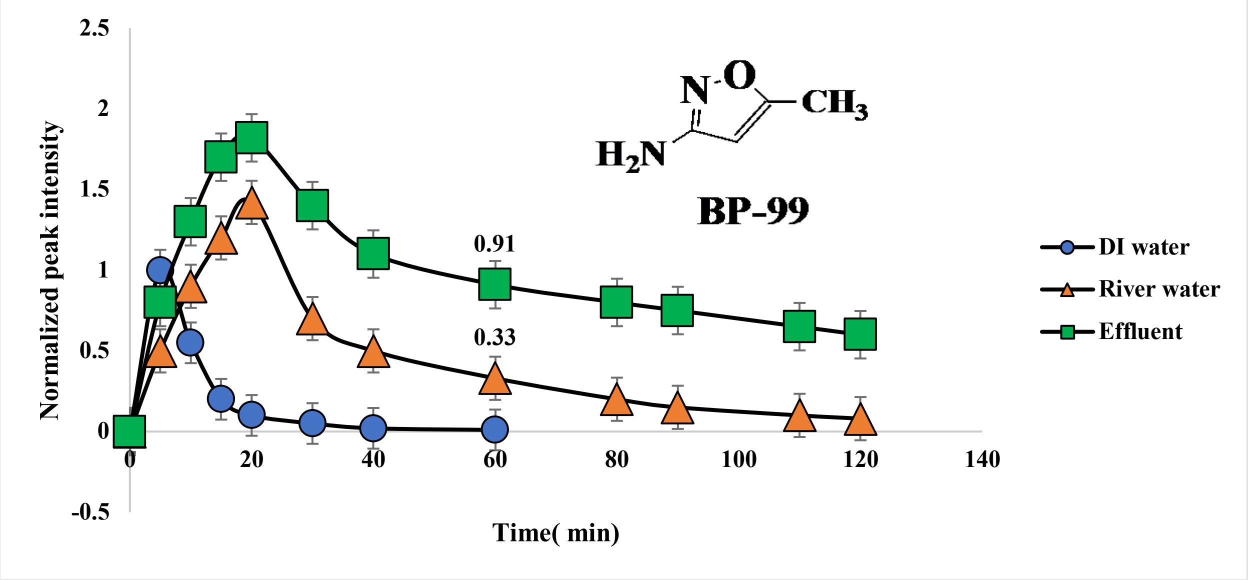

Figure 4.55. The effect of water matrix on BP-99 evolution;
Experimental conditions: UVC (40 W) intensity =10 mJ/cm^2, reaction time = 30 min, solution volume=3L (irradiated), 4L (total), temperature 18- 20 °C, airflow rate= 0.5 L/min, water recirculation rate= 2 L/min, pH = 5.5- 7, H_2O_2 dose = 6 mM

4.7.4.2 Effect of non-target constituents on BP-270 evolution

Formation and destruction of BP-270 occurred simultaneously in the aqueous medium. However, the rate of formation during the first 30 minutes was much higher due to higher concentration of H_2O_2. The maximum concentration of BP-270 was observed between 15 to 30 minutes of reaction, where the maximum concentration of OH radical was imminent as well. After 30 minutes, the concentration of BP-270 was reduced, implying further oxidation by OH radicals. The formation of BP-270 was the result of hydroxylation of SMX aromatic rings. A subsequent degradation of molecules could be attributed to simultaneous further oxidation by both OH radical and UV irradiation. In Figure 4.56, as much as HCO_3 concentration increased, the concentration of BP-270 decreased. This could be attributed to the competition of bicarbonate and SMX to consume OH radicals.

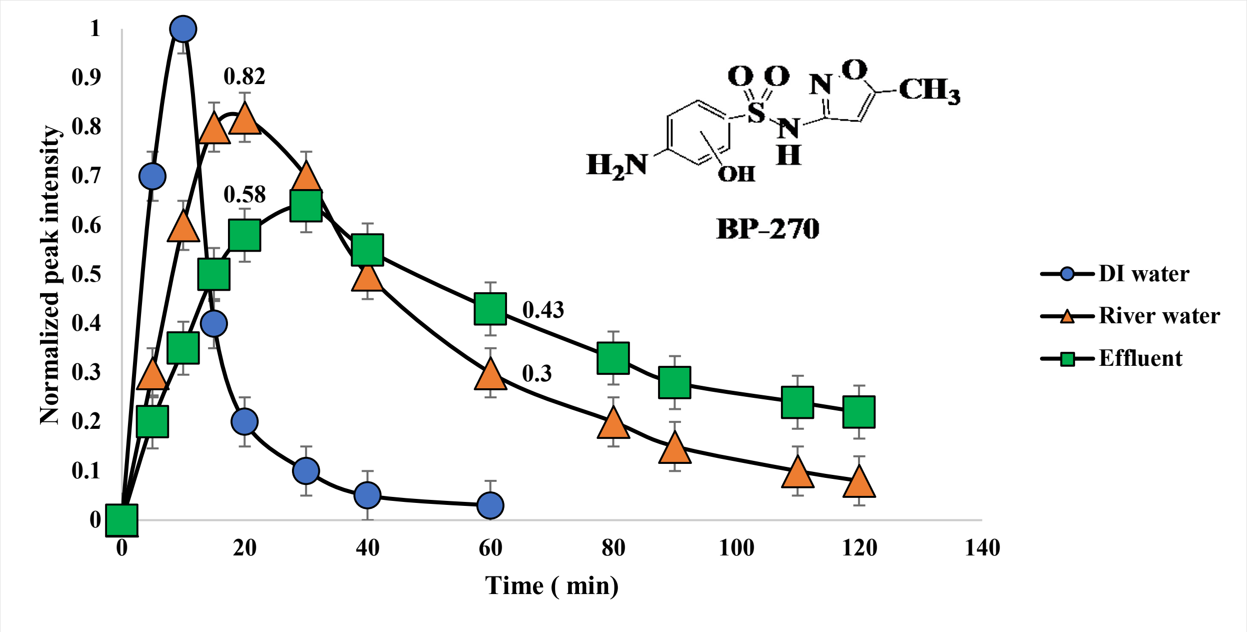

Figure 4.56. The effect of water matrix on BP-99 evolution;
Experimental conditions: UVC (40 W) intensity =10 mJ/cm^2, reaction time = 30 min, solution volume=3L (irradiated),4L (total), temperature 18- 20 °C, airflow rate= 0.5 L/min, water recirculation rate=2 L/min, pH = 5.5-7, H_2O_2 dose = 6 mM

Partial conclusion (oxidant dose effect)

The evolution of SMX by-products was studied in river water and effluent matrices. The by-products revealed different behavior with respect to the degree of non-target constituents' concentration in the medium. Higher concentrations of non-target constituents resulted in lower degradation rate and higher treatment time. Therefore, in river water samples, SMX by-products showed higher removal rate than effluent.

4.7.5 Mineralization: Reaction pathway and degradation mechanism

Figure 4.57 confirmed an accumulation of SMX's BPs in the first 60 minutes of reaction. At longer reaction time, the COD concentration, which is an indicator of BPs accumulation, was reduced. The flattering rate of the COD curve increased after the 120 min reaction time which is an evidence of the presence of identified and unidentified BPs during this period.

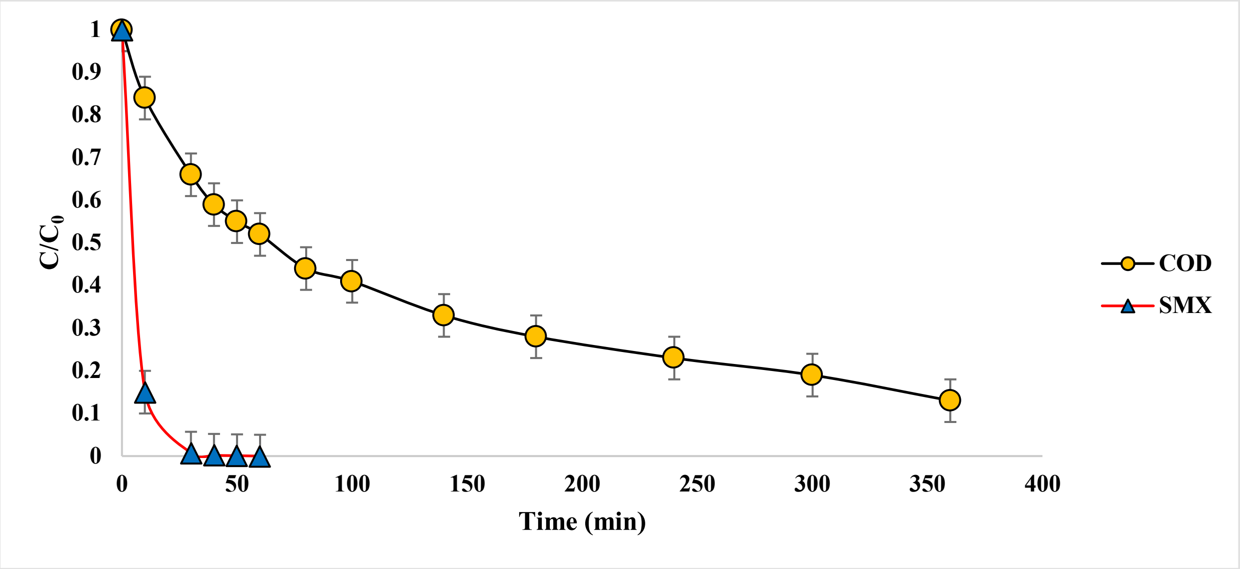

Figure 4.57. Degradation rate of SMX and chemical oxygen demand (COD) rate as degree of mineralization Experimental conditions: UVC (40 W) intensity =10 mJ/cm^2, reaction time = 360 min, solution volume=3L (irradiated),4L (total), temperature 18- 20 °C, water recirculation rate= 2 L/min

Furthermore, based on information obtained by LC-MS QTOF and LC-MS-MS analyses and following a discussion in Phase 5, several SMX transformation products were identified. However, the intensity of all peaks was not high enough and/or their lifetime was short; therefore, four major degradation products of SMX were selected due to of their higher stability in medium and much higher abundances. The structure of four major by-products (BP-99, BP-270, BP-288, BP172) were assigned based on their accurate mass to charge ratio and information regarding the SMX structure and possible forms of new transformation products.

Figure 4.58 depicts the evolution of SMX four major BPs. All four major BPs formed at the beginning of SMX oxidation. The concentration of BPs increased along with degradation of

SMX and reached the maximum at initial time of reaction. At best condition, the abundance of BPs reduced after 10 minutes of reaction. However, as long as SMX existed in the medium, the BPs were present even in complete removal of SMX, both BP-99 and BP-270 were found at low concentrations in the water samples.

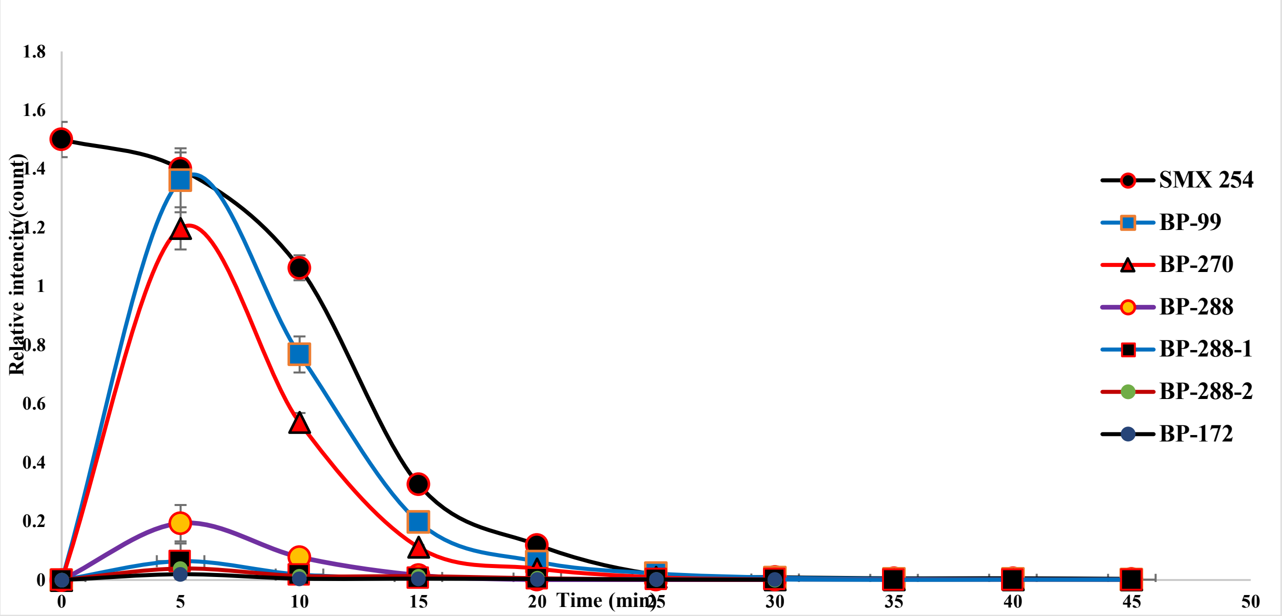

Figure 4.58. Evolution of SMX and its four major by-products during the time. Experimental conditions: UVC (40 W) intensity =10 mJ/cm^2, reaction time = 60 min, solution volume=3L (irradiated), 4L (total), temperature 18- 20 °C, water recirculation rate= 2 L/min

Accordingly, based on accumulated data in previous sections, four major degradation pathways were proposed which finally led to the mineralization of SMX.

4.7.6 Mineralization, end- products evolution

Fig. 4.57 and Fig. 4.59 demonstrated the DOC removal and formation of ammonia (NH_4^+), Nitrate (NO_3^-) and sulfate (SO_4^{-2}) respectively. Evaluation of reaction mineralization was performed on account of reaction end-products. Formation of ammonia, nitrate and sulfate as oxidation end-products was a strong indicator of reaction mineralization. During 360 minutes of reaction, COD curve descended and its concentration decreased by 87% (Fig. 4.57); However, the concentration of the ions in the water sample increased (Fig. 4.59).

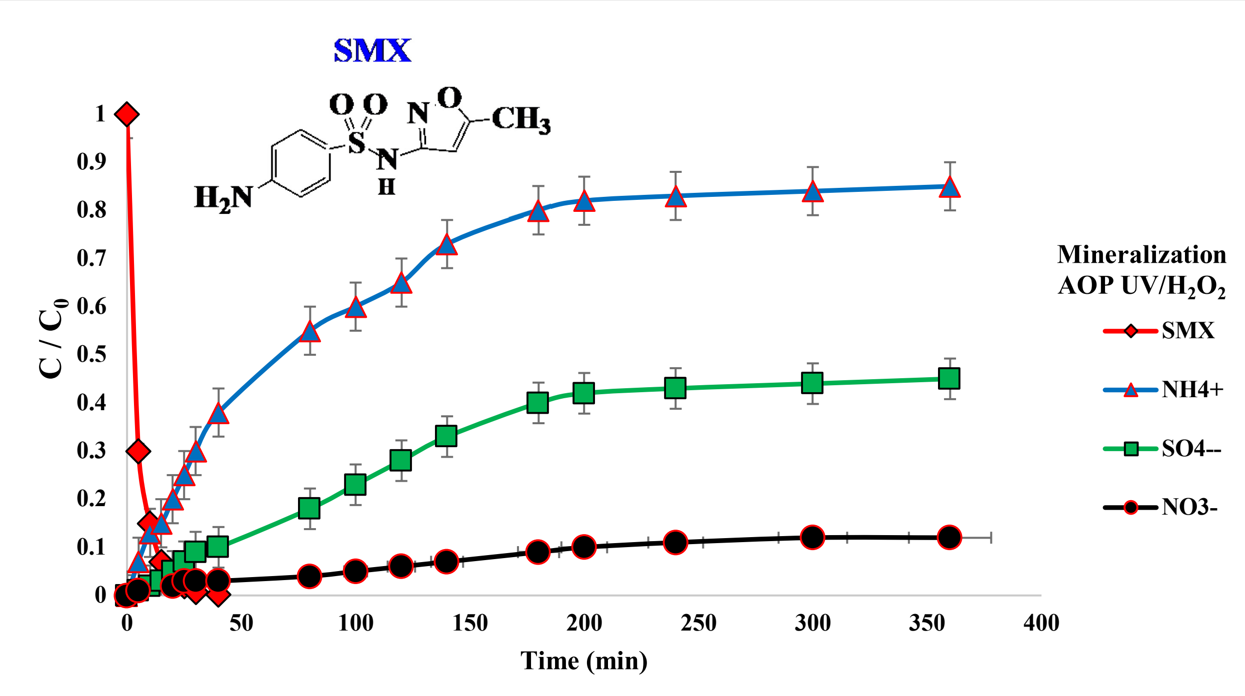

Figure 4.59. Oxidation of SMX and formation of end-products' ions as mineralization indicators Experimental conditions: UVC (40 W) intensity =10 mJ/cm^2, reaction time = 360 min, solution volume=3L (irradiated),4L (total), temperature 18- 20 °C, water recirculation rate= 2 L/min

The major BPs include identified BP-99 (A), BP-172 (B), BP-270 (C) and BP-288 (D). The proposed pathways are illustrated in Fig. 4.60. The pathway A shows formation of BP-99 which is the result of the S-N bound cleavage in SMX molecule by OH attack to the sulfonamide bond in the middle of molecule. This pathway is the major route of SMX degradation during the oxidation reaction of SMX. This by-product had major abundance and longer lifetime in comparison to other BPs. Another possible route was proposed based on the pathway B. In pathway B, the formation of BP-172 occurred. The pathway was proposed as the cleavage of S-N bound of SMX and addition of hydroxyl radical to the part of the SMX molecule including aromatic ring and carry the sulfone moiety. Simultaneously, another reaction occurred during oxidation of SMX molecule, which led to pathway C. The formation of BP-270 is probably the effect of attacking the aromatic benzene ring by OH radicals. Hydroxylation of SMX aromatic rings led to formation of stable species named BP-270. This by-product appeared with a high intensity peak and lasted in the medium even after the parent SMX ion was eliminated in water sample. Pathway D is proposed as dihydroxylation of isoxazole ring to form BP-288. Simultaneously, based on LC-MS-MS accurate mass information and possible molecule structural considerations, the isomers of BP-288 were formed in the medium. BPs-288 had fewer peak intensities in comparison to other major BPs.

Mineralization of the SMX molecule was carried out by continuing the oxidation with a longer time, i.e. more than two hours (Fig .4.59).

It can be assumed that the final products contained $CO_2 + H_2O + SO4^{-2} + NO_3^{-} + NH4^{+}$.

Based on the abundance of by-products and their lifetime, the major pathway for SMX degradation in this study may be proposed by hydroxylation of molecule aromatic ring, S-N bound cleavage and subsequent sulfone moiety abstraction.

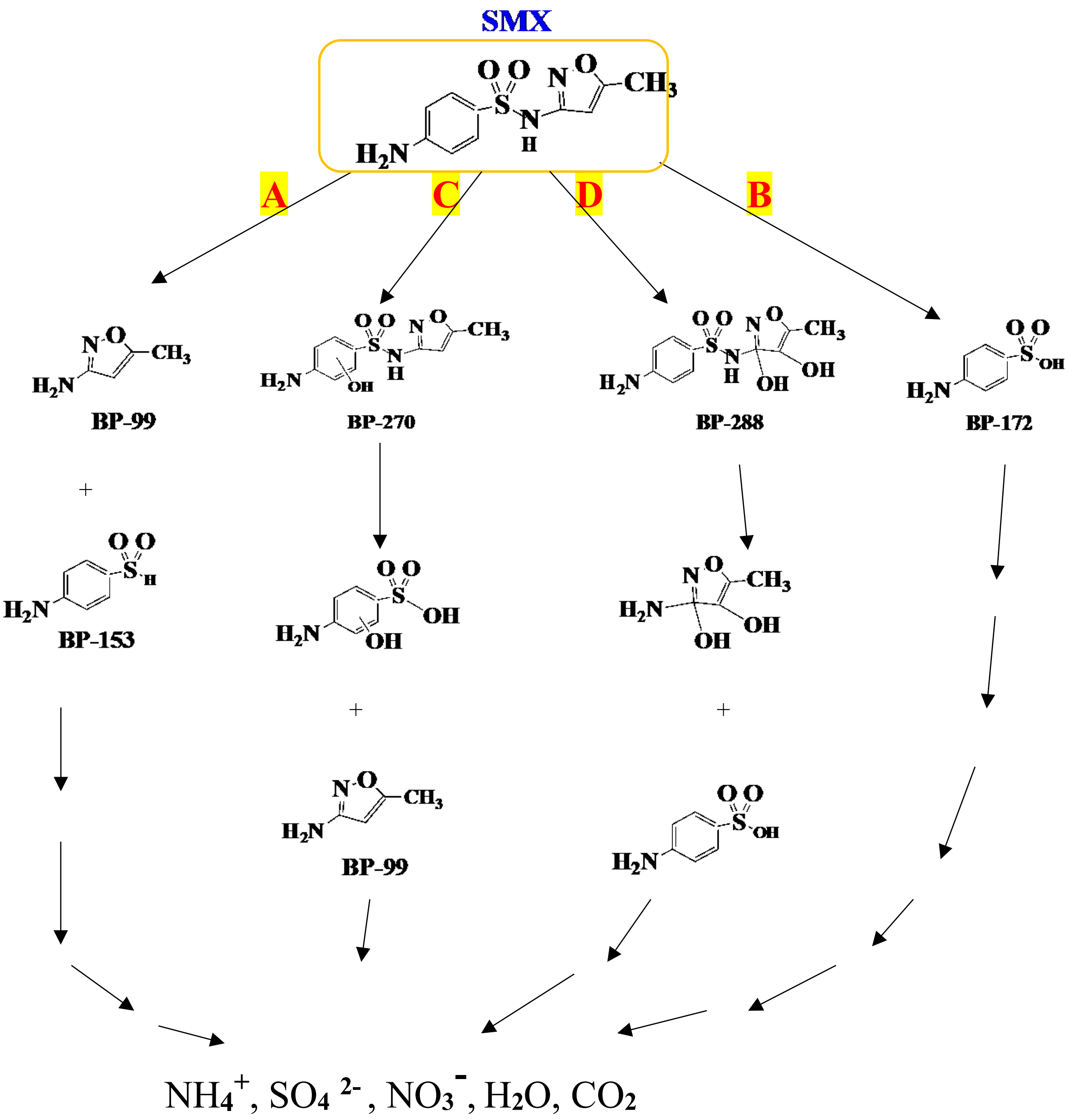

Figure 4.60. The proposed pathway degradation of SMX by UV/H_2O_2 AOP

4.7.7 Potential toxicity of by-products

4.7.7.1 Relationship between chemical structure and toxicity

Miscellaneous chemicals in the form of household products, food additives, pharmaceuticals and cosmetics are widely entered into the environment on a daily basis (Riva et al. 2018; Sui et al. 2015). By different route of exposure, e.g. ingestion, these chemicals could affect human health and safety. Toxicity of a chemical compound can be measured quantitatively like LD50 and qualitatively such as immunotoxicity for certain cell types (Narko et al. 2020). Furthermore, toxicity of a chemical can be evaluated with the toxicity endpoint like carcinogenicity and mutagenicity (Nekooki-Machida et al. 2009; Xu et al. 2020).

The relationship between toxicity and chemical structure of a compound has high levels of importance for precautionary measures for both human health and regulatory bodies such as EPA and FDA (Banerjee et al. 2018; Barratt 2000; Lin et al. 2008). Chemicals with different morphologies can result in different degrees of toxicity (Petkova et al. 2005; Inaba et al. 2005; S. Lee et al. 2007). A modification in bounds between atoms in a molecule, will result in the structure change which might be associated with the different levels of toxicities (Campioni et al. 2010; Kayed et al. 2009). Researchers also found a direct relationship between a structure of a molecule and cytotoxicity (Campioni et al. 2010; Yoshiike et al. 2007). In another study, the role of the functional group on toxicity activity was assessed (Wu et al. 2013). For example, in the trichothecene, a hydroxyl group in C_3 position in the molecule, enhances toxicity; while if the OH was removed by a hydrogen, the toxicity reactivity decreased.

Researchers also found that the position of a functional group in a molecule can alter toxicity. For example in a phenyl molecule, substitution of X moiety with any additional or alternative functional group, reduces toxicity activity (Coats 1990). Other factors such as isomeric configuration, shape and molecular volume have considerable effect on toxicity. The importance of lipophilic functional groups such as halogen and alkyl are responsible for delivery of neurotoxicants to the site of toxic action. It has been also confirmed that high lipophilicity is the main character of an insecticide chemical which penetrates the cell and nerve of an insect. In another publication, the authors recognized that the transport of antibiotics to the human body would be fulfilled through hydrophobic interaction of antibiotics to the phase protein of blood plasma (Azad et al. 2012).

4.7.7.2 Impact of aromaticity on by-product toxicity

In section 4.4.3, Table 4.9, miscellaneous SMX degradation by-products were reported due to their identification by LC-MS-MS analysis. These intermediate by-products appeared in the water solution, including low molecular weight and high molecular weight organics. Low molecular weight included aldehydes and carboxylic acids and higher molecular weight by-products were SMX dimer and other organic compounds with m/e = 502, 518 and 523. All these transformation by-products appeared in the solution matrix. When high molecular weight by-products appeared in the medium, the aromaticity of the solution increased. By increasing the aromaticity, the toxicity of the medium increased in a short period of treatment. According to the study conducted by Kroflič, Grilc, and Grgić (2015), elevation of aromaticity would result significantly to the toxicity and hazard to living organisms with a possible increase of human carcinogenicity. Appearance of low molecular weight moieties such as aldehydes and ketones, may elevated the toxicity of sample solution.

4.7.7.3 Impact of hydroxylation on by-product toxicity

Formation of BP-270 and BP-288 may affect the toxicity of the sample solution. According to the study conducted by Wu et al. 2013, hydroxyl moieties could alter the toxicity of a molecule. Hydroxylation of SMX molecules, in Ortho position of aromatic ring of BP-270, and in Ortho, Meta and Para position of BP-288 and its isomers, may increase the toxicity of the medium. This phenomenon was interestingly depicted in Figures 4.30-b and 4.31 for evolution of BP-288 and its isomers. As it is seen in Fig. 4.30, the highest toxicity was recorded at 5-10 minutes of reaction, where BP-288 and its isomers had maximum abundance. After 10 minutes, with a fast-descending rate, the concentration of BP-288 went down and other BP- 288 isomers faced a decreasing rate, but with moderate rate. However, BP- 288 was not stable as BP- 270 and disappeared in 45 minutes of reaction (Fig. 4.31).

On the other hand, BP-270 was more stable and existed in the sample solutions even after complete disappearance of parent ions at very low concentration (Fig.4.58). In the context of considering the relative relation between the abundance of BP- 270 and toxicity, we can see the evolution of toxicity based on the evolution of BP-270 shown in Figures 4.50, 4.52, 4.54, 4.56. As it is depicted in these figures, experimental conditions and technological parameters may affect the toxicity of the medium. For all conditions, the maximum toxicity reached during 5- 10 minutes of reaction as BP- 270 generated maximum peaks. However, in non-adjusted experiment conditions, an increase of toxicity was imminent. For example, at highest H_2O_2 dose, the relative toxicity reached to the maximum value; but at the H_2O_2 dose between 6 – 12 mM, the relative toxicity was minimal (Fig. 4.54). The evolution of BP-270 in different matrices is depicted in Fig. 4.56. As it was discussed in section 4.7.4, BP-270 revealed different behavior with respect to the degree of no-target constituents’ concentration in the medium. In DI water matrix, BP-270 had maximum abundance in 10 minutes of reaction and it lasted until 60 minutes. However, in river water and effluent matrix, the trend of BP- 2870 is different. The maximum peak appeared between 20-30 minutes and it lasted more than 120 minutes of reaction. Therefore, the relative toxicity of BP- 270 in DI water sample was lower than river water and effluent matrices. However, compared to the river water sample, relative toxicity was higher in effluent samples during UV/ H_2O_2 AOP treatment.

4.7.7.4 Partial conclusion (toxicity)

The following conclusion can be obtained considering relationship between toxicity and aromaticity in the sample solution and hydroxylation of aromatic ring of SMX molecule:

- formation of by-products may result in toxicity elevation especially at the 5-10 minutes at the beginning of the oxidation reaction;
- technological parameters such as exposure time, H_2O_2 dose and aeration, affect the level of toxicity;
- by extending the treatment time, over 20-30 minutes, the toxicity trend tends to descend;
- some by-products, with higher molecular weight and more stability, could express higher toxicity than low molecular weight and unstable compounds;
- aqueous matrix type showed a tremendous effect on by- products evolution and toxicity;
- river water matrix showed lower by-products formation and lower toxicity than effluent matrix. This phenomenon was attributed to the impact of OH radical scavengers such as carbonate, bicarbonate and other scavenger ions;
- Hybrid system application played very important role in minimization the toxicity level. The elimination of miscellaneous organics by MEBR compartment as pre-treatment unit,

would results in COD abatement from 150 to 5 mg/L. Treatment of low COD effluent by AOP setup in AO/MEBR, would results in minimum by-products formation and lower toxicity.

4.7.8 Conclusion and remarks of Phase 8:

Advanced oxidation of sulfamethoxazole (SMX), as one of the important pharmaceutical emerging contaminants, was comprehensively analyzed and monitored in different sample matrices. Accurate mass of SMX ion and its four major by-products including BP-99, BP-270, BP-288, BP-172, identified and quantified by an LC-Q-TOF and LC-MS-MS spectrometry respectively. The effect of technological parameters had an extensive effect on by-products evolution. By adjusting the pH= 5-6, aeration = 0.5-1 L/min and H_2O_2 dose = 3-6 mM, the by-products formation descended to the minimum abundance. It could be concluded that formation of by-products may result in toxicity elevation especially at the 5-10 minutes at the beginning of the oxidation reaction. By continuing the treatment time, more than 20-30 minutes, the toxicity trend descends.

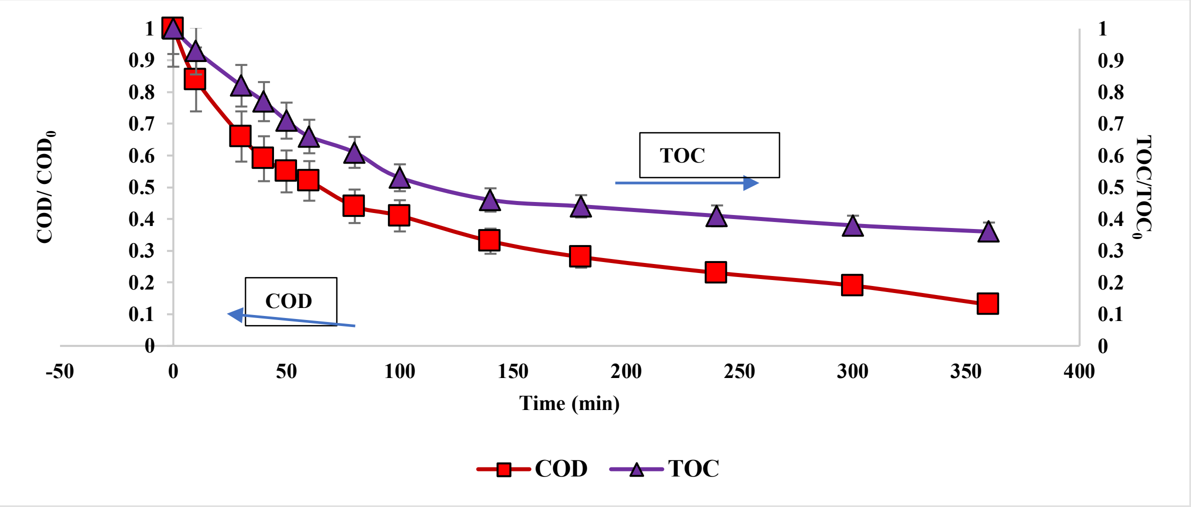

Figure 4.61. TOC and COD removal during SMX degradation

In addition, the evolution of SMX by-products was studied in river water and effluent matrices. The by-products revealed different behavior with respect to degree of no-target constituents' concentration in river water and effluent matrices. Therefore, in river water samples, SMX by-products showed higher removal rate and required lower treatment time than effluent matrix. By continuing the treatment time, SMX by-products disappeared in the medium. However, TOC and COD remained in the medium until the certain time (Figure 4.61). Formation of ammonia (NH_4^+), Nitrate (NO_3^-) and sulfate (SO_4^{-2}) as SMX end- products were strong indicators of mineralization process (Figure.4.59). This phenomenon was validated by the SMX oxidation pathway as well (Figure. 4.60).

5 Conclusions and Recommendations

5.1 Conclusions

As a promising technology for water treatment, advanced oxidation processes (AOPs) have been proposed in this research. Despite a large number of publications referred to the lab scale research, AOPs often failed to be applied in plant scale facilities widely due to their limitations. To overcome AOPs limitations a novel hybrid AO/MEBR system comprising of an AOP coupled with membrane electro bioreactor (MEBR) was proposed. This study verified the effectiveness of the novel hybrid AO/MEBR system to remove organic matter emerging contaminants while controlling their by-products.

This main objective was accomplished in eight phases and several stages as follows.

1) An AOP UV/H_2O_2 reactor was designed and manufactured to receive maximum UV irradiation with a low energy (40 W) UV lamp. Degradation of SMX, PCM and EE2 as target pollutants by sole UVC photolysis was between 30-40%. However, SMX revealed higher elimination within the same period of time compared to PCM and EE2 samples. This phenomenon could be attributed to SMX higher molar absorption coefficient.

   The rate of degradation by AOPs was found to be much higher than UV sole irradiation. The results showed more than 99% removal of ECs including SMX, PCM and EE2.
2) A pilot plant reactor was designed and manufactured to evaluate AOP UV/O_3 technology for ECs removal efficiency in large scale semi-continuous flow. By developing an engineered multiple ozone dissolution approach, the pilot benefited higher ozone concentration in liquid film more than nominal values, which led to saving energy (no ozone in off gas flow-cell).

The result showed maximum removal of PCM, SMX and CAF in both ozonation and AOP UV/O_3 (more than 99%). The target pollutants achieved deficient degradation by sole UV-C fluence in both bench scale and pilot plant. However, Advanced oxidation showed superior removal efficiency in both UV/H_2O_2 AOP and UV/O_3 AOP pilot.

3) An AO/MEBR hybrid system for effluent treatment was developed for production of superior quality of reclaimed water in accordance with sustainable development principles. Residual organic matter (EfOM) and TOC were removed by more than 60% in 360 min. Simultaneously, ECs and their by-products were degraded by more than 99% in 60 minutes. The effluents from the MEBR pilot plant could be degraded and removed COD between 71% to 83% by the hybrid system within 240 minutes of reaction. All effluent samples (effluent 1,2,3 and 4) had almost the same COD removal rate after application of the hybrid system. Applying aeration (1.0 L/min, DO = 9.3 mg/L) in combination with the adjusted operational conditions (pH = 6-7 and H_2O_2 = 12 mM) revealed a considerable effect on COD removal (83%). Comparing the COD removal of emerging contaminants (SMX, PCM), the effluents required much more time to get the same COD removal compared to DIW matrix. On the other hand, the spiked effluent samples (effluent+ SMX), showed less removal (by 6% compared to sole effluent and by 18% compared to SMX in DI water samples) in 60 minutes of reaction, because of the matrix effect on UV irradiation and complex mixture of effluents. The load of PCM to the MEBR had inhibitory effect on the microbial community. Therefore, there was not significant reduction of PCM and COD of effluent (7% for PCM and 1% for COD). The ultrafiltration membrane was not able to inhibit PCM species as emerging micropollutants. This finding enhanced the clarity of our understanding of an MEBR unit's ability to remove COD and nutrients when it was affected by a moderate load of PhACs.

4) The best technological parameters were provided for AO-MEBR hybrid system when wastewater effluent and surface water were reclaimed (pH = 5- 5.5, aeration = 0.5-1 L/min, H_2O_2 = 6 - 7 mM). The results revealed a strong relationship between technological parameters and removal efficiency (more than 10%).

5) A model was developed to predict water and wastewater treatment efficiency by response surface methodology based on central composite design. This model also could be used for investigating the effect of technological parameters on each other and on the water and wastewater treatment efficiency. The regression analysis of variance, using ANOVA, with R^2 value of 0.98 confirmed the reliability of predicted quadratic polynomial model which had a good fitness to the experimental values.

6) The accurate mass of SMX ion and its four major by-products that are BP-99, BP-270, BP-288, BP-172, were obtained by LC-Q-TOF and quantified by LC-MS-MS spectrometry. Technological parameters had an extensive role in by-products evolution. By-products were controlled and minimized by adjusting technological parameters. Therefore, in the range of pH= 5-6, aeration = 0.5-1 L/min and H_2O_2 dose = 3-6 mM, by-products formation descended to the minimum abundance. It could be concluded that formation of by-products may result in toxicity elevation, especially at the first 5-10 minutes of the oxidation reaction. By continuing the treatment time, more than 20-30 minutes, the toxicity trend went to the descending values. In the river water samples, by-products showed higher removal rate than effluent matrix. This behavior could be attributed to the lower non-target constituent’s concentration in river water samples.

7) The main transformation pathway of SMX degradation by AOP UV/H_2O_2 was proposed. The major pathway was fulfilled through S-N bound cleavage and formation of BP-99 and also hydroxylation of SMX aromatic ring to form BP-270. By continuing the reaction oxidation to 360 minutes, mineralization of SMX reached a maximum level. Furthermore, mineralization was validated by appearing of $CO_2 + H_2O + SO4^{-2} + NO_3^{-} + NH4^{+}$ ions and mineral acids as SMX end-products during AOP UV/H_2O_2 treatment.

8) Both UV/H_2O_2 AOP and UV/O_3 AOP pilot advanced oxidation technologies, found to be the feasible methods to remove refractory emerging contaminates efficiently.

   The AO/MEBR hybrid system could remove simultaneously the refractory emerging contaminants (ECs), bacteria, pathogens, metals, nutrients, phosphorous, ammonia, nitrates and COD at elevated levels, controlling and minimized by-products and toxicity and saved energy. Therefore, the AO-MEBR hybrid system found to be a feasible and effective technology to improve the quality of effluent; leading to improved potential of water recovery from sewage.

5.2 Remarks and contribution of research

This study evaluated degradation of pharmaceutical emerging contaminants (ECs) such as sulfamethoxazole, paracetamol, 17-alpha ethynylestradiol and caffeine by advanced oxidation (AOP) methods. Ozone UV, UV/H_2O_2 AOP, and UV/O_3 AOP pilot scale, in semi- continuous mode, removed ECs efficiently. Investigations showed that, advanced treatment of target pollutants by AOP methods at best operational condition, led to mineralization and formation of

CO_2 and water. Technological parameters such as pH, oxidant dose and aeration had considerable effect on oxidation reaction rate and reaction efficiency.

The investigation showed that the novel AO - MEBR hybrid system efficiently removed EfOM, ECs and BPs with low energy consumption which reclaimed wastewater and produced superior quality water. The by-products of SMX, which accumulated at the initial time of reactions, were detected by LC-MS-MS analytical method. The major by-products abundance was higher than SMX parent ions and remained in the medium even after the disappearance of target pollutants. By applying best technological parameters, the abundance of BPs was minimized and controlled.

Based on an extensive literature review, almost all studies reported their results under manipulated lab scale experimental conditions such as synthetic wastewater and / or DI water matrix. The strength of this research was conducting the experiments in real wastewater, effluent and river water at pilot scales. Furthermore, analytical measurements were conducted by the most advanced analytical instruments such as LC-MS-MS, which required preparation of a special analytical method.

1) Development of an AO/MEBR hybrid system produced superior quality of reclaimed water with sustainable development principles

Several studies proved that even an advanced treatment method like MBR, could not remove high loads of miscellaneous ECs in wastewater. The developed MEBR, as a component of the novel hybrid system, achieved superior quality of the effluent with respect to ammonia, COD and other nutrients. However, the results in section 4.7 showed that if sole MEBR is applied, it cannot remove high loads of organic matter. In fact, most ECs (PCM) pass through the ultra-filter membrane in MEBR and still exist in the effluent. The results showed that by installing the

UV/H_2O_2 AOP downstream the MEBR, the novel AO/MEBR hybrid system could efficiently remove PCM, SMX and EE2. The main achievement of the new AO-MEBR hybrid system, was increasing the treatment efficiency by reducing substrate concentration, i.e. DOC. Reduction of the substrate from influent, would increase OH radical's reactivity. Due to the fact that substrates behave as OH radical scavengers, therefore, the lower concentration of substrates would result in lower concentration of OH radical scavengers. The second important achievement of the AO-MEBR hybrid system was mitigation of by-products precursors. By reducing the DOC concentration, BPs precursors were decreased, which in turn resulted in toxicity mitigation and a high quality of reclaimed water achieved. The third important achievement of the AO-MEBR hybrid system was providing a condition that led to faster degradation rates, which in return, the minimum energy was consumed.

2) Energy consumption mitigation

According to equation 3.7, the higher rate of degradation led to minimum energy consumption in AOP methods. Therefore, the AO-MEBR system which eliminates the OH radical scavengers, can accelerate degradation rate and save the energy required for treatment. In this study a pre-treatment unit (such as MEBR) was applied and the results showed elimination of OH radical scavengers' concentrations. In return, minimum energy consumption was achieved.

In the UV/O_3 AOP pilot system, by developing an engineered multiple ozone dissolution approach, the pilot benefited from higher ozone concentration in liquid film more than nominal values. This approach led to minimum energy consumption for maximum removal efficiency of SMX, PCM and CAF. Technological parameters had a critical role in achieving higher removal efficiency. In this research, local optimization and surface response methodology were applied to find optimal values for aeration rate, oxidant dose and pH. By applying best condition, faster reaction rates were achieved, which led to shorter reaction time and saving energy.

3) By- products identification, reduction and control

Transformation by-products also behaved as OH radical scavengers and reduced reaction performance. The results showed that application of MEBR for reduction and control of BPs was imminent due to elimination of by-products precursors. MEBR was applied as a pre-treatment unit and AOP was placed downstream of MEBR to eliminate residual EfOM, ECs and their by-products. This design pushed the AOP to be selective in order to target micropollutants removal, maximize reaction performance, saving energy, reduce by-product formation and destroy pathogens, simultaneously.

The results showed that almost all SMX and other ECs species were removed from water samples within a short period of reaction. However, partial mineralization of SMX was acquired during the initial time of photolysis reaction. This phenomenon could be described by high abundance of BPs formation during the SMX oxidation process. Time-of-flight mass spectrometry identified major by-products such as BP-99, BP-172, BP 270 and BP 288. The lifetime of BP- 99 revealed to be the highest and even parent SMX ions disappeared in the water solutions. Furthermore, BP-270 was formed at high concentration and remained in the media until to the end of treatment. Two other BPs (BP-288 and BP- 172) were removed in a shorter period.

It was concluded that the by-products which formed during the UV/H_2O_2 oxidation of the parent compound, accumulated at the initial reaction period. The high concentrations of BP-270 and BP-99 were present even after the entire removal of SMX. This phenomenon might bring a potential hazard and toxicity to the output of water treatment facilities. The study showed that technological parameters including pH, oxidant dose and aeration had significant effects on BPs evolution. However, when the best operational conditions were applied, the by-products abundance and toxicity were controlled and minimized.

Contribution

In summary, the contribution is listed as following:

- Designing a hybrid system which enhanced the level of wastewater treatment potential to reuse the wastewater as a source of water
- Discovery of SMX individual by-products including their abundances, stability, lifetime higher than parent compound
- Defining BPs evolution in DI, real effluent and river matrices
- Finding the impact of technological parameters on BPs evolution in DI water matrices
- Defining of an influence of technological parameters on BPs evolution in real water matrices including river water and wastewater
- Defining the best conditions for faster and shorter reaction time and saving energy
- Developing a model by RSM to investigate and predict removal, and technological parameters interaction
- Defining end-product reaction mechanism by pathway mapping and mineralization (NH_4^{+1}, NO_3^{-1}, SO_4^{2-} mineral acids)
- Defining a relationship between by-products' chemical structure and toxicity
- Finding a control to minimize toxicity by the hybrid system
- Designing a treatment system for simultaneous removal of ECs and effluent organics

- Elucidating the importance of applying a pre-treatment unit to minimize by-products precursors
- Applying parameters to a pilot scale (a limited study in pilot scale)
- Investigating BPs evolution in real water matrices (effluent and river)
- Saving the energy by the hybrid system
- Controlling and minimizing BPs by hybrid system by eliminating BPs precursors
- Investigating the contribution of super oxide radical to the reaction (air, no air and N_2 purge)
- Investigating the relation between energy consumption and technological parameters

5.3 Recommendations for future work

Based on excellent results of current research, in order to obtain more improvement for AO-MEBR hybrid system and AOP as well, the following recommendations are suggested.

- The electro bioreactor (EBR) chamber in the MEBR pilot facility, could partially remove the target compound, paracetamol (PCM). Therefore, the study for application of a new nano-filtration membranes is recommended.

- On the other hand, PCM as an EC negatively affected the bacterial activity. Furthermore sulfamethoxazole (SMX) as an antibiotic drug spiked to the EBR and might killed some portion of bacteria in the EBR chamber. Therefore, in future work, an investigation is recommended for adapted bacteria community to have more ability to remove higher ECs concentrations and wider range of miscellaneous ECs as well.

- Both components of the hybrid system are designed to work at semi-continuous flow individually. In other words, the hybrid system is designed like a semi-continuous - batch - semi-continuous system. However, this design had satisfactory results and no differences of efficiency are expected in comparison to a fully semi-continuous system. But, in order to simulate a pilot scale to a plant scale design, an interface between the MEBR and AOP should be applied. Thus, some aspects of engineering components (e.g. flow distribution, mass transfer, retention time and UV irradiation change) should be adjusted for full scale AO-MEBR.

- The effectiveness of both AOP UV/H_2O_2 and AOP UV/O_3 for model ECs was demonstrated. Comparing other AOPs methods such as photo Fenton and photocatalysis to the applied methods is recommended. The future studies by other AOP methods could be performed in terms of other model ECs, energy consumption and by-products evolution.

- The novel hybrid AO/MEBR system could save energy by applying a MEBR unit, since AOPs are expensive methods to reach maximum mineralization. However, some portion of the model ECs passed through the membrane, then, an enhancement in membrane type would result in higher ECs removal and more energy saving.

- Developing a model to predict a wider range of BPs control is recommended.
- Developing a kinetic model for rate of reaction to illustrate a method to measure quantum yield is also suggested.

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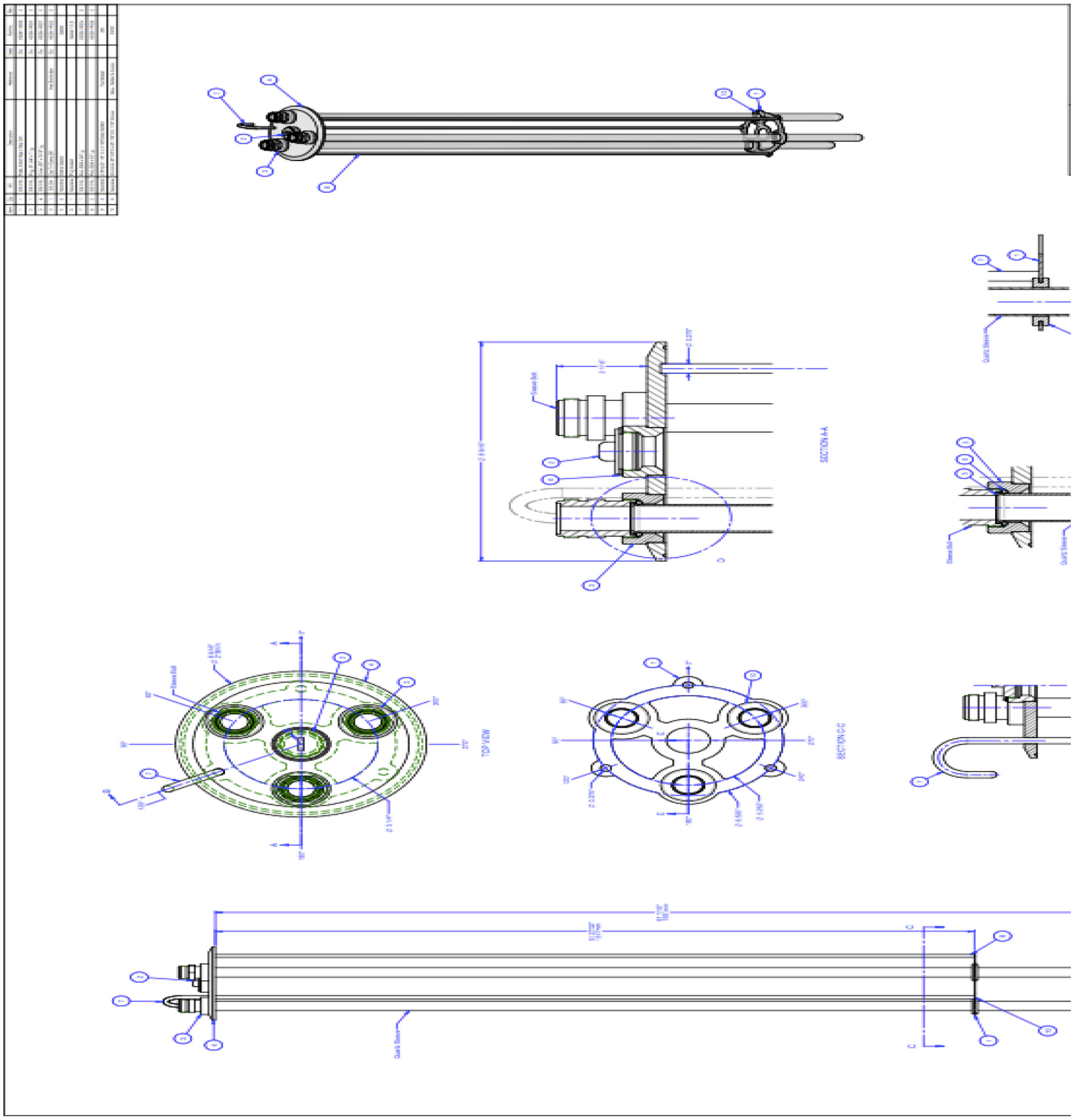
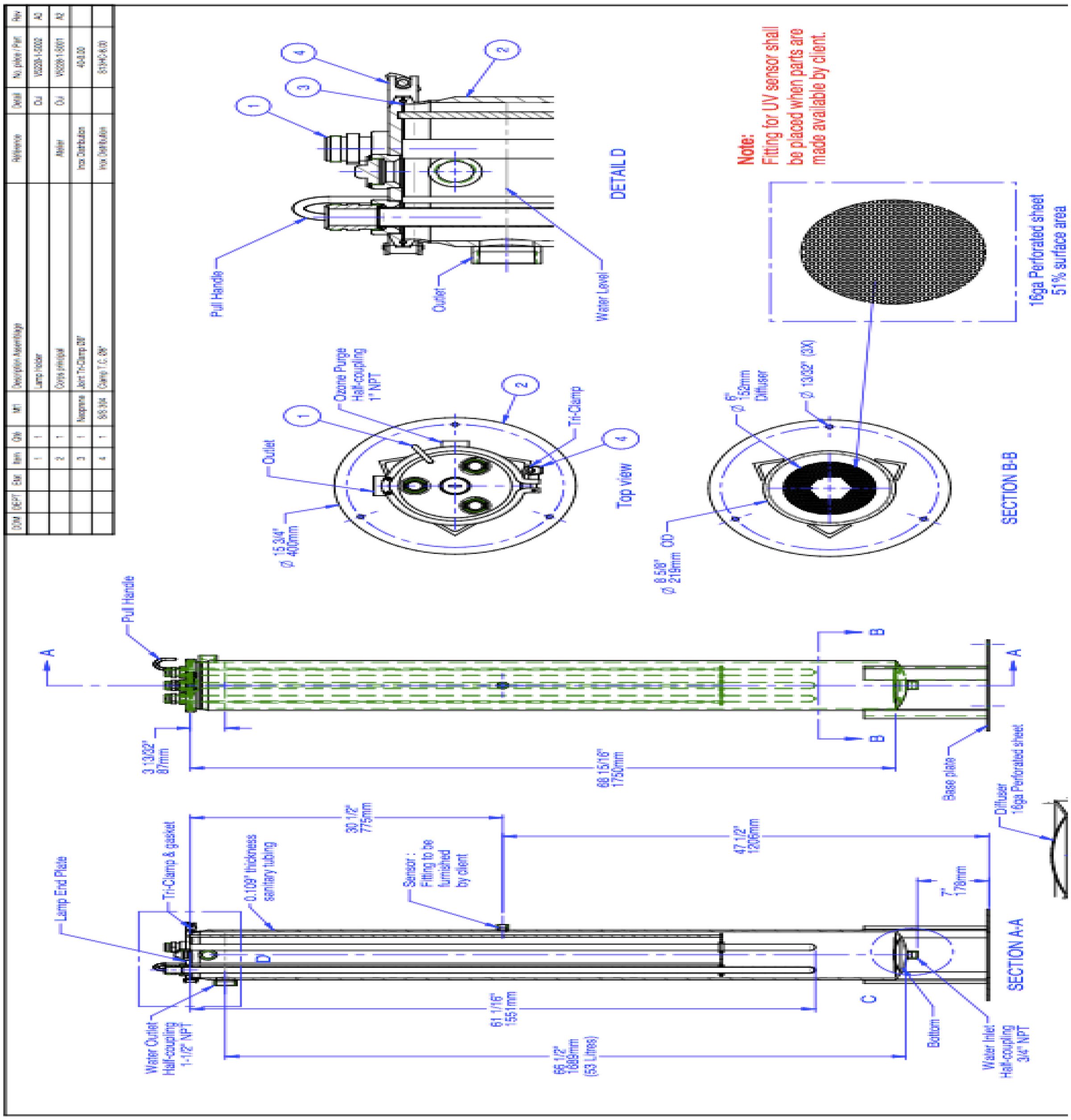
7 Appendix

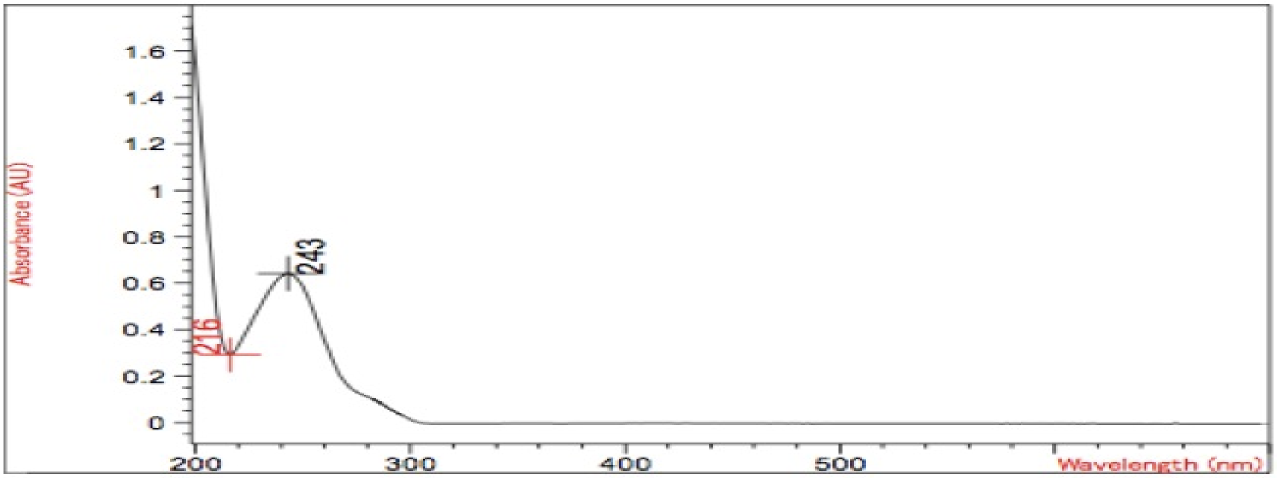


A1. AOP reactor design: Main UV chamber and UV lamps holder

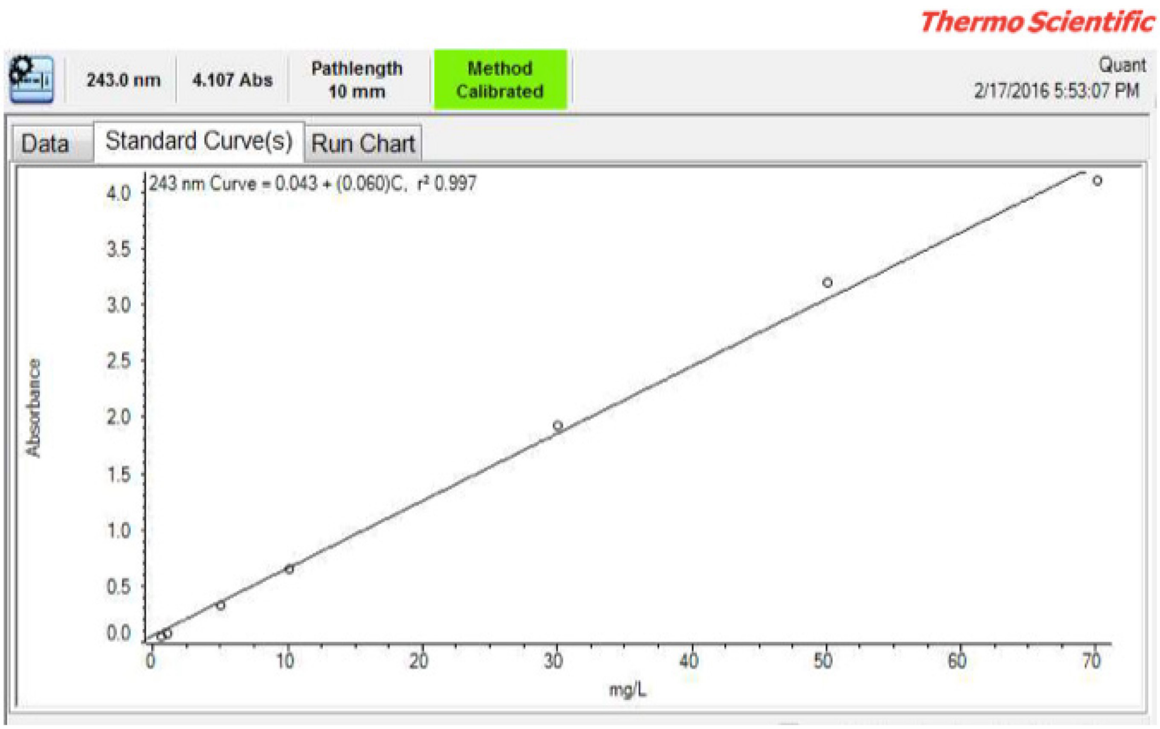


A2. AOP reactor design: Perforated plate and UV positioning

A3. (a) UV-Vis. Spectrophotometer evolution 201(left); (b)Spectrophotometer Cary 8454 (right)



A4. Paracetamol UV –Vis. scan and maximum absorption at 243



243.0 nm

4.107 Abs

Pathlength 10 mm

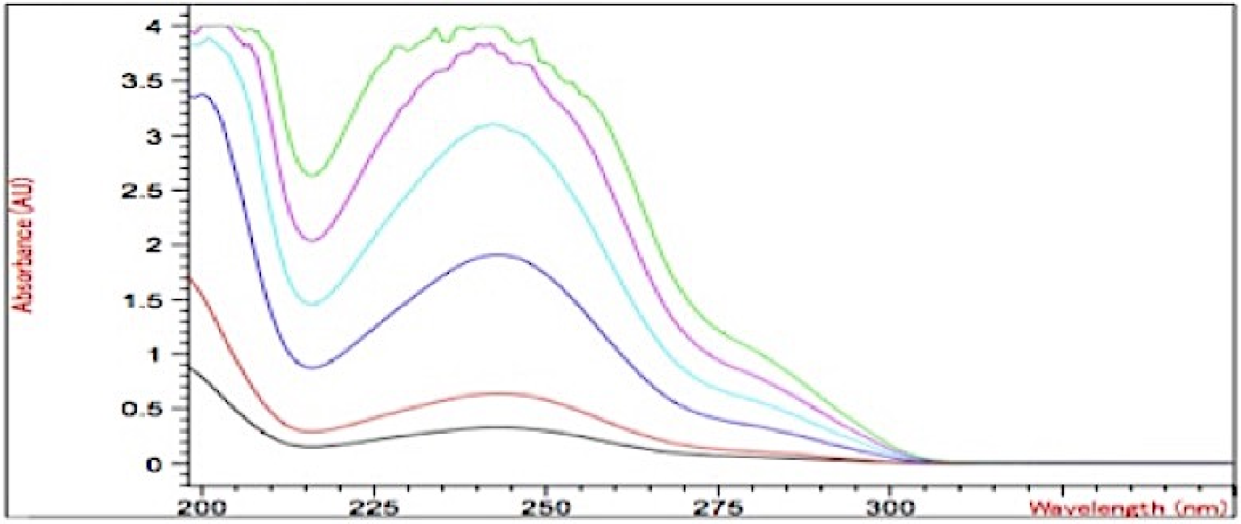
Method Calibrated

Quant

2/17/2016 5:53:07 PM

243 nm Curve = 0.043 + (0.060)C, r^2 0.997

A5. Calibration curve for PCM (0-70 mg/L)



A6. Paracetamol standard samples (5,10,30,50,70,90 mg/L) UV –Vis. scan and their maximum absorption at 243 nm.

A7 (a) TOC and COD measurement by HACH DRB200 (right); (b) HACH DR2800 (left)

A.8. (a)Agilent 6210 Time-of-Flight LC/MS (left); (b)Waters Quattro micro LC/MS/MS (right))