Treatment of Primary Influent Wastewater during Wet Weather Flow by Powdered Activated Carbon – Catalyzed Ozonation: From Fundamentals to Application

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ABSTRACT

Cities equipped with combined sewers to accommodate domestic and industrial wastewater as well as storm water runoffs, encounter the need to prevent seasonal overflows into water bodies. An extensive literature review pertaining to the treatment of primary influent (PI) during wet weather conditions determined that a coagulation/ flocculation/ sedimentation process was required for at least the removal of suspended solids. Ozonation was deemed promising especially for the oxidation of micropollutants (MPs) and disinfection. Yet, although ozone (O_3) is a renowned strong oxidant, several MPs are not sufficiently reactive with O_3 which calls for a process upgrade. Powdered activated carbon (PAC) was favourable to catalyze the ozonation because of its adsorbing capacity. There has been limited and conflicting knowledge pertaining to PAC-catalyzed ozonation especially in the ambiguously described catalytic mechanisms. The objective of this study was to propose a complete treatment for PI during wet weather flow by optimizing the operational parameters in conventional primary treatment and exploring single or PAC-catalyzed ozonation as a supplementary step for MPs' degradation and disinfection. This was addressed through a meticulous investigation of the catalytic mechanisms using a mixture of pharmaceuticals, personal care products, herbicides and perfluorinated compounds which have different affinities towards O_3.

Initially, the enhanced primary treatment of municipal PI during wet weather conditions was studied through a comprehensive approach from bench to full scale. Three metal-based coagulants were tested in a series of jar tests. Aluminum sulfate (alum) outperformed other coagulants since 1 mg of aluminum added as alum with low mixing was able to remove 22 Nephelometric Turbidity Units (NTUs), 19 mg of oxygen as chemical oxygen demand (COD) and 0.8 mg of ortho-phosphate (ortho-P). The removal of total suspended solids (TSS) depended mostly on rapid mixing while COD and ortho-P removals depended on slow mixing and coagulant dose. In bench and full-scale operations, the addition of polymer did not lead to any pronounced improvements. Turbidity and percent ultraviolet transmittance showed good correlation with TSS and ortho-P which evoked their use as surrogates for online process control.

PAC was then used to catalyze the ozonation of a mixture of seventeen MPs at near environmental concentrations in clean water matrix. Thirteen of those MPs were studied for the first time by PAC-catalyzed ozonation. The latter improved the removal of O_3-resistant MPs by up to 27% and promoted faster specific degradation rates. Radical probing experiments showed that scavenging hydroxyl radical ($^{\bullet}OH$) did not have a significant impact on MPs removals, while scavenging other reactive oxygen species was more influential. A detailed study by Electron Paramagnetic Resonance (EPR) spectroscopy ascertained that the decomposition of O_3 in presence of PAC at neutral pH did not boost the generation of free $^{\bullet}OH$. Instead, it likely produced adsorbed $^{\bullet}OH$ as PAC$^{\bullet}$–HO and other strong oxidizing species like [$^1O_2$+PAC]. Thus, free $^{\bullet}OH$ did not play any significant role in PAC-catalyzed ozonation. The effect of varying the O_3 specific dose as g O_3/g DOC (dissolved organic carbon) on the removal of those MPs by single and PAC-catalyzed ozonation was also investigated. Most MPs were more prone for removal by catalytic ozonation where faster removal kinetics were obtained. Carbamazepine, an anticonvulsant, and Atrazine, an herbicide, were found to be good surrogates for fast and slow reacting compounds, respectively. The removal kinetics were strongly dependant on the level of DOC.

After establishing a better understanding of the catalytic mechanisms, single and PAC-catalyzed ozonation were explored for the first time during wet weather flow for organics removal, disinfection, MPs' reduction and toxicity abatement. Overall, applying either ozonation process after the primary treatment was more efficient than applying them simultaneously. PAC-catalyzed ozonation was particularly favourable for the removal of organics and O_3-resistant MPs. Both single and PAC-catalyzed ozonation achieved 4 log removal of *E. coli*, and reduced the acute and genetic toxicity and the estrogenic activity of PI. A detailed cost analysis revealed that in post treatment, single ozonation would cost 0.06 to 0.32 \$/m^3 while PAC-catalyzed ozonation would cost 0.32 to 0.63 \$/m^3 for a flow rate ranging between 100 and 600 MLD. A comprehensive performance assessment demonstrated that PAC-catalyzed ozonation was promising for PI treatment during wet weather flow with one drawback related to the disposal of PAC.

PREFACE

The research described in this thesis is an original work that I, Mirna Alameddine, planned, designed, performed, interpreted and analyzed under the supervision of Dr. Mohamed Gamal El-Din in the Department of Civil and Environmental Engineering at the University of Alberta. The thesis was designed in a paper-based format with chapters (2-6) representing stand-alone papers that have been published, submitted or will be submitted for publication. I conducted the experimental work and prepared the manuscript. Post-doctoral fellows in our research group contributed to the analysis of samples and editing of manuscripts. All the contributions are further detailed below:

- Chapter 2: A version of this chapter will be submitted to Journal of Environmental Management as "A Review of Coagulation and Advanced Oxidation Processes for the Treatment of Primary Influent Wastewater during Wet Weather Flow Conditions". Mr. Abdulrahim Al Umairi will be the co-author of the manuscript. Dr. Mohamed Gamal El-Din contributed to the research planning and manuscript revision. Dr. Pamela Chelme-Ayala, Dr. Zuo Tong How and Dr. Shailesh Sable contributed to the revisions and edits.
- Chapter 3: A version of this chapter was published as "Alameddine, M., Al Umairi, A. R., Shaikh, M. Z., & Gamal El-Din, M. (2020). Bench to Full-Scale Enhanced Primary Treatment of Municipal Wastewater under Wet Weather Flow for Minimized Pollution Load: Evaluation of Chemical Addition and Process Control Indicators. *Can. J. of Civ. Eng.* doi: https://doi.org/10.1139/cjce-2019-0515". Mr. Abdulrahim Al Umairi and Mr. Mohammed Zakee Shaikh were the co-author of the manuscript, they contributed to the experimental work and write-up. Dr. Mohamed Gamal El-Din contributed to the research planning and manuscript

revision. Dr. Pamela Chelme-Ayala and Dr Selamawit Ashaghre Messele contributed to the manuscript revision and edit. Mr. Abdul Mohammed contributed to the manuscript revision.

- Chapter 4: A version of this chapter was submitted to Applied Catalysis B: Environmental (June 30, 2020) as: "Alameddine, M., Siraki, A., Tonoyan, L., & Gamal El-Din, M. Treatment of a Mixture of Pharmaceuticals, Herbicides and Perfluorinated Compounds by PAC-Catalyzed Ozonation: Insight into the Non-Free $^{\bullet}$OH Contingent Mechanisms". Dr. Mohamed Gamal El-Din contributed to the research planning and manuscript revision. Dr Arno Siraki and Dr Lusine Tonoyan contributed to the EPR analysis. Dr. Shailesh Sable contributed to the experimental planning and manuscript revision. Dr. Zuo Tong How contributed to the samples' analysis and manuscript revision. Dr. Pamela Chelme Ayala contributed to the manuscript revision and editing. Mrs. Bing Lin from EPCOR Water Services contributed to the manuscript revision.
- Chapter 5: A version of this chapter will be combined with a version of Chapter 6 and submitted to the Journal of Hazardous Materials. Dr. Mohamed Gamal El-Din contributed to the research planning and manuscript revision. Dr. Zuo Tong How contributed to the samples analysis and manuscript revision. Dr. Pamela Chelme-Ayala contributed to the revision and editing.
- Chapter 6 will be combined and jointly submitted with a version of Chapter 5 to Journal of Hazardous Materials (September, 2020) as: "Alameddine, M., How, Z.T., & Gamal El-Din, M. Advancing the Treatment of Primary Influent Wastewater during Wet Weather Flow by Single versus PAC-catalyzed Ozonation for Micropollutants Removal, Disinfection and Toxicity Abatement". Dr. Mohamed Gamal El-Din contributed to the research planning and manuscript revision. Mr. Abdulrahim Al Umairi contributed to the wastewater samples collection. Dr. Zuo Tong How contributed to the experimental planning, samples analysis and manuscript revision. Dr. Pamela Chelme-Ayala contributed to the manuscript revision and editing. Mrs. Bing Lin from EPCOR Water Services contributed to the revision and editing.

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DEDICATION

To the soul of a beautiful person watching over me for the past seven years,

To my amazing parents and siblings,

To the most wonderful husband who always has my back,

And to the most precious little girl who cannot wait to flip through these pages…

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ABBREVIATIONS

Alum	Aluminum sulfate
ANOVA	Analysis of Variance
CapEx	Capital Expenditure
CFS	Coagulation/ Flocculation/ Sedimentation
COD	Chemical Oxygen Demand
CSO	Combined Sewer Overflow
DOC	Dissolved Organic Carbon
EPR	Electron Paramagnetic Resonance
EPT	Enhanced Primary Treatment
$FeCl_3$	Ferric chloride
FT-IR	Fourier-transform infrared spectroscopy
M	Molar
mM	milli Molar
MLD	Mega liters per day
MPN	Most Probable Number
MP	Micropollutant
NaN_3	Sodium azide
OpEx	Operational and Maintenance Expenditure
O_3	Ozone
$^1O_2$	Single Oxygen
$O_2^{-\bullet}$	Superoxide
$^\bullet OH$	Hydroxyl radical

OH^-	Hydroxyl ion
Ortho-P	Orthophosphate
PAC	Powdered Activated Carbon
PACl	Polyaluminum chloride
*p*BZQ	Para-benzoquinone
PI	Primary Influent
PT-CO	Post treatment – Catalytic ozonation
PT-SO	Post treatment – Single ozonation
pH_{pzc}	Point of zero charge
ppb	Parts per billion
ppm	Parts per million
rpm	Rotations per minutes
ST-CO	Simultaneous treatment – Catalytic ozonation
ST-SO	Simultaneous treatment – Single ozonation
SS	Suspended solids
TBA	Tertiary butyl-alcohol
TOC	Total Organic Carbon
TSS	Total Suspended Solids
UVA	Ultra-violet absorbance
UPLC-TOF-MS	Ultra-performance liquid chromatography time-of-flight mass spectrometry
WWTP	Wastewater Treatment Plant
XPS	X-ray photoelectron spectroscopy
%UVT	Percent Ultra-violet Transmittance

CHAPTER 1: Introduction and Research Objectives

1.1. Background

1.1.1. Combined Sewer Overflow (CSO): occurrence and environmental concerns

Combined sewer overflows (CSOs) occur seasonally when the capacity of a wastewater network is exceeded due to increased volumes from heavy rainfalls and snow melts. In such cases, wastewater treatment plants (WWTPs) become unable to accommodate the excess wastewater that is usually of domestic and industrial type diluted by storm water runoffs. This excess ends up overflowing to the closest water stream as per the combined sewer system design. The volume of untreated or poorly treated CSO and the frequency of its discharge will essentially contribute to the concentration of pollutants including pathogens, organic and inorganic compounds in the receiving water body (Kay et al., 2016; Tondera et al., 2016). It will consequently affect its suitability for drinking or recreational purposes. Problems with irresponsible and unsafe CSO discharge can further transcend, impacting the aquatic ecosystem and public health with detrimental waterborne diseases (Jalliffier-Verne et al., 2016). In Canada, it is reported that 87% of the population is connected via a wastewater collection network to certain type of treatment, and only few treatment plants undertake the initiative to store and treat CSO. As such, local direct discharges from CSO have not been routinely monitored (Canada, 2019; CWN, 2018). Treatment options to mitigate CSO include physical and chemical processes applied on primary influent wastewater. As such, coagulation/ flocculation/ sedimentation has been tested and applied for the elimination of conventional parameters such as turbidity, suspended solids and chemical oxygen demand (El Samrani et al., 2008a; Gibson et al., 2016; Jung et al., 2015; Wang et al., 2015b). Also, tertiary reed beds were used to maximize the removal of biochemical oxygen demand, total suspended solids, and ammonia to match target values in tertiary treatment systems (Green et al., 1999). Ultraviolet irradiation (Tondera et al., 2015; Wojtenko et al., 2001a), ozone (Tondera et al., 2015; Wojtenko et al., 2001b), performic acid (Chhetri et al., 2015; Chhetri et al., 2014; Tondera et al., 2016), and peracetic acid (Chhetri et al., 2016; Chhetri et al., 2014; Coyle et al., 2014) were reportedly effective methods to address disinfection, a prominent topic for alleviating the environmental impacts of CSO. While each treatment provides part of the solution, there is an arising need for a comprehensive approach towards the treatment of primary influent during wet weather conditions to prevent the discharge of raw CSO. This approach should be set to target three areas of concern: conventional macropollutants (contaminants present at high concentrations), pathogens, and micropollutants (natural or manmade contaminants present at very low concentrations).

1.1.2. Micropollutants (MPs) in wastewater effluents: occurrence, and health and environmental concerns

Micropollutants (MPs) are natural or anthropogenic compounds present in the environment at very low concentrations. They exist in different classes including: pharmaceuticals, personal care products, herbicides, pesticides, industrial products and surfactants (Stamm et al., 2016). It was reported that the number of known and registered MPs in Europe exceeded 100,000, many of which can find their way to the aquatic environment through point and non-point sources (Eggen et al., 2014). They can provoke undesirable impacts on the environmental and public health when inappropriately disposed of. For example, MPs belonging to the group of endocrine disrupting compounds (EDCs) are known to affect the reproductive system in aquatic animals (Eggen et al., 2014). Other MPs have expressed toxic levels for specific aquatic species by virtue of their high biological activity aligned with their intended uses such as antibiotics and insecticides (Eggen et al., 2014; Stamm et al., 2016). The risk to the public health arises when the receiving water body is intended for human use, either through recreation or consumption. Some herbicides and pesticides have been associated with possible carcinogenicity and risk of acute toxicity (Bozoglu, 2011), and some perfluorinated compounds have been linked to cancer, damages to the bones, liver, and immune, reproductive and developmental systems (Khalil et al., 2016; Pelch et al., 2019). Amid all those risks and until now, there are no national standards or guidelines to regulate the permissible concentrations of MPs in the final effluent in North America. Many of those MPs have been registered under a list of Contaminants of Emerging Concerns (CECs) or were allocated a maximum contaminant level goal in drinking water (Health Canada, 2019; USEPA, 2010) to protect the public health, while there is a growing motive for their regulation. In contrast, several European countries, primarily Switzerland, are pioneering the research and application of MPs removal techniques as well their regulations in effluent wastewater. In fact, Waters Protection Ordinance, a Swiss act implemented in 2016 required the removal of at least 80% of the content of influent wastewater in trace organic pollutants by monitoring six MPs in a list of twelve including carbamazepine, mecoprop, diclofenac and others (Joss et al., 2016; WPO, 2020).

CSOs can be as a relevant source of MPs as WWTPs and thus can imply comparable adverse effects (Shu et al., 2016). To better elucidate, it is estimated that conventional WWTPs are more effective for macropollutants removal than for MPs removal with no guarantee for meeting safe and acceptable concentrations in the final effluent. Ryu et al. (2014) alleged that physical, chemical and biological processes in a WWTP can decrease the MPs in the effluent by 28% as compared to 97% decrease in suspended solids and 86% decrease in chemical oxygen demand. Qi et al. (2015) traced the removal of some MPs in WWTPs. The authors confirmed that the effect of the treatment processes on their removal can be inconsistent between WWTPs and dependent on the characteristics of each MP. The researchers also ascertained that coagulation/ flocculation was not very effective for the removal of the majority of the studied MPs.

1.1.3. Ozonation for MPs degradation and wastewater treatment

While upgrading and optimizing the conventional wastewater treatment for enhanced removal of suspended solids and organics can result in better removal of hydrophobic MPs, other hydrophilic MPs difficult to degrade will persist. Subsequently, introducing advanced tertiary treatment is recommended. In particular ozonation and adsorption are praised for their ability to remove persistent compounds and for their cost and energy efficiencies (Das et al., 2017; Margot et al., 2015; von Sonntag & von Gunten, 2012). Ozone (O_3) is widely recognized for its oxidation and disinfection properties. It was deemed effective in wastewater treatment in multiple studies on the ozonation of real wastewater for the removal of MPs in secondary effluents (Altmann et al., 2014; Can & Çakır, 2010; Huber et al., 2005; Ikehata et al., 2008; Jin et al., 2016; Lee et al., 2014b; Nothe et al., 2009; Wildhaber et al., 2015; Zhou et al., 2015). Also, applying ozonation for wastewater disinfection has been known and practised for a while (Xu et al., 2002). In CSO treatment, ozonation was only studied for disinfection.

Single ozonation is one way for applying O_3. It was examined for the removal of several MPs as a standalone treatment for model compounds (Seredyńska-Sobecka et al., 2005), or in combination with other processes such as following secondary treatment of real wastewater (Huber et al., 2005; Lajeunesse et al., 2013; Lee et al., 2013; Nothe et al., 2009). Yet the fact that many MPs exhibit limited reactivity with molecular O_3 prompted the addition of a catalyst in an attempt to improve the removals. This has become the recent trend in O_3-based advanced oxidation processes (AOPs) mainly to promote the degradation of organics through an indirect pathway that involves the generation of radicals. Free radicals are capable of oxidizing more compounds by virtue of their non-selectivity and strong oxidizing potential. Carbon-based catalysts are common in the literature and have been applied in different forms, alone and in combination with other catalysts. The interest in carbon material is mainly associated with its practicality in terms of cost and ease of application, in addition to its potential dual role as catalyst and adsorbent. Powdered activated carbon (PAC) is a potential good candidate. Studies on PAC-catalyzed ozonation are limited and have focused on only one (Faria et al., 2008a; Faria et al., 2008b; Faria et al., 2009; Goncalves et al., 2012; Gonçalves et al., 2013a; Gonçalves et al., 2014; Guzman-Perez et al., 2011) or a small mixture of four MPs only (Rozas et al., 2017). Those studies were performed using high concentration of target compounds in clean water and they seldom addressed the matrix effect while claiming free hydroxyl radicals as the main oxidants.

1.2. Research scope and hypotheses

This thesis pursued the enhanced treatment of primary influent wastewater during wet weather conditions as an alternative for the discharge of untreated CSO into water bodies. It elaborated on two treatment methods: coagulation/ flocculation/ sedimentation and ozonation processes. The studies were performed at bench and full-scale levels on real wastewater samples and on model compounds to explore practical treatment solutions as well as fundamental knowledge in catalytic mechanisms. The following hypotheses initiated this research and steered the objectives:

1) Enhanced primary treatment for the removal of conventional wastewater contaminants from primary influent wastewater during wet weather conditions can be sufficient to meet the target value for effluent discharge.
2) The contribution of coagulant aids to the overall removal efficiency of major macropollutants is minimal compared to that of the coagulant.
3) The use of PAC as catalyst is effective for the removal of O_3-resistant MPs during ozonation processes. Its dual role as catalyst and adsorbent depends on the matrix composition and concentration of target compounds.

4) The mechanism of PAC-catalyzed ozonation is driven by different pathways that rely on reactive oxygen species at the surface or in the interface between PAC and the bulk solution:
    a. Molecular O_3 and reactive oxygen species oxidize the organic molecules adsorbed onto the surface of the catalyst;
    b. The catalyst initiates O_3 decomposition into radicals which oxidize the organic MPs adsorbed onto the catalyst surface or in solution;
    c. O_3 reacts with the surface of the catalyst producing surface radicals which react with organic molecules available in solution or with the adsorbed organic molecules producing organic radicals that will be further oxidized by hydroxyl radicals and molecular O_3 in solution;.
5) The apparent (i.e., overall) removal kinetics of MPs in a mixture differ from theoretical kinetics of individual compounds due to the competition between pollutants. However, similar trends in the removal rates are expected in complex mixtures.
6) Single and PAC-catalyzed ozonation are beneficial additions to the enhanced primary treatment (EPT) of the primary influent wastewater during wet weather conditions for both disinfection and MPs removal.
7) PAC-catalyzed ozonation can demonstrate a superior performance compared to single ozonation by favouring disinfection and toxicity reduction.
8) Cost is one considerable limitation for the application of PAC-catalyzed ozonation due to the significant addition implied by the catalyst.

1.3. Research objectives

The main thesis objectives are presented below according to their appearance in the thesis:

Chapter 3 addressed hypotheses 1 and 2 and its objectives were:

1) To compare the performance of metal-based coagulants and anionic and cationic polymers as coagulant-aids; and
2) To define the optimum conditions for coagulation/ flocculation/ sedimentation process for the removal of conventional contaminants from primary influent (PI) wastewater during wet weather flow.

Chapter 4 addressed hypotheses 3 and 4 and its objectives were:

1) To determine the optimum catalyst dose to catalyze the decomposition of ozone and maximize the degradation of selected MPs;
2) To compare the removal efficiencies of single and catalytic ozonation in a diversified mixture of MPs, from different categories and with different affinities towards ozone; and
3) To study the catalytic mechanisms involved in the ozonation and catalytic ozonation of selected MPs in a clean water matrix using radical probing and other available methods.

Chapter 5 addressed hypothesis 5 and its objectives were:

1) To study the matrix effect on the single ozonation and catalytic ozonation of selected MPs and the kinetics of their degradation by single and catalytic ozonation.

Chapter 6 addressed hypotheses 6, 7 and 8 and its objectives were:

1. To study the impact of single and catalytic ozonation on the removal of organic contaminants and the disinfection of PI during wet weather;
2. To assess the feasibility of single and PAC-catalyzed ozonation for the treatment of PI during wet weather conditions.

1.4. Thesis organization

This thesis consists of seven chapters that were logically organized following the research stages to meet the above-mentioned objectives.

- Chapter 1 provides a general background on the environmental and public health concerns that are associated with the free disposal of untreated wastewater during wet weather conditions. It highlights the growing interest in addressing the removal of micropollutants in particular and tackles the gap in the knowledge pertaining to their treatment as well as that of wastewater during wet weather conditions in particular. Chapter 1 also enlists the research objectives and thesis organization.
- Chapter 2 compiles an extensive literature review on the treatment of wastewater during wet weather flow and the application of ozonation methods for the degradation of micropollutants.
- Chapter 3 reports the optimum chemical dosing for the enhanced primary treatment of PI during wet weather conditions. It also compares data from bench and full-scale applications.
- Chapter 4 explores the mechanisms involved in PAC-catalyzed ozonation through radical probing and electron paramagnetic resonance. The chapter presents the effect of PAC on the decomposition of ozone and how PAC-catalyzed ozonation improves the removal of model compounds. The study uses a diversified mixture at a neutral pH (pH 7) that includes seventeen micropollutants belonging to different categories (pharmaceuticals and personal care products, herbicides and perfluorinated compounds). Eight of those micropollutants are studied for the first time with PAC-catalyzed ozonation, at near environmental concentrations.
- Chapter 5 addresses the effect of ozone specific dose on the removal of MPs in a buffered mixture at neutral pH by single and PAC-catalyzed ozonation. It benchmarks the removals by PAC-catalyzed ozonation compared to single ozonation and determines surrogate MPs. Removal kinetics and formation of intermediates are also tackled in this chapter.

- Chapter 6 provides a comprehensive approach towards the application of single and PAC-catalyzed ozonation for the treatment of PI during wet weather conditions. This approach includes a performance assessment based on the removal of conventional parameters and micropollutants as well as disinfection and toxicity levels. The chapter also comprises a detailed cost analysis to evaluate the feasibility of the studied treatments.
- Chapter 7 wraps up the thesis by summarizing the major findings and conclusions. It depicts the objectives that were met and provides insights for future work.

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CHAPTER 2: Literature Review

2.1. Treatment of Combined Sewer Overflow

2.1.1. Introduction

Wastewater collection networks represent a fundamental component of a city's infrastructure and its wastewater treatment process. In areas where those networks are designed to accommodate storm water runoffs in addition to regular domestic and industrial wastewaters, they become known as combined sewers. Their operation varies seasonally reaching full capacity during events of heavy rain and intensive snow melts. In such cases, wastewater treatment plants (WWTPs) to which those networks are connected and which are theoretically designed to operate with a small footprint, become unable to contain the excess wastewater during wet weather conditions which ends up overflowing to the closest water stream as per the combined sewer system design. According to the USEPA (2018), this phenomenon is known as combined sewer overflow (CSO) and it consists of regular untreated wastewater diluted by storm water. The volume of poorly treated or untreated CSO and the frequency of its discharge will essentially contribute to the concentration of pollutants (including pathogens, organic and inorganic compounds) in the receiving water body (Kay et al., 2016; Tondera et al., 2016), and consequently affect its suitability for drinking or recreational purposes. Problems with irresponsible and unsafe CSO discharge can further transcend, impacting the aquatic ecosystem and public health with detrimental waterborne diseases (Jalliffier-Verne et al., 2016).

CSO is commonly characterized in terms of its mass loading of macropollutants including, metals, suspended solids (SS), total nitrogen (TN), *Escherichia coli* (*E. coli*), biochemical oxygen demand (BOD), chemical oxygen demand (COD), total phosphorus (TP) and orthophosphate (ortho-P) (Diaz-Fierros et al., 2002; Gasperi et al., 2012; Irvine et al., 2005; Kwon et al., 2014);

Pongmala et al. (2015); (Soonthornnonda & Christensen, 2008). Among the metals studied in CSO, zinc and copper were the most abundant with concentrations reaching up to 3525 µg/L and 1180 µg/L, respectively. Other CSO constituents include around 180 mg/L of BOD, around 270 mg/L of COD, 240 mg/L of total solids, 280 mg/L of TP, and 70 mg/L of ortho-P (Gasperi et al., 2008). It is believed that CSO discharges increase the level of *E. coli* in the aquatic environment in a cumulative manner (by 0.5 to 2 log) (Madoux-Humery et al., 2016). It also participates to the mass load of metal contaminants in the receiving environment (Irvine et al., 2005). Recently, there have been a growing interest in studying the contribution of CSO to the release of micropollutants (MPs) into the environment (Evans et al., 2016; Gasperi et al., 2008; Madoux-Humery et al., 2016).

The objective of this section in Chapter 2 is to provide a comprehensive literature review regarding the applied and potential CSO treatment processes for the removal of macro and micropollutants and for disinfection. This section also aims to provide an overview of the gaps and limitations in those processes and some recommendations to overcome them.

2.1.2. Treatment options for the removal of macropollutants from CSO

The term “macropollutants” is used to refer to conventional contaminants that are available at high concentrations, in the range of mg/L. Macropollutants include organics, inorganics, and pathogens (Verlicchi et al., 2012). These compounds are usually regulated in the final wastewater effluent on different governmental levels. To target their removal from CSO, physical and chemical processes that can be applied during primary treatment or for disinfection are the most common in literature. As such, coagulation/ flocculation/ sedimentation processes using aluminum sulfate (alum), ferric chloride ($FeCl_3$) or polyaluminum chloride (PACl) have been applied to study the elimination of macropollutants (namely: turbidity, SS, COD) (El Samrani et al., 2008a; Gibson et al., 2016; Jung et al., 2015; Wang et al., 2015b). Also, in a successful attempt, tertiary reed beds were used to maximize the removal of BOD, total suspended solids (TSS), and ammonia (NH_4-N) from CSO and match target values in tertiary treatment systems (Green et al., 1999). The disinfection of CSOs has also been a prominent topic with ultra-violet irradiation (UV) (Tondera et al., 2015; Wojtenko et al., 2001a), ozone (O_3) (Tondera et al., 2015; Wojtenko et al., 2001b), performic acid (Chhetri et al., 2015; Chhetri et al., 2014; Tondera et al., 2016), and peracetic acid (Chhetri et al., 2016; Chhetri et al., 2014; Coyle et al., 2014) proven to be effective. In comparison, studies on the removal of MPs from CSO are still scarce (Jung et al., 2015; Pongmala et al., 2015).

Evidence of full scale applications of the optimum coagulant dose are rarely available in literature where most studies are limited to bench scale applications (Baghvand et al., 2010; El Samrani et al., 2008b; Guida et al., 2007; Wang et al., 2015b). Software models were built for real time reading using sensors which help, to a certain extent, with the prediction of chemical doses especially during wet weather flow (Ratnaweera & Fettig, 2015; Tik & Vanrolleghem, 2017).

Coagulation is the process during which colloids are destabilized and aggregated forming larger particles able to settle out. In wastewater treatment, colloids are particles with a size ranging between 0.001 and 1 µm and are normally in suspension because of Brownian motion, the random movement and collision with water molecules. On the other hand, flocculation is the process of formation of larger particles or flocs due to colloidal aggregation which can be induced by mixing and velocity gradients. In chemical coagulation/ flocculation, a coagulant and a flocculent are added. The coagulant is the chemical (natural or synthetic polymer or a metal salt) that initiates colloidal destabilization. The flocculent is the chemical (typically an organic polymer) that promotes flocculation and strengthens the formed flocs (Metcalf & Eddy, 2014). Polymers act through charge neutralization, polymer bridging or electrostatic patch. During charge neutralization, the polymer reduces the surface charge of the negatively charged colloids in wastewater diminishing the forces of repulsion between them which keep them in suspension, and amplifying the forces of attraction, which result in the formation of microflocs (Lee et al., 2014a). During polymer bridging, polymers adsorb to the particle surface forming loops and tails making the particle more likely to bind with another one that has similarly adsorbed polymers and thus producing larger and sturdier flocs. In cases where the flocculent is abundantly added, it is expected that the particle surface will become excessively covered with polymers and that polymer bridging will no longer become possible, instead particles re-stabilization would take place. In electrostatic patch, cationic polymers adsorb onto the surface of negatively charged colloids forming cationic or positive ″patches″ at the adsorption site that attract to the negative sites on other colloids and result in particle aggregation. The resulting flocs are usually stronger than those formed by charge neutralization but weaker than those obtained by polymer bridging (Lee et al., 2014a). While cationic polymers are more prone to function by charge neutralization and electrostatic patch (Lee et al., 2014a), they are less applied than anionic polymers which are widely used and seem to act by polymer bridging (Haydar & Aziz, 2009).

In one study (El Samrani et al., 2008a), two metal-based coagulants $FeCl_3$ and PACl were tested and compared for the chemical coagulation of CSO without the addition of coagulant-aids. The aluminum-based coagulant (i.e., PACl) was privileged for being more effective in the reduction of turbidity (that was associated with the removal of metals, namely: copper, lead, zinc and chromium), and for having lower optimum dose than $FeCl_3$. Coagulant although overdosing would result in metals resuspension and release. It was thus recommended to match the necessary coagulant dose with the fluctuating CSO quality parameters that can be predicted by its conductivity. Alum was also applied in the coagulation/ flocculation of CSO where a dose of 100 mg/L was found to maximize UV transmittance to 85%. When coupled with a cationic polymer the latter was recognized for fast-acting, enhancing the formation of larger flocs and increasing the turbidity removal, although it had no major impact on TSS or UV transmittance (Gibson et al., 2016). In coagulation with aluminum-based salts, it is the salt hydrolysis product that is responsible for particles destabilization. As such, when alum dissociates in water, it forms metal complexes known as coordination compounds which undertake the destabilization process (Metcalf and Eddy, 2003). Some of the important precipitation reactions (during chemical phosphorous removal) that take place when alum is added to wastewater include the reaction between alum and calcium bicarbonate producing aluminum hydroxide precipitate that can enmesh and remove colloids (Reaction 2.1), and between alum and phosphorus producing insoluble aluminum phosphate (Reaction 2.2).

$$Al_2(SO_4)_3 \cdot 18\,H_2O + 3\,Ca(HCO_3)_2 \leftrightarrow 3\,CaSO_4 + 2\,Al(OH)_3 + 6\,CO_2 + 18\,H_2O \qquad \textit{Reaction 2.1}$$

$$Al^{3+} + PO_4{}^{3-} \leftrightarrow AlPO_4 \qquad \textit{Reaction 2.2}$$

2.1.3. Treatment options for the removal of micropollutants from CSO and wastewater effluents and for disinfection

Micropollutants (MPs) are natural or anthropogenic compounds present in the environment at very low concentrations that can provoke undesirable impacts on the environmental and public health. There are different classes of MPs including: pharmaceuticals, personal care products, herbicides, pesticides, industrial products and surfactants (Stamm et al., 2016).

As the problem of disposal of MPs without appropriate treatment arose, researchers started shedding more light on their occurrence, sources and eventually treatment options (Kay et al., 2016; Lee et al., 2014b). Unsurprisingly, CSOs can be as a relevant source of MPs (pharmaceuticals, personal care products, herbicides and pesticides) as WWTPs and thus they can imply comparable adverse effects on aquatic and terrestrial fauna and flora (Shu et al., 2016). Nevertheless, until now, there are no national standards or guidelines to regulate the permissible concentrations of MPs in the final effluent in North America. Most of those MPs have been registered under a list of Contaminants of Emerging Concerns (CECs) or were allocated a maximum contaminant level goal in drinking water (USEPA, 2010) to protect the public health, while there is a growing motive for their regulation. In contrast, several European countries, primarily Switzerland have been leading the way in regulating MPs in effluent wastewater in addition to researching and applying techniques for their removal. Meanwhile there have been screening and modeling approaches to estimate the overall load of MPs in the environment and mitigate their cost-prohibitive and impractical quantification (Arlos et al., 2014; Johnson & Williams, 2004; Launay et al., 2016; Mutzner et al., 2016; Tolouei et al., 2019).

In an attempt to evaluate the overall wastewater treatment efficiency for the removal of MPs, there have been several studies surveying the fate of MPs in conventional WWTPs and the capacity of different advanced oxidation processes (AOPs) for their degradation. Accordingly, it is estimated that conventional WWTPs are less effective for MPs removal compared to macropollutants removal. Interestingly, the removal efficiency of the treatment still does not guarantee meeting safe and acceptable concentrations in the effluent for final disposal. Ryu et al. (2014) alleged that physical, chemical and biological processes in a WWTP can decrease the MPs in the effluent only by 28% as compared to 97% decrease in suspended solids and 86% decrease in COD. Qi et al. (2015) traced the removal of some MPs in WWTPs. The authors confirmed that the effect of the treatment processes on their removal can be inconsistent between WWTPs and dependent on the characteristics of each MP. Overall, coagulation/ flocculation was not very effective for the majority of the studied MPs. It was however confirmed that activated sludge and bioreactors can remove 40% to 60% of pharmaceuticals and personal care products (PPCPs) (Miege et al., 2009; Sui et al., 2011) and generally more than 70% of the non-polar compounds. Their removal mechanism consists mainly of sorption (onto suspended solids or dissolved colloidal matter), biotransformation (by microorganisms as growth material, or by enzymes in side reactions) or volatilization (during aeration). Polar compounds are less removed in those processes. Other researchers (Das et al., 2017; Lee et al., 2011; Margot et al., 2015; Qi et al., 2015; Sui et al., 2010) further confirmed that activated sludge and biodegradation were less efficient compared to oxidation which removed more than 70% of selected PPCPs. Table 2.1 shows the removal efficiency and effluent occurrence of selected MPs from three different categories in conventional WWTPs.

While upgrading and optimizing the conventional wastewater treatment for enhanced removal of TSS, BOD, DOC and ammonium can result in better removal of hydrophobic MPs, other hydrophilic MPs that are difficult to degrade persist. Therefore, introducing tertiary treatment is recommended. In particular ozonation and adsorption are praised for their ability to remove persistent compounds as well as for their cost and energy efficiency (Das et al., 2017; Margot et al., 2015; von Sonntag & von Gunten, 2012).

Table 2.1 Percent removal and effluent concentrations of selected MPs in typical WWTPs (Adapted from:(Margot et al., 2015) and (Das et al., 2017))

Micropollutant		**Class**	**Typical WWTP % Removal**	**Typical Effluent Concentration (ng/L)**
		Pharmaceuticals and Personal Care Products (PPCPs)		
1	Carbamazepine	Anticonvulsant	16	140-832
2	Carbendazim	Antifungal	30	81-100
3	Clindamycin	Antibacterial	10	50-115
4	Fluconazole	Antifungal	15	108-110
5	Gemfibrozil	Lipid-regulating agent	39	1-420
6	Ibuprofen	Anti-inflammatory	80	81-460
7	Sulfamethoxazole	Antibacterial	44	238-1190
8	Naproxen	Anti-inflammatory	40	27-462
9	Trimethoprim	Antibacterial	35	150-482
10	Ethinylestradiol	Semisynthetic Estrogen	60	0-5
11	Triclosan	Antiseptic	90	75-200
		Herbicides		
12	Atrazine	Herbicide	23	4-10
13	2,4-Dichlorophenoxyacetic Acid	Herbicide	-	13
14	Mecoprop	Herbicide	25	424-500
15	Diazinon	Insecticide	40	40-173
		Industrial Compounds		
16	Perfluorooctanoic Acid	Surfactant	1	13
17	Heptadecafluoro-octanesulfonic acid	Surfactant	1	12

In fact, O_3 was an effective oxidant in wastewater treatment as concluded in multiple studies on the ozonation of real wastewater for the removal of MPs in secondary effluents (Altmann et al., 2014; Can & Çakır, 2010; Huber et al., 2005; Ikehata et al., 2008; Jin et al., 2016; Lee et al., 2014b; Nothe et al., 2009; Wildhaber et al., 2015; Zhou et al., 2015). Similarly, applying ozonation for wastewater disinfection purposes has also been known and practised for a while (Xu et al., 2002).

However, in CSO treatment, ozonation was only studied for disinfection. Wojtenko et al. (2001b) presented a comprehensive review for the application of ozonation in CSO treatment including advantages and disadvantages (Table 2.2). Tondera et al. (2015) used a synthetic CSO by highly diluting the influent wastewater with groundwater (1:7 to 1:3 as influent wastewater:

groundwater). The authors performed the ozonation experiments in semi-batch systems with relatively high specific O_3 doses ranging between 0.6 and 4.8 g O_3/g DOC applied over 15 minutes contact time to mainly target disinfection. The researchers reported 3.4 log removal of *E. coli* with 8.4 -12.1 mg/L O_3 and concluded that ozonation was efficient for the reduction of bacteria, viruses and parasite.

Table 2.2 The advantages and disadvantages of applying ozonation for the disinfection of CSO (Adapted from (Wojtenko et al., 2001b))

Ozonation Advantages	Ozonation Disadvantages
▪ Very strong disinfectant	▪ Unstable, must be manufactured in-situ
▪ Does not require purchase, shipment, storage or handling of chemicals	▪ High capital cost, operation and maintenance cost
▪ Does not require large space	▪ Difficult to quantify in water
▪ Easily adaptable to existing facilities	▪ Requires relatively high equipment maintenance
▪ Requires short contact time	▪ Must be coupled with biological filtration to minimize potential regrowth
▪ Effective for a wide range of microbes	
▪ Low half-life (no toxic residual)	▪ Reacts with organics (substrates for microbial growth)
▪ Improves the receiving water quality by: effluent decolourization, turbidity and odor reduction, increase in dissolved oxygen concentration	▪ Safety consideration: O_3 is toxic and corrosive
▪ No toxicity to aquatic life after ozonation	▪ No full-scale application of O_3 for CSO treatment

2.1.4. Bridging the gaps for improved CSO treatment

The primary treatment of PI during wet weather flow is inevitable at least for solids removal. Yet its operation necessitates optimizing the process parameters to case-specific applications which also means upscaling bench scale experiments and testing various chemicals.

There are several concerns associated with the ozonation of PI during wet weather and wastewater in general. While the ultimate role of O_3 is the oxidation of specific target compounds, the complexity of a wastewater matrix entails the presence of O_3 sinks such as nitrites and nitrates. It is estimated that the stoichiometry of their reaction with O_3 is 1:1 in molar concentration (Lee et al., 2013). Due to the presence of such compounds, ozonation is often applied after biological treatment to optimize its efficiency. Thus, these factors are to be accounted for when adjusting the O_3 dosage in complex matrices especially in CSO treatment.

Also, ozonation is known to affect the chemical structure and composition of wastewater (Jin et al., 2016). However, it has been claimed that although there is a variety of ozonation by-products (bromate, aldehydes, ketones, peroxide), only very low concentrations of those compounds have been identified in the effluent and receiving waters (Wojtenko et al., 2001b). Therefore, the best approach to study the impact of the treatment on the overall toxicity of the effluent is under real environmental conditions and in real wastewater. Analyzing samples from the receiving water might also be needed.

2.1.5. Conclusions

Given the uniqueness of the wastewater during wet weather flow in terms of variability in its quality and frequency of occurrence, there is a need for an appropriate and convenient treatment that can be relatively fast and economic and can secure enhanced contaminants elimination. Achieving high removal of suspended solids and organic matter, pathogens and MPs are the top priority for a full comprehensive treatment. Due to the time limitations, an optimum treatment must be limited to few steps only. Therefore, primary treatment through coagulation, flocculation and settling combined with or followed by another treatment step that can guarantee disinfection and removal of MPs are needed. Among the several options, ozonation appears to be a viable treatment. A careful optimization of all the operation conditions is needed in order to achieve a comprehensive treatment and secure the best possible effluent quality before discharge.

2.2. Micropollutants degradation by PAC-catalyzed ozonation

2.2.1. Introduction

Ozone (O_3) is a strong selective oxidant and disinfectant. It is applied in water and wastewater treatment to oxidize, disinfect or assist other processes. For instance, during pre-ozonation, O_3 is applied prior to coagulation to destabilize particles and enhance their removal process. In aqueous systems, O_3 undergoes direct or indirect reactions (Beltran, 2004). In direct O_3 reactions, molecular O_3 reacts with other chemical species through oxidation-reduction, substitution (i.e. nucleophilic and electrophilic reactions) and cycloaddition. These reactions are governed by kinetics and produce by-products such as aldehydes, ketones, carboxylic acids and polymers. Alternatively, in indirect O_3 reactions, targeted species do not react with molecular O_3 but rather with hydroxyl radicals ($^{\bullet}OH$) that are a product of O_3 decomposition in water either through reaction with hydroxyl ions (OH^-) or through direct interactions with other species (Beltran, 2004). $^{\bullet}OH$ can initiate a series of chain reactions that either consume the $^{\bullet}OH$ or form radical intermediates producing another $^{\bullet}OH$. Depending on the net production of $^{\bullet}OH$, a compound can be classified as an initiator (reacting with O_3 to form the $^{\bullet}OH$), promoter (reacting with the $^{\bullet}OH$ to from another $^{\bullet}OH$ via chain reactions) or inhibitor (reacting with and consuming the $^{\bullet}OH$) in the ozonation process (Staehelin & Hoigne, 1985; Westerhoff et al., 1999). Also, some species in the aqueous system can react easily and preferentially with $^{\bullet}OH$, and are thus known as $^{\bullet}OH$ scavengers or O_3 decomposition inhibitors. Such species include: carbonates and bicarbonates, tertiary-butanol (TBA), p-chlorobenzoate (pCBA), and excess natural organic matter (NOM) (Beltran, 2004; Stucki, 1988).

Single ozonation is one common technique that has been tested to oxidize a variety of micropollutants (MPs). It was examined for the removal of several MPs as a standalone treatment for model compounds (Seredyńska-Sobecka et al., 2005), or in combination with other processes such as following secondary treatment of real wastewater (Huber et al., 2005; Lajeunesse et al., 2013; Lee et al., 2013; Nothe et al., 2009). Nevertheless, studies have identified several MPs with limited reactivity with ozone such as: phthalate (Beltran et al., 2002; Jin et al., 2012; Ning et al., 2007), bezafibrate, iomeprol (Altmann et al., 2014), benzotriazole (Altmann et al., 2014; Hollender et al., 2009), atenolol (Hollender et al., 2009), MPs with amine groups (Hubner et al., 2015), pesticides (Broseus et al., 2009), and saturated aliphatic compounds (Jin et al., 2012).

Recent trends in O_3-based advanced oxidation processes (AOPs) suggest the application of catalysts to improve the generation of radicals and thus the removal of compounds that are less reactive with molecular O_3. In order to improve the overall performance of ozonation, and thus the removal of organics and mineralization, a catalyst can be applied to accelerate the rate of O_3 reactions without undergoing any significant chemical reaction. Two types of catalytic ozonation processes can be discerned: homogeneous catalytic ozonation (HoCO) with water soluble catalyst, and heterogeneous catalytic ozonation (HeCO) with an insoluble catalyst. Some of those catalysts are listed in Table 2.3. In environmental applications, the latter is generally preferred over HoCO for being more cost-efficient, easily separable from the reaction media, and safer to the environment and public health, especially since the catalyst in HoCO remains in solution raising concerns about added pollutants (Beltran, 2004). The application of catalytic ozonation for the removal of MPs in aqueous systems is still a work in progress given the wide variety of available catalysts along with the huge list of MPs that exhibit different chemical structures and characteristics and the complexity in discerning the exact mechanisms involved in the process. So far, most of the work in this field has been performed on model compounds or simulated media with the exception of only few studies that tackled real wastewater samples (Kolosov et al., 2018; Mecha et al., 2016; Melero et al., 2009; Sui et al., 2012).

Table 2.3 Soluble and insoluble catalysts applied in HoCO and HeCO and available in literature

Catalytic ozonation process	Catalyst	Reference
HoCO	Transition metals: Mn^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+}, Zn^{2+}, Cu^{2+}, Ni^{2+},Ti^{2+}	(Guo et al., 2018)
	Ultraviolet light	(Mecha et al., 2016)
	Solar light	(Agustina et al., 2005)
HeCO	Iron oxides	(Wang & Bai, 2017)
	Titanium oxide	(Rodriguez et al., 2012)
	Aluminum Oxide	(Nawrocki & Fijołek, 2013)
	Carbon xerogel	(Alvarez et al., 2008; Orge et al., 2012)
	Multiwalled carbon nanotubes	(Gonçalves et al., 2013b; Oulton et al., 2015)
	Granular Activated Carbon	(Gümüs & Akbal, 2017)
	Powdered Activated Carbon	(Rozas et al., 2017)

Carbon-based catalysts are common in literature and have been applied in different forms, alone and in combination with other catalysts. The interest in carbon material is mainly associated with its practicality in terms of cost and ease of application, in addition to its potential dual role as catalyst and adsorbent. As such, multi-walled carbon nanotubes (Fan et al., 2014; Gonçalves et al., 2010; Gonçalves et al., 2013b; Liu et al., 2011; Oulton et al., 2015; Restivo et al., 2012), carbon nanofibers (Restivo et al., 2013), and activated carbon (AC) in powder or granular forms (Faria et al., 2008b; Goncalves et al., 2012; Gonçalves et al., 2013a; Gonçalves et al., 2014; Merle et al., 2010; Rozas et al., 2017; Sanchez-Polo et al., 2005) have been examined as single catalysts. Also, multi-walled carbon nanotubes with manganese oxide (Jalali, 2016; Sui et al., 2012), AC with cerium oxide (Faria et al., 2009), and granular activated carbon (GAC) with transition metals (Hammad Khan & Jung, 2008) have been investigated as combinations of catalysts. Studies on HeCO with PAC only are generally limited and focus on one (Faria et al., 2008a; Faria et al., 2008b; Faria et al., 2009; Goncalves et al., 2012; Gonçalves et al., 2013a; Gonçalves et al., 2014; Guzman-Perez et al., 2011) or a small mixture of four MPs only (Rozas et al., 2017). Those studies were performed using high concentration of target compounds in clean water and they seldom addressed the matrix effect.

The objective of this section in Chapter 2 is to provide an overview of the catalytic ozonation studies performed using PAC as well as the role of the catalyst in the mechanism of O_3 decomposition and MPs degradation. This section also addresses some limitations and discrepancies in the approach to PAC-catalyzed ozonation and means to mitigate them.

2.2.2. Fundamentals of the catalytic mechanisms in PAC-catalyzed ozonation: approaches and main findings

Faria et al. (2008a) studied the removal of oxamic and oxalic acids at a concentration of 1 mM each (equivalent to 90 mg/L) in a semi-batch system with 500 mg/L granular activate carbon (GAC) and ozone supplied at 150 cm^3/ min over 2 to 3 hours. The study was performed at natural acidic pH and at pH 7 with phosphate buffer. The latter was found to slow down the removal of target compounds. This effect was associated with the possibility of phosphate buffer adsorbing onto the surface of GAC, limiting its interaction with O_3. At neutral and basic pH, the oxidation of oxamic acid by single or catalytic ozonation was reported very unlikely to happen unless the concentration of hydroxyl radicals is significantly increased. That is because under these conditions, oxamic acid is present in a stable hydrophilic form, and any removal would be due to adsorption. In contrast, catalytic ozonation demonstrated positive impact on the removal of oxalic acid. The addition of TBA inhibited its removal by catalytic ozonation at neutral pH. The removal pattern differed at acidic pH because of the impact of the solution pH on the surface functional groups of GAC (pH_{pzc}), on the dissociation of the target compound (pka) and on the O_3 decomposition pathway. At acidic pH, the addition of TBA did not impact the removal of oxalic acid. This observation was linked to the fact that lower solution pH promotes surface interactions between GAC and oxalic acid and demotes the interactions with radical species in the bulk. This conclusion was contrasted with findings from another study (Beltran et al., 2002).Two different mechanisms were proposed for the removal of oxalic acid during catalytic ozonation. The first mechanism suggests surface reactions by adsorption-surface reaction-desorption and the second suggests interactions in the bulk between oxalic acid and the active radical species, products of O_3 decomposition. The difference between the removal of oxalic and oxamic acids was associated with their chemical structure.

Faria et al. (2008b) researched the removal of sulfanilic acid and benzenesulfonic acid in a similar experimental setup, using the same doses of ozone (150 cm^3/min), PAC (500 mg/L) and target compounds (1 mM equivalent to 173.2 mg/L and 158.18 mg/L respectively) at natural acidic pH and neutral pH (in the presence of phosphate buffer). At acidic pH complete removal was achieved for benzenesulfonic acid within 80 min, and the removal rate improved with catalytic ozonation. A major improvement was observed in the reduction of total organic carbon (TOC), since the oxidation of benzenesulfonic acid produced several intermediates, better mineralization was attained in catalytic ozonation systems. With catalytic ozonation at neutral pH, a small improvement in the removal of benzenesulfonic acid was observed while the most obvious impact was on TOC reduction. Maleic and oxalic acids were identified as oxidation intermediates for benzenesulfonic acid. The former was produced at the beginning of the reaction and oxidized by molecular O_3 while the latter formed later during the reaction and persisted and was more abundant at neutral pH. In fact, oxalic acid tends to react better with hydroxyl radicals than with molecular O_3 and its presence indicates the conversion of the parent compound. The addition of TBA prevented the removal of benzenesulfonic acid which proved that its degradation mainly occurs through the radical pathway. With sulfanilic acids, there were no major improvements in the compound's removal when catalytic ozonation was performed, yet a significant increase in TOC removal was noted. The addition of TBA had no impact on the removals. Intermediates that formed during its oxidation process were oxalic and oxamic acids. The fact that oxamic acid is refractory to oxidation justified the lower TOC removal compared to benzenesulfonic acid. The concentrations of ammonium and nitrate were also monitored throughout the process. Nitrate was more abundant at neutral pH while ammonia dominated at acidic pH. Monitoring these products was deemed important to indicate the possible mechanisms of reactions.

Faria et al. (2009) studied the removal of three different dyes in a catalytic ozonation system with the same O_3 and GAC doses as above. The authors also tested cerium oxide as an alternative catalyst at the same dose as GAC. The study was performed in simulated and real matrices of textile effluent after sludge treatment with target compounds at concentrations between 30 and 50 mg/L at natural pH (pH between 5 and 6). Experiments showed that adsorption had a minimal impact on the removal of dyes compared to single ozonation which also allowed an 88% reduction of TOC within 2 hours. In catalytic ozonation with GAC the removal of dyes did not significantly improve, yet the removal of TOC was accelerated. Cerium oxide was found superior to GAC as it showed better mineralization over a long reaction time. The initial concentration of the target compounds and the presence of carbonates and bicarbonates in the matrix were also examined. Carbonates addition did not show any significant impact, while increasing the concentration of dyes lowered the mineralization level. The applicability of single and catalytic ozonation in the treatment of treated (with activated sludge) and untreated effluent wastewater from textile plants was assessed. In treated wastewater, the level of mineralization achieved by single ozonation was lower than by catalytic ozonation with 30% and 57% TOC removal, respectively, after 30 min. This level was significantly lower when the treatments were applied to raw wastewater for the same duration with 6% TOC removal by single ozonation and around 18% by catalytic ozonation. The study claimed that the mechanisms of catalytic ozonation with AC for the removal of those dyes relied on interactions with the surface functional groups of the catalyst where $^{\bullet}OH$ did not play any major role. There was no attempt to prove this claim by investigating the impact of radical scavengers on the removal of target compounds.

Merle et al. (2010) examined the removal of 2,4 dichlorophenol and nitrobenzene in a semi-batch reactor using 250 mg/L of each of the target compounds with 30 L hr^{-1} (equivalent to 500 cm^3/ min) of O_3 and 1000 mg/L GAC at a natural neutral pH. The study reported that the rate constant of O_3 decomposition was proportional to the catalyst dose. It was also reported that while catalytic ozonation had no impact on the removal of 2,4 dichlorophenol which could be completely removed by single ozonation, it only improved the removal rate of nitrobenzene. Four by-products of the single ozonation of nitrobenzene were then identified and quantified: ortho-, meta- and para-nitrophenol and acetic acid. Their concentrations varied throughout the reaction with acetic acid being generated at significantly higher concentrations than the other products. During catalytic ozonation, the same by-products were identified and their removal rates were relatively enhanced. A mass balance for the chemical oxygen demand (COD) of nitrobenzene was performed where the theoretical COD was calculated, the final COD was measured, and the actual COD of the by-products was then calculated by subtracting COD final from COD theoretical. The theoretical COD of the by-products was computed upon their quantification and then compared to the actual COD of the by-products and was found lower. This meant that there were probably some other by-products that formed but were not quantified. It was also noticeable that the final COD obtained after 4 hours of single ozonation of nitrobenzene was more than 4 times higher than the value obtained after catalytic ozonation for the same period. In contrast, results of 2,4 dichlorophenol oxidation revealed the formation of eight by-products that were monitored over time. COD generation and evolvement with time did not differ between single and catalytic ozonation. The reaction pathways for the oxidation of both compounds were determined accordingly.

Guzman-Perez et al. (2011) studied in a semi-batch system, the removal of 10 mg/L atrazine from a clean water matrix with pH adjustment, using 5 mg/L O_3 and 250-1000 mg/L PAC. The study found that catalytic ozonation increased the removal rate of atrazine in comparison with adsorption and single ozonation (with removals of 80%, 20% and 55% respectively). It also accelerated the rate of O_3 decomposition compared to single ozonation at acidic pH. It was noticed that different types of AC catalysts with similar surface area and pH_{pzc} exhibited the same catalytic activity. The application of $^{\bullet}OH$ scavenger TBA revealed a decrease in the rate of atrazine removal. TBA adsorbed to a limited extent onto PAC, it slowed down the removal of atrazine, confirming that removals occurred in the bulk solution rather than on the surface of the catalyst. The study showed that after complete O_3 depletion (30 min), at acidic pH 3, the role of adsorption in atrazine removal became more pronounced, as more sites were available on the surface of AC for adsorption. At acidic pH, O_3 adsorbed better onto the surface of the catalyst that had a high pH_{pzc} value of 9.82, while at neutral and basic pH, the hydroxyl surface groups as well as the abundant hydroxyl ions in solution were the major initiators of O_3 decomposition. The kinetics of atrazine removal by catalytic ozonation were performed and the ratio of $^{\bullet}OH$ to O_3 concentration, known as R_{ct} was computed for the different pH conditions studied. The rate constants for O_3 decomposition and atrazine removal, as well as R_{ct} were higher at neutral pH than those at basic pH where more hydroxyl ions OH^- are available that promote the decomposition of O_3. Those values also increased linearly as the catalyst dose increased; yet there was no obvious relationship between those constants and pH. As such, it was concluded that pH plays a major role in defining the type of interaction between O_3 and the surface of AC. It was claimed that at lower pH, O_3 adsorbs on the surface of PAC where OH^- is scarce, while at neutral and basic pH it reacts with the hydroxyl groups that adsorb onto PAC. This led to the conclusion that there are two different mechanisms involved during catalytic ozonation and that the pH of the solution is the factor that determines which mechanism can take place.

In another semi-batch system, Goncalves et al. (2012) studied the removal of 50 mg/L sulfamethoxazole in water using 150 cm^3/ min O_3 and 140 mg/L AC or multi-walled carbon nanotubes (MWCNT) at natural pH of 4.8. After characterization, the surface area of GAC was reportedly larger and consisted mainly of micropores with basic surface groups and pH_{pzc} of 8.5. Complete removal of sulfamethoxazole was achieved within 30 min of either single or catalytic ozonation. In contrast, adsorption with GAC removed 60% of sulfamethoxazole after 3 hours and more TOC compared to single ozonation. Catalytic ozonation also allowed better TOC removal than single ozonation with 45% reduction in TOC achieved in 3 hours. Scavenging $^{\bullet}OH$ by addition of TBA during single and catalytic ozonation led to faster removal of sulfamethoxazole. As such, it was concluded that the mechanism of sulfamethoxazole removal was based on the reaction with molecular O_3 and that the purpose of catalyst addition was the improvement of mineralization. The study further investigated the formation of oxidation intermediates and by-products and tracked their evolvement with time. Two intermediates: 3-amino-5-methylisoxazole, p-benzoquinone, and four by-products: oxamic acid, oxalic acid, pyruvic acid ad maleic acid were identified. Sulfate, nitrite, nitrate and ammonium were also monitored during the reaction considering that the parent compound sulfamethoxazole contains sulfur and nitrogen. While it was reported that all the sulfur content could be transformed to sulfate in single or catalytic ozonation, nitrogen content of sulfamethoxazole was partially converted into ammonium at the beginning of the reaction, in addition to nitrate and other unidentified nitrogenated species. The products were identified in both single and catalytic ozonation but in different proportions. As a result, two pathways for the degradation of sulfamethoxazole during single and catalytic ozonation were suggested depending on the catalyst in use. Microtox bioassays with *Vibrio fischeri* were performed before treatment and after 30 min and 3 hours of single and catalytic ozonation. It was revealed that with both treatments, the toxicity increased after 30 min reaction time and then decreased again after 3 hours while remaining higher than the toxicity of the untreated sulfamethoxazole solution. It was noticeable that the acute toxicity with single ozonation was always higher than that with catalytic ozonation. The intermediates and by-products that were obtained during single or catalytic ozonation were deemed more toxic than the parent compound.

The removal of bezafibrate in a similar reaction set up was studied by Gonçalves et al. (2013a). 20 mg/L of the target compound were subjected to 150 cm^3/ min of O_3 and 140 mg/L carbon-based catalysts: GAC or MWCNT at natural pH of 4.4. According to the catalysts characterization, GAC had larger surface area and was more basic (pH_{pzc} value of 8.5) than MWCNT. Also, oxygenated surface groups on both materials were minimal and represented only around 1% by weight. The results showed that bezafibrate removal by adsorption with GAC was 95% and 70 % with MWCNT within 5 hours. Both single and catalytic ozonation achieved full removal of bezafibrate in 20 min, yet catalytic ozonation led to higher level of mineralization with the removal of 60 to 73% of TOC (with MWCT and GAC respectively) after 5 hours. A faster removal of bezafibrate was noted when $^\bullet$OH scavenger TBA was added, implying that the mechanism of bezafibrate removal relied on molecular O_3. The authors recognized that the presence of 0.5 mM TBA in those experiments interfered significantly with TOC results and opted not to track the effect of TBA addition in the system on TOC removal. The potential for catalyst reuse was evaluated in terms of the impact on bezafibrate and TOC removal: while reusing the catalyst had no impact on the degradation of bezafibrate, it was obvious that it limited the level of mineralization. Further investigations using temperature programmed desorption (TPD) spectra revealed that ozonation promoted the formation of oxygenated groups on the surface of the catalyst which tend to reduce the electron density around the catalyst, translating into lower catalytic activity. Ozonation also led to an increase in the overall surface area of the catalyst MWCNT. A closer look at the intermediates and by-products formed during single and catalytic ozonation of bezafibrate resulted in the identification of six different compounds that were monitored over 5-hours reaction time and linked to TOC results. It was claimed that within the first few minutes, unsaturated organic compounds were formed and then transformed by reaction with molecular O_3 into lower molecular weight organics such as carboxylic acids (mainly oxamic acid and oxalic acid) that accumulated throughout the 5 hours. Inorganic ions were also produced and monitored, as such it was believed that all chlorine content of bezafibrate was transformed into chlorine ion Cl^- within 30 min, 60 min and 2 hours of catalytic ozonation with MWCNT, catalytic ozonation with GAC, and single ozonation, respectively. Nitrogen content was also converted to nitrite, nitrate and ammonia, it entered in the composition of unsaturated organic by-products and finally formed nitrate and some unidentified nitrogenated compounds. The study also noted that the simultaneous use of O_3 and catalyst improved the removal of bezafibrate oxidation by-products by means of adsorption onto the catalyst. It suggested possible bezafibrate degradation pathways during single and catalytic ozonation that culminate in the formation of oxamic, oxalic and pyruvic acids in addition to inorganic ions: nitrite, nitrate, ammonium and chloride. Microtox® bioassays with *Vibrio fisheri* showed a more pronounced increase in toxicity in the first 3 hours of single ozonation compared to catalytic ozonation. This was justified by the adsorption capacity of the catalyst that targeted both bezafibrate and its oxidation intermediates and by-products.

Carbon-based catalysts were also used to study the removal of erythromycin in catalytic ozonation (Gonçalves et al., 2014). 140 mg/L GAC or MWCNT before and after impregnation with cerium oxide were used along with 150 cm^3/ min O_3 during the catalytic ozonation of 50 mg/L erythromycin in a semi-batch system at a natural pH of 6.5. The carbon-based catalysts in their different forms were characterized in terms of surface area following Brunauer-Emmett-Teller (BET) theory, surface chemistry with X-ray photoelectron spectroscopy (XPS), structure with X-ray diffraction (XRD) and morphology with Transmission Electron Microscopy (TEM). AC with and without CeO_2 revealed a higher surface area when compared to MWCNT. Upon impregnation with CeO_2, Ce^{4+}/Ce^{3+} were identified on the surface of the carbon material. Results revealed that more TOC was removed by adsorption with MWCNT than with AC (46% and 25% removal respectively after 5 hours of contact time) which was linked to the surface and textural properties of both materials. The addition of catalyst enhanced the reduction of TOC compared to single ozonation, and the highest level of mineralization was achieved during catalytic ozonation with CeO_2/MWCNT. Three experiments were conducted with MWCNT as catalyst to assess its reutilization. The largest decline in the catalyst activity was observed between the first two cycles where the TOC removal decreased. Following the results of TPD analysis, it was noted that ozonation oxidized the surface of MWCNT producing more oxygenated surface groups that eventually became more abundant every time ozonation took place. The more oxygenated surface groups were present on the catalyst's surface, the less the electron density and thus the lower the catalytic effect in O_3 decomposition. Also, BET results showed that ozonation had little impact on the MWCNT surface texture translated in a small increase in the surface area from one run to the next. When investigating the by-products of catalytic ozonation, six compounds were recognized including oxamic, oxalic and pyruvic acids. Those compounds were tracked during the 5 hours reaction time, where it was noticed that they formed at different times and in varying concentrations depending on the catalyst used. Similarly, because of the nitrogen content of erythromycin, nitrate, nitrite and ammonium ions were monitored during the experiments. Nitrate was the most abundant and it was detected in catalytic ozonation experiments at higher concentrations than in single ozonation experiments, which was justified by the better removal of erythromycin in the presence of catalyst. The study also indicated the formation of unidentified nitrogenated by-products that contributed to the total TOC in addition to nitrogenated gases that satisfied the nitrogen mass balance. Two pathways were suggested for the removal of erythromycin by catalytic ozonation. In the first pathway, the catalyst initiated O_3 decomposition into radicals, and reactions occurred in the bulk solution between those radicals and the organic pollutants. In the second pathway, the interaction between molecular O_3 and the catalyst's surface generated surface oxygenated radicals that reacted with the organic pollutant, intermediates and by-products on the surface by chemisorption. Those adsorbed compounds could still react with molecular O_3 and $^{\bullet}OH$ in the bulk becoming more hydrophilic, which caused them to desorb back into the bulk solution resulting in a TOC increase. Microtox® bioassays on *Vibrio fischeri* unveiled that single ozonation increased the acute toxicity by 42%, and the application of AC and CeO_2 in catalytic ozonation increased it further to 43% and 54%, respectively, despite the higher TOC removal. The study noted that the toxicity level decreased with longer reaction time, and that AC caused lower acute toxicity than MWCNT and its impregnation with ceria decreased the acute toxicity.

So far, all the studies presented above showcased the removal of one compound at a time and at significantly high concentrations compared to the real environmental concentrations. The first approach towards investigating the impact of catalytic ozonation on a mixture of MPs, at relatively low levels, was undertaken by Rozas et al. (2017) who performed the study on a mixture of 4 compounds: atrazine, carbamazepine, diclofenac and triclosan at concentrations 2.8, 2.8, 2.9 and 2.3 mg/L, respectively. Experiments were performed in a semi-batch system, with 2.4 L/ hr O_3 (40 cm^3/ min) and 20 mg/L PAC in ultrapure water with pH adjusted to 7.5 using HNO_3 and

NaOH, and in river water at natural neutral pH. The compounds were initially individually studied then studied in a mixture. When studied individually with single ozonation, atrazine was removed by 98% within 30 min while the other 3 compounds were completely removed within the first 4 min. Those results were comparable to findings from other studies. The reactivity of O_3 with these 4 compounds varied depending on their chemical structures and compositions. In contrast, in a mixture of compounds in ultrapure water, 90% of atrazine was removed in 30 min of single ozonation, and the application of PAC-catalyzed ozonation improved the removal in 20 min. In order to explain this improvement, adsorption experiments with higher PAC doses were conducted and they showed less than 35% removal of all compounds except triclosan that was removed by 75% in 30 min contact time. The addition of TBA slowed the removal of atrazine which confirmed that the mechanism of its oxidation involved $^{\bullet}OH$, but did not impact the removal of the 3 other compounds verifying that molecular O_3 is the main driver for their oxidation. In general, the results were similar in pure and natural (river) water despite the fact that in ultrapure water pH dropped to 4.5 upon addition of O_3 while it remained neutral in river water due to the buffering effect of the low DOC level. Moreover, FTIR results showed that ozonation of PAC significantly affected the alcohol, carbonyl, aromatic and hydroxyl surface functional groups which reflected on the ability of PAC to adsorb organic compounds or generate hydroxyl radicals during catalytic ozonation. A closer look at the intermediates and by-products of the mixture's ozonation led to the identification of 5 different carboxylic acids: oxalic, oxamic, maleic, fumaric and acetic acids that were constantly present in the system. As such, since those carboxylic acids are refractory to O_3, they can justify why TOC removal reached a plateau at 40% after 15 min of catalytic ozonation in ultrapure water. Toxicity tests were performed using *Daphnia magna* and they confirmed that toxicity of the initial mixture in ultrapure water, decreased with both single and catalytic ozonation and that the latter was more efficient in reducing the toxicity: 45% and 80% toxicity reduction by single and catalytic ozonation, respectively, after 15 min.

In summary, the key findings pertaining to the catalytic mechanisms in PAC-catalysed ozonation as reported in literature are available in Table 2.4.

Table 2.4 Summary of the key findings in literature pertaining to ozonation catalyzed by activated carbon

Effect of pH
▪ Solution pH affects: – The O_3 decomposition pathway; – The surface functional groups of the catalyst; – The dissociation of target compounds ▪ Abundance of hydroxyl surface groups on PAC and abundance of hydroxyl ions in the bulk solution promote the decomposition of O_3 (at neutral and basic pH); ▪ Buffer can adsorb onto the catalyst and limit its interaction with O_3.
Effect of O_3 on the catalyst's surface
▪ Oxidation of the catalyst's surface and formation of oxygenated surface groups; ▪ Reduction of electron density; ▪ Increased surface area of the catalyst; ▪ Reduced catalytic and adsorption capacities to be considered for catalyst's reuse.
Effect of radical scavenger TBA
▪ Faster degradation of target compounds proves that the degradation occurs mainly via direct pathway by reaction with molecular O_3; ▪ Decreased or inhibited removal of target compounds proves that the degradation occurs via indirect radical pathway in the bulk solution.
Removal Mechanism in catalyzed ozonation
▪ Reaction between target compounds adsorbed on the surface of the catalyst and O_3 or radicals in the bulk solution can cause them to desorb and increase TOC; ▪ Decomposition of O_3 into radicals in the bulk solution that react with target compounds; ▪ Reaction between target compounds and surface oxygenated radicals formed upon decomposition of O_3 on the catalyst's surface; ▪ Removal of target compounds by adsorption on the catalyst.
Impact of catalytic ozonation
▪ While single and catalytic ozonation can have a comparable effect on the removal of target compounds, catalytic ozonation can enhance TOC removal promoting mineralization; ▪ Catalytic ozonation reduces the acute toxicity (Microtox®) more than single ozonation.

2.2.3. Bridging the gaps for better understanding and application of PAC-catalyzed ozonation

2.2.3.1. Catalyst characterization

Detailed characterization of the catalyst is common in most studies on AC-catalyzed ozonation mainly with the purpose of proving or justifying the speculated catalytic mechanism. It includes the measurement of pH_{pzc}, and surface area with N_2 adsorption isotherm, in addition to the characterization of the surface structure and chemistry with X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) and the quantification of adsorbed material with Fourier-transform infrared spectroscopy (FTIR). There is no doubt that these techniques help demonstrate the changes on the surface of PAC during the catalytic ozonation process, the doubt arises upon the interpretation of the causes of those changes should they exist.

Moreover, the exact composition of AC has an important role. For instance according to Sanchez-Polo et al. (2005), determining the ash content of AC can affect the interpretation of the catalytic mechanism since some metals on the surface of AC can act as catalysts. Also, it is claimed that those metals in addition to the basic surface functional groups induce the decomposition of O_3 in catalytic ozonation. For this reason, pre-treating AC with O_3 prior to AC-catalyzed ozonation can reduce the basic surface functional groups and the surface area. And while this does not affect the pores, it still can reduce the efficiency of AC in the treatment and therefore longer exposure time will be required. This study concluded that AC is an initiator or promoter of O_3 decomposition rather than a catalyst. In a later study (Sánchez-Polo et al., 2007), it was concluded that the role of AC when coupled with O_3 in drinking water treatment is to catalyze the degradation of O_3 and formation of $^{\bullet}OH$ along with the adsorption of organic matter and alkalinity reduction. Alvarez et al. (2008) agreed with the previous study stating that O_3 chemisorbs onto the surface of AC by oxidizing the surface basic groups and that the presence of ash catalyzes its decomposition. The authors confirmed that the reuse of AC as catalyst is inefficient unless it is preceded by a reactivation process to reproduce basic functional groups. Jaramillo et al. (2010) further confirmed that O_3 reacts with the basic surface groups generating acidic oxygenated groups. Dehouli et al. (2010) supported the concept of O_3 sorption onto AC but refuted that it reacts with basic groups. Instead, the authors suggested that O_3 and OH^- from the bulk adsorb on the AC surface and react together. The researchers argued that the presence of basic negatively charged groups on AC results in the repulsion of OH^-, thus preventing the interaction with O_3. Dehouli et al. thus concluded that the presence of acidic groups affects the interaction between O_3 and AC.

2.2.3.2. Dosage

The common ranges of applied O_3 doses for MPs' removal are reported per mg DOC as specific O_3 doses: 0.21 - 1.53 mg O_3/mg DOC (Song et al., 2017; Zimmermann et al., 2011). Several studies exceeded those values disregarding the importance of oxidant dosage in real applications in WWTPs in terms of increased cost, by-products formations and effluent toxicity.

Literature unveils a wide range of PAC doses (10 to 1000 mg/L) and particle sizes applied in catalytic ozonation in a clean water matrix. These significantly wide ranges were often coupled with high doses of target compounds in the mg/L range which clearly exceeded the real environmental concentrations and only satisfied research purposes. It was reported that 2 – 3 g PAC/g DOC is the common specific PAC dose applied in secondary treatment (Rizzo et al., 2019). Still, the majority of the research on this topic showed no attempt to justify the doses of O_3 or catalyst used. The effect of the catalyst dose was rarely presented with any data showing the least catalyst dose required to achieve catalytic activity under certain conditions. In practicality, less is more which means that maintaining the doses of O_3 and the catalyst at a minimum to achieve the maximum removal of contaminants is the most efficient option.

2.2.3.3. Catalytic mechanisms and pathways – Concept validation

Studying the mechanisms involved in the degradation of a specific compound or a mixture of compounds by catalytic ozonation is reported in literature through an evaluation of the effect of radical scavenger addition on the removals. TBA is the most used $^{\bullet}OH$ scavenger in literature on catalytic ozonation and its applied doses have not been justified. In AC-catalyzed ozonation, it was never clear if the dose of the radical scavenger added is related to the dose of the oxidant or that of the target compound, and if the radical scavenger can interfere in the catalytic ozonation system for instance by adsorbing onto the AC and affecting its interaction with O_3 and target compounds. Faria et al. (2008a) reported two mechanisms of AC catalytic ozonation. In the first mechanism, AC acts as an initiator for O_3 decomposition into $^{\bullet}OH$ in solution which in turn oxidizes the adsorbed MPs. In the second mechanism, molecular O_3 adsorbs and reacts with the AC surface generating surface radicals that attack the adsorbed MPs so that degradation occurs on the surface of the catalyst. These two proposed mechanisms assume that all degradation reactions occur on the surface and do not consider reactions in the bulk especially since not all types of MPs have high affinity for adsorption. Moreover, the organic carbon that is introduced in the system along with TBA contributes to the TOC measured and thus affects the interpretation of the level of mineralization that could be achieved.

It is remarkable that all studies on PAC-catalyzed ozonation resorted to TBA to scavenge $^{\bullet}OH$ as one approach towards proving the catalytic mechanism. There was no attempt to evaluate the formation and role of other types of radicals presumably because it is common to assess catalysis by the generation of $^{\bullet}OH$, yet the mechanism can be more complex and other strong oxidizing agents or radicals can undertake major roles in the degradation of target compounds.

Current trends in studying catalytic ozonation mechanisms resorted to investigating the formation of radials through electron paramagnetic resonance (EPR) spectroscopy as an alternative to radical probing (Song et al., 2019; Wang et al., 2019b). EPR is however not new, it has been applied for decades to identify free radicals: it involves using a spin trap to capture the free radical and form the adducts that are detected by EPR spectroscopy (Buettner, 1987). To the best of our knowledge this technology has not been used in PAC-catalyzed ozonation yet. It is crucial to consider however the strong adsorbing capacity of PAC and the impact that entails on the spin traps used in EPR systems and therefore the accuracy of the results.

2.2.3.4. Intermediates, by-products and toxicity tests

It is possible that the identification of intermediates and by-products during catalytic ozonation is one of the most meticulous tasks in the study. That is because they can form in very small concentrations posing challenges for quantification. They can also help justify the evolution of TOC through the experiment, and exacerbate the pollution and toxicity problems since some have been recognised as more toxic than the parent compound. Actually, toxicity tests have been performed in clean matrices with one or a few MPs using different types of Microtox® assays with *vibrio fischeri* (Goncalves et al., 2012; Gonçalves et al., 2014) and *daphnia magna* (Rozas et al., 2017). This approach might not be fully relevant as it does not portray realistic concentrations occurring in wastewater effluents and does not consider the synergistic effect of the mixture of contaminants, so it cannot reflect the real environmental hazard imposed on the receiving waters.

2.2.3.5. Matrix effect

In real water or wastewater applications, the complexity of the matrix has a huge implication on the reaction pathways and eventually on removals. Many factors can interfere or compete for the reaction with molecular O_3 and the radicals produced in the system which can hinder the removal of targeted compounds in wastewater. As such, there are many considerations for upscaling a bench scale study to a full-scale application for the degradation of specific pollutants.

One important parameter that cannot be overlooked when studying the efficiency of catalytic ozonation in real matrices is dissolved organic carbon (DOC) which is known to promote O_3 decomposition (at low concentrations), scavenge $^{\bullet}OH$ radicals (at high concentrations) and possibly reduce the catalyst's activity by adsorbing to its surface. Sanchez-Polo et al. (2005) proved that the effect of DOC on the catalyst's activity is not very significant; the authors ascertained that the presence of catalyst (AC) boosted the AOP with DOC adsorption. Kovalova et al. (2013) compared DOC removal by adsorption onto PAC to that by oxidation with O_3 and attested that the level of mineralization by O_3 was minimal compared to that by PAC.

Alkalinity and nitrites are other parameters that can weigh in the ozonation process and they can readily react with O_3 (Lee et al., 2013). They are rarely taken into account when real matrix is studied while they can impact the O_3 dosage. Similarly, the microbiological quality of the treated matrix affects O_3 consumption during treatment. Thus, considering O_3 for both disinfection and oxidation must entail satisfying the initial O_3 demand of the wastewater and securing enough residual to react with the target components.

2.2.3.6. Experimental limitations

The effect of pH in these oxidation experiments is of utmost importance, and is often neglected in the analysis of results. The high concentration of target compounds is reflected in the initial pH of the solution which has been mostly leaning towards the acidic side. Those studies tend to adjust the pH instead of using buffer. The importance of the solution's pH lies in the huge impact pH has on the interactions between the oxidant, the catalyst and the target compound. On one hand, it is not new that O_3 decomposition pathway is driven by the solution pH, whereby in acidic environment, the direct pathway is favored, i.e. the reaction between molecular O_3 and the target compound; yet in basic environment the indirect pathway is favoured, and that is the molecular O_3 decomposition into $^{\bullet}OH$ and the subsequent reaction between those radicals and the target compound. On the other hand, the solution pH affects the surface characteristics of PAC when assessed against the pH_{pzc}. As such, when the solution pH exceeds the pH_{pzc} of AC, more basic surface functional groups are expected, while when pH is lower than pH_{pzc} more acidic surface functional groups are expected. The surface chemistry of AC plays an important role in the interaction with O_3 and the target compounds. Finally, the solution pH also affects the chemistry of the target compound: if the solution pH is higher than pKa, of the compound, the latter is expected to be present in the system mainly in the deprotonated form, and if the pH is lower than pKa, the protonated forms are expected to be more abundant. The prevalence of the acidic or basic form of the target compound can be connected to the possibility of its adsorption onto the surface of AC.

At the same time, attempting to maintain the pH during the experiment at a fixed preferred value through the addition of buffer risks the introduction of species in the system that can interfere with the interaction between O_3/AC/target compound through either influencing the O_3 decomposition rate or adsorbing onto the surface of the catalyst or preferentially affecting the abundance of either the protonated or deprotonated form of the target compound. In contrast, a simple pH adjustment is performed to ensure specific initial conditions but is not enough to mitigate for the pH changes incurred by the reactions and impacting their pathways and thus cannot reasonably simulate real applications in natural waters and wastewaters. Accordingly, discussing the role of the pH in the reaction mechanism is of high importance.

In a catalytic oxidation system using activated carbon, a very renowned adsorbent, adsorption becomes a crucial means of removal not only for the target compound, but also for any other species in the system. These include the buffer where there might be some interaction between the buffer and the surface of AC hindering or affecting the interaction with O_3 and generation of radicals. Another limitation comes with the addition of organic $^{\bullet}OH$ scavengers, such as TBA, which add up to the total organic carbon and interfere with reporting the total level of mineralization achieved in catalytic ozonation.

2.2.3.7. Fate of the catalyst: recovery and reuse or disposal

When PAC in particular is used to catalyze the decomposition of O_3, important issues can arise pertaining to its application in WWTPs. First, there is the issue of its fate: recuperation and regeneration or recuperation and safe disposal or discharge with the effluent without risks to the receiving environment. This requires a meticulous understanding of the PAC size and the difficulty of its recuperation after suspension. If the recuperated PAC is destined for reuse, then there is a need for its reactivation especially after the surface changes caused by exposure to O_3 and adsorption of organic matter. If not, the recuperated PAC should be destined for final disposal with the other sludge generated at the WWTP. If those cannot be applicable, then disposal with the effluent is the least cumbersome yet a detailed assessment regarding its effect on the aquatic life and sediments is needed. Second, there is the issue of the additional cost it can entail for purchase, storage and disposal if any specific disposal measures are required. This can only be addressed through a case-specific cost analysis.

2.2.4 Conclusions

The use of O_3 for the oxidation of MPs has been tested and recommended by many researchers. Yet the fact that many MPs are not reactive with molecular O_3 prompted the addition of a catalyst such as PAC to enhance the formation of radicals. Those are capable of oxidizing more compounds by virtue of their non-selectivity and strong oxidizing potential. The exact mechanism of formation of those radicals along with the mechanism of oxidation of MPs appear to be case-specific. Significant efforts have been made to assess the efficiency of catalytic ozonation at bench-scale level. However, scale-up, cost analysis, and full-scale applications need further investigation.

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CHAPTER 3 Bench to Full-scale Enhanced Primary Treatment of Municipal Wastewater under Wet Weather Flow for Minimized Pollution Load: Evaluation of Chemical Addition and Process Control Indicators [1]

3.1. Introduction

Wastewater collection networks represent a fundamental component of a city's infrastructure and its wastewater treatment process. In areas where those networks are designed to accommodate storm water runoffs in addition to regular domestic and industrial wastewaters, they become known as combined sewers. Their operation thus varies seasonally, reaching its full capacity during events of heavy rain and intensive snow melts. In such cases, wastewater treatment plants (WWTPs) to which those networks are connected become unable to contain the excess wastewater during wet weather conditions. Consequently, untreated wastewater ends up overflowing to the closest water stream as per the combined sewer system design. According to the USEPA (2018) this is known as combined sewer overflow (CSO) and it includes regular untreated wastewater diluted by storm water. The volume of poorly treated or untreated CSO and the frequency of its discharge will essentially contribute to the concentration of pollutants (including pathogens, organic and inorganic chemicals) in the receiving water body, and consequently will affect its suitability for drinking or recreational purposes. Problems with the discharge of untreated CSO can transcend, impacting the aquatic ecosystem and public health with detrimental waterborne diseases (Jalliffier-Verne et al., 2015). It is reported that in Canada, 87% of the population is connected via a wastewater collection network to certain type of treatment,

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and that only few treatment plants undertake the initiative to store and treat CSO. As such, direct discharges from CSO have not been routinely monitored (Canada, 2019; CWN, 2018).

CSO is commonly characterized in terms of its mass loading of macropollutants. Some of its major constituents include around 45-114 NTUs, 83-600 mg/L of total suspended solids (TSS), 30-180 mg/L of biochemical oxygen demand (BOD), 80-200 mg/L of chemical oxygen demand (COD), 80-190 mg/L of total phosphorus, and 30-50 mg/L of ortho-phosphate (ortho-P) (El Samrani et al., 2008a; Gasperi et al., 2008; Li et al., 2004). CSOs can also be a relevant source of micropollutants (MPs) (pharmaceuticals, personal care products, herbicides and pesticides) as WWTPs (Kay et al., 2016; Phillips et al., 2012) and thus imply similar adverse effects on aquatic and terrestrial fauna and flora (Shu et al., 2016). Ryu et al. (2014) estimated that physical, chemical and biological processes in a WWTP can decrease the MPs in the effluent by 28% as compared to 97% decrease in suspended solids and 86% decrease in COD. This relatively low removal sheds the light on the importance of screening and modeling approaches to estimate the overall load of MPs in the environment and mitigate their cost-prohibitive and impractical quantification (Arlos et al., 2014; Johnson & Williams, 2004; Launay et al., 2016; Mutzner et al., 2016; Tolouei et al., 2019).

During wet weather conditions El Samrani et al. (2008a) demonstrated that the aluminum-based coagulant PACl was more efficient than $FeCl_3$ for CSO treatment. It had a lower optimum dose and allowed a pronounced reduction of turbidity and associated metals such as copper, lead, zinc and chromium. Gibson et al. (2016) reported similar effect on turbidity removal with alum coupled with a cationic polymer; yet, no major impact on TSS removal or percent ultraviolet transmittance (%UVT) was observed.

As a matter of fact, the addition of a coagulant that comes as a natural or synthetic polymer or a metal salt, initiates the colloidal destabilization and aggregation resulting in the formation of larger particles able to settle out. Different mechanisms can be involved in the particles removals depending on the water quality and coagulant dose (Pourrezaei et al., 2011). Particularly, during coagulation with aluminum-based salts, the salt hydrolysis product is responsible for particles destabilization (Exall & Marsalek, 2013). Two important precipitation reactions take place when alum is added to wastewater. The first one occurs between alum and calcium bicarbonate and produces aluminum hydroxide precipitate that can enmesh and remove colloids (Reaction 3.1). The second one occurs between alum and phosphorus and produces insoluble aluminum phosphate (Reaction 3.2) (Cao et al., 2010).

$$Al_2(SO_4)_3 \cdot 18\,H_2O + 3\,Ca(HCO_3)_2 \leftrightarrow 3\,CaSO_4 + 2\,Al(OH)_3 + 6\,CO_2 + 18\,H_2O \quad \textit{Reaction 3.1}$$

$$Al^{3+} + PO_4{}^{3-} \leftrightarrow AlPO_4 \quad \textit{Reaction 3.2}$$

Following coagulation, larger particles or flocs are formed during flocculation by colloidal aggregation. This process is induced by mixing and polymer addition to strengthen the formed flocs (Young et al., 2000). Settling entails the separation of solids from the liquid and is the last step in the process. In real applications, settling can take place in sedimentation tanks often enhanced by plate settlers that promote large surface area and short settling distance. While the role of plate settlers is to maximize the particles removal, their efficiency remains a function of their geometric design, the wastewater quality and flow conditions (Sarkar et al., 2007).

To the best of our knowledge no study on the treatment of wet weather primary influent (PI) or CSO has comprehensively addressed the upscaling of coagulation conditions and the evaluation of process control indicators. Most studies were limited to bench or pilot-scale levels (El Samrani et al., 2008b; Exall & Marsalek, 2013; Li et al., 2003; Zhu et al., 2007). Evidence of full-scale application of the optimum coagulant dose is also scarce in literature (Baghvand et al., 2010; El Samrani et al., 2008b; Guida et al., 2007; Wang et al., 2015b). Few studies only evaluated the performance of disinfectants at full-scale level using performic acid and peracetic acid (Chhetri et al., 2016; Chhetri et al., 2015; Chhetri et al., 2014). In this study, we undertook a practical approach towards the EPT of CSO to maximize the output, i.e. the quality of the effluent, while minimizing the chemical input.

The main objective of this chapter was to evaluate the performance of different coagulants and coagulant aids for the enhanced primary treatment of municipal wastewater during wet weather conditions at bench-scale level. The application of those compounds at full-scale level was investigated in order to optimize the EPT at the WWTP, its online process control, and the overall discharge of suspended solids and ortho-phosphate into the receiving environment.

3.2. Material and methods

3.2.1. Wastewater

Samples of municipal wastewater were collected in 20 L plastic pails from the influent stream (i.e., primary influent (PI)) to the Enhanced Primary Treatment (EPT) unit of a WWTP in central Edmonton between November 2016 and March 2017 and between August and October 2017 (Figure 3.1). The collected grab samples of PI during wet weather flow were transported to the laboratory for a preliminary characterization for TSS. During dry weather, PI samples were diluted with deionized water to the desired TSS concentration to emulate the average TSS value during wet weather flow. The obtained wastewater was immediately used in the coagulation/ flocculation experiments.

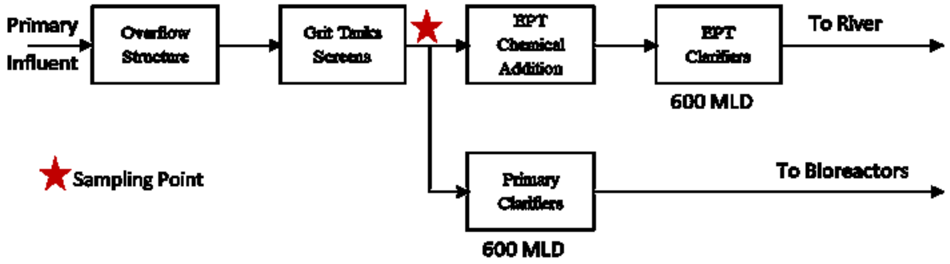


Figure 3.1 Simplified representation of the EPT system

3.2.2. Coagulants and polymers

All coagulants and chemicals used in the laboratory analyses were purchased from Fisher Scientific, except PACl which was obtained from ClearTech in the form of a stock solution of 4.6 mol/L. Polymers were purchased from SNF Inc., BASF, Kemira and AS Paterson. Stock solutions of coagulants and polymers were prepared in the laboratory by dissolving the respective solutes in deionized water to the desired concentration; they were then stored at 4 °C for up to four days until used in the jar test.

3.2.3. Jar test

During the coagulant and polymer optimization studies, three B-KER^2 Jar Test apparatuses with 3-inch wide Phipps & Bird stirrers were used for each mixing condition to cater for duplicate test runs. Jars and stirrers were thoroughly cleaned with phosphate-free detergent and rinsed with deionized water before and after each use. At the beginning of each experiment, jars were filled with 2 L of homogenized wastewater, then the designated doses of coagulants and polymers were consecutively added to the jars before turning the impellers on. In all experiments, one jar remained free of chemical addition to represent the effect of mixing only. Rapid and slow mixing were performed sequentially before stopping the impellers and carefully removing the stirrers in each apparatus to avoid any media disturbance. Settling was then allowed for one hour after which the supernatant was collected with syringes immersed at 2 inches below the surface. Samples were stored in dark glass bottles at 4°C for analysis.

A 2^3 factorial design was adopted to determine the impact of rapid and slow mixing conditions and coagulant doses on the coagulation/ flocculation process of the wastewater (Table 3.1). These factors were selected due to their influence on the destabilization and aggregation process as well as their easy manipulation at bench-scale level. Keeping in mind that these factors are among the most important ones impacting the coagulation / flocculation efficiency and that various other factors have also been studied such at pH and temperature (Afzal et al., 2011; Chelme-Ayala et al., 2012; Chelme-Ayala et al., 2011a; Pourrezaei et al., 2010).

Table 3.1 Details of the 2^3 factorial design used for the coagulants assessment.

Factor	High Level	Low Level
Rapid Mixing Gt	68400 (300 rpm – 3 min)	9300 (150 rpm – 1 min)
Slow Mixing Gt	27600 (30 rpm – 20 min)	6000 (15 rpm – 10 min)
Coagulant Dose	125 mg/L Alum (10.14 mg Al/L) 105 mg/L PACl (10.14 mg Al/L) 61 mg/L $FeCl_3$ (20.95 mg Fe/L)	50 mg/L Alum (4.05 mg Al/L) 42 mg/L PACl (4.05 mg Al/L) 24 mg/L $FeCl_3$ (8.38 mg Fe/L)

In total, there were four replicates for each measurement performed in the factorial design. Three different coagulants were tested: alum, PACl and $FeCl_3$. Literature was screened to identify the most common applicable doses of alum in the treatment of wet weather PI. In general, doses ranged between 25 and 200 mg/L, with 100 mg/L alum being identified for maximum COD removal and %UVT (Gibson et al., 2016; Jung et al., 2015; Wang et al., 2015b). Accordingly, the alum doses decided upon in this study were 50 and 125 mg/L as they represent a reasonable range of values. Metal-equivalent doses were then calculated to identify the corresponding doses of PACl and $FeCl_3$ (Table 3.2). They were elaborated based on the molar equivalent for the consumption of the same amount of alkalinity (Reactions 3.1 and 3.3), according to which 2 moles of $FeCl_3$ are equivalent to 1 mole of alum. 1.25 mg/L cationic polymer (Table 3.7) was also uniformly added in all jars along with the coagulant.

Table 3.2 Calculations of metal-equivalent coagulant doses.

Coagulant	**Coagulant Molecular Weight (MW) (g/mol)**	**Active Species: Molecular Weight (g/mol)**	**Coagulant dose (mg/L)**	**Metal concentration (mM)** $= \left(\frac{\text{Coagulant dose } (\frac{mg}{L})}{\text{Coagulant MW } (\frac{mg}{mol})}\right) \times n^*$	**Metal-equivalent Dose (mg Al or Fe/L)**
Aluminum Sulfate: Alum ($Al_2O_{12}S_3.18H_2O$)	666.42	Al: 27 g/mol	25	0.07	2.03
			50	0.15	4.05
			75	0.23	6.08
			100	0.30	8.10
			125	0.37	10.14
			150	0.45	12.15
Ferric Chloride ($FeCl_3$)	162.2	Fe: 55.84 g/mol	24.34	0.15	8.38
			60.85	0.37	20.95
Coagulant	**Density** (g/mL)	**Metal-equivalent Dose** (mg Al/L)	**Volume of PACl required in 2 L Jar** (mL)	**Mass of PACl required in 2 L Jar** (mg)	**Coagulant dose** (mg/L of PACl)
Polyhydroxyl Aluminum Chloride ** (PACl)	1.37	4.05	0.061	83.57	41.78
		10.14	0.154	210.98	105.49

Notes:

* n= mol of Active species in 1 mol of coagulant.

** PACl (Clear PAC 180) with a Specific Gravity of 1.37 (according to the manufacturer) was obtained in a solution form and was characterized in the lab for Al content. Results indicated the Al content of PACl as 131589.16 mg Al/L and calculations were made accordingly.

Reference equations for Alum and $FeCl_3$ in wastewater:

$Al_2(SO_4)_3 \cdot 18H_2O + 3Ca(HCO_3)_2 \Leftrightarrow 3CaSO_4 + 2Al(OH)_3 + 6CO_2 + 18H_2O$

$2FeCl_3 + 6H_2O + 3Ca(HCO_3)_2 \Leftrightarrow 3CaCl_2 + 2Fe(OH)_3 + 6CO_2 + 12H_2O$

Two levels of rapid mixing with Gt values 68400 and 9300 and two levels of slow mixing with Gt values 27600 and 6000 were applied. Where "G" is the velocity gradient and "t" is the mixing time. Conversions from rpm-min to Gt are presented in Table 3.3.

$$2FeCl_3 + 6\,H_2O + 3\,Ca(HCO_3)_2 \leftrightarrow 3\,CaCl_2 + 2\,Fe(OH)_3 + 6\,CO_2 + 12\,H_2O \quad \textit{Reaction 3.3}$$

Table 3.3 Conversion of mixing conditions from rpm, min to Gt (Based on B-KER^2 – Phipps & Bird Specifications).

Factor	Level	Speed		Time		Gt
		rpm	G (s^{-1})	T (min)	t (s)	
Rapid Mixing	High	300	380	3	180	68400
	Low	150	155	1	60	9300
Slow Mixing	High	30	23	20	1200	27600
	Low	15	10	10	600	6000

Eight anionic polymers (labeled A to H) and one cationic polymer were arbitrarily selected and their performances as coagulant aids were evaluated at a bench scale using a jar test with alum as the primary coagulant. Similar mixing conditions were applied with all polymers uniformly injected with alum. After one hour of settling time, samples were collected from the supernatant. They were screened for TSS, turbidity and ortho-P. The polymer that revealed highest removals was selected and investigated under a range of dose combinations to identify the optimum condition for full-scale operation. All polymers were prepared from stock solutions and applied with a ratio of 100:1 as coagulant: polymer.

3.2.4. Full-scale application of alum/polymer

Different dose combinations of alum and polymer were tested at the existing EPT plant at the WWTP. The coagulant was dosed with mixing in the channel connected to the primary clarifier and the flocculent was dosed downstream with mixing in the channel connected to the flocculation chambers. Settling took place in the primary clarifier equipped with plate settlers for a retention time of approximately one to two hours.

3.2.5. Analytical methods

Samples were analyzed according to the Standard Methods for the Examination of Water and Wastewater (2012) for TSS (APHA (2017): Method 2540 D, using 0.45 μm filter paper), and COD (Method 5220 D). HACH method was used to measure ortho-P in filtered samples (HACH 8114 based on Standard Method 4500-P C). pH and turbidity were determined using Accumet Research AR20 pH/conductivity meter (Fischer-Scientific) and T-100 handheld Oakton Turbidity meter, respectively. UV absorbance (UVA) was measured at 254 nm using Thermo Scientific GENESYS 10S UV-Vis Spectrophotometer, and the %UV Transmittance (%UVT) was calculated using Equation 3.1. Data was analyzed using Microsoft Excel® which was also used to run the Three Factor ANOVA statistical test.

$$\%UVT = 100 \times 10^{-UVA} \qquad \textit{Equation 3.1}$$

3.3. Results and discussion

3.3.1. Wastewater quality

As part of this study, samples of PI during real wet weather conditions were collected at different rain occasions and analyzed for TSS. The average obtained TSS value was 150 mg/L. Accordingly; during dry weather, PI samples were diluted with deionized water to emulate real wastewater during wet weather flow. Also, during wet weather conditions and a flow rate of 1000 MLD, the recorded turbidity and ortho-phosphate values were 128 NTUs and 6.6 mg PO_4^{3-}/L respectively, while at lower flow rate of 276 MLD, those values increased to 212 NTUs and 12.7 mg PO_4^{3-}/L. The sampling period extended over one year with a total of 12 samples. Details on all parameters are included in Table 3.4.

Table 3.4 Water quality parameters of the untreated diluted primary influent (PI) used in the bench-scale experiment and the influent wastewater to the WWTP in the full-scale runs.

		pH	Turbidity (NTU)	TSS (mg/L)	%UVT	COD (mg O_2/L)	Ortho-P (mg PO_4^{3-}/L)
Bench-scale	**Range**	7.17-7.88	43-110	98-167	*N.M.*	160-361	2.10-6.35
	Average (±STDEV)	7.38 (±0.22)	88 (±22)	137 (±29)	*N.M.*	293 (±71)	4.48 (±1.88)
Full-scale	**Range**	6.71-7.29	87-192	138-364	33-57	*N.M.*	0.88-11.10
	Average (±STDEV)	7.13 (±0.16)	150 (±31)	224 (±59)	44 (±6.85)	*N.M.*	6.54 (±2.44)

*N.M. = Not measured

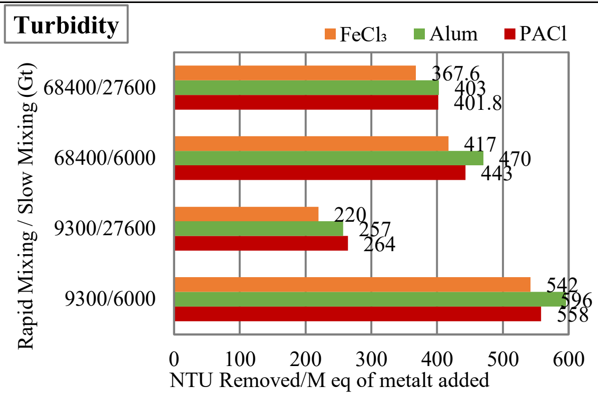
3.3.2. Performance assessment of coagulants

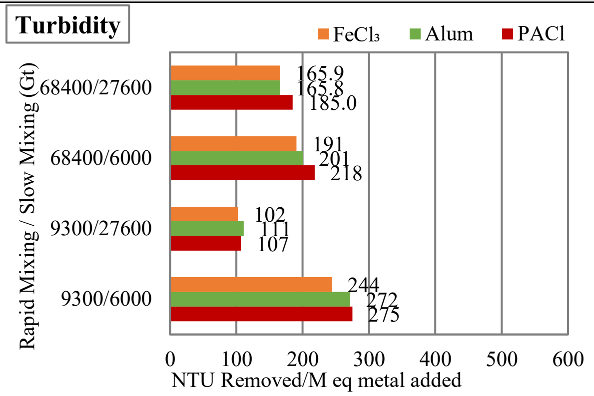
In general, the capacity of each coagulant to eliminate pollutants varied with the dose and mixing conditions. Neither mixing conditions nor coagulant type and dose affected the final pH of the wastewater which dropped slightly upon coagulant addition. At lower coagulant doses, the pH ranged between 6.90-7.21 for alum, 7.16-7.34 for PACl and 7.11-7.29 for $FeCl_3$. At higher coagulant doses, the pH of treated samples ranged between 6.35-6.99 for alum, 6.85-7.21for PACl and 6.74-7.10 for $FeCl_3$.

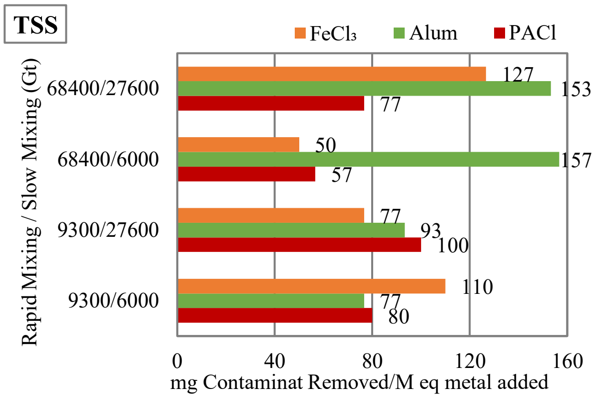
According to Figure 3.2, turbidity removal ranged widely between 102 and 600 NTUs/M of equivalent metal. The highest removal was obtained with low dose of alum and low level rapid and slow mixing. Alum and PACl revealed close performances with removals often more than double those with $FeCl_3$. It was also noticeable that at lower coagulant doses, higher removals were achieved throughout the four mixing conditions.

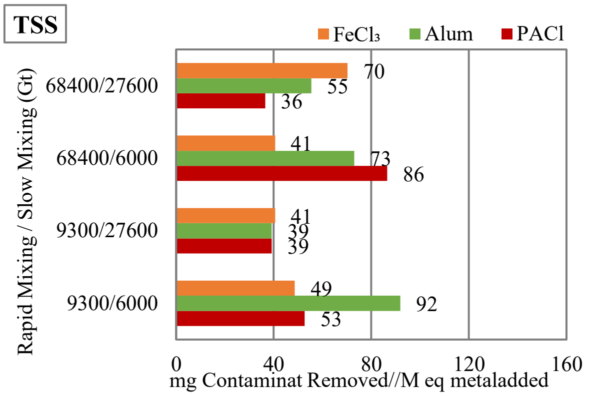
Results of TSS removal indicated that alum outperformed other coagulants. At low alum doses, the removal of TSS was the highest with high level rapid mixing (153 mg TSS removed by M equivalent of of Al added as alum). In contrast, at high alum doses, low level of rapid and slow mixing were optimum. This is in-line with the sweep coagulation mechanism that dominates at high coagulant doses and the efficiency of which is maximized by lower mixing intensity (Wei et al., 2015). Mixing showed different impact on TSS removal with PACl mainly because the flocs formed with PACl are more sensitive to breakage, and their settling velocity changes inversely with Gt (Dempsey et al., 1985; Yu et al., 2009). This is largely due to the fact that PACl acts on particles removal by sweep flocculation, which entails their enmeshment during precipitation (Wang et al., 2015a). So, at low dose where charge neutralization takes place, intensive rapid mixing provoked their irreversible shear, and at high dose, where sweep flocculation is in effect, intensive slow mixing lead to the same result. It is worth noting that in all cases, the final recorded TSS value was less than the target value set by the WWTP (30 mg/L).

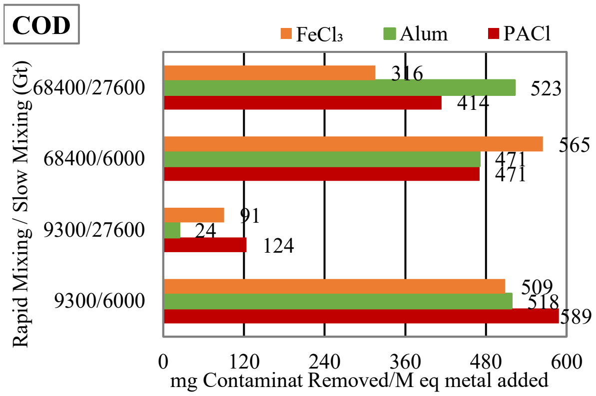
Low Coagulant Dose: 24 mg/L FeCl$_3$ (8.38 mg Fe/L), 50 mg/L Alum (4.05 mg Al/L) and 42 mg/L PACl (4.05 mg Al/L)	**High Coagulant Dose:** 61 mg/L FeCl$_3$ (20.95 mg Fe/L), 125 mg/L Alum (10.14 mg Al/L), and 105 mg/L PACl (10.14 mg Al/L)

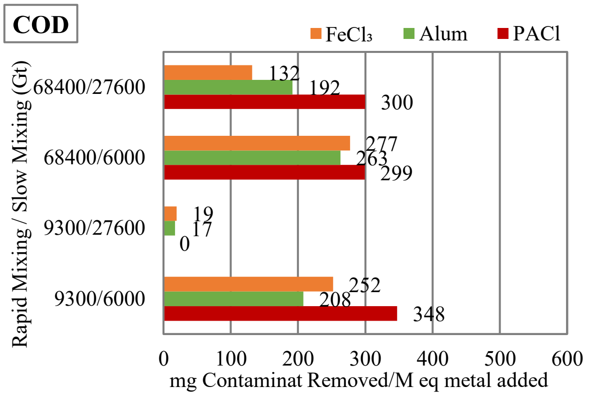












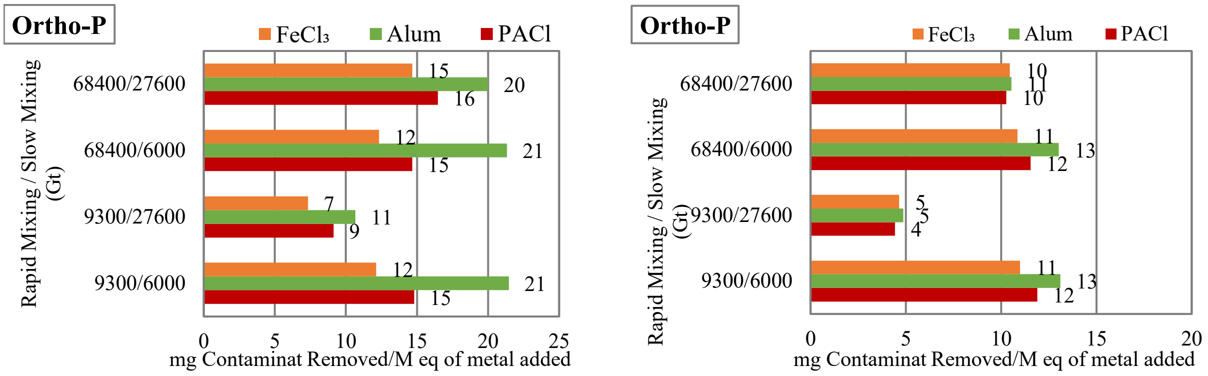


Figure 3.2 Mass of contaminant removed by 1 M equivalent of active metal at high and low coagulant doses. The effect of mixing and settling on the removal was excluded in the calculation. In untreated wastewater, the parameters ranged as follows: Turbidity 47.2-106.0 NTU; TSS 99-167 mg/L; COD 160-361 mg O_2/L; and Ortho-P 2.10-6.35 mg P/L.

With COD removal, the tested coagulant doses and mixing conditions turned out to have different effects. The condition of low-level rapid mixing with high level slow mixing was consistently the least favourable for all three coagulants, regardless of the dose. In most cases, PACl revealed better COD removal reaching up to almost 590 mg COD removed by M equivalent of active Al added as PACl. In fact, PACl is expected to exceed alum as it is a pre-polymerized coagulant that brings pre-formed stable aluminum hydroxide polymeric species to the matrix upon its addition. These species are also formed when alum is used and they are the product of alum hydrolysis (Jiang & Graham, 2010). Yet, with PACl application, they are readily available for longer time which justifies their higher potential for charge neutralization. Studies have demonstrated that for these reasons, PACl has high capacity to adsorb and remove dissolved organic carbon which would also imply removal of natural organic matter and lower COD (Jiang & Graham, 2010; Smoczynski et al., 2014). Alternatively, studies suggested increasing the dose of alum to improve COD removal (Zhou et al., 2008). Both Al-based coagulants were generally more efficient than $FeCl_3$ with which removal ratios ranged between 91 and 509 mg COD removed by M equivalent of Fe added as $FeCl_3$ at low dose.

The removal of ortho-P was best achieved with alum under all mixing conditions and doses, with the highest removal being 21 mg ortho-P removed by M equivalent of Al added. Similar to the results above, low coagulant doses lead to higher removal ratios, and $FeCl_3$ remained the least efficient among the three coagulants. The mixing intensity did not show significant impact on the removal of ortho-P which was also reported elsewhere (Ebeling & Ogden, 2004). Such observation can be associated with the formation of phosphate complexes that are influenced by pH and coagulant dose. When Al-based coagulants are applied, aluminum monomer species that form by the coagulant hydrolysis have the dominant effect on the formation of phosphate complexes (Trinh & Kang, 2015). It has been reported that iron-based coagulants are more effective for the removal of phosphate, while aluminum-based coagulants are more effective for the removal of COD (Smoczynski et al., 2014). This is not supported by our results that showed that $FeCl_3$ was less effective for the removal of both ortho-P and COD when applied in iron-equivalent doses comparable to those of the aluminum-based coagulants. This disagreement regarding the efficiency of both metal-based coagulants can be due to the different experimental conditions applied in both studies. As such, Smoczynski et al. (2014) used synthetic wastewater along with higher doses of aluminum and iron-based coagulant doses: 235 mg Al/L and 452 mg Fe/L, while we applied lower doses of both coagulants (10.14 mg Al/L and 20.95 mg Fe/L, equivalent to 0.37 mM of metal) on real wastewater.

The two components of mixing addressed in this study: intensity and time are generally capable of mitigating the effect each other. On one hand, studies have demonstrated that intense mixing provokes the breakage of flocs which results in small hard to settle particles and thus high turbidity (Yukselen & Gregory, 2004). On the other hand, long mixing time could reverse flocs breakage, yet this is not always guaranteed and tends to be less significant in metal-based coagulants (Yu et al., 2011; Yukselen & Gregory, 2004). For all those reasons added to the extra power requirements for mixing, high level rapid mixing conditions are generally not favoured.

Since, during the analysis of variance, the effects with values near-zero are generally attributed to experimental error or noise (Anderson, 2015), factors in the current ANOVA showing such effects were considered negligible regardless of their p-values. Overlooking all three coagulants, it could be noticed that while turbidity removal was unilaterally impacted by coagulant dose, there was no agreement on the factors, impacting the removal of TSS, COD and ortho-P across the studied coagulants (Table 3.5).

Table 3.5 Results of the Three-Factor ANOVA test showing the interactions between contaminants percent removals and the three factors: rapid mixing, slow mixing, and coagulant dose at 95% confidence level.

Factors	**Alum**							
	Turbidity % Removal		**TSS % Removal**		**COD % Removal**		**Ortho-P % Removal**	
	p-value	Effect *(±1.38)*	p-value	Effect *(±1.38)*	p-value	Effect *(±3.63)*	p-value	Effect *(±1.11)*
Rapid Mixing A	**0.000**	-5.71	**0.000**	-7.32	0.103	-6.15	0.051	-2.28
Slow Mixing B	0.151	1.24	0.207	1.78	**0.000**	-19.30	0.878	-0.17
Coagulant Dose C	**0.000**	5.53	**0.017**	3.52	0.278	-4.03	**0.000**	18.35
AB	**0.009**	-2.37	**0.000**	-6.78	**0.001**	-13.79	0.159	-1.61
AC	**0.004**	-2.63	**0.019**	-3.47	**0.033**	-8.20	0.829	0.24
BC	**0.026**	-1.99	**0.004**	-4.35	**0.000**	-21.09	**0.000**	-17.02
ABC	0.618	0.42	0.134	2.13	0.115	-5.94	0.051	2.28
	PACl							
	Turbidity % Removal		**TSS % Removal**		**COD % Removal**		**Ortho-P % Removal**	
	p-value	Effect *(±1.38)*	p-value	Effect *(±1.40)*	p-value	Effect *(±3.20)*	p-value	Effect *(±2.05)*
Rapid Mixing A	**0.015**	-1.24	**0.001**	-5.40	0.046	-6.75	0.924	-0.20
Slow Mixing B	**0.000**	3.84	0.772	0.41	**0.000**	-16.60	**0.007**	-6.09
Coagulant Dose C	**0.000**	11.32	**0.002**	4.89	**0.003**	10.61	**0.000**	22.29
AB	**0.005**	-1.48	**0.000**	-10.35	0.216	-4.07	0.282	2.26
AC	**0.000**	2.94	**0.000**	8.98	0.360	-2.98	**0.027**	4.83
BC	**0.000**	-5.65	**0.000**	-5.95	**0.004**	-10.27	**0.000**	-27.74
ABC	**0.000**	2.89	0.501	-0.96	0.080	5.85	**0.005**	6.39
	FeCl$_3$							
	Turbidity % Removal		**TSS % Removal**		**COD % Removal**		**Ortho-P % Removal**	
	p-value	Effect *(±1.38)*	p-value	Effect *(±1.35)*	p-value	Effect *(±3.55)*	p-value	Effect *(±1.34)*
Rapid Mixing A	**0.006**	-2.14	0.265	-1.54	0.057	-7.10	**0.000**	12.11
Slow Mixing B	**0.001**	2.61	**0.000**	-5.93	**0.000**	-18.81	**0.000**	-23.54
Coagulant Dose C	**0.000**	9.30	0.484	0.96	0.987	0.06	**0.000**	16.27
AB	0.479	-0.51	0.366	-1.24	**0.000**	-20.98	**0.000**	14.40
AC	0.871	-0.12	**0.000**	9.48	0.852	0.67	**0.000**	14.13
BC	0.741	0.24	**0.000**	-12.76	**0.004**	-11.48	**0.000**	-41.41
ABC	0.358	-0.67	0.294	1.45	0.757	1.11	**0.000**	15.50

As such, factors affecting TSS removal by alum and the extent of this effect differed from those with PACl and FeCl$_3$. In fact, all three studied factors (coagulant dose, mixing time and mixing speed) showed a minor effect on the removal of turbidity and TSS. Similar results were obtained by Zhu et al. (2010) during the treatment of liquid swine manure. COD removal by alum was mostly affected by slow mixing alone and slow mixing and coagulant dose combined, while with PACl and FeCl$_3$ slow mixing was the most impactful. Factors affecting the removal of ortho-

P by alum and PACl were the same (coagulant dose only and slow mixing and coagulant dose). It must be highlighted that slow mixing and/or coagulant dose combined unveiled the highest effect for the removal of ortho-P and COD across all three coagulants. So, in order to maximize the contaminants removal, these factors must be optimized.

The following ANOVA models (Table 3.6) were developed to predict the percent removal of the different contaminants with each factor at two levels.

Table 3.6 ANOVA models.

Turbidity % Removal by:	
Alum	88.57 – 5.71 A + 5.53 C – 2.37 AB – 2.63 AC – 1.99 BC
PACl	89.49 – 1.24 A + 6.84 B + 11.32 C – 1.48 AB + 2.94 AC – 5.65 BC + 2.89 ABC
$FeCl_3$	81.46 – 2.14A + 2.61 B + 9.30 C
TSS % Removal by:	
Alum	90.29 – 7.32 A + 3.52 C – 6.78 AB – 3.47 AC + 4.35 BC
PACl	86.36 – 5.40 A + 4.89 C – 10.35 AB + 8.98 AC – 5.95 BC
$FeCl_3$	85.66 – 5.93 B + 9.48 AC – 12.76 BC
COD % Removal by:	
Alum	58.33 – 19.30 B – 13.79 AB – 8.20 AC – 21.09 BC
PACl	63.47 – 6.75 A – 16.60 B + 10.61 C – 10.27 BC
$FeCl_3$	57.52 – 18.81 B – 20.98 AB – 11.48 BC
Ortho-P % Removal by:	
Alum	80.88 + 18.35 C – 17.02 BC
PACl	68.36 – 6.09 B + 22.29 CB + 4.83 AC – 27.74 BC + 6.39 ABC
$FeCl_3$	57.17 + 12.11 A – 23.54 B + 16.27 C + 14.40 AB + 14.13 AC – 41.41 BC + 15.50 ABC

3.3.3. Optimization of the alum dose

The above analysis deemed alum and PACl comparable for the removal of contaminants, yet alum is more cost efficient than PACl (with approximately 300 USD /MT of alum compared to 600 - 715 USD /MT of PACl), so it can be considered the best coagulant for full-scale application. In order to further optimize its dosage, a jar test was performed with a broader range of alum doses (0 to 150 mg/L) that were evaluated for the removal of TSS (Figure 3.3). Results demonstrated that with an alum dose of 75 mg/L, the final average TSS was 33 mg/L. Further increasing the alum dose decreased the TSS to below the target value of 30 mg/L to reach near a plateau. Therefore, we recommended 75 mg/L alum as the typical dose because higher doses would incur higher costs with minimal returns.

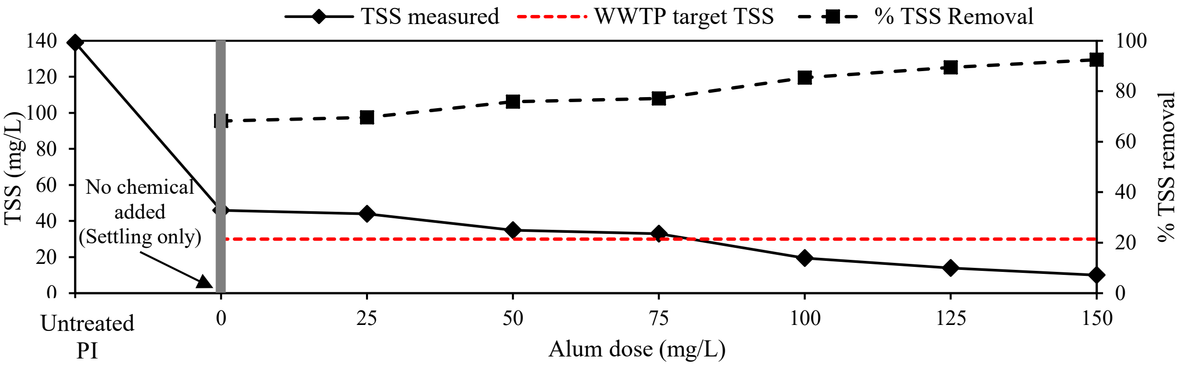


Figure 3.3 Effect of alum dosage on the removal of TSS from wastewater during wet weather conditions.

3.3.4. Effect of polymer type on the performance of alum in the treatment of wastewater during wet weather flow

As alum was deemed the best coagulant for wastewater treatment, an attempt was made to further improve its performance under the effect of different types of polymers. The WWTP is currently implementing anionic polymer A along with alum. Therefore, 7 other types of anionic polymers and 1 cationic polymer were put to test to assess the role of polymer addition. The chemical and physical properties of all polymers are available in Table 3.7.

Table 3.7 Chemical and physical properties of the polymers used in this study.

Polymer	Chemical Composition	Concentration (%)	Type	Density (g/cm^3)	pH
A	Distllates (petroleum , hyrdotreated light	20 to 23	Anionic	1	6 to 8
	Alcohol, c12-14, ethoxylated	0 to 3			
	Alcohol, c10-16, ethoxylated	0 to 3			
	Alcohol, c12-16, ethoxylated	0 to 3			
	Alcohol, c13-15, ethoxylated, branched and linear	0 to 3			
B	Distillates (petroleum) , hydrotreated naphthenic acid	15 to 40	Anionic	1.1	3.9-4.4
	Alcohol, c12-15,ethoxylated, propoxylayted	1 to 5			
C	Distillates petroleum, hyrdotreated light	22 to 25	Anionic	1.1	6 to 9.5
	Alcohol, c10-16, ethoxylated	0 to 3.6			
	Alcohol, c12-14, ethoxylated	0 to 3.6			
	Alcohol, c12-16, ethoxylated	0 to 3.6			
	(Z)-octadec-9-enylyamine, ethoxylayted	1.2 to 1.6			
	Ammonium acetate	2 to 10			
D	Distillates petroleum, hyrdotreated light	22 to 25	Anionic	1.1	5 to 8 at 5 g/L
	Alcohol, c12-16, ethoxylated	0 to 3.6			
	Alcohol, c12-14, ethoxylated	0 to 3.6			
	Alcohol, c10-16, ethoxylated	0 to 3.6			
	(Z)-octadec-9-enylyamine,ethoxylayted	1.2 to 1.6			
	Ammonium acetate	2 to 10			
E	Distillates (petroleum), hydrotreated naphthenic acid	20 to 45	Anionic	1.1	5 to 8 at 5 g/L
	Poly(oxy-1,2-ethanediyl), a-tridecyl-w-hydroxy-,branched	<3			
F	Poly(oxy-1,2-ethanediyl), a-tridecyl-w-hydroxy-,branched	<3	Anionic	1.1	5 to 8 at 5 g/L
	Distillates (petroleum), hydrotreated naphthenic acid	20 to 45			
G	Distillates (petroleum) hydrotreated light	<30%	Anionic	1	6 to 8
	Alcohol, C12-16, Ethoxylated	<5%			
	Alcohol, C12-14, Ethoxylated	<5%			
	Alcohol, C10-16, Ethoxylated	<5%			
H	Distillates (Petroleum) Hydrotreated Light	20 to 28 %	Anionic	1	6 to 8
	Alcohol, C10-16, Ethoxylated	<5%			
	Alcohol, C12-16, Ethoxylated	<5%			
Cationic	COCO DIETHANOLAMIDE	>=0.5 < 1 %	Cationic	0.62	4 at 10 g/L

The dose of coagulant: polymer was maintained constant at 100:1 and the mixing conditions were fixed at 300 rpm - 1 min for rapid mixing and 30 rpm - 20 minutes for slow mixing. Following the previous set of experiments, it was decided to investigate the performance of 75 mg/L alum applied with 0.75 mg/L polymer in terms of turbidity, TSS, % UVT and ortho-P removal. The obtained results (summarized in Figure 3.4) showed that while all tested polymers exhibited comparable performances, Alum with the anionic polymers A and B showed the best removal for all three tested parameters. All treated samples met the TSS and %UVT design values for the EPT effluent (30 mg/L and 40% respectively).

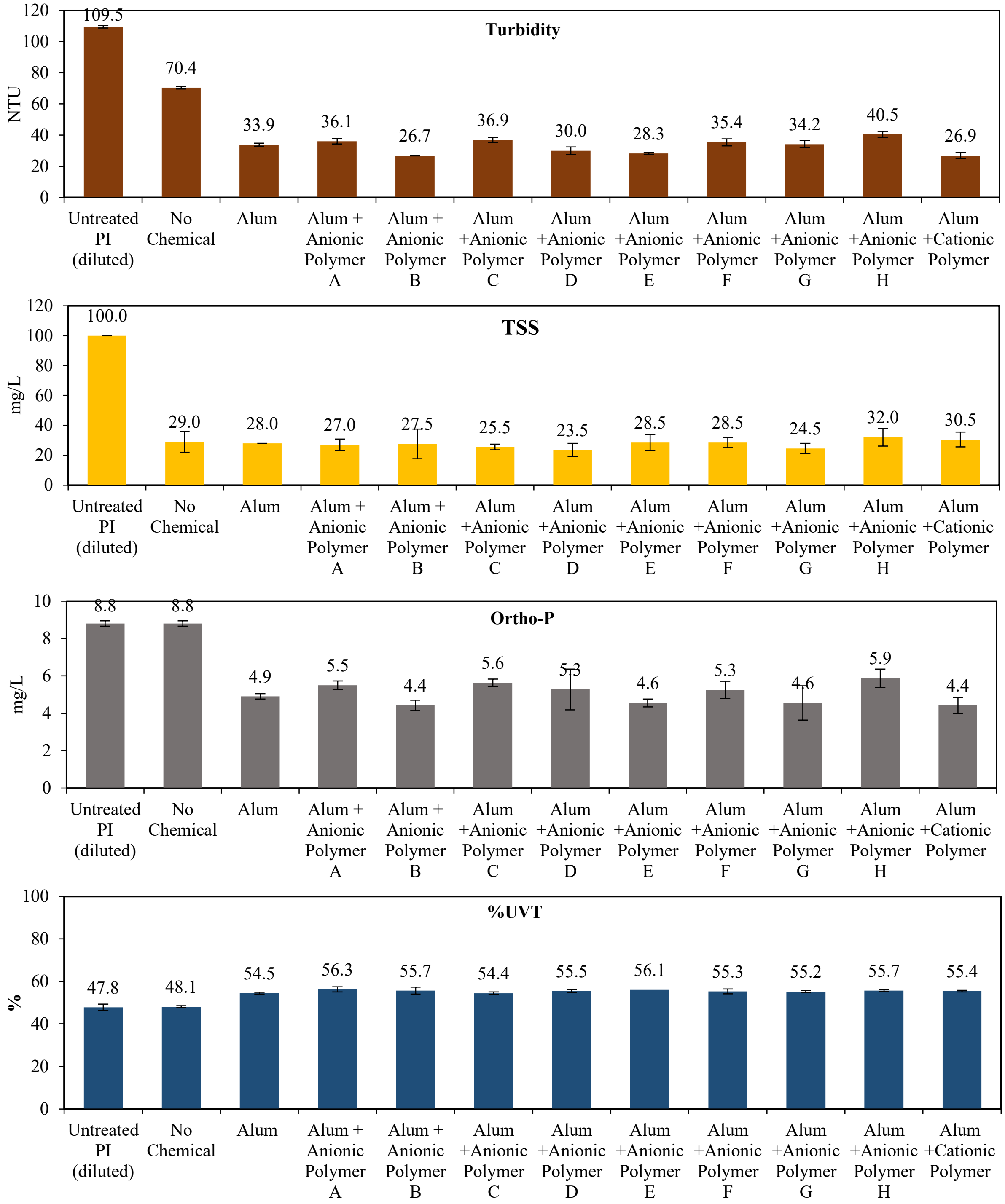


Figure 3.4 Effect of polymer addition on turbidity, TSS, ortho-P and %UVT (applied alum dose is 75 mg /L and polymer dose is 0.75 mg/L).

The addition of anionic polymer was further evaluated and the experiments were limited to polymer A which the WWTP was using during its operations at the time of this study. Thus, alum was applied with and without polymers A, (in doses ranging between 25/0.25 and 150/1.5 mg/L as alum/polymer (mg/L)) during a jar test and samples were analyzed for turbidity, TSS and ortho-P removal (Figure 3.5). With mixing only and no chemical addition, turbidity and TSS were significantly reduced compared to ortho-P. Adding alum only without polymers led to better removals compared to adding alum with polymer which is in line with findings from another study (Aguilar et al., 2005). An average alum dose of 75 mg/L achieved the target EPT effluent TSS value set by the WWTP (30 mg/L). Increasing the doses of alum and polymer did not efficiently improve the removals as samples treated with 125:1.25 alum/polymer could barely reach a final TSS value close to 30 mg/L. This may be referred to a mechanism of re-stabilization of particles in suspension due to the tremendous increase in the positively charged aluminum species (Saritha et al., 2017).

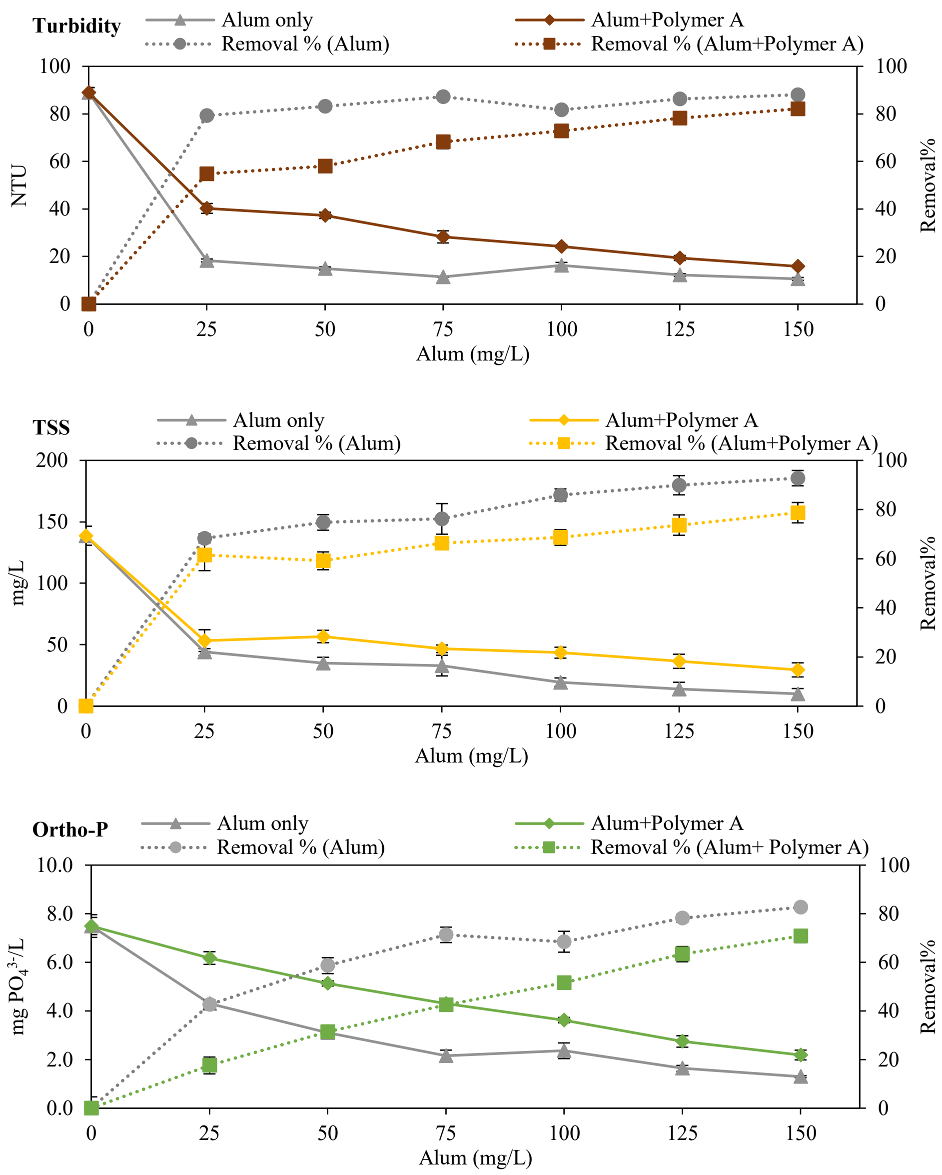


Figure 3.5 Impact of alum dose applied with anionic polymer A in a fixed dose ratio of 100:1 (as alum: polymer in mg/L) on the removal of turbidity, TSS and Ortho-P.

The removal of ortho-P is usually influenced by the wastewater quality including: initial ortho-P concentration, TSS, and pH, in addition to the type and dose of chemical added, and mixing conditions (Hussain et al., 2011). The pH of all tested samples was between 7.13 and 7.22 without adjustment, which is the optimum pH for ortho-P removal by alum and iron-based coagulants. During coagulation process, different aluminium and phosphate complexes are formed under specific pH values. It is reported that phosphorus adsorbs onto the hydrolysis products of the metal-based coagulants, this chemisorption results in precipitates that separate easily from the liquid. Changes in the pH can affect the favorable conditions for the formation of phosphate-aluminum complexes and the adsorption and desorption mechanisms (Smoczynski et al., 2014). The solubility diagram of aluminum hydroxide shows that pH dictates the form of hydrolysis products which are positively charged at low pH and negatively charged at high pH. It was found that the favourable pH for ortho-P removal by precipitation of aluminum phosphate ($AlPO_4$) is between 6 and 8 (David Jenkins & Menar, 1970). In this study, the removal of ortho-P was noticed to improve when higher chemical doses were applied; however less improvement was observed when alum doses exceeded 125 mg/L (Figure 3.5). Moreover, the application of anionic polymer might be hindering the removal of ortho-P as alum alone was able to achieve better removal.

3.3.5. Effect of alum and polymer addition during full-scale application

A detailed description of water quality parameters in the influent and effluent of the WWTP is available in Table 3.8.

Table 3.8 Water quality parameters of untreated and treated samples during full-scale application of Alum and Alum + Polymer A at the WWTP.

Sample ID	Date	Flow rate (MLD)	HRT (hr)	Turbidity (NTU)	TSS (mg/L)	Ortho-P (mg/L)	%UVT
PI*	18-Aug	131.5	2.92	126	208	11.25	24
PI	19-Aug	239	1.61	86.45	200	6.65	33
Alum (100 mg/L)	19-Aug			26	26	1	44
PI	24-Aug	250.7	1.53	164	240	9.9	30
EPT Effluent**	24-Aug			73.55	54	9	36
PI	13-Sep	259.7	1.48	165.5	188	7.75	36
EPT Effluent	13-Sep			72.1	32	8.88	48
PI	13-Sep	320	1.2	120.5	244	7.25	42
Alum + Polymer (A) (75/1.45) mg/L	13-Sep			30.75	38	2	45
PI	13-Sep	263	1.46	113.5	138	7.125	46
Alum + Polymer (A) (75/1.45) mg/L	13-Sep			23.35	26	0.88	51
PI	14-Sep	214	1.79	190	364	8.88	40
EPT Effluent	14-Sep			67.1	40	4.75	51
PI	14-Sep	269	1.43	149	200	6.75	44
Alum 75	14-Sep			42.9	44	1.38	52
PI	19-Sep	192	1	164.5	218	5.06	50
PI	19-Sep						
Alum + Polymer (B) (75/1.1) mg/L	19-Sep			21.2	28	0.88	53
PI	19-Sep	272	0.71	154	180	4	56
Alum + Polymer (B) (75/1.1) mg/L	19-Sep			68.55	64	0.5	68
PI	19-Sep	232	0.83	177.5	176	6.12	46
EPT Effluent	19-Sep			82.75	60	7.88	48
PI	19-Sep	306	0.63	215	360	2.63	62
Alum + Polymer (B) (75/1.1) mg/L	19-Sep			62.8	98	0.5	65
PI	20-Sep	144.7	1.33	190	248	9.38	38
EPT Effluent	20-Sep			197.5	150	8.5	41
PI	20-Sep	179.3	1.07	191.5	280	5.75	41
Alum + Polymer (B) (75/0.75) mg/L	20-Sep			57.3	56	2.5	45
PI	20-Sep	162.5	1.18	170.5	280	7.75	42
Alum + Polymer (B) (75/0.75) mg/L	20-Sep			35.15	40	1.38	45
PI	21-Sep	247.7	0.78	124.5	200	0.88	57
Alum + Polymer (B) (75/0.75) mg/L	21-Sep			14.085	14	0.25	62
PI	01-Oct	226	0.85	221	296	9.1	33
EPT Effluent	01-Oct			124	76	9.9	41
PI	02-Oct	167	1.15	147	244	11.1	43
Alum + Polymer (A) (75/0.75) mg/L	02-Oct			39.55	48	3.9	47

Notes:
* PI = Primary Influent to the WWTP.
** EPT Effluent = effluent from the primary clarifier without any chemical addition (i.e., after mixing and settling only).

The initial TSS values for all events from the full-scale application ranged between 168 to 296 mg/L. As shown in Figure 3.6, the results of coagulant addition were in line with the findings from the jar test confirming that 100 mg/L of alum was capable of achieving the target TSS design value (30 mg/L). In fact, this is expected since the primary clarifier is provided with lamella plate settlers to maximize the removal of suspended solids. Moreover, better removal was achieved with the lower dose of alum: polymer A 75/0.75 mg/L when the initial TSS was less than 200 mg/L. Yet, when initial TSS exceeded 200 mg/L, the same alum dose of 75 mg/L was unable to achieve the required removal even when increasing the polymer dose to 1.1 mg/L. It is therefore preferable to adjust the alum dose when the TSS values in the incoming PI are higher than 200 mg/L. Pollutants removals induced by the application of chemicals were evaluated against removals under the effect of lamella plate settlers (indicated by "No chemicals" in Figure 3.6). Results showed that the chemical addition is crucial for ortho-P reduction whereas the effect of lamella settler alone was almost null because ortho-P removal is mainly associated with precipitation (Gasperi et al., 2010; Mohammed & Shanshool, 2009). However, there was a noticeable reduction in TSS and turbidity where the main mechanism of removal is settling. In some cases, the effects of lamella settler on TSS reduction were comparable with the values obtained when chemicals were added. These findings are comparable to those reported by the effect of mixing only in the jar tests.

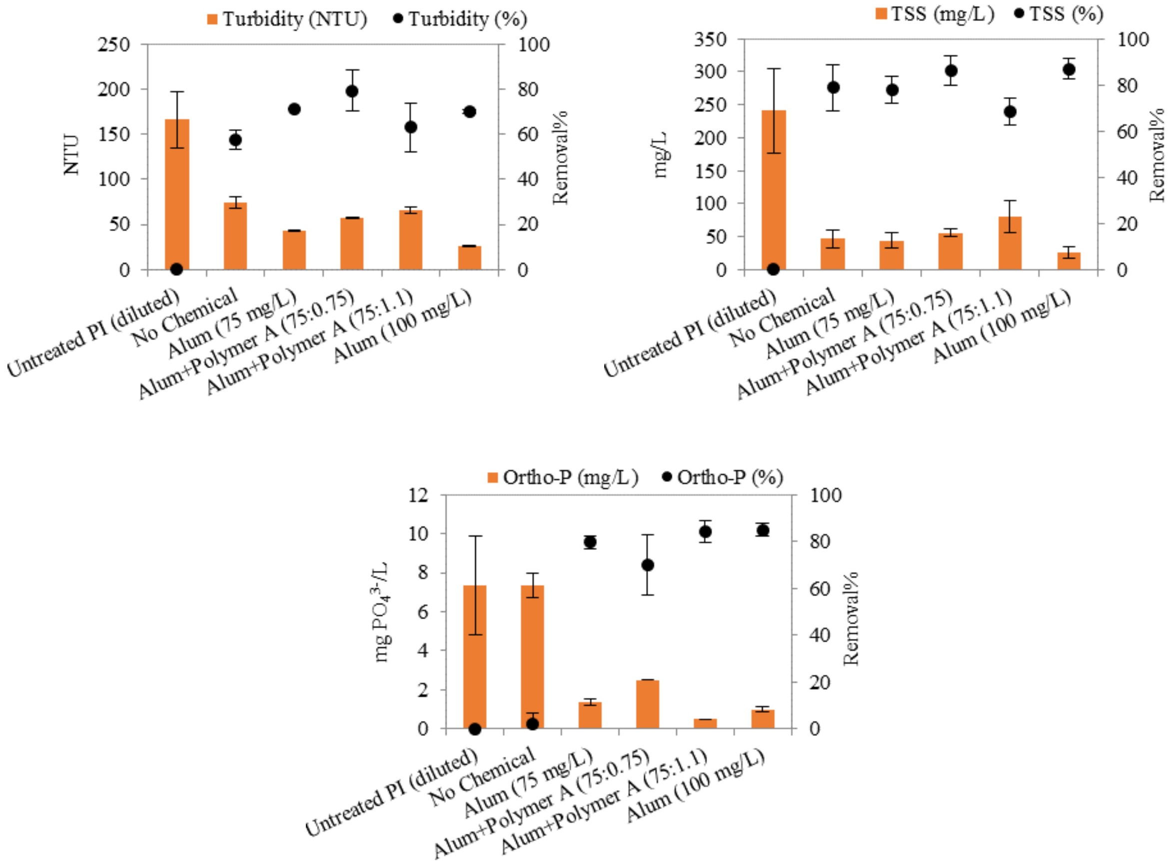


Figure 3.6 Removal of turbidity, TSS and ortho-P during the full-scale application of alum and alum + polymer A.

There are multiple physical and chemical factors affecting the process of coagulation/ flocculation such as the dose and type of chemical and its application point, reactor type, background effects and mixing intensities and times. In fact, it is possible to compare bench -scale with full-scale experiments by using the mean velocity gradient G or Gt values assuming the mixing environments will be the same under constant G or Gt (Cornwell & Bishop, 1983). Yet, during the jar tests, both chemicals were simultaneously added at the beginning of rapid mixing with known mixing intensities while during full-scale operation, the coagulant is mixed with the inflow to the coagulation tank and the polymer is mixed later with the outflow into the flocculation chamber. In addition, on either scale the temperature was not controlled, it varied between 5 and 20°C at full scale while room temperature was maintained during jar tests. Indeed, the comparison between bench and full-scale was strictly based upon the chemical addition. So, although the jar test could not mimic the exact operation conditions, our results acquired from bench-scale experiments were comparable to the results of the full-scale operation in terms of contaminants removals on mass basis (Figure 3.7). Bench and full-scale data (Figures 3.5 and 3.6) showed that polymer addition had no major contribution to the removal of turbidity, TSS and Ortho-P. Hence the addition of polymer was not a sustainable option neither economically nor environmentally.

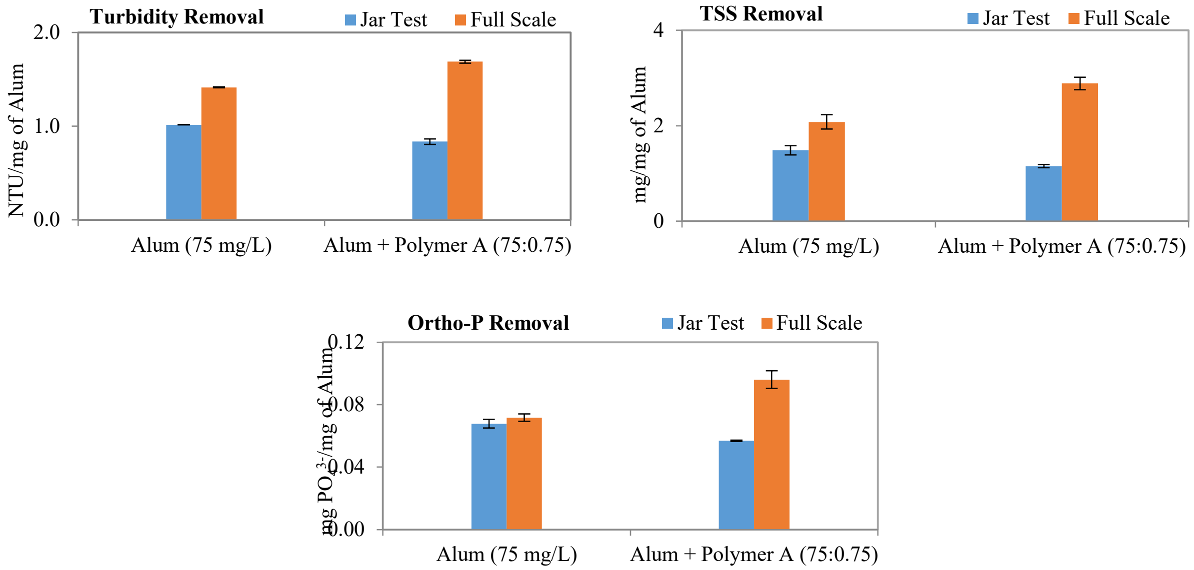


Figure 3.7 Comparison between bench-scale and full-scale applications of 75 mg/L alum only and 75 mg/L alum + 0.75 mg/L polymer for the removal of turbidity, TSS and ortho-P.

3.3.6. Effective parameters for online process control

Investigating the correlation between different wastewater parameters is technically and economically beneficial. According to Ratnaweera and Fettig (2015), pH, turbidity, TSS, UVA and ortho-P are relevant parameters to evaluate the coagulation/ flocculation/ sedimentation process, and they are typically monitored by online sensors. Ortho-P is occasionally measured to monitor the influent and effluent quality. For these reasons, correlations between the different parameters were studied in order to investigate downsizing the analysis to the most effective parameter for online process control.

Results obtained from the full-scale analysis revealed no strong association between the influent flow rate and any of the measured parameters. So, flow rate cannot be a reliable indicator for process control. Also, besides the redundant correlation between TSS and turbidity, there was a strong correlation between %UVT and ortho-P (Figure 3.8). This signifies that measuring turbidity and UVA during operation can help predict rough estimates of TSS and ortho-P and adjust the required coagulant dose without the hassle of multiple sample analyses. This is known as feed-forward control scheme where the quality of the influent is monitored to adjust the chemical dosing. (Ratnaweera & Fettig, 2015). Mass removal ratios can be used here to approximate the required coagulant dose.

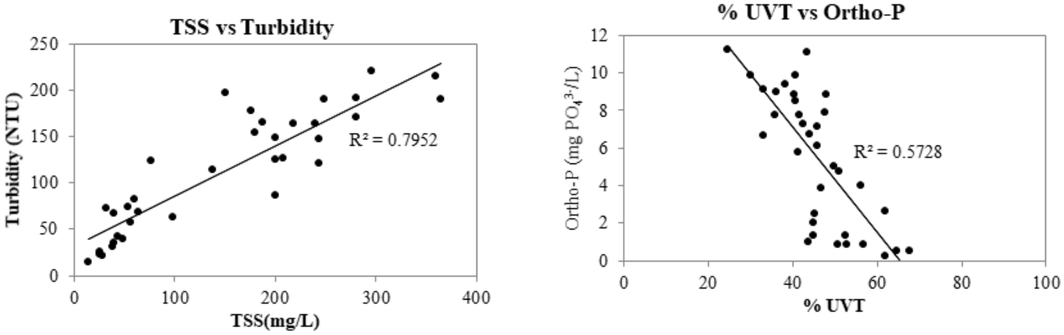


Figure 3.8 Correlations between contaminants measured at full-sale level.

At bench-scale level, our results showed a good correlation between turbidity and TSS, TSS and COD, and COD and ortho-P (Fig. 9). The strongest linear correlations were between turbidity and TSS at both full-scale and bench-scale levels, where the R^2 values were 0.80 and 0.85 respectively (Figure 3.9). These results comply with those obtained by Grayson et al. (1996) who studied the correlation between turbidity and TSS and turbidity and total phosphorus in samples collected from a river catchment area and identified strong linear correlations with R^2 values of

0.86 and 0.90, respectively. It is noteworthy that the strength of such correlations is site specific and changes according to the tested wastewater matrix (Hannouche et al., 2011). Nevertheless, more data is essential to reduce the uncertainty and validate those correlations.

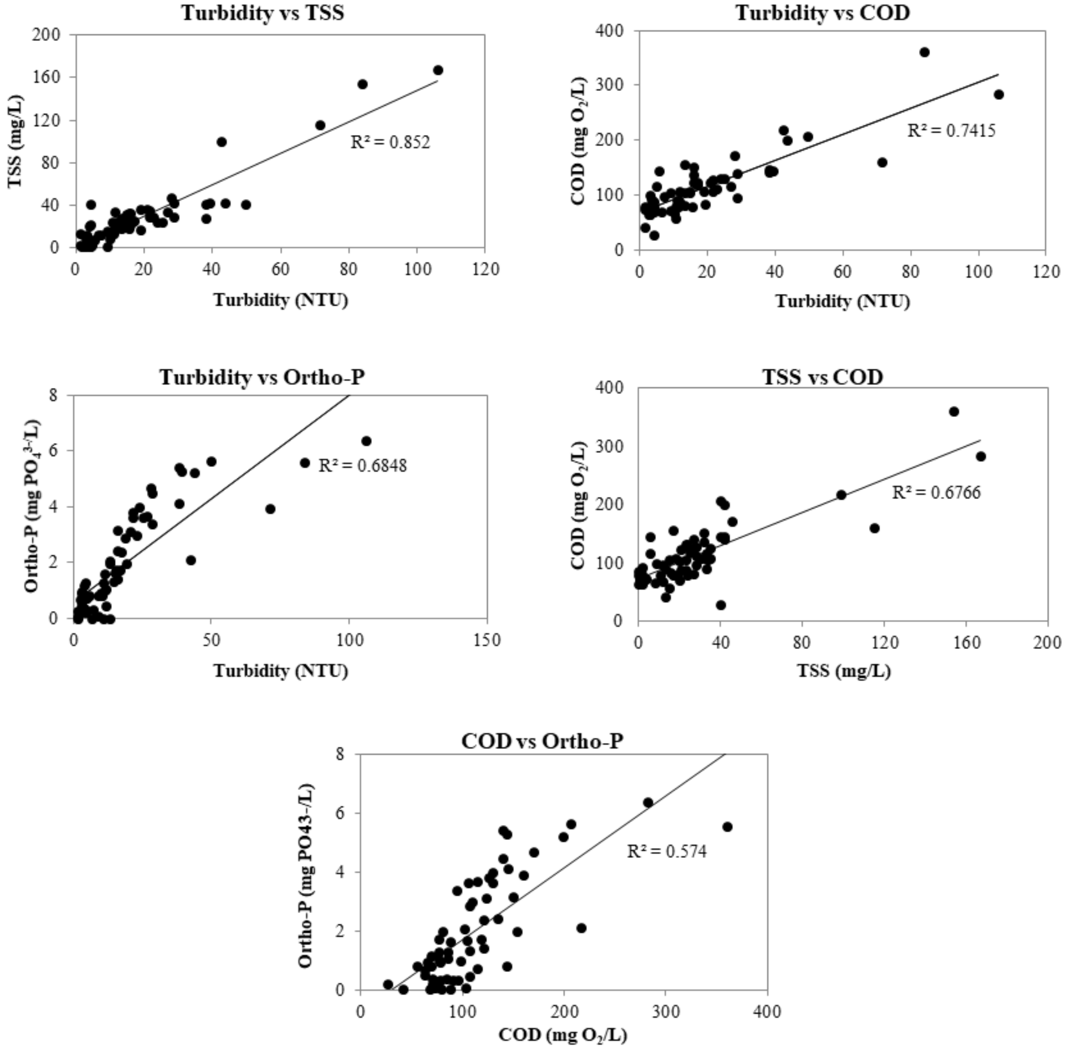


Figure 3.9 Correlations between contaminants measured at bench-scale level.

3.3.7. Implications of these removals on the monitoring of micropollutants

As discussed previously, CSOs are a considerable source of micropollutants. So, in order to assess the overall efficiency of the EPT and the need for any additional treatment, it is important to monitor not only conventional pollutants, but also micropollutants of concern. Thus, in order to estimate the elimination of MPs during EPT, the correlation between differential UVA_{254} (ΔUVA_{254}) and removal of MPs was surveyed from different studies. In the present study we project that UVA can serve not only for process control, but also as a surrogate parameter to estimate the removal of micropollutants during the EPT of CSO. Micropollutants removal correlates with ΔUVA_{254} in advanced oxidation and adsorption processes where an increase in ΔUVA_{254} is associated with higher removal of trace organics reaching up to 95% depending on the chemical structure and properties of the compound (Altmann et al., 2016; Altmann et al., 2015; Ning et al., 2007; Sui et al., 2010; Zhang et al., 2015; Ziska et al., 2016). In coagulation/ flocculation/ sedimentation processes, UVA_{254} was found to be an accurate surrogate parameter for trihalomethane formation in alum-treated waters (Pifer & Fairey, 2014). In the current study, ΔUVA_{254} ranged between 15% and 40% with the use of 75 mg/L alum at bench and full-scale levels. This range can be associated with up to complete removal of some trace organics by ozonation (Chys et al., 2017). In this WWTP final effluent, Shu et al. (2013) and Kerr et al. (2008) reported on the occurrence of some micropollutants such as carbamazepine, diclofenac, ibuprofen, gemfibrozil, mecoprop, diazinon and others at varying concentrations. In contrast, CSO contributes up to 10% of the total discharged load of trace organic compounds with low removal efficiency in a WWTP and up to 90% of those with high removal efficiency (Phillips et al., 2012). As such, we anticipate that the EPT of CSO can still achieve some removal of those compounds that have low water solubility, which entails hydrophobic interactions and sorption onto particulate matter (Margot et al., 2015). Other hydrophilic compounds can also aggregate with metal ions during the treatment with alum. Alum treatment can as such remove up to 75% of some micropollutants (Kim & Zoh, 2016) which can translate in higher ΔUVA_{254}. Moreover, the removal of selected MPs by different oxidants will be investigated extensively in other phases of this study.

3.3.8. Recommended future interventions

The local municipality projects that by 2020, the WWTP would contribute around 10% of the total TSS loading to the adjacent river among which 10 % (2700 Kg/d) would be attributed to the EPT effluent (at a concentration of 30 mg/L) compared to 72% to the final effluent (at a concentration of 7 mg/L) and 18% to the combined bypasses. Thus, the EPT was put under the Combined Sewer Overflow Control Strategy set by the city to control the discharges into the river (City-of-Edmonton, 2009). Despite prioritizing TSS, there are several macro and micropollutants that can implicate detrimental effect to the environment receiving the EPT effluent. It is believed that the discharge of CSO cumulatively increases the level of *E. coli* in the aquatic environment by 0.5 to 2 log (Madoux-Humery et al., 2016). The disinfection of CSOs was effectively achieved by ultraviolet irradiation (Tondera et al., 2015; Wojtenko et al., 2001a), ozone (Tondera et al., 2015; Wojtenko et al., 2001b), performic acid (Chhetri et al., 2015; Chhetri et al., 2014; Tondera et al., 2016), and peracetic acid (Chhetri et al., 2016; Chhetri et al., 2014; Coyle et al., 2014). Therefore, further polishing steps will be required for disinfection and oxidation purposes to minimize the environmental impact of the EPT effluent.

3.4. Conclusions

This study provided a practical solution for the enhanced primary treatment of municipal primary influent under wet weather conditions and proposed the best parameters for online process control. It demonstrated that alum is the best coagulant for the EPT. In fact, alum and PACl were both capable of maximizing the removal of major macropollutants under different mixing scenarios. However, the former had the advantage of cost efficiency and was therefore considered for further optimization. A dose of 75 mg/L alum without any polymer was guaranteed to achieve the target levels of TSS and reduce turbidity by 87% and ortho-P by 71%. While the addition of polymer as a coagulant aid is the current practise at the WWTP, our results showed that this is not sustainable neither economically nor environmentally, as it adds costs by increasing the demand for chemicals with insignificant contribution to the reduction of the load of pollutants into the receiving environment.

Overall, bench and full-scale applications of coagulant and coagulant aid, despite their dissimilarities, unveiled comparable results especially for turbidity and TSS removal. The role of temperature in the overall optimization of the treatment process can be further investigated particularly where major seasonal and diurnal fluctuations are forecasted. The removal of macropollutants presented in this study correlated with that of micropollutants can serve as a guide for additional treatment with small footprint and high efficiency in order to refine the EPT of CSO. This treatment should consider sustainable options for disinfection and oxidation.

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CHAPTER 4: Treatment of a Mixture of Pharmaceuticals, Herbicides and Perfluorinated Compounds by PAC-Catalyzed Ozonation: Insight into the Non-Free •OH Contingent Mechanisms [2]

4.1 Introduction

With the relentless advancements in agricultural, industrial and health care sectors matching the continuous evolvement in human lifestyle, new environmental challenges are constantly surfacing. One common problem emerging from those sectors is the presence of micropollutants (MPs) in the environment. MPs such as pharmaceuticals, personal care products, herbicides, insecticides and industrial compounds are manmade synthetic chemicals or naturally available products that have been detected in the environment at very low concentrations; however, they are capable of exerting adverse ecological impacts (Stamm et al., 2016). They find their way from production, to utilization to point or non-point disposal into landfills, soils and wastewaters, and are eventually detected in surface, ground and drinking waters (Barbosa et al., 2016). Nowadays, there is ample literature on the occurrence, fate and treatment of MPs. Yet treatment options remain under the spotlight because MPs vary in chemical structure and reactivity and accordingly numerous techniques to remove them are continuously investigated for both efficiency and practicality. Advanced oxidation processes (AOPs) constitute a viable option for the abatement of MPs that are hardly biodegradable and tend to resist conventional treatments (Ikehata et al., 2008; Ikehata et al., 2006) .

The exposure to ozone (O_3) in a single ozonation process can selectively transform MPs into other products via direct oxidation/reduction, cycloaddition, electrophilic substitution or nucleophilic reactions (Beltran, 2004). While many MPs demonstrated high removals by single

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[2] A version of this chapter was submitted to Applied Catalysis B: Environmental

ozonation, literature identified some MPs that are insufficiently reactive with O_3 such as: phthalate (Jin et al., 2012; Ning et al., 2007), bezafibrate, iomeprol (Altmann et al., 2014), benzotriazole (Altmann et al., 2014; Hollender et al., 2009), atenolol (Hollender et al., 2009), MPs with amine groups (Hubner et al., 2015), pesticides (Broseus et al., 2009; Chelme-Ayala et al., 2011b), and saturated aliphatic compounds (Jin et al., 2012). In general, the common range of applied O_3 doses for the removal of MPs is reported per mg of dissolved organic carbon (DOC): 0.2 - 1.5 mg O_3/mg DOC (Song et al., 2017; Zimmermann et al., 2011).

In order to improve the performance of ozonation in the degradation of MPs, catalysts are added to accelerate the rate of O_3 reactions, boost the removal and mineralization and reduce toxicity, all without undergoing significant chemical changes (Goncalves et al., 2012; Gonçalves et al., 2013a; Gonçalves et al., 2014; Wang et al., 2019a). There has been a specific interest in carbon-based catalysts associated with its practicality in terms of cost and ease of application, in addition to its potential dual role as catalyst and adsorbent. As such, powdered activated carbon (PAC) is used to catalyze the ozonation process by virtue of its ability to act as adsorbent material, or reaction support, or radical initiator or promoter or all of them combined (Rozas et al., 2017). The main factors reported to impact the catalytic activity of PAC are associated with its physical and chemical properties (including surface area, porosity, functional groups and pH_{pzc} (Pereira et al., 2014)), its concentration as well as its exposure time to O_3 (Alvarez et al., 2008; Sanchez-Polo et al., 2005). The activated carbon's (AC) surface area and its basic surface functional groups, in addition to the higher solution pH were found to enhance the rate of O_3 decomposition (Faria et al., 2006). The stability of PAC as a catalyst and its reusability have also been arguable (Feng et al., 2019). It is noticeable that many studies on catalytic ozonation with PAC in clean water matrix were limited to one MP or a small mixture of MPs at concentrations significantly higher than their expected environmental occurrence, i.e. in parts per million (Faria et al., 2008a; Faria et al., 2008b;

Goncalves et al., 2012; Gonçalves et al., 2013a; Gonçalves et al., 2014; Guzman-Perez et al., 2011; Merle et al., 2010; Rozas et al., 2017). Faster degradation was noted when MPs were treated individually compared to when they were treated in a mixture because of the competitive effect (Rozas et al., 2017). Literature unveils a wide range of AC dosage (10 to 850 mg/L) and particle sizes (75 to 300 µm) that can be applied in catalytic ozonation (Sanchez-Polo et al., 2005).

The mechanisms involved in catalytic ozonation with AC are numerous, generally complex and not completely understood. AC can act as an initiator for O_3 decomposition into $^{\bullet}OH$ in solution which in turn oxidizes the adsorbed MPs. Also, molecular O_3 can adsorb onto and react with the AC surface generating surface radicals that attack the adsorbed MPs (Faria et al., 2008b). A series of surface reactions have been presented and summarized to elucidate the role of AC in catalyzing the ozonation of organic compounds (Xing et al., 2014). The process was claimed to be relying mainly on $^{\bullet}OH$. The decomposition of O_3 on the surface of AC was proposed to produce ozonide ion radicals ($O_3^{-\bullet}$), perhydroxyl radicals ($HO_2^{\bullet}$) and superoxide anion radicals ($O_2^{-\bullet}$) as intermediates in a chain reaction. Hydrogen peroxide (H_2O_2) was reported as another intermediate product that eventually reacts with AC and forms $^{\bullet}OH$. It was also recognized that $^{\bullet}OH$ can react with AC and form some other unidentified species. And, even though those compounds can diffuse in the solution where they can promote the decomposition of O_3 into $^{\bullet}OH$ to undertake the oxidation of target compounds, this diffusion is likely inefficient. The formation of those compounds was confirmed in a later study (Biernacki et al., 2015), where it was noted that the adsorbed $^{\bullet}OH$ can further react with the AC and transfer the free electron from the oxygen atom to a carbon atom resulting in $AC^{\bullet}$–OH a compound that is stabilized by resonance.

The objective of the current study was to examine the efficiency of PAC-catalyzed ozonation for the removal of MPs in a diverse mixture of 17 MPs. The mixture included 8 pharmaceuticals and personal care products, 3 herbicides and 2 surfactants (perfluorinated compounds) that were considered for the first time in PAC-catalyzed ozonation at near-environmental concentrations. The study also aimed to provide a better understanding of the catalytic mechanisms in an O_3+PAC system by identifying and monitoring the formed reactive species. This was also meticulously tackled through the inhibition effect of three different radical scavengers added to the O_3+PAC system and through a detailed Electron Paramagnetic Resonance (EPR) spectroscopic analysis.

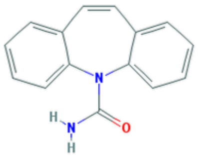
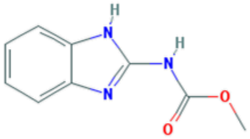
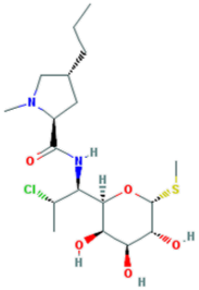
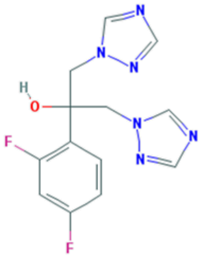
4.2 Material and methods

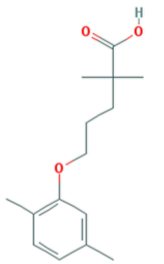
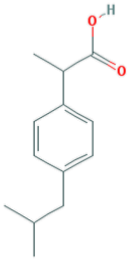
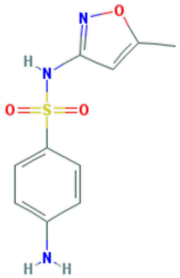
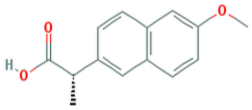
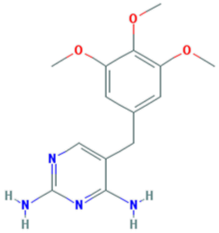
4.2.1. Chemicals and standards

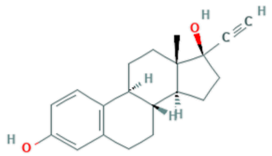
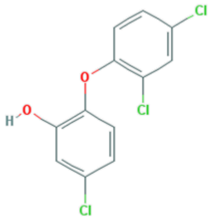
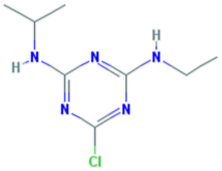
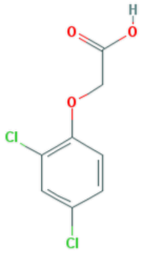
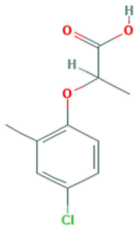
All used chemicals: potassium indigo trisulfonate, phosphoric acid, sulfuric acid, sodium tetraborate, tertiary butanol, sodium thiosulfate, *para*-benzoquinone, sodium azide, were purchased from Sigma Aldrich, Canada. Commercial PAC WPX with a particle size of 45 µm was acquired from Calgon Carbon.

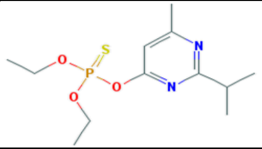
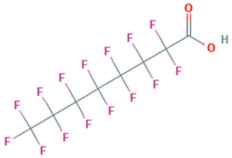
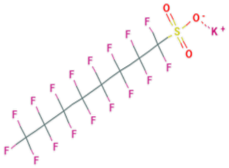
In this study, seventeen MPs were selected to represent three different categories: pharmaceuticals and personal care products, herbicides and industrial products. The list of all MPs along with their respective classes, structures, and chemical and physical characteristics are provided in Table 4.1.

Table 4.1 List of Micropollutants included in this study.

#	**Micropollutant:** Molecular Formula	**Abbreviation**	**Structure**	**Class**	**MW (g/mol)**	**pKa**	**log kow**	**Water Solubility**
Pharmaceuticals and Personal Care Products (PPCPs)								
1	**Carbamazepine** $C_{15}H_{12}N_2O$	**CBZ**		Anticonvulsant	236.27	13.9	2.45	18 mg/L at 25 °C
2	**Carbendazim** $C_9H_9N_3O_2$	**CDM**		Antifungal	191.19	4.29	1.52	8 mg/L at 24 °C
3	**Clindamycin** $C_{18}H_{33}CN_2O_5S$	**CLN**		Antibacterial	424.18	7.60	2.16	30.61 mg/L at 25 °C
4	**Fluconazole** $C_{13}H_{12}F_2N_6O$	**FCZ**		Antifungal	306.10	2.27 0.25	0.25	4363 mg/L at 25 °C

5	**Gemfirbozil** $C_{15}H_{22}O_3$	**GFL**		Lipid-regulating agent	250.34	4.42 4.77	4.77	11 mg/L at 25 °C
6	**Ibuprofen** $C_{13}H_8O_2$	**IBU**		Anti-inflammatory	206.29	5.30 4.91	3.97	21 mg/L at 25 °C
7	**Sulfamethoxazole** $C_{10}H_{11}N_3O_3S$	**SMX**		Antibacterial	253.05	1.6-5.7	0.79	610 mg/L at 37 °C
8	**Naproxen** $C_{14}H_{14}O_3$	**NPX**		Anti-inflammatory, Anti-rheumatic	230.09	4.15	3.18	15.9 mg/L at 25 °C
9	**Trimethoprim** $C_{14}H_{18}N_4O_3$	**TMP**		Antibacterial	290.32	7.12 6.3	0.91	400 mg/L at 25 °C

10	Ethinylestradiol $C_{20}H_{24}O_2$	**EE2**		Semisynthetic Estrogen	296.41	10.40	3.67	11.3 mg/L at 27 °C
11	**Triclosan** $C_{12}H_7Cl_3O_2$	**TCN**		Antiseptic	289.54	7.90	4.76	10 mg/L at 20 °C
				Herbicides				
12	**Atrazine** $C_8H_{14}ClN_5$	**ATZ**		Herbicide	215.69	1.60	2.61	34.7 mg/L at 26 °C
13	**2,4-Dichlorophenoxya-cetic Acid** $C_8H_6Cl_2O_3$	**2,4-D**		Herbicide	221.03	2.73	2.81	677 mg/L at 25 °C
14	**Mecoprop** $C_{10}H_{11}ClO_3$	**MCP**		Herbicide	214.65	3.78	3.13	880 mg/L at 25 °C

15	**Diazinon** $C_{12}H_{21}N_2O_3PS$	**DZN**		Insecticide	304.35	2.60	3.81	60 mg/L at 20 °C
			Industrial Compounds					
16	**Perfluorooctanoic Acid** $CF_3(CF_2)_6COOH$	**PFOA**		Surfactant	414.07	1.30	4.81	2290 mg/L at 24 °C
17	**Heptadecafluoro-octanesulfonic acid** $CF_3(CF_2)_7SO$ K	**PFOS**		Surfactant	538.22	1.0	4.49	3200 mg/L at 25 °C

Note: References:

[1] R. Broseus, S. Vincent, K. Aboulfadl, A. Daneshvar, S. Sauve, B. Barbeau, M. Prevost, Water Res. 43 (2009) 4707-4717.
[2] M. Patel, R. Kumar, K. Kishor, T. Mlsna, J. Charles U. Pittman, D. Mohan, Chem. Rev. 119 (2016) 3510-3673.
[3] P. Westerhoff, Y. Yoon, S. Snyder, E. Wert, Envrion. Sci. & Technol. 39 (2005) 6649-6663.

Some of these MPs have been found in ng/L to µg/L levels in the primary influent to a wastewater treatment plant (CBZ, FCZ, GFL, IBU, SMX, TMP, EE2, TCN), others are regulated by the Canadian Guidelines for Drinking Water Quality (ATZ, 2,4-D, DZN, PFOA, PFOS) (Health Canada, 2019). Out of the 17 MPs in the mixture, 13 MPs were studied for the first time in the O_3+PAC system: CDM, CLN, FCZ, GFL, IBU, NPX, TMP, EE2, 2,4-D, MCP, DZN, PFOA, PFOS. MPs were supplied by Sigma Aldrich, Canada and Supelco, Canada. A stock solution of borate buffer was prepared with a 1:1 mixture of sodium tetraborate and sulfuric acid and its pH was adjusted to 7 using sulfuric acid and sodium hydroxide. Stock solutions of the radical scavengers *tert*-butanol (TBA), *para*-benzoquinone (*p*-BZQ), sodium azide (NaN_3) and the O_3 quencher sodium thiosulfate were all prepared in MilliQ water and stored at 4 °C until used. All glassware used in the experiments were ozonated for 30 minutes in a washtub to ensure they were O_3 demand-free prior to each experiment.

4.2.2. Catalyst characterization

The surface area of PAC including the volume of micropores and mesopores were identified using the N_2 adsorption-desorption isotherm. The surface functional groups were identified by X-ray photoelectron spectroscopy (XPS; Kratos AXIS Ultra spectrometer, Shimadzu, Columbia, USA, equipped with monochromatic Al Kα source) and the data were analyzed using XPS Vision-2 instrument software. Fourier-transform infrared spectra (FT-IR) were acquired from Thermo Scientific NICOLET 8700 FT-IR and used to assess the adsorption of materials onto the surface of PAC throughout the treatments. The point of zero charge pH_{pzc} of the catalyst was measured following the solid addition method detailed elsewhere (Pourrezaei et al., 2014).

4.2.3. Experimental procedures

All experiments were performed in duplicate 100 mL round bottom flask glass reactors with no free headspace, wrapped in aluminum foil at room temperature and atmospheric pressure. Seventeen individual stock solutions of MPs were prepared in MilliQ water at concentrations ranging between 5 and 100 ppm in conformity with their solubility limit at 20°C. Each solution was sonicated for 20 min to ensure complete dissolution and stored at 4°C in the dark until used. O_3 was generated from dry oxygen using the O_3 Generator Model GSO-30 and was bubbled into O_3 demand-free water (ODFW) in an ice bath to obtain a saturated stock solution. Experiments were performed with continuous stirring. Samples were withdrawn at fixed time intervals and analyzed for residual O_3 via the Indigo Method (Bader & Hoigne, 1981) with UV absorbance at 600 nm measured using UV spectrophotometer. Samples collected for MPs analysis were filtered with 0.22 µm nylon syringe filters into 1.5 mL amber polypropylene vials where 0.64 mM sodium thiosulfate was added to quench the residual O_3. All samples were stored at 4 °C until analysis.

4.2.4. Analytical methods

The analysis of MPs was performed using ultra-performance liquid chromatography – quadrupole time of flight mass spectrometry UPLC-qTOF-MS (Xevo G2-S, Waters). ACQUITY UPLC BEH C18, 50 x 2.1 mm column, at 50°C was utilized with an injection volume of 10 µL. MPs were analyzed using either positive or negative ionization modes. In positive ionization mode, the mobile phase consisted of water with 0.1 % formic acid (solvent A) and acetonitrile with 0.1 % formic acid (solvent B). In negative ionization mode, 0.02% ammonium hydroxide in water (solvent A) and 0.02% ammonium hydroxide in acetonitrile (solvent B) were used. Details of the monitoring mode and mass are available in Table 4.2.

Table 4.2 Monitored mass (*m/z*) and detection mode for the 17 micropollutants.

MP		Monitored mass (*m/z*)	Mode
1	CBZ	237.103	Positive
2	CDM	192.077	Positive
3	CLN	425.188	Positive
4	FCZ	307.112	Positive
5	GFL	249.149	Negative
6	IBU	205.123	Negative
7	SMX	254.060	Positive
8	NPX	231.102	Positive
9	TMP	291.146	Positive
10	EE2	295.170	Negative
11	TCN	286.962	Negative
12	ATZ	216.102	Positive
13	2,4-D	218.962	Negative
14	MCP	213.032	Negative
15	DZN	305.109	Positive
16	PFOA	412.966	Negative
17	PFOS	498.930	Negative

Electron paramagnetic resonance (EPR) measurements were performed using BRUKER ELEXSYS EPR spectrometer operated at 0.0001 T modulation amplitude, 100000 Hz modulation frequency, 9.839293 x 10^9 Hz microwave frequency and 0.02 W microwave power. Signals were acquired at 3504.95 G center field. Spin traps 5,5-diemthyl-1-1 pyrroline-N-oxide (DMPO), 2,2,6,6-tetramethylpiperidine (TEMP), 2-methyl-2-nitrosopropane (MNP), N-*tert*-butyl-*α*-phenylnitrone (PBN) were supplied by Dojindo Molecular Tech. Inc. All experiments were run *in-situ* in 1.5 mL reactors incubated at 20 °C with 1000 rpm shaking. Samples were collected after 10 minutes reaction time using three capillary tubes and measurements were subsequently performed.

4.3. Results and discussion

4.3.1. Catalyst characterization

PAC was manufactured from bituminous coal. Its total surface area measured 632 m^2 g^{-1} with a total pore volume of 0.452 cm^3 g^{-1} and it consisted mainly of micropores (S_{micro} = 544 m^2 g^{-1}, V_{micro} = 0.282 m^3 g^{-1}) and few mesopores (S_{meso} = 88 m^2 g^{-1}, V_{meso} = 0.170 m^3 g^{-1}). The deconvolution of XPS spectra indicated that the major constituents of PAC surface were carbon, hydrogen and oxygen. Peaks formed for C=C (284.6 eV), C-OH (285.2 eV) and C(O)O (289.6 eV) (Feng et al., 2019). The pH_{pzc} value for the catalyst was 10 as shown in Figure.4.1. Accordingly, the catalyst presented a basic character.

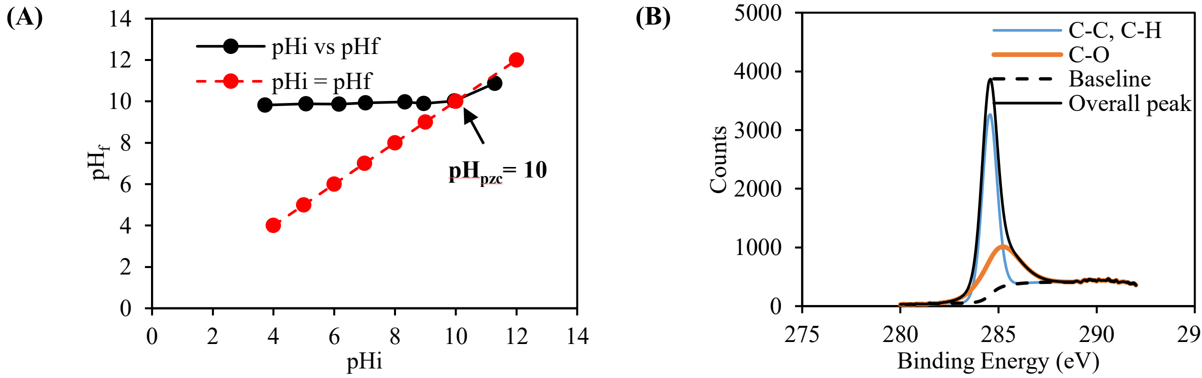


Figure 4.1 Assessed PAC characteristics: **(A)** pH_{pzc} by Solid Addition Method; **(B)** XPS spectra for untreated PAC.

4.3.2. Ozone decomposition in single and catalytic ozonation

An initial screening of the O_3 and PAC dose combinations was performed. Single ozonation experiments were conducted using a mixture of 17 MPs at 500 µg/L each with two doses of O_3 (5 mg/L and 10 mg/L). The results showed that doubling the O_3 dose (10 mg/L) improved the MPs removal by up to 45% after 10 minutes of exposure time (Figure 4.2).

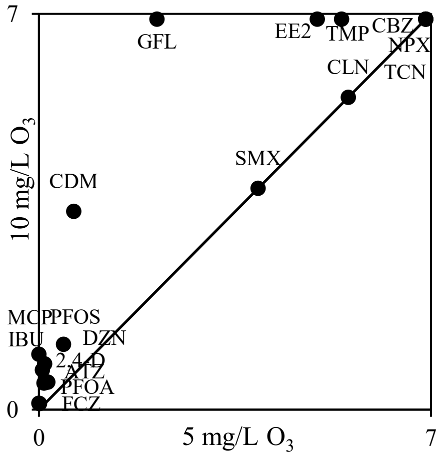


Figure 4.2 Comparison between the MPs removal (Ln C_0/C) in a mixture with two O_3 doses: 5 mg/L and 10 mg/L after 10 minutes of single ozonation (in borate buffer pH 7; Mixture of 17 MPs with 500 ppb each).

The dose of O_3 was then fixed at 10 mg/L and the O_3 decomposition kinetics were evaluated against PAC doses ranging between 0 and 500 mg/L for 10 minutes in buffer at pH 7 (Figure 4.3).

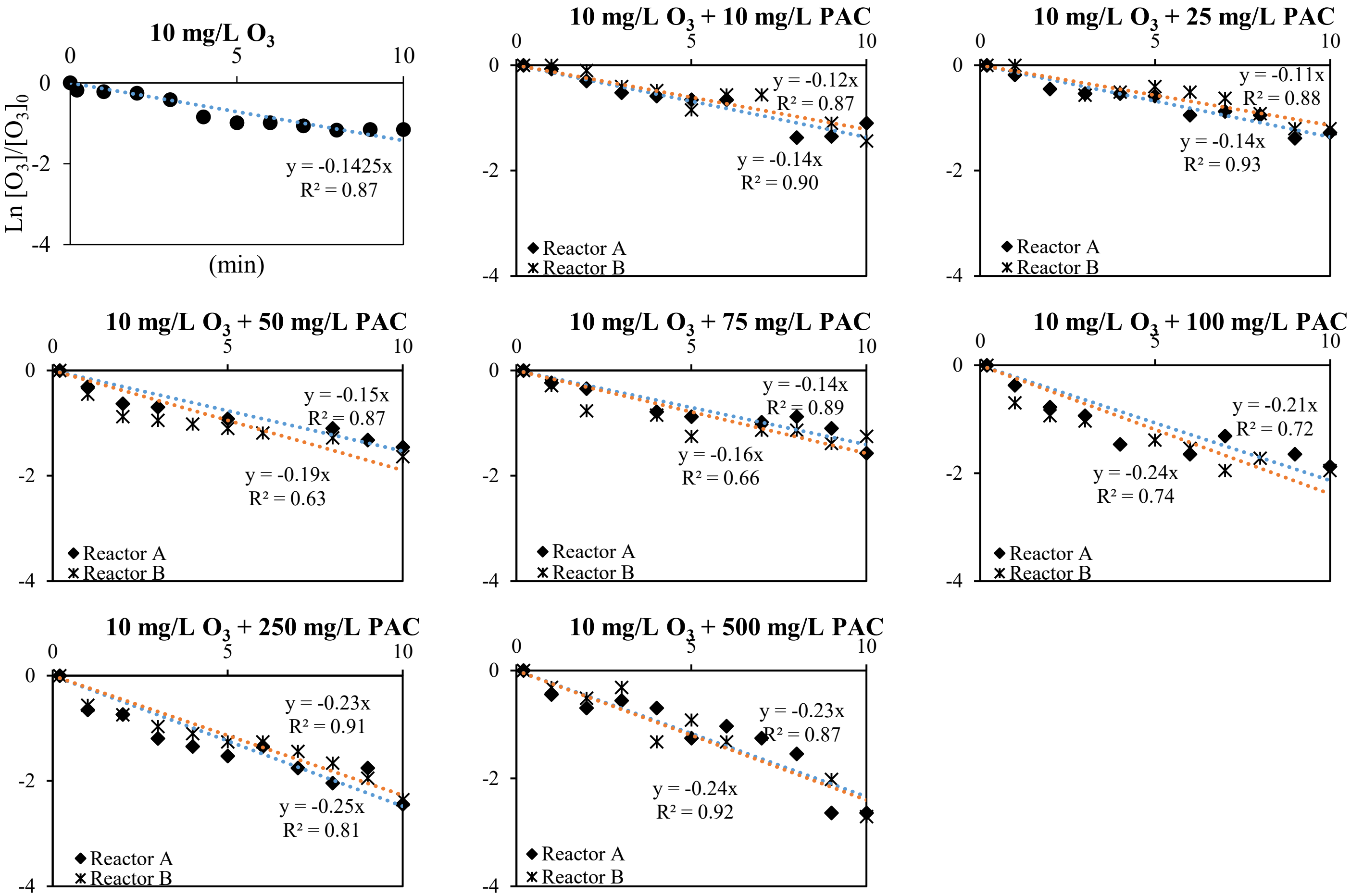


Figure 4.3 O_3 decomposition kinetics in clean matrix using 10 mg/L O_3 in borate buffer at pH 7 and different doses of PAC. (x axis represents time in min; y axis represents ln $[O_3]/[O_3]_0$ where $[O_3]_0$ is the residual O_3 at time = 12 seconds)

Figure 4.4 illustrates the effect of PAC dose on the initial O_3 demand IOD and first-order rate constant of O_3 decomposition. The relationship between PAC dose and IOD was linear, revealing a significantly high IOD in presence of higher PAC doses: 66% of the applied O_3 dose was utilised in the first 12 seconds in presence of 500 mg/L PAC. On the other hand, the relationship between PAC dose and the rate of O_3 decomposition was not exactly linear as shown elsewhere in semi-batch reactors at pH 2 and 7 (Biernacki et al., 2015; Merle et al., 2010). However, the calculated rate constants were comparable to those reported at pH 7. In this study, increasing the PAC dose from 0 to 75 mg/L resulted in a ratio $\Delta k/\Delta PAC$ equal to 0.00013. That ratio increased to 0.003 when the PAC dose increased from 75 to 100 mg/L and then decreased to 0.000025 between higher PAC doses 100-500 mg/L. It is therefore noticeable that at a PAC dose of 100 mg/L the rate of O_3 decomposition increased substantially. This observed trend could be explained by a minor catalytic effect that PAC at low doses and small particle size (µm level) had on O_3: in this case PAC could mimic the impact of a substrate rather than a catalyst (Biernacki et al., 2015). It was therefore noticeable that the PAC dose was correlated with the demand for O_3, yet it did not reveal similar correlation with the rate of O_3 decomposition because of the high demand in the batch reactor.

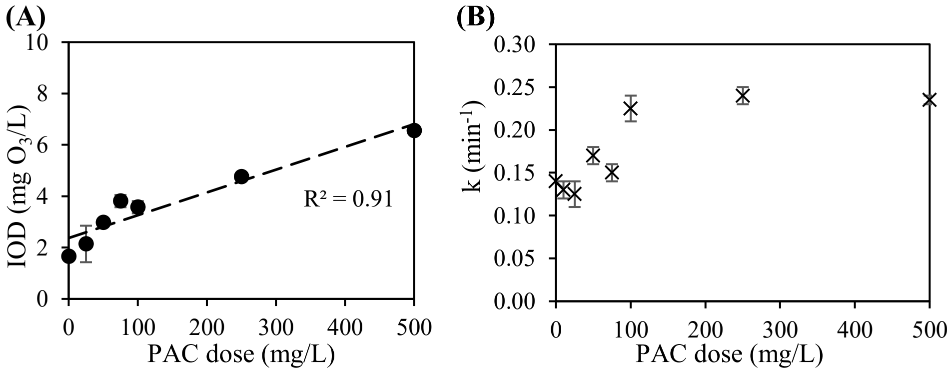


Figure 4.4 Effect of PAC dose on (A) the initial O_3 demand (IOD) in the first 12 seconds; and (B) the first-order rate constant of O_3 decomposition in borate buffer at pH 7 (O_3 dose: 10 mg/L – PAC doses: 0; 25; 50; 75; 100; 250; 500 mg/L – Borate Buffer, pH 7).

To further investigate, 10 mg/L O_3 was applied with 25 mg/L PAC on a buffered mixture of 17 MPs and the removals were compared to those achieved with 10 mg/L O_3 and 100 mg/L PAC as shown in Figure 4.5. While the rate of O_3 decomposition was higher with 25 mg/L PAC (similar to the rates obtained in buffered water), significantly less removals were noticed for: FCZ, IBU, TCN, ATZ, 2,4-D, MCP, DZN, PFOA and PFOS. These results are comparable to literature (Xing et al., 2014). They also further ascertain that at low doses, PAC did not catalyze the decomposition of O_3 but rather acted as a target compound.

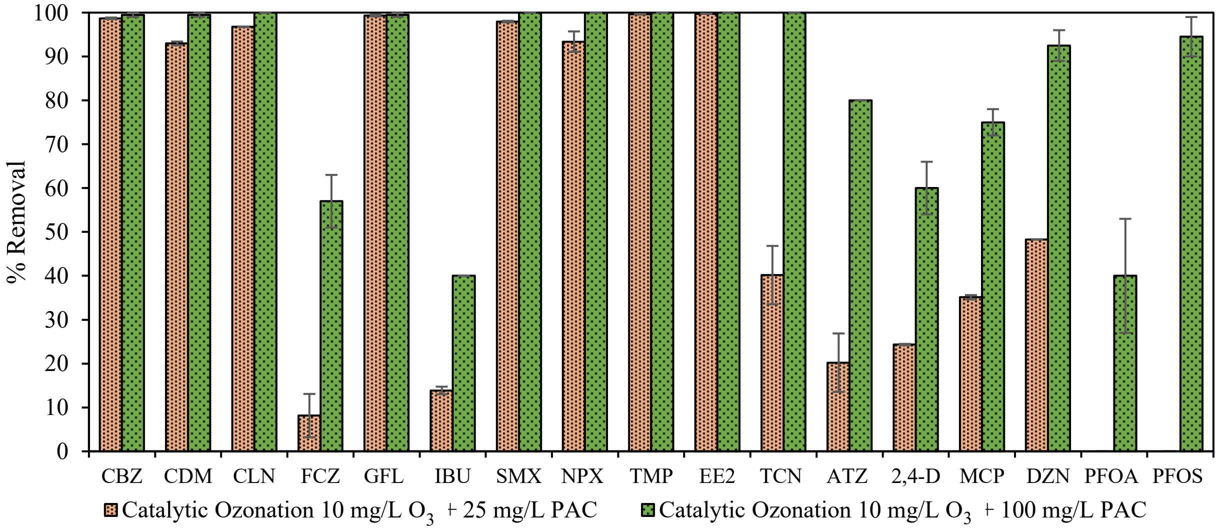


Figure 4.5 Changes in the percent removal of MPs after 1 min of catalytic ozonation using different PAC doses: 25 mg/L PAC vs 100 mg/L PAC. The rates of O_3 decomposition were 1.74 L mg^{-1} min^{-1} with 25 mg/L PAC and 0.14 L mg^{-1} min^{-1} with 100 mg/L and (O_3: 10 mg/L; PAC: 25 mg/L – 100 mg/L; borate buffer pH 7; Mixture of 17 MPs with 500 ppb each).

The impact of buffer type on the kinetics of O_3 decomposition in presence of PAC in clean water was also evaluated. Experiments were performed with 10 mg/L O_3 and 100 mg/L PAC in presence of equimolar borate buffer or phosphate buffer to achieve neutral pH. It was obvious that both buffers accelerated the decomposition of O_3 in comparison with a system at natural pH (pH 5.3). The O_3 decomposition rate constant in presence of borate buffer at pH 7 was 14.8 times higher than that in natural pH 5.3, while that in presence of phosphate buffer was and 3.7 times higher. These results are generally expected because of the high dependence of O_3 chemistry in aqueous systems on the pH whereby at higher pH more hydroxyl ions are available to initiate the decomposition of O_3 (Beltran, 2004). However, the difference noted in the effect of each buffer can be attributed to their possible interference with the chemistry of O_3 decomposition through the interaction with the catalyst surface.

Experiments performed on the mixture of 17 MPs were conducted in near-environmental conditions with each of the MPs added at a low initial concentration (500 μg/L) in presence of 4 mM borate buffer to maintain a neutral pH. The O_3 dose was fixed a 10 mg/L, with a theoretical specific dose equivalent to 2.2 g O_3/g DOC. The O_3 decomposition kinetics (Figures 4.9 and 4.10 below) confirmed that O_3 decomposed faster in the absence of MPs. Also, its decomposition rate almost doubled with the addition of PAC in clean buffered water, while it increased by 1.3 times in the presence of MPs (from 0.11 min^{-1} to 0.14 min^{-1}). This discrepancy in the effect of PAC on the decomposition of O_3 in presence and absence of target compounds can be attributed to the dual role of PAC as catalyst and adsorbent. Thus, when some MPs adsorb onto the surface of PAC, they could reduce the number of active sites capable of initiating O_3 decomposition which resulted in a smaller effect on the rate constant compared to when there were no target compounds to occupy potentially active sites.

4.3.3. Removal of micropollutants

In the list of 17 MPs treated in this study, only 4 MPs: ATZ (Fan et al., 2014; Guzman-Perez et al., 2011; Restivo et al., 2013; Rozas et al., 2017), CBZ (Rozas et al., 2017), TCN (Rozas et al., 2017) SMX (Goncalves et al., 2012; Gonçalves et al., 2013b) were previously examined with carbon material-based catalytic ozonation in clean water matrix. In most of those studies, the compounds were studied at higher concentrations in mg/L, individually or within a small mixture.

In this study, nine MPs were completely removed within the first minute of oxidation by single or catalytic ozonation: CBZ, CDM, CLN, GFL, SMX, NPX, TMP, EE2 and TCN (Figure 4.6). Since, these MPs demonstrated high reactivity with O_3 at low concentrations, ozonation turns out to be sufficient for their degradation.

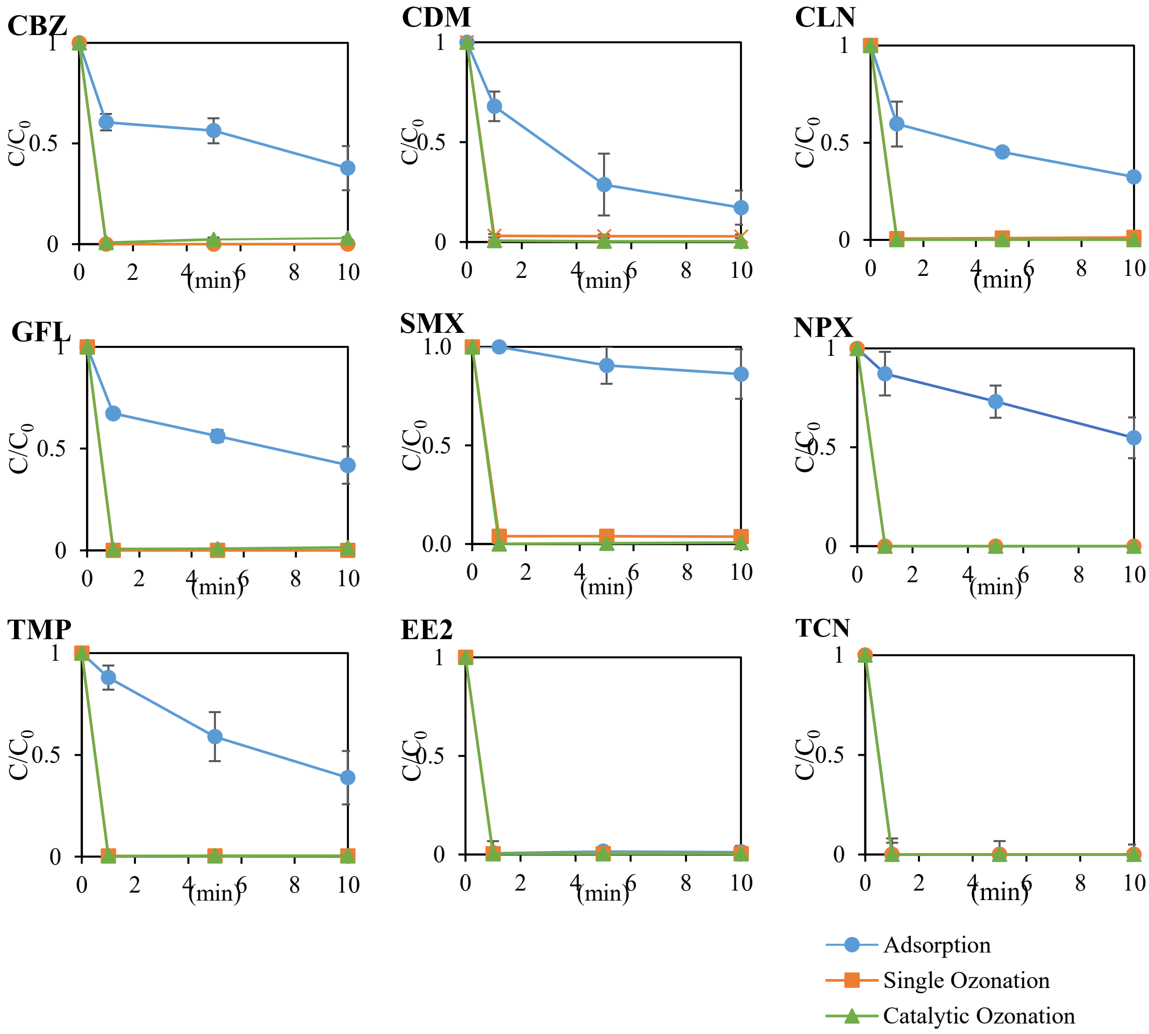


Figure 4.6 MPs that were completely removed within the first 1 minute of oxidation in a buffered mixture of 17 MPs: adsorption (blue circle), single ozonation (orange, square), catalytic ozonation (green, triangle). (MPs mixture: 500 ppb each; O_3: 10 mg/L; PAC: 100 mg/L).

The removal results of the other eight MPs: FCZ, IBU, ATZ, 2,4-D, MCP, DZN, PFOA and PFOS after 10 minutes of adsorption, single and catalytic ozonation are summarized in Figure 4.7-A. The reactions in single and catalytic ozonation were almost complete within the first 1 minute of treatment since the largest drop in concentration occurred in the first minute after which there was no significant removal. It was expected that under these experimental conditions, with 2.2 g O_3/g DOC, the reaction would proceed in a fast manner due to the high oxidant to pollutant ratio in a batch system. In order to elucidate whether the observed removal during catalytic ozonation was facilitated by enhanced oxidation or by adsorption, the synergistic effect was calculated as the sum of the removals during adsorption and during single ozonation. It was then compared with the catalytic effect represented by the obtained removals during catalytic ozonation (Figure 4.7-B). FCZ was the main MP that demonstrated the catalytic effect, followed by 2,4-D. In contrast, the removal of MCP and PFOA during catalytic ozonation lingered on the border line which highlights the probable role of synergy, while the removal of the other 4 MPs remained lower than that calculated by the synergistic effect. These results ascertain that the observed removals during catalytic ozonation occur for two reasons: simultaneous oxidation and adsorption as noted for MCP and PFOA, and degradation favoured by the catalytic mechanism, as noted for the remaining MPs. Generally, catalytic ozonation led to faster apparent degradation rate for most of those MPs (with the exception of IBU and PFOS, Figure 4.7-C) in comparison with single ozonation and adsorption. Also, as shown in Figure 4.8, the specific degradation rates of most MPs were higher in catalytic ozonation than in single ozonation. In particular, those rates increased 4.4 times for FCZ and 1.1 times for IBU, while they increased around 2.3 times for herbicides, 1.2 times for PFOA and PFOS. The faster removal of PFOA was mostly due to its adsorption onto PAC in catalytic ozonation. Knowing that PFOS exhibits a very low reactivity with O_3 (Dai et al., 2019b); its remarkably high removal in 1 minute that decreased with time can be associated with the foaming phenomenon observed in the ozonation experiments. It is thus possible that PFOS attached to the foam that formed during mixing by virtue of its hydrophobicity as reported elsewhere (Dai et al., 2019a).

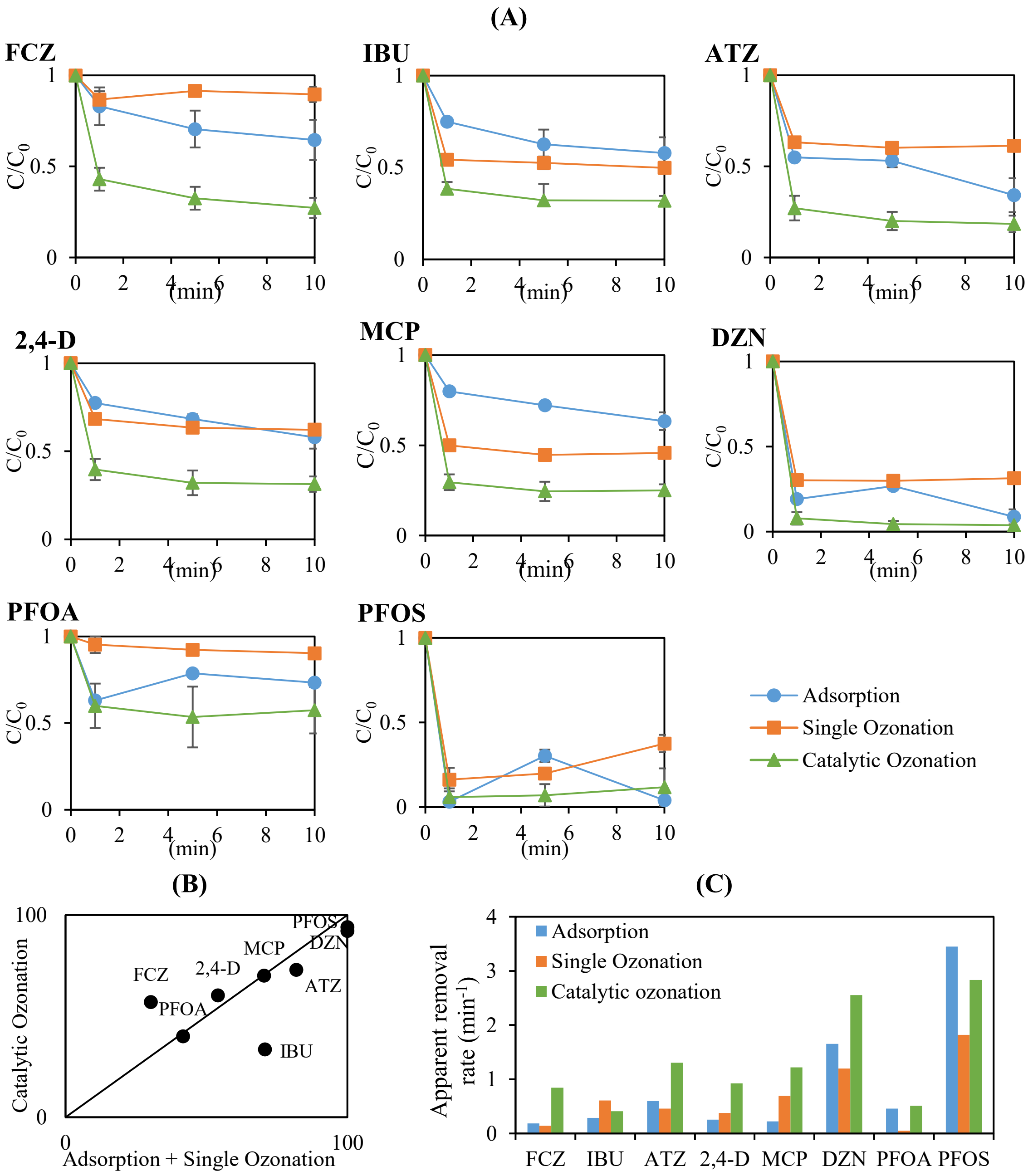


Figure 4.7 (A) Removal of MPs in a buffered mixture of 17 MPs by different treatments: Adsorption (blue circle), Single Ozonation (orange, square), Catalytic ozonation (green, triangle); **(B)** Comparison between the 1 minute percent removal by synergistic effect (Adsorption + Single Ozonation) versus catalytic effect (catalytic ozonation) where C_0 represents the initial concentration of the MPs and C represents their concentration at 1 minute; **(C)** Comparison between the apparent degradation rate (k in min^{-1}) calculated for the first minute of the treatment.

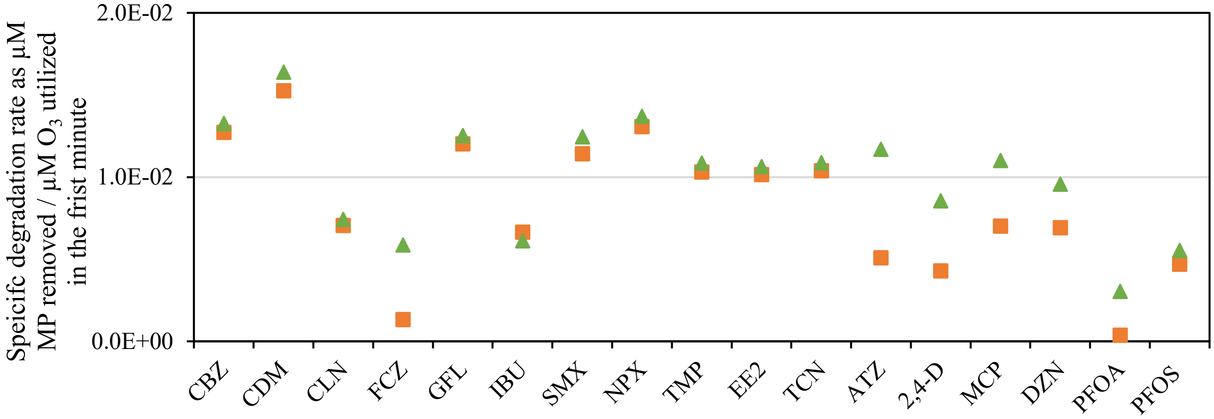


Figure 4.8 Specific degradation rate for each MP in the mixture as µM of MP removed per µM O_3 utilized in 1 minute (MPs mixture: 500 ppb each; O_3: 10 mg/L; PAC: 100 mg/L, borate buffer pH 7).

4.3.4. Formation of reactive oxygen species (ROS)

4.3.4.1. Catalyst surface changes

To study the impact of O_3 and MPs on the surface of PAC, experiments were performed in a batch reactor and all reagents were mixed for 30 minutes. PAC was then allowed to decant; the supernatant was removed and PAC was dried in the oven at 100 °C for 2 hours. The recovered PAC was analyzed by FT-IR spectroscopy. The obtained spectra indicated that the surface of PAC did not undergo any significant permanent changes upon a 30 minutes exposure to borate buffer at pH 7 only, or to O_3 (10 mg/L) at natural pH of 5.3, or to the mixture of MPs at natural pH of 5.9. In contrast, in the presence of borate buffer at pH 7, some surface changes were depicted when PAC was added to the mixture of MPs alone and together with O_3 (Figure 4.9). This can be explained by the mutual interactions between pH_{pzc}, pH of the solution, and pKa of the MPs (Feng et al., 2019). In a buffered solution at pH 7, PAC with a basic pH_{pzc} of 10 loses some of its surface electron density, and its surface becomes positively charged attracting more hydroxide ions (OH^-). When O_3 was applied under these conditions, the nucleophilic sites on PAC surface were targeted by the electrophilic sites in the O_3 molecule. As such, better catalysis was expected for a basic catalyst's surface, exhibiting higher electron density and more nucleophilic oxygenated surface groups (Gonçalves et al., 2010). With PAC, it is possible that the interaction between O_3 and the catalyst's surface resulted in radicals that can adsorb or diffuse to the bulk. The formation of these short-lived radicals did not translate into major changes on the surface groups. Other studies reported changes on the surface of PAC upon exposure to O_3. For instance, the one hour contact between PAC and O_3 through continuous O_3 bubbling resulted in changes in C-OH and C=C bonds that were associated with the capacity of the carbon material (multi-walled carbon nanotube) for adsorption and $^{\bullet}OH$ generation (Rozas et al., 2017). It was also claimed that, depending on the nature and properties of AC, O_3 oxidized its outermost surface and increased the amount of oxygenated groups without causing any significant textural changes (Faria et al., 2006). It is therefore probable that O_3 did not have any pronounced impact on the surface of PAC utilized in this study because of its type and the O_3 exposure time and method.

The new FT-IR bands that formed in the presence of MPs, whether in adsorption only or in catalytic ozonation (Figure 4.9), corresponded to the groups alkene C=C and hydroxyl -OH (forming at 3110-3200 cm^{-1}), carboxylic salt –COONa, carbonyl group C=O (forming at 1414 cm^{-1}), and to the cyano group –CN (forming at 1199 cm^{-1}) (Coates, 2006). Those bands were generally narrower and less intense in catalytic ozonation. Therefore, all those detected groups on the surface of PAC can be attributed to the interactions between: the surface of PAC, MPs, O_3, and buffer at pH 7.

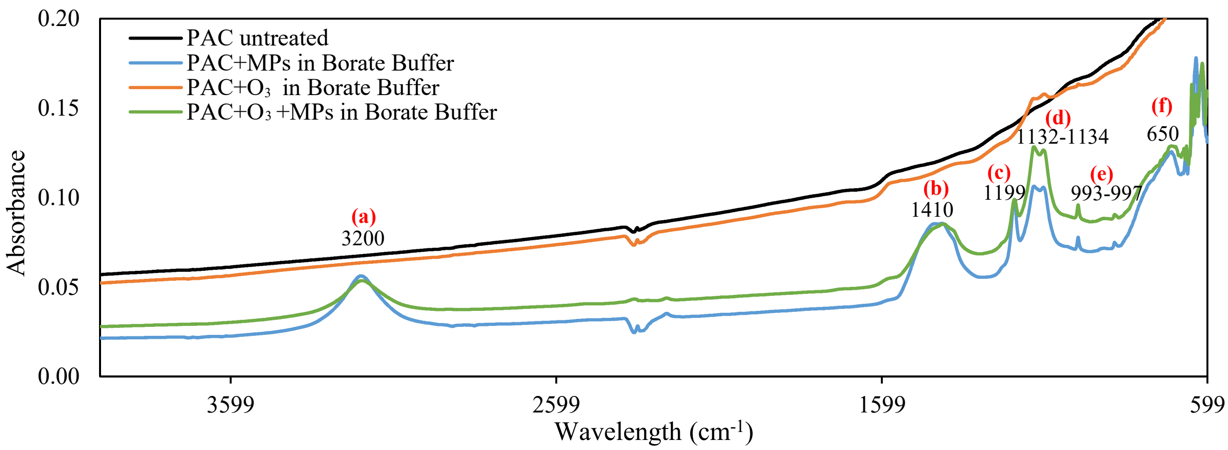


Figure 4.9 FT-IR Spectra for PAC samples recovered after 30 minutes exposure to O_3 and/or the mixture of MPs (with 4 mM borate buffer pH 7, 10 mg/L O_3, 100 mg/L PAC, mixture of 17 MPs at 500 ppb each).
(**a**): -OH, C=C; (**b**): -OH, C(=O)(-O), COONa; (**c**): C-O, C-O-SO_3^-, -CN; (**d**): C-N, -SO_4^{2-}, C-F, C-O-C; (e): aromatic C-H; (**f**): C-Br, O-H

4.3.4.2. Competitive radical test

Quenching tests were performed in the presence of different radical scavengers to explore the indirect radical pathways for degradation involving ROS in single and catalytic ozonation. Three scavengers were tested at a molar concentration equivalent to ten times that of the principal oxidant O_3. As such, the following compounds were added: 2mM TBA to scavenge $^{\bullet}OH$ ($k_{TBA/\bullet OH} = (3.8\text{-}7.6) \times 10^8\ M^{-1}.s^{-1}$ (Wang et al., 2019b)), 2 mM *p*-BZQ to scavenge superoxide radicals ($O_2^{-\bullet}$) ($k_{p\text{-}BZQ/\bullet O_2^-} = 2 \times 10^9\ M^{-1}.s^{-1}$ (Wang et al., 2019b)) and 2 mM NaN_3 to scavenge singlet oxygen ($^1O_2$) ($k_{NaN_3/^1O_2} = 2 \times 10^9\ M^{-1}.s^{-1}$(Wang et al., 2015c)). It is worth noting that while those scavengers target mainly one radical, they can still react with other compounds. For instance, *p*-BZQ and NaN_3 are also strong $^{\bullet}OH$ scavengers as they react with $^{\bullet}OH$ at half or more than half the rate of their reactions with their main target radicals ($k_{p\text{-}BZQ/\bullet OH} = 1.2 \times 10^9\ M^{-1}.s^{-1}$ (Schuchmann et al., 1998) and $k_{NaN_3/\bullet OH} = 1 \times 10^9\ M^{-1}.s^{-1}$ (Wang et al., 2015c)). Each of those scavengers was tested individually then all three scavengers were added together in catalytic and non-catalytic ozonation experiments. While, the most pursued impact of scavengers' addition is attacking the radicals responsible for the oxidation of MPs that favour the indirect pathway, two other impacts can also emerge. The first is the termination of O_3 decomposition, and therefore allowing residual O_3 to persist longer in solution to oxidize the MPs that are preferentially removed through the direct pathway. The second is the opposite: the promotion of O_3 decomposition which eventually means depleting the available residual O_3, responsible for the direct pathway. In these experiments, the effect of scavenger addition on the decomposition of O_3 varied with the type of matrix and presence of catalyst. That effect was more pronounced in the non-catalytic than in the catalytic O_3 decomposition (Figures 4.10 and 4.11), which hints to the presence of free radicals in both systems due to the auto-decomposition of O_3 initiated by OH^- at neutral pH. NaN_3 promoted the non-catalytic O_3 decomposition in clean water and inhibited it in the mixture of MPs. It can be noticed that the inhibition / promotion effect of each scavenger changed between systems.

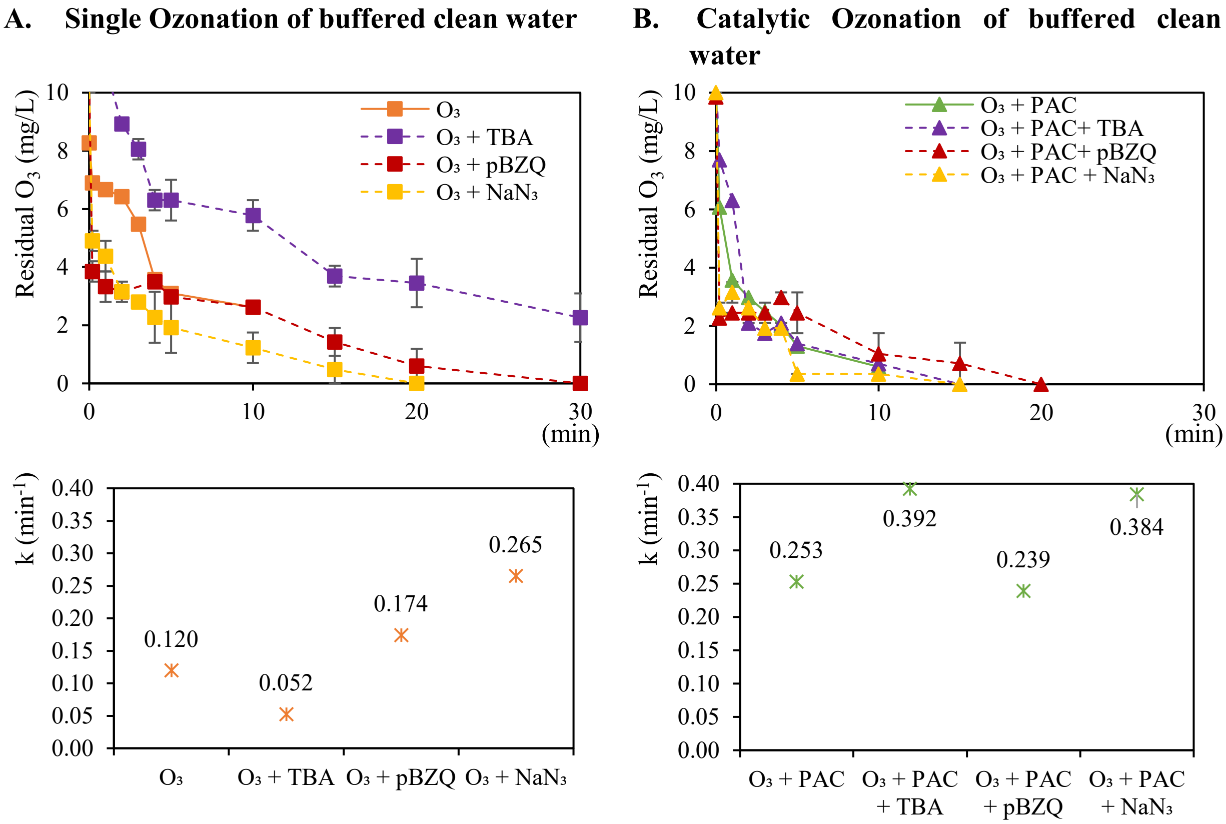


Figure 4.10 Measured residual O_3 in buffered clean water at pH 7, during single ozonation (O_3) and catalytic ozonation (O_3 + PAC) with and without radical scavengers. O_3: 10 mg/L; PAC: 100 mg/L; TBA: 2 mM; p-BZQ: 2 mM; NaN_3: 2 mM.

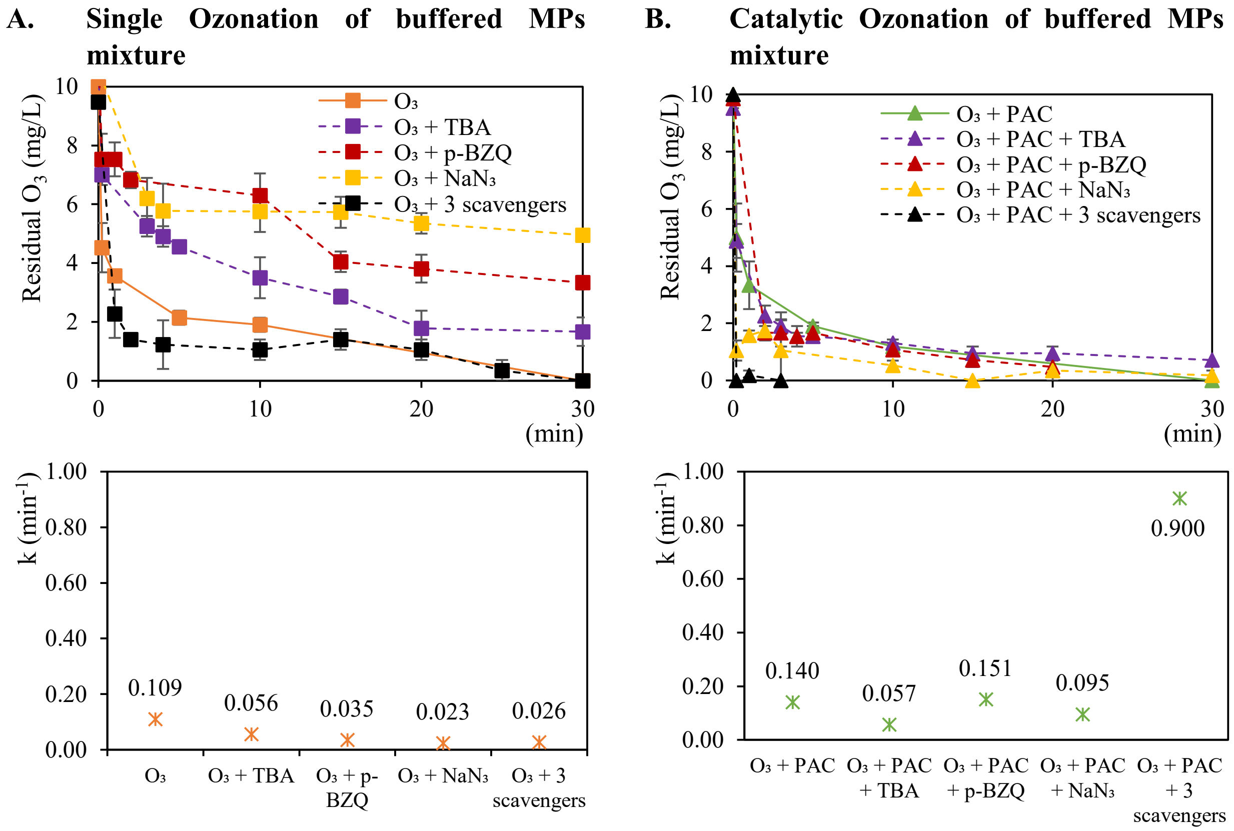
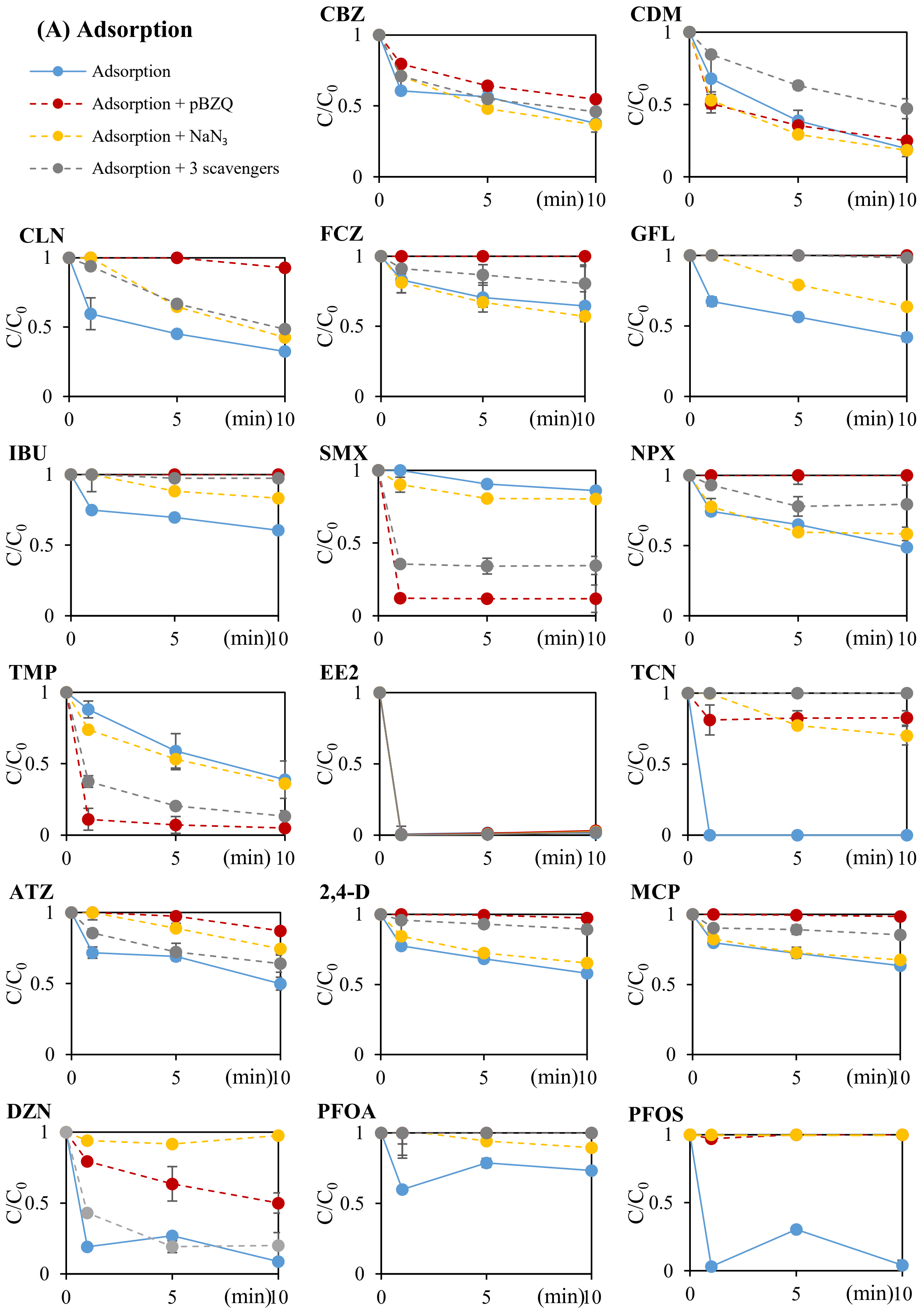
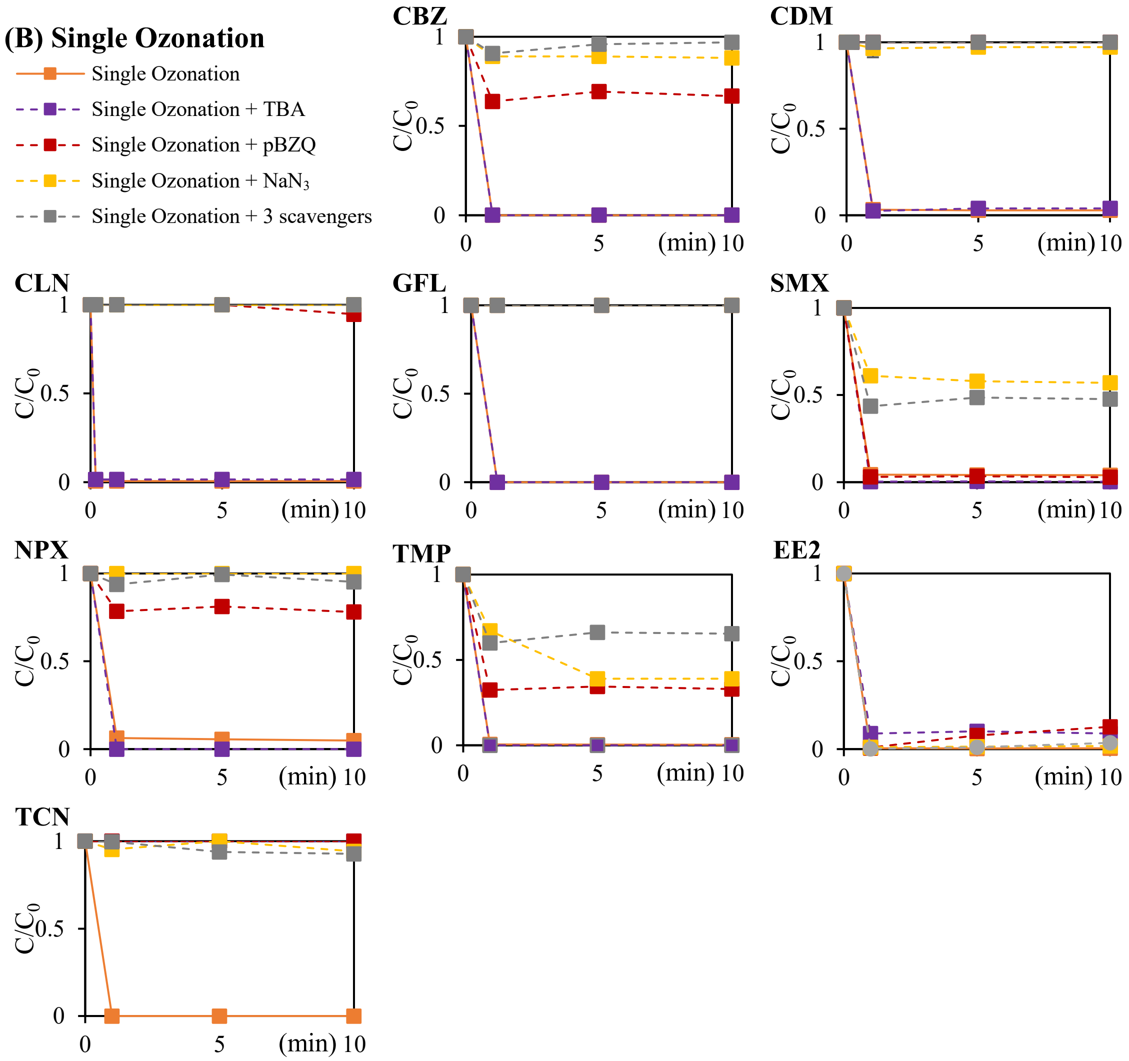


Figure 4.11 Measured residual O_3 in buffered mixture of 17 MPs pH 7, during single ozonation (O_3) and catalytic ozonation (O_3 + PAC) with and without radical scavengers. Mixture of 17 MPs: 500 ppb each; O_3: 10 mg/L; PAC: 100 mg/L PAC; TBA: 2 mM; *p*-BZQ: 2 mM; NaN_3: 2 mM.

On the other hand, the detailed data for the effect of adding scavengers on the removal efficiencies (by PAC, O_3 and O_3+PAC) of MPs is available in Figure 4.12.


(A) Adsorption
Adsorption
Adsorption + pBZQ
Adsorption + NaN$_3$
Adsorption + 3 scavengers
CBZ
CDM
CLN
FCZ
GFL
IBU
SMX
NPX
TMP
EE2
TCN
ATZ
2,4-D
MCP
DZN
PFOA
PFOS
C/C$_0$
0
0.5
1
0
5
(min) 10


(B) Single Ozonation
Single Ozonation
Single Ozonation + TBA
Single Ozonation + pBZQ
Single Ozonation + NaN$_3$
Single Ozonation + 3 scavengers
CBZ
CDM
CLN
GFL
SMX
NPX
TMP
EE2
TCN
C/C$_0$
0
0.5
1
0
5
(min) 10

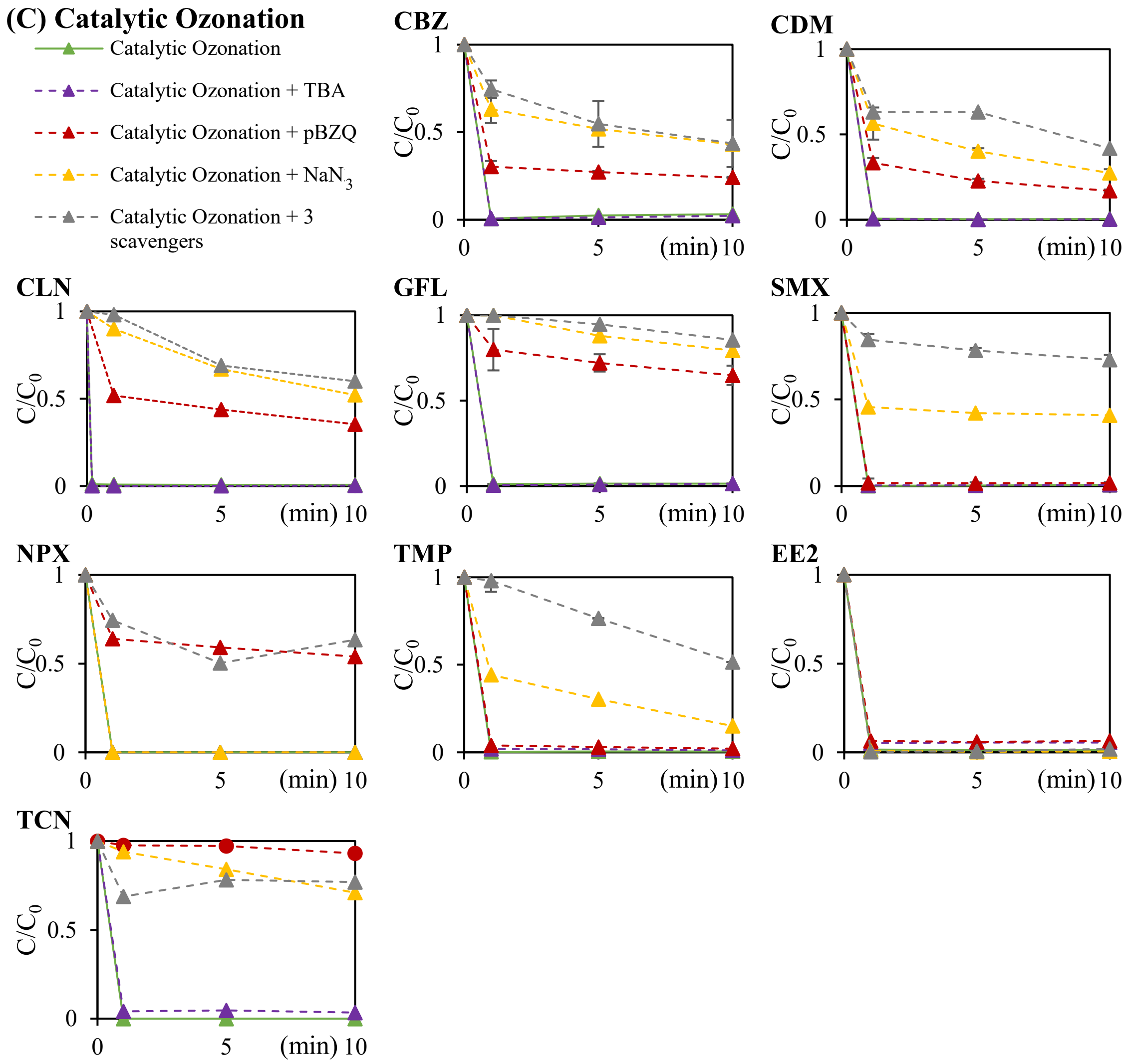


Figure 4.12 Effect of radical scavenger addition on the removal of each MP in a mixture of 17 MPs in borate buffer, pH 7 by **(A)** Adsorption; **(B)** Single Ozonation; **(C)** Catalytic ozonation (Mixture of 17 MPs: 500 ppb each; borate buffer: 4 mM; O_3: 10 mg/L; PAC: 100 mg/L; TBA: 2 mM; *p*-BZQ: 2 mM; NaN_3: 2 mM).

Control experiments to explore the effect of radical scavenger addition on the removal by adsorption during 10 minutes were performed. Since TBA is reported to poorly adsorb onto the surface of PAC and thus is more likely to scavenge free radicals in the bulk (Biernacki et al., 2015; Xing et al., 2014), experiments to assess the effect of TBA on the removal of MPs by adsorption were not performed. Nevertheless, *p*-BZQ seemed to infer some interaction with the surface of PAC whereby it almost completely inhibited the removal of more than half of the studied MPs (CLN, FCZ, GFL, IBU, NPX, 2,4-D, MCP, PFOA, PFOS). The inhibition of MPs adsorption was unlikely to be due to *p*-BZQ as adsorption experiment with 100 mg/L PAC in presence of 2 mM *p*-BZQ in buffer showed little adsorption of *p*-BZQ on PAC with 3% (±0.35%) dissolved organic carbon (DOC) removal at 10 minutes. The effect of NaN_3 was generally more moderate and differed between MPs. It was noted elsewhere that 0.01 %W/W of NaN_3 did not seem to affect the adsorption of 1 µg/L CBZ and NPX, onto 5 mg/L of granular activated carbon over a long period of 21 days (Yu et al., 2005). This means that NaN_3 did not impact the adsorption of CBZ and NPX which matched our results. However, it was also reported that NaN_3 can affect the adsorption capacity of AC by implying changes in the ionic strength of the solution (Yu et al., 2005) or by affecting the AC's surface properties (Klimenko et al., 2010). These could possibly explain why the addition of all three scavengers at the same time led to a decrease in removal for most MPs.

In single ozonation (Figure 4.13), all three scavengers showed relatively comparable effect for the inhibition of the removal of MPs. This was especially remarkable in the degradation of herbicides and PFAS. Some compounds showing full removal with single ozonation such CBZ, CLN, GFL, NPX, TMP, TCN were almost completely stopped from degrading by the addition of one or more radical scavengers. This is likely due to the very fast O_3 decomposition in presence of the three scavengers as displayed in Figure 4.11.

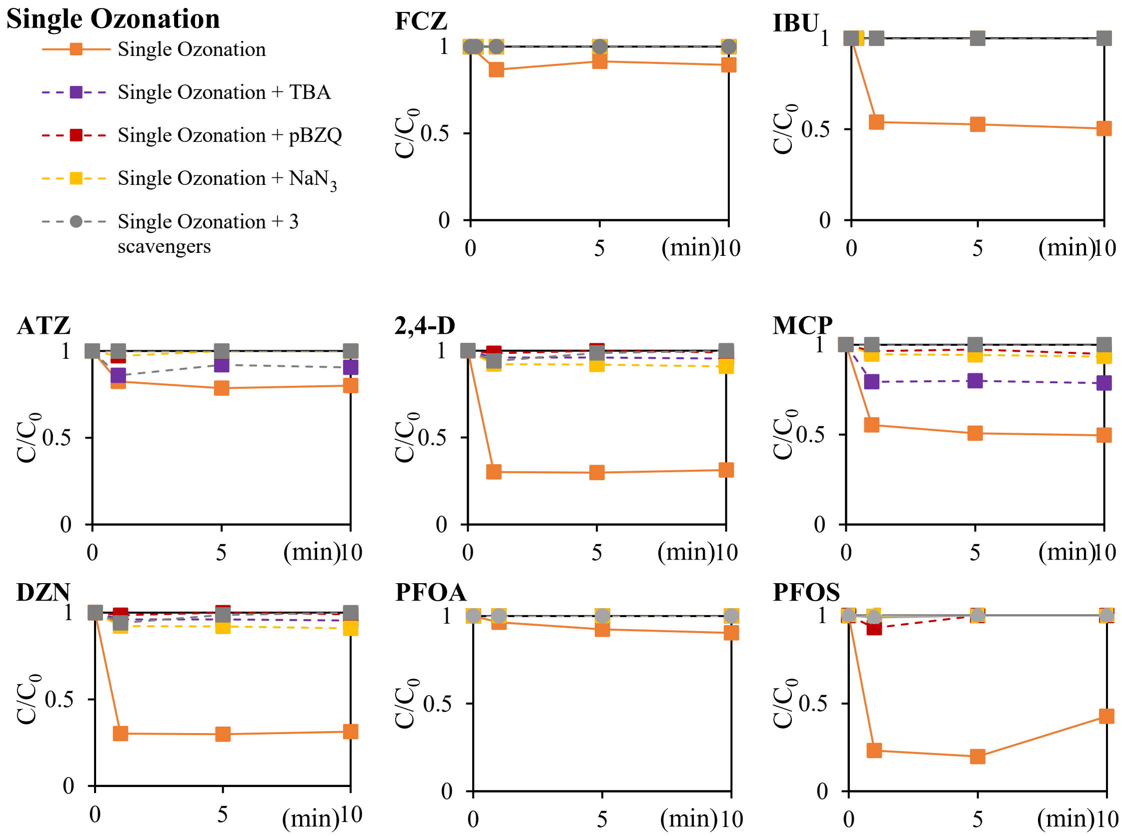


Figure 4.13 Inhibition effect of TBA, *p*-BZQ and NaN_3 added individually and combined during Single ozonation, with a buffered mixture of 17 MPs after 10 minutes of treatment (O_3: 10 mg/L, MPs in mixture: 500 ppb each; borate buffer pH 7; TBA: 2 mM; *p*-BZQ: 2 mM; NaN_3: 2 mM; exposure time: 10 minutes).

Among the three scavengers, TBA was less impactful indicating that $^{\bullet}OH$ was the least dominant oxidant in the ozonation system (Table 4.3). Also, it seemed that the removal of EE2 was favoured when any or all of the radicals were scavenged. It was reported that EE2 is highly reactive with O_3, with almost complete (99.7%) removal using 10 mg/L O_3 and 10 µg/L EE2 at neutral pH (Maniero et al., 2008). This suggested that reaction with EE2 was more favorable with molecular O_3 than the ROS formed. For most of the remaining MPs, the combination of all three scavengers revealed similar complete scavenging effect as NaN_3 only. In single ozonation, the removal of most MPs was completely stopped upon the addition of one or a combination of scavengers, except for ATZ, 2,4-D and MCP that showed a drop from 20%, 69% and 50% to 10%, 5% and 21% respectively upon addition of TBA. Also, some removal was noted for 2,4-D and

MCP with 1% and 5%, respectively, in presence of *p*-BZQ and 9% and 7% in presence of NaN_3 (Table 4.3).

Table 4.3 Percent removal in single and catalytic ozonation before and after the addition of radical scavengers

MP	No scavengers	TBA	*p*-BZQ	NaN_3	TBA+*p*-BZQ+NaN_3
% Removal by Single Ozonation at 10 min					
FCZ	10	0	0	0	0
IBU	50	0	0	0	0
ATZ	20	10	0	0	0
2,4-D	69	5	1	9	0
MCP	50	21	5	7	0
DZN	3	7	0	0	0
PFOA	10	0	0	0	0
PFOS	57	0	0	0	0
% Removal by Catalytic Ozonation at 10 min					
FCZ	70	60	25	29	21
IBU	68	56	11	17	9
ATZ	81	70	36	41	35
2,4-D	68	61	15	1	18
MCP	75	69	16	0	20
DZN	96	92	71	3	45
PFOA	43	46	15	11	0
PFOS	88	98	0	20	0

In PAC-catalyzed ozonation (Figure 4.14), the removal of MPs was reduced in presence of TBA, *p*-BZQ, NaN_3 or all three scavengers combined. The only cases of complete inhibition were for 2,4-D, MCP and DZN in presence of NaN_3 (1%, 0%, 3% respectively); and for PFOA and PFOS in presence of the three scavengers. Even though when radicals were scavenged in catalytic ozonation, many MPs could still be degraded. This might be due to an alternative removal pathway: either adsorption or oxidation by other strong oxidizing species. Such species were probably associated simultaneously with the mixture of MPs and catalyst. These results do not match what was reported in literature where the effect of scavenger was slightly more pronounced in catalytic than in non-catalytic ozonation, when the assessment was based on the removal of one compound only (Guzman-Perez et al., 2011).

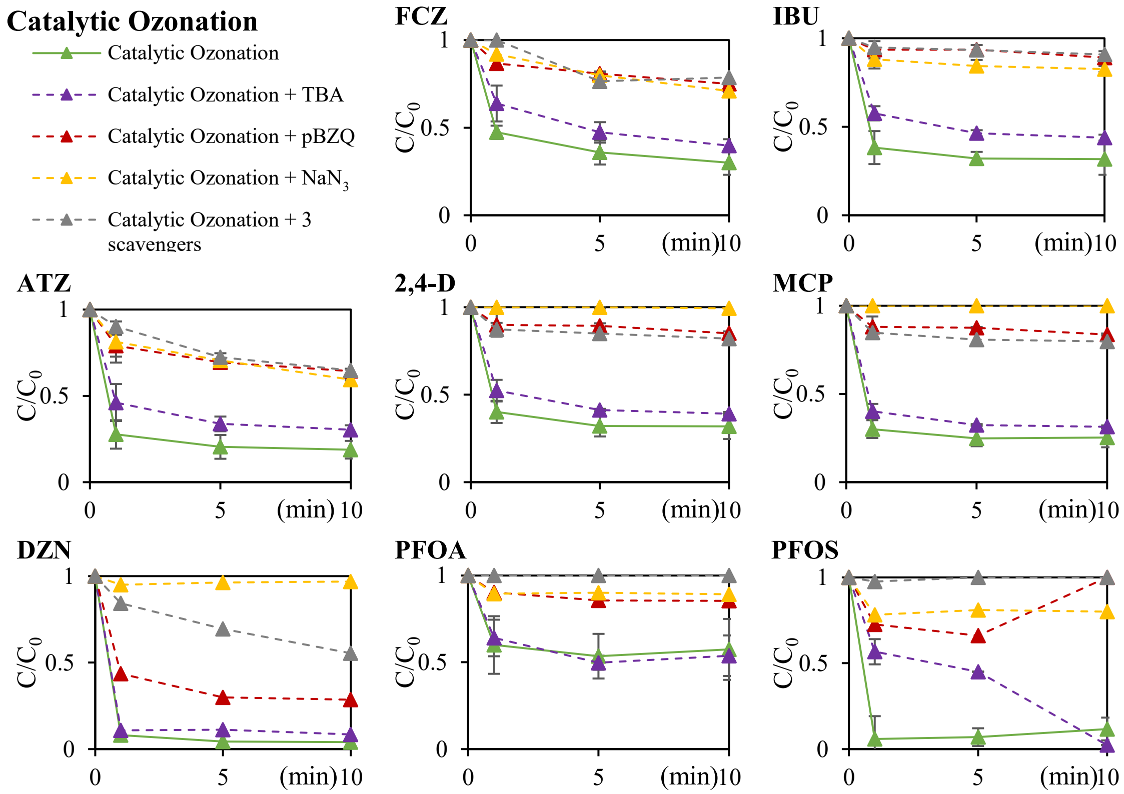


Figure 4.14 Inhibition effect of TBA, *p*-BZQ and NaN_3 added individually and combined during Catalytic Ozonation, with a buffered mixture of 17 MPs after 10 minutes of treatment (O_3: 10 mg/L, PAC, 100 mg/L; MPs in mixture: 500 ppb each; borate buffer pH 7; TBA: 2 mM; *p*-BZQ: 2 mM; NaN_3: 2 mM; exposure time: 10 minutes).

All examined radicals: $^{\bullet}OH$, $O_2^{-\bullet}$, $^1O_2$ were involved, to different extents, in the indirect pathway in both single and catalytic ozonation of the mixture of MPs, with $^{\bullet}OH$ being the least impactful. It is also possible that carbon-centered radicals formed in both systems either as intermediates in the MPs degradation or by virtue of the interaction between O_3 and PAC. This was because *p*-BZQ that scavenges $O_2^{-\bullet}$, can also react with alkyl radicals (Denisov, 2006), which meant that its inhibition effect could be associated with the scavenging of both radicals, despite its minimal impact on the decomposition of O_3. A complex system was thus formed in single and catalytic ozonation of the mixture of MPs. $^1O_2$ was likely to lead the oxidation mechanism as selectively removing it by adding NaN_3 showed the largest impact. $^1O_2$ can contribute in the pathway of O_3 decomposition into $^{\bullet}OH$ or work directly as an oxidant. When the short-lived $^1O_2$

is generated as an intermediate in the reaction between O_3 and OH^- in solution, then the resulting $^{\bullet}OH$ would be free in the bulk. As such, the addition of TBA should have resulted in the same inhibition effect as the addition of NaN_3. Yet, that was not the case, since scavenging $^1O_2$ was more impactful than scavenging •OH in the bulk by TBA. Instead, it is very plausible that most $^1O_2$ formed either in the bulk during the oxidation of organic compounds (which explains the results obtained with the addition of NaN_3 in single ozonation) or on the surface of PAC upon its reaction with O_3 where it can still diffuse to the bulk.

4.3.4.3. Identification of ROS by EPR spectroscopy

A thorough investigation of the formation of ROS during single and catalytic ozonation processes was conducted with EPR. It was first observed that a characteristic signal for DMPO–OH adduct of DMPO and free $^{\bullet}OH$ (quartet signal with hyperfine splitting couplings of $a_N = a_H = 14.9G$ with a peak intensity ratio of 1:2:2:1) was obtained in single ozonation at pH 7 (Figure 4.15-A). This confirmed the formation of free $^{\bullet}OH$ in the bulk solution at pH 7 due to the non-catalytic, auto-decomposition of O_3 by reaction with ^-OH. The same characteristic signal was also obtained with phosphate buffer at neutral pH (Figure 4.16). In contrast, the decomposition of O_3 catalyzed by PAC generated strong oxidative species or radicals, other than $^{\bullet}OH$, that formed a DMPO-X adduct (with 7 lines 1:2:1:2:1:2:1 and a hyperfine splitting constant $a_N = 7.32$) in clean water at pH 7 with borate buffer. This DMPO-X represents an oxidized form of DMPO. There was no $O_2^{-\bullet}$ trapped since there no signal for DMPO-OOH (sextet signal) was obtained. Similarly, a DMPO-X adduct with a different spectrum (triple triplets) was obtained using phosphate buffer which further confirmed the absence of free $^{\bullet}OH$ in the bulk solution upon PAC-catalyzed O_3 decomposition. Other spin traps were then tested in an attempt to capture any formed radicals. With TEMP (Figure 4.15-B) a triplet signal (3 lines at equal intensity) was obtained representing the typical spectrum for TEMPO which indicates the presence of $^1O_2$. Yet this signal was also obtained with TEMP and buffer only which means it could be an artifact. With MNP (Figure 4.15-C), a signal was detected in catalytic ozonation only representing a radical dimerization product of MNP: MNP was oxidized before trapping any radical, so neither $^1O_2$ nor carbon-based radicals $C^\bullet$ were trapped. With PBN (Figure 4.15-D) a signal for PBN-OH (triplet of doublets) was detected in single ozonation affirming the presence of $^\bullet OH$, while there was no spectrum obtained in catalytic ozonation. While such observations ascertained that free $^\bullet OH$ could not be captured in the bulk in PAC-catalyzed ozonation, there was still a possibility that $^\bullet OH$ was formed on the surface or in the interface between PAC and the bulk. This possibility was supported by the reduction in DMPO–X signal intensity upon addition of TBA in borate buffer and in phosphate buffer (Figure 16). That was also proven after sample (PAC+ aqueous O_3) centrifugation and PAC separation where only the bulk was analyzed and the spectrum for DMPO–X was also reduced. Actually, in a proposed mechanism for the decomposition of O_3 on AC (Biernacki et al., 2015), it was suggested that when $^\bullet OH$ form near the surface, they can adsorb onto the surface of PAC where a transfer of free electron is likely to occur and result in a carbon-based radial $AC^\bullet$–OH. It is likely that species such as AC–$^\bullet OH$ or $AC^\bullet$–OH were responsible for the oxidation of DMPO into DMPO-X and that in presence of PAC the formed $^\bullet OH$ preferentially remained in proximity of the surface rather than diffused to the bulk solution.

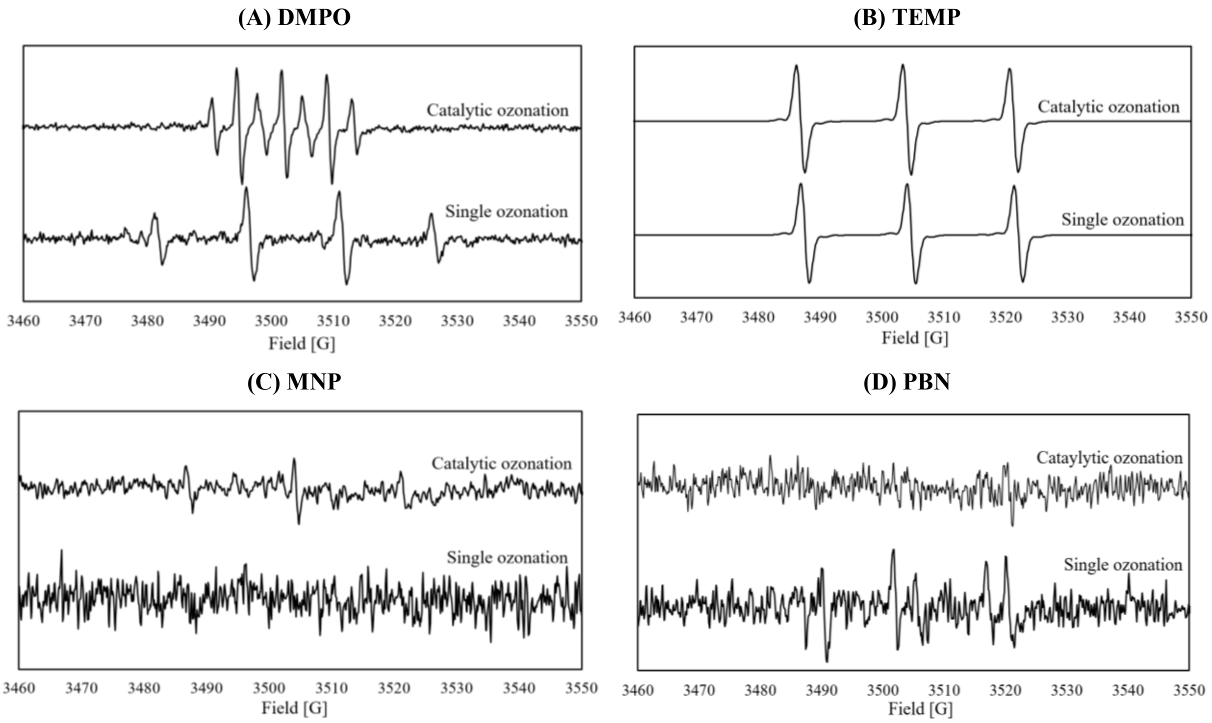
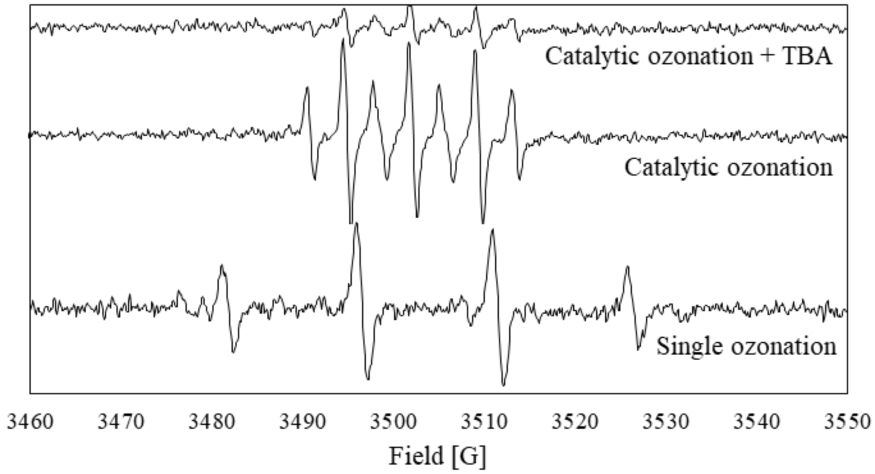


Figure 4.15 EPR spectra obtained in clean water with **(A)** 100 mM DMPO, featuring a spectrum for DMPO-OH (quartet signal) in single ozonation, and a signal with 7 lines representing DMPO-X in catalytic ozonation; **(B)** 5.9 M TEMP, featuring a signal with 3 lines at equal intensity in both single and catalytic ozonation; **(C)** 20 mM MNP, featuring no spectrum in single ozonation, and low-intensity signal in catalytic ozonation; **(D)** 2.5 M PBN, featuring a spectrum for PBN-OH (triplet of doublets) in single ozonation, and no signal in catalytic ozonation.

(Experimental conditions: Single Ozonation: 10 mg O_3/L in 4 mM borate buffer; Catalytic Ozonation: 10 mg O_3/L+100 mg PAC/L in 4 mM borate buffer)


(A) Borate Buffer

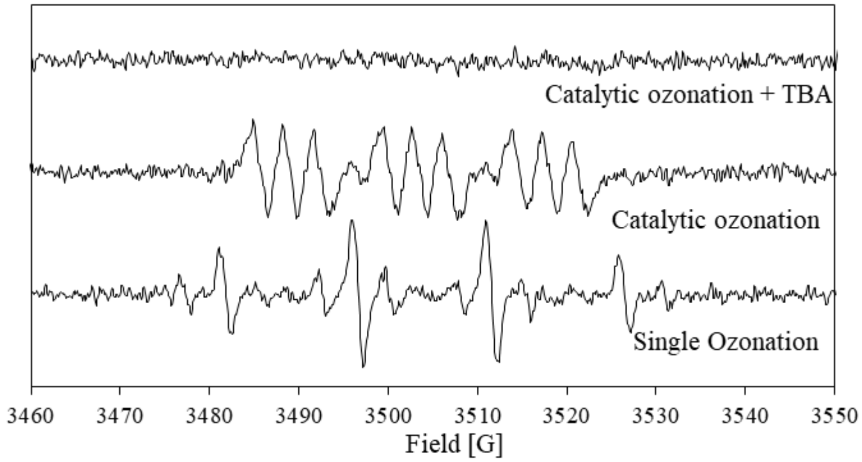

(B) Phosphate Buffer

Figure 4.16 EPR spectra obtained with 100 mM DMPO in clean water under different experimental conditions: Single ozonation with 10 mg O_3/L; Catalytic Ozonation with 10 mg O_3/L and 100 mg PAC/L; Catalytic Ozonation in presence of TBA with 10 mg O_3/L and 100 mg PAC/L and 2 mM TBA; in **(A)** Borate buffer, and **(B)** Phosphate buffer.

On the other hand, there was no proof of the formation of $^1O_2$, $O_2^\bullet$ or carbon-centered radicals during PAC catalyzed ozonation since the characteristic spectra for the respective adducts with DMPO, TEMP or MNP were not obtained. Despite the fact that no free reactive oxygen species (ROS) were detected in the bulk, it was hard to demonstrate their occurrence on the surface of PAC or in the interface. In a possible scenario, with the presence of ROS in the solution, the paramagnetic centers on PAC surface, i.e. the formed carbon-centered radicals –C$^\bullet$, could transform into –C–O$^\bullet$ as suggested in literature (Wieckowski et al., 2015).

When the EPR analysis was performed in a mixture of MPs, an intense spectrum for DMPO-OH was obtained during single ozonation revealing the abundant formation of free •OH in the bulk in comparison with the free •OH formed in clean water. Yet, in catalytic ozonation it seems that DMPO-OH spectrum decreased and a new spectrum emerged signaling the formation of other radicals or strong oxidative species (Figure 4.17). The addition of TBA to scavenge free •OH did not reveal any significant impact on the intensity of that spectrum. These findings were in conformity with the radical scavenging tests using TBA presented in section 4.3.4.1 where the addition of TBA only slightly inhibited the removal of MPs. As such, it can be confirmed that there were no free •OH in the bulk solution during catalytic ozonation with PAC, and thus free •OH did not partake in the catalytic oxidation of MPs.

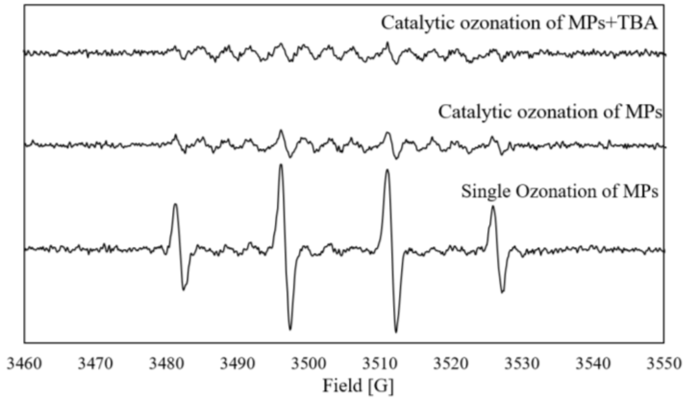


Figure 4.17 EPR spectra obtained with 100 mM DMPO in a mixture of 17 MPs at 250 ppb each in 4 mM borate buffer pH 7, under different experimental conditions: Single Ozonation: 10 mg O_3/L; Catalytic Ozonation: 10 mg O_3/L+100 mg PAC/L; Catalytic Ozonation + TBA: 10 mg O_3/L+100 mg PAC/L+2 mM TBA.

4.3.5. Proposed catalytic ozonation mechanisms

Based on these radical scavenging and EPR experimental results, it can be concluded that •OH was not the key species in the catalytic mechanism. Instead other strong oxidizing species were probably responsible for the removal of target MPs in single ozonation and in PAC-catalyzed ozonation besides adsorption. By employing PAC as a catalyst, it seemed that it maintained its adsorbing role in addition to its role as initiator/promoter for O_3 decomposition. The latter was clearly justified when the rate of O_3 decomposition increased upon addition of PAC in clean water. Figure 4.18 displays a proposed schematic for the MPs removal mechanism by O_3 and PAC. In this figure, it is suggested that O_3 decomposition in presence of PAC and MPs at pH 7 takes place at two different levels simultaneously. O_3 reacts with OH^- and MPs in the bulk solution and with the surface of PAC. In this case with basic surface, PAC tends to lose its electron density when in solution and gain more protons which will facilitate the adsorption of deprotonated MPs (with pKa higher than pH 7 of the solution) making the adsorption pathway favourable for some MPs. Also, the now acidic PAC surface attracts electrophilic species such as O_3 and radicals with free electrons like $^{\bullet}OH$, O_2^- and $^1O_2$ driving most of the reaction to occur on the surface/interface.

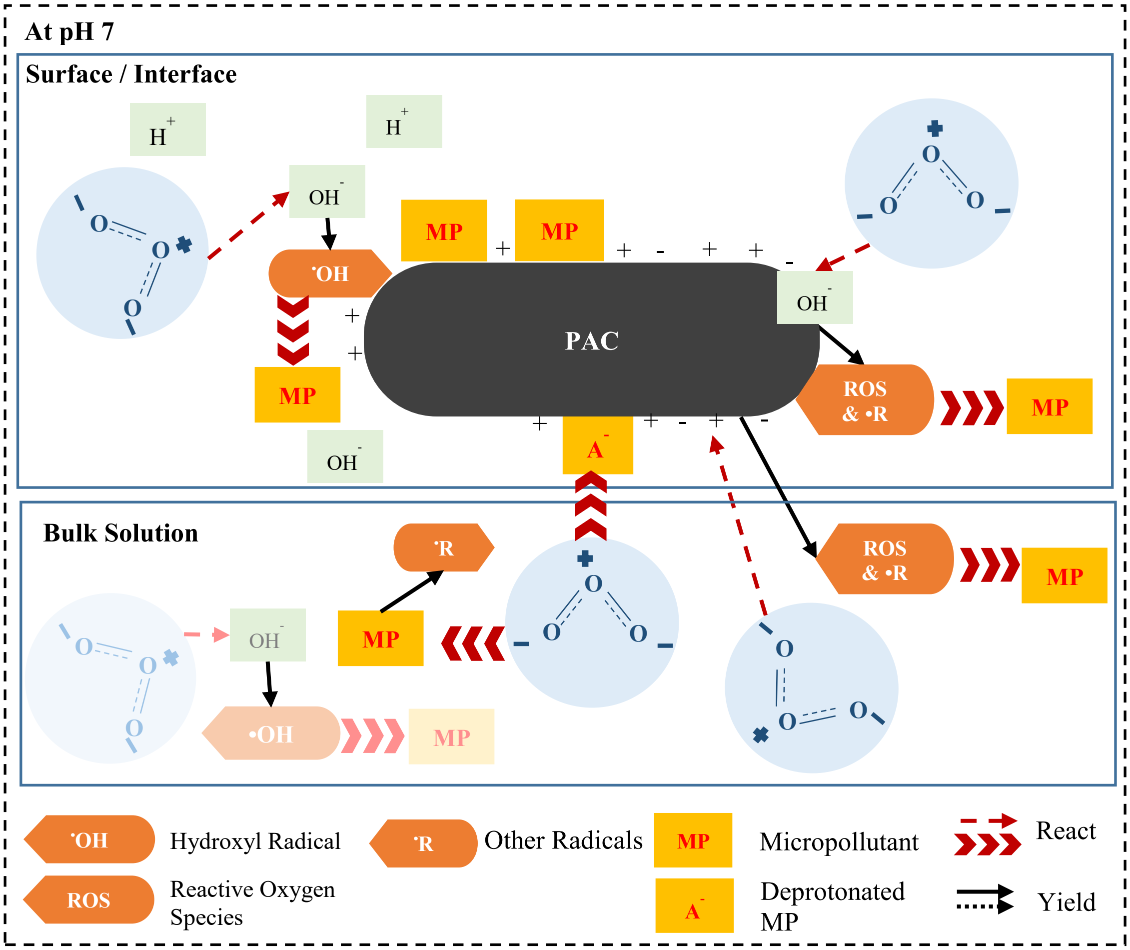


Figure 4.18 Suggested removal mechanisms in PAC-catalyzed ozonation.

In a complex matrix with a diverse mixture of MPs, the application of $^1O_2$ scavenger NaN_3 showed a significantly more pronounced inhibition effect for the removal of MPs in single and catalytic ozonation than TBA. This implies that $^1O_2$ was formed in O_3 + MPs in the bulk solution as intermediate or as product of the reaction of O_3 with either OH^- or MPs in the mixture (Equations 4.2 - 4.3 and 4.5). In its turn $^1O_2$ could further react to form $^{\bullet}OH$ in the bulk. It can also directly oxidize MPs in the bulk (Equation 4.6) as discussed earlier. When in water, H_2O molecules can chemisorb onto the surface of PAC and result in adsorbed hydroxyl groups as PAC–OH and H^+ (Equation 4.7). In O_3 + PAC + MPs an additional source of $^1O_2$ and potentially other radicals is possibly the reaction between O_3 and the surface of the hydrated PAC (PAC-OH) (Equation 4.8), and thus there could be more $^{1}O_2$ generated in a catalytic than in non-catalytic system. The formed $^{1}O_2$ can either diffuse to the bulk or adsorb onto the surface of PAC forming an oxidizing species that targeted MPs and resulted in oxidized MPs removed by PAC (Equation 4.9). The ${}^{\bullet}OH$ that form due to the interaction between O_3 and PAC (Equation 4.8) was more likely to adsorb on the surface forming a carbon-based radical PAC•–HO that can undertake the oxidation of MPs, rather than diffuse to the bulk (Equation 4.10). This was also suggested elsewhere (Biernacki et al., 2015).

Reactions in the bulk, radicals' formation in the bulk:

O_3 decomposition in water

$O_3 + H_2O \rightarrow {}^{\bullet}OH + O_2$ *Equation 4.1*

$O_3 + OH^{-} \rightarrow {}^{\bullet}O_2^{-} + HO_2^{\bullet} + HO_3^{\bullet} + O_3^{-\bullet}$ *Equation 4.2*

$2{}^{\bullet}O_2^{-} + 2H^{+} \rightarrow {}^{1}O_2 + H_2O_2$ *Equation 4.3*

$O_3 + HO_2^{\bullet} \rightarrow {}^{\bullet}OH + 2O_2$ *Equation 4.4*

Reactions with MPs in solution

$O_3 + MP \rightarrow {}^{1}O_2 + MPO$ *Equation 4.5*

${}^{1}O_2/{}^{\bullet}OH + MP \rightarrow MPO$ *Equation 4.6*

Reactions with the surface of PAC, radicals' formation on the surface/interface:

$PAC + H_2O \rightarrow PAC\text{–}OH + H^{+}$ *Equation 4.7*

$O_3 + PAC\text{–}OH \rightarrow {}^{1}O_2;\ {}^{\bullet}O_2^{-};\ {}^{\bullet}OH$ *Equation 4.8*

$[{}^{1}O_2 + PAC] + MPs \rightarrow PAC\text{–}MPO$ *Equation 4.9*

${}^{\bullet}OH + PAC \rightarrow PAC^{\bullet}\text{–}HO + MPs \rightarrow PAC\text{-}MPO$ *Equation 4.10*

Hydrogen peroxide (H_2O_2) can also build up in the homogeneous bulk phase through reactions between ${}^{\bullet}OH$ molecules (Equation 4.11) or between ${}^{\bullet}OH$ and $HO_3^{\bullet}$ formed in Equation 4.2

(Equation 4.12). It is then terminated by auto-decomposition or reaction with O_3, ${}^{\bullet}O_2^{-}$, $HO_2^{\bullet}$ (Zhao et al., 2008) (Equations 4.13 - 4.14 and 4.15). Yet, in our catalytic system, H_2O_2 did not seem to play any significant role where it measured less than 1 mg/L throughout the PAC-catalyzed ozonation experiments.

$$ {}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 + O_2 \qquad \textit{Equation 4.11} $$

$$ {}^{\bullet}OH + HO_3^{\bullet} \rightarrow H_2O_2 + O_2 \qquad \textit{Equation 4.12} $$

$$ H_2O_2 + O_3 \rightarrow {}^{\bullet}OH + HO_2^{\bullet} + O_2 \qquad \textit{Equation 4.13} $$

$$ H_2O_2 + HO_2^{\bullet} \rightarrow {}^{\bullet}OH + HO_2 + O_2 \qquad \textit{Equation 4.14} $$

$$ H_2O_2 + {}^{\bullet}O_2^{-} \rightarrow {}^{\bullet}OH + OH^{-} + O_2 \qquad \textit{Equation 4.15} $$

4.4. Conclusions

In conclusion, while PAC is recognized for its high adsorption capacity, using it solely for adsorption ends up as a relatively slow process. Yet combining PAC with O_3 has proven effective for the degradation of organic micropollutants from different classes, and affinities towards adsorption and catalytic ozonation. In fact, MPs with limited reactivity with O_3 were removed by at least 68% within 10 minutes only of PAC-catalyzed ozonation with 10 mg/L O_3 and 100 mg/L PAC. In most cases, the parent compound degraded within the first minute. The catalytic mechanism with PAC relied heavily on the catalyst and the mixture of target compounds that substantially participated in the formation of radicals in PAC catalyzed the ozonation by initiating, promoting and terminating the decomposition of O_3. PAC also acted as a support for radicals and intermediates generated in the solution by MPs oxidation. Unlike what has been reported previously, free ${}^{\bullet}OH$ was not the key radical, instead, singlet oxygen ${}^{1}O_2$ and superoxide radical ${}^{\bullet}O_2^{-}$ dictated the mechanism that was mainly shifted to the interface between PAC and the bulk solution. These results provided a new insight on the catalytic mechanisms involved in the ozonation process and can set the ground for further applications in real environmental matrices.

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CHAPTER 5: Assessment of the Effect of Ozone Specific Dose on the Removal of Micropollutants in a Mixture by Single and PAC-catalyzed Ozonation through Benchmarks and Kinetics[3]

5.1. Introduction

Trace organic compounds such as pharmaceuticals, personal-care products, endocrine disrupting compounds, industrial surfactants, and others are frequently detected in the aquatic environment (Alexander et al., 2012). Commonly referred to as micropollutants (MPs), they occur in environmental waters at very low concentrations and can provoke adverse impacts to the environmental and public health (Stamm et al., 2016). Research has proved that treatment methods based on oxidation processes such as ozonation, are effective for their degradation in natural and synthetic media (Kolosov et al., 2018; Mecha et al., 2016; Melero et al., 2009; Sui et al., 2012). It is the presence of compounds that are not sufficiently reactive with molecular ozone (O_3) that prompts the addition of a catalyst to the process (Beltran, 2004) to improve the overall performance of ozonation. Powdered activate carbon (PAC) is one of the carbon-based catalysts that were tested in catalytic ozonation. It has the advantage of a high adsorption capacity by virtue of its small particle size. The dose selection of both O_3 and PAC is very critical for the efficiency of PAC-catalyzed ozonation. Generally, the tested PAC doses ranged between 20 mg/L (Rozas et al., 2017) and 500 g/L (Faria et al., 2008b), while O_3 doses were commonly reported as specific doses realtive to the dissolved organic carbon (DOC) ranging between 0.21 - 1.53 mg O_3/mg DOC (Song et al., 2017; Zimmermann et al., 2011) with seldom doses outside this range such as 4.8 mg O_3/mg DOC (Tondera et al., 2015). The efficiency of PAC-catalyzed ozonation for the removal of several MPs that are simultaneously present in the same medium was approached in a mixture of four MPs

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[3] A version of this chapter will be submitted jointly with a version of chapter 6 to Journal of Hazardous Materials.

only (Rozas et al., 2017). MPs were monitored individually and in a mixture where they were reported to degrade in a slower fashion.

Despite the significant advances in analytical chemistry, the quantification of MPs has been cost-prohibitive and impractical due to the large number of structurally diverse compounds and the increasing frequency of their detection (Oulton et al., 2010). Therefore, mathematical models and surrogate parameters have been developed to understand and predict the behavior of MPs (Arlos et al., 2014; Johnson & Williams, 2004). In practical environmental applications, the use of surrogate parameters to predict the behavior of MPs has been extensively studied for municipal wastewater treatment (Acero et al., 2000). Surrogates used for municipal wastewaters included total organic carbon (TOC), chemical oxygen demand (COD), ultraviolet absorbance at 254 nm (UVA_{254}), and UV fluorescence (Gerrity et al., 2012; Lee et al., 2013). It was alleged that the selection of a specific surrogate parameter depends on the water treatment step being monitored (Bourgeois et al., 2001). Accordingly, in O_3-based treatments, UVA_{254}, total fluorescence, and dissolved organic carbon (DOC) were counted as promising surrogate parameters (Chys et al., 2018; Gerrity et al., 2012). Nevertheless, relying on these surrogates to estimate the removal of MPs is rather a holistic approach that looks at the general load of MPs and overlooks specific categories of compounds according to their predicted response to the treatment.

For a better understanding of the removals and as an alternative for actively measuring the exact concentrations of each compound, benchmarking which is the concept of assessing how one compound performs in comparison with another compound in the same media, can be used (McLachlan et al., 2016). In environmental studies, it was applied to estimate the behaviour of one pollutant relative to another pollutant that has been well studied and understood (McLachlan et al., 2016). It was also utilized to evaluate the performance of different treatments such as adsorption with different types of adsorbents for the degradation of pollutants under multiple conditions (Ling et al., 2017).

The objective of this study was to assess the effect of O_3 specific dose on the performance of PAC-catalyzed ozonation for the degradation of a mixture of MPs in a clean matrix at neutral pH. The removals by PAC-catalyzed ozonation were benchmarked with single ozonation and adsorption. Correlations were developed between MPs to identify potential surrogate MPs for compounds with known or unknown reactivity towards O_3. Removal kinetics were attempted in batch experiments and intermediates were screened for both treatments.

5.2. Material and methods

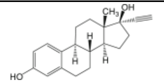
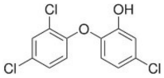
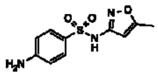
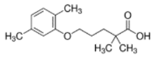
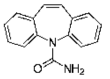
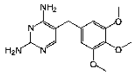
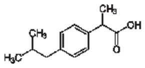
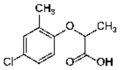
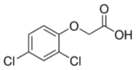
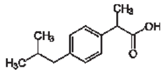
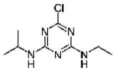
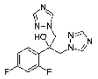
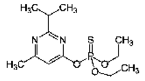
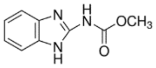
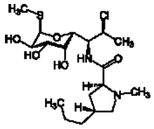
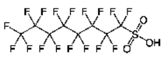
5.2.1. Micropollutants and reagents

All micropollutants selected in this study were supplied by Sigma Aldrich, Canada and Supelco, Canada. Individual stock solutions of each MP were prepared in MilliQ water at concentrations ranging between 5 and 100 mg/L in conformity with their solubility limit at 20 °C. They were then sonicated for 20 minutes to ensure complete dissolution and used to prepare a stock mixture of MPs that was also sonicated for 20 minutes. All solutions were stored at 4 °C in the dark. Chemicals such as potassium indigo trisulfonate, phosphoric acid, sulfuric acid, sodium tetraborate, and sodium thiosulfate were purchased from Sigma Aldrich, Canada. Commercial PAC WPX with a particle size of 45 µm and a measured surface area of 632 m^2/g was acquired from Calgon Carbon. Further details on the characteristics of PAC are available in Chapter 4, section 4.3.1. Borate buffer was prepared in a stock solution with a 1:1 mixture of sodium tetraborate and sulfuric acid. The O_3 quencher sodium thiosulfate was prepared in MilliQ water and stored at 4 °C until used. All glassware used in the experiments were ozonated for 30 minutes in a washtub to ensure they were O_3 demand-free prior to each experiment.

5.2.2. Target mixture

A mixture of seventeen MPs belonging to the three different categories: pharmaceuticals and personal care products, herbicides and industrial products or surfactants was prepared in buffered water at pH 7. The MPs are enlisted in Table 5.1 along with their concentrations in the influent wastewater to a wastewater treatment plant in Alberta. Only four MPs were previously studied in a catalytic ozonation system with PAC: CBZ (Rozas et al., 2017); SMX (Goncalves et al., 2012); TCN (Rozas et al., 2017) and ATZ (Guzman-Perez et al., 2011; Rozas et al., 2017). The other thirteen were studied for the first time in the O_3+PAC system: CDM, CLN, FCZ, GFL, IBU, NPX, TMP, EE2, 2,4-D, MCP, DZN, PFOA, PFOS. To date, five MPs are regulated in the Guidelines for Canadian Drinking Water Quality (ATZ: 0.0005 mg/L; DZN: 0.02 mg/L; 2,4-D: 0.1 mg/L; PFOS: 0.0006 mg/L; PFOA: 0.0002 mg/L) (Health Canada, 2019). Also five MPs are regulated under the Environmental Quality Guidelines for Alberta Surface Waters (ATZ: 1.8 µg/L; 2,4-D: 4 µg/L; DZN: 0.17 µg/L ; EE2: 0.5 ng/L; MCP: 13 µg/L) (Alberta Environment & Sustainable Resource Development (ESRD), 2014). Two MPs are listed under the Canadian Water Quality Guidelines for the protection of Aquatic Life (in fresh water: ATZ: 1.8 µg/L; CBZ: 10 µg/L) (Canadian Council of Ministers of the Environment (CCME), 2014). There are still no national guidelines for the permissible concentrations in wastewater effluents.

Table 5.1 Characteristics and occurrence of the studied MPs.

Name Formula	Abbreviation	**Structure**	**Use**	**Influent conc. (ng/L)****	
				2011	**2019**
Ethinylestradiol $C_{20}H_{24}O_2$	EE2		PPCP*: Semisynthetic estrogen	287-2,260	3,500
Triclosan $C_{12}H_7Cl_3O_2$	TCN		PPCP: Antiseptic	1,210-946	N/D
Sulfamethoxazole $C_{10}H_{11}N_3O_3S$	SMX		PPCP: Antibacterial	597-1,420	4,900
Gemfibrozil $C_{15}H_{22}O_3$	GFL		PPCP: Lipid-regulating agent	94-185	600
Carbamazepine $C_{15}H_{12}N_2O$	CBZ		PPCP: Anticonvulsant	549-1,060	N/D
Trimethoprim $C_{14}H_{18}N_4O_3$	TMP		PPCP: Antibacterial	265-366	5,200
Naproxen $C_{14}H_{14}O_3$	NPX		PPCP: Anti-inflammatory, Anti-rheumatic	3,280-8,090	N/D
Mecoprop $C_{10}H_{11}ClO_3$	MCP		Herbicide	N/A	4,600
2,4-Dichlorophenoxyacetic Acid $C_8H_6Cl_2O_3$	2,4-D		Herbicide	N/A	4,700
Ibuprofen $C_{13}H_8O_2$	IBU		PPCP: Anti-inflammatory	7,580-13,100	2,600
Atrazine $C_8H_{14}ClN_5$	ATZ		Herbicide	N/A	N/D
Fluconazole $C_{13}H_{12}F_2N_6O$	FCZ		PPCP: Antifungal	N/A	100
Diazinon $C_{12}H_{21}N_2O_3PS$	DZN		Herbicide	N/A	N/D
Carbendazim $C_9H_9N_3O_2$	CDM		PPCP: Antifungal	N/A	N/D
Clindamycin $C_{18}H_{33}ClN_2O_5S$	CLN		PPCP: Antibacterial	N/A	N/D
Perfluorooctanoic Acid $CF_3(CF_2)_6COOH$	PFOA		Surfactant	N/A	N/D
Heptadecafluoro-octanesulfonic Acid $CF_3(CF_2)_7SO_3H$	PFOS		Surfactant	N/A	N/D

Notes: *PPCP = Pharmaceutical and Personal care product; N/A: Not available; N/D: Not detected;
** Concentrations in the influent wastewater to a wastewater treatment plant in Alberta.

5.2.3. Experimental procedures

5.2.3.1. Ozonation experiments

All experiments were performed in duplicates using 100 mL round bottom flask glass reactors wrapped in aluminum foil at room temperature and atmospheric pressure. O_3 was generated from dry oxygen using the O_3 Generator Model GSO-30 and was bubbled into O_3 demand-free water (ODFW) in an ice bath to obtain a saturated O_3 stock solution. A measured volume of O_3 stock solution was transferred to each reactor to achieve the desired final concentration. Reactors were then immediately capped with no free headspace, and stirred with a magnetic stirrer over a multi-position stir plate. Samples were withdrawn at fixed time intervals and analyzed for residual O_3 via the Indigo Method (Bader & Hoigne, 1981) with UV absorbance at 600 nm measured using Ultrospec 2100 UV-Visible spectrophotometer. Samples collected for MPs analysis were filtered with 0.22 µm nylon syringe filters into 1.5 mL amber polypropylene vials containing sodium thiosulfate to quench the residual O_3. All samples were stored at 4 °C in the dark until analysis.

5.2.3.2. Kinetics study

In this study, the O_3 specific dose was manipulated by varying the mass concentration of the MPs in the mixture, while keeping the mass concentrations of O_3 and PAC fixed throughout the experiments at 10 mg/L and 100 mg/L respectively. The concentrations of O_3 and PAC were selected in accordance with the study presented in Chapter 4, Figures 4.3 and 4.4. By changing the concentration of MPs in the mixture, or in other terms the DOC, the O_3 demand changed and thus the concentration of O_3 available to carry on the reaction changed. This is further discussed in section 5.3.3 below. MPs' removal kinetics were therefore attempted under the different O_3 specific doses in a batch reactor, following the same experimental procedure presented above.

5.2.4. Analytical methods

The analysis of MPs was performed using ultra-performance liquid chromatography – quadrupole time-of-flight mass spectrometry UPLC-qTOF-MS (Xevo G2-S, Waters). ACQUITY UPLC BEH C18, 50 x 2.1 mm column, at 50 °C was utilized with an injection volume of 10 µL. MPs were analyzed using positive or negative ionization modes. In positive ionization mode, the mobile phase consisted of water with 0.1 % formic acid (solvent A) and acetonitrile with 0.1 % formic acid (solvent B). In negative ionization mode, 0.02% ammonium hydroxide in water (solvent A) and 0.02% ammonium hydroxide in acetonitrile (solvent B) were used. Details of the detection mode and monitored masses are available in Table 4.2 in Chapter 4.

5.2.5. Detection of intermediates

Literature was screened for the common intermediates and by-products that are produced during the oxidation process of each MP. The same analytical methods detailed above were employed to detect the presence of those compounds in the collected samples.

5.3. Results and discussion

5.3.1. Effect of O_3 specific dose on the removal of MPs by single ozonation

Table 5.2 summarizes the expected removals of the MPs in the mixture by adsorption onto PAC and by ozonation as reported in literature, along with their reported rate constants. The MPs were classified in four groups following their reactivity with molecular O_3 and with hydroxyl radicals ($^{\bullet}OH$). The reported second order rate constants were obtained for each MP studied individually rather than in a mixture with other MPs. Neither adsorption onto PAC nor ozonation seemed able to provide an effective solution for the degradation of all MPs from the different categories. While ozonation was less efficient for the removal of MPs in groups II and III in addition to POFA and PFOS, adsorption onto PAC did not reveal high removal either, except for FCZ, PFOA and PFOS. Those three MPs were reportedly better removed by adsorption than by single ozonation. It is worth noting that the removal levels reported in literature were possibly a function of specific experimental conditions. For instance, the removal of PFOA and PFOS by adsorption onto activated carbon was evaluated in presence and absence of effluent organic matter (Yu & Hu, 2011). It was determined that the adsorption decreased in the presence of effluent organic matter where higher adsorbent doses would be required for mitigation.

Table 5.2 Summary of the removal of MPs by adsorption and single ozonation in different media as reported in literature and their reported rate constants at pH 7 and 20 ºC, following similar classification used elsewhere (Guo et al., 2018; Lee et al., 2013).

MP	Removal in Literature				Kinetics in Literature		
	By PAC	**References**	**By O_3**	**References**	**k_{O3} ($M^{-1}s^{-1}$)**	**$k_{\bullet OH}$ ($M^{-1}s^{-1}$)**	**References**
Group I: $k_{O3} > 1x10^4\ M^{-1}s^{-1}$							
EE2	Intermediate/High	(Westerhoff et al., 2005)	High	(Broseus et al., 2009)	$7×10^9$	$9.8×10^9$	(Huber et al., 2003)
TCN	Intermediate/High	(Rozas et al., 2017; Westerhoff et al., 2005)	High	(Rozas et al., 2017)	$3.8×10^7$	$9.6×10^9$	(Suarez et al., 2007; Wert et al., 2009)
SMX	Intermediate/Low	(Kovalova et al., 2013; Margot et al., 2013; Rizzo et al., 2019; Westerhoff et al., 2005)	High	(Goncalves et al., 2012; Kovalova et al., 2013; Margot et al., 2013; Rizzo et al., 2019)	$5.7×10^5$	$5.5×10^9$	(Dodd et al., 2006)
GFL	Intermediate/Low	(Westerhoff et al., 2005)	High	(Uslu et al., 2015)	$4.9×10^5$	$7.1×10^9$	(Jin et al., 2012; Razavi et al., 2009)
CBZ	Low	(Margot et al., 2013; Rozas et al., 2017)	High	(Margot et al., 2013; Rozas et al., 2017)	$3×10^5$	$8.8×10^9$	(Huber et al., 2003; Wert et al., 2009)
TMP	High	(Margot et al., 2013; Westerhoff et al., 2005)	High	(Kovalova et al., 2013; Margot et al., 2013)	$2.7×10^5$	$6.9×10^9$	(Dodd et al., 2006; Wert et al., 2009)
NPX	High Intermediate/Low	(Margot et al., 2013) (Westerhoff et al., 2005)	Intermediate/High	(Margot et al., 2013)	$2×10^5$	$9.6×10^9$	(Huber et al., 2005; Wert et al., 2009)
Group II: $10 \leq k_{O3} < 1x10^4\ M^{-1}s^{-1}$							
MCP	Intermediate	(Margot et al., 2013)	Intermediate	(Margot et al., 2013)	101	$1.9×10^9$	(Beltrán & Rey, 2018)
2,4-D	Low	(Javier-Benitez et al., 2004)	Low	(Javier-Benitez et al., 2004)	29.1	N/A	(Xiong & Graham, 2008)
Group III: $k_{O3} < 10\ M^{-1}s^{-1}$ and $k_{\bullet OH} > 1x10^9\ M^{-1}s^{-1}$							
IBU	Intermediate/Low	(Westerhoff et al., 2005)	Intermediate	(Betancur-Corredor et al., 2016)	9.6	$7.4×10^9$	(Beltrán & Rey, 2018; Wert et al., 2009)
ATZ	Low Intermediate	(Rozas et al., 2017) (Margot et al., 2013; Westerhoff et al., 2005)	Low	(Guzman-Perez et al., 2011; Margot et al., 2013; Rozas et al., 2017)	6	$3×10^9$	(Acero et al., 2000; Beltrán & Rey, 2018)
FCZ	Intermediate/High	(Kovalova et al., 2013; Margot et al., 2013)	Low	(Kovalova et al., 2013; Margot et al., 2013)	<1	N/A	(Lee et al., 2014b)
DZN	Intermediate/Low	(Ku et al., 1998)	Intermediate/Low	(Ku et al., 1998)	$1.7\text{-}3.2×10^{-3}\ \mathbf{s^{-1}}$	$8.4×10^9$	(Ku et al., 1998; Real et al., 2007)
Group IV: Data Not Available							
CDM	High	(Margot et al., 2013)	High	(Margot et al., 2013)	N/A	N/A	
CLN	High	(Margot et al., 2013)	High	(Kovalova et al., 2013; Margot et al., 2013)	N/A	N/A	
PFOA	Intermediate/High	(AWWA, 2019; Yu & Hu, 2011)	Low – Intermediate/High (pH 11)	(Lin et al., 2012)	N/A	$<3×10^7$	(Trojanowicza et al., 2018)
PFOS	Intermediate/High	(AWWA, 2019; Yu & Hu, 2011)	Low – Intermediate/High (pH 11)	(Lin et al., 2012)	N/A	$<3×10^7$	(Trojanowicza et al., 2018)

Notes:

N/A = Not available; N/D = Not detected; Low removal: <50%; Intermediate removal: 50-80%; High removal: > 80

In order to investigate the efficiency of single ozonation for the degradation of MPs in a diverse mixture, four different O_3 specific doses were applied to the mixture of MPs. The percent removal of each MP was separately calculated, and divided by 17, the total number of MPs in the mixture. The data was plotted in Figure 5.1 to show the percentage contribution of each MP to the total MPs removed. As the O_3 specific dose increased, the cumulative percent removal of MPs increased. The smallest O_3 specific dose tested (0.27 g O_3/g DOC) was able to remove 47% of the MPs in the mixture. The effect of increasing this dose was mainly observed through the improved removal of the less reactive MPs which eventually increased the cumulative removal. It was also noticeable that the relationship between the O_3 specific dose and the cumulative % removal of MPs in the mixture was linear for the first 3 doses, which fall within an acceptable range of applied doses (Song et al., 2017; Zimmermann et al., 2011). At the highest O_3 specific dose, which represented almost a 10 times dose increase, the cumulative percent removal increased only from 73% at 2.17 g O_3/g DOC to 79% at 21.64 g O_3/g DOC revealing near a plateau. This is better represented by the ratio of the differential cumulative % removal over the differential O_3 specific dose. This ratio was equal to 14 when the O_3 specific dose increased from 0.27 to 2.17 g O_3/g DOC; and it was reduced to 0.3 when the dose increased from 2.17 to 21.64 g O_3/g DOC. A similar trend was observed elsewhere on the DOC removal that slowed down after certain O_3 specific dose (Molnar et al., 2012). This was expected as a portion of the O_3 specific dose was used to satisfy the demand of fast reacting compounds. The less reactive ones have a limited capacity to react with O_3 thus increasing the dose would not considerably impact their removals. As such, three doses were studied in PAC-catalyzed ozonation: the low and high ends of the common range of O_3 specific doses, i.e. 0.27 and 2.17 g O_3/g DOC which also showed a significant improvement in the degradation of MPs, as well as the extreme O_3 specific dose 21.64 g O_3/g DOC for comparison.

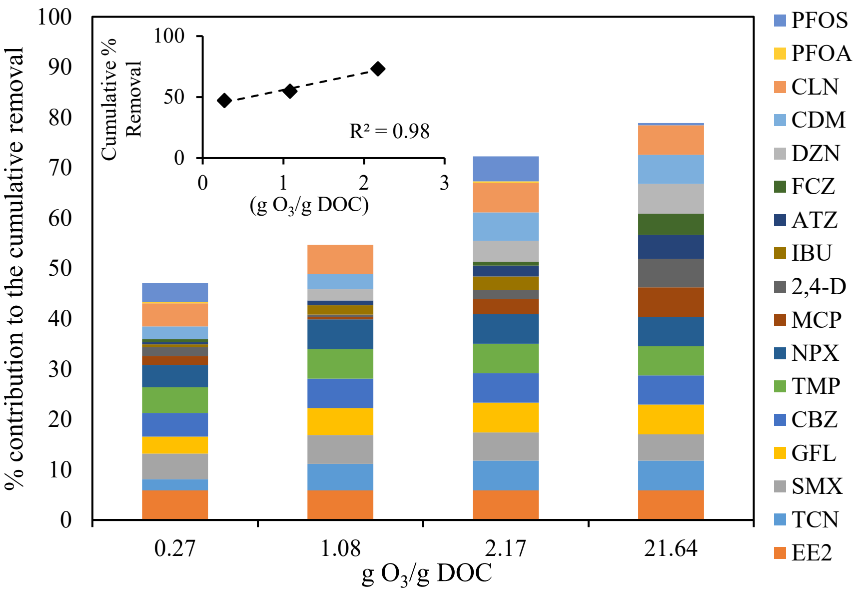


Figure 5.1 Percent contribution of each MP in the mixture to the total cumulative removal after 1 minute of single ozonation under different specific O_3 doses, and linear correlation between the O_3 specific dose and the total % cumulative removal.

5.3.2. Effect of O_3 specific dose on the decomposition of O_3 in single and catalytic ozonation

The O_3 decomposition and one-minute removal of MPs under the three different O_3 specific doses are illustrated in Figure 5.2. It was noticeable that the higher the O_3 specific dose, the higher the residual O_3 and accordingly the more the O_3 available for reaction. Moreover, O_3 seemed to be degrading in more than one kinetic regime, with the first regime being the fastest. Similar behaviour was reported elsewhere where it was suggested that this is caused by the reaction with compounds that are highly or moderately reactive with O_3 (Benitez et al., 2007; Buffle et al., 2006; Chelme-Ayala et al., 2011b; Elovitz & von Gunten, 2008; Guo et al., 2018). Also, there was clearly a faster O_3 decomposition in the presence of PAC. In parallel, the removal rate of MPs as mg removed in 1 minute/mg O_3 applied, generally decreased as the O_3 specific dose increased because of the lower mass concentration of MPs at high O_3 specific dose. Yet, the removal rate reached its maximum for more MPs in the latter case than in any other condition because of the higher residual O_3. Also, it was noticeable that MPs belonging to group I exerted higher removal rates compared to other MPs under the different O_3 specific doses. Moreover, the removal trend of MPs could only be detected at very high O_3 specific doses probably because this was the only condition that secured enough O_3 to oxidize slow-reacting MPs towards reaction completion.

Fast-reacting MPs belonging to group I were identified at below detection limit in both single and PAC-catalyzed ozonation. They could be considered equivalent to natural organic matter that exerted instantaneous O_3 demand (IOD). Therefore, their removal kinetics in a mixture could not be monitored and they are better studied individually through competition kinetics (Jin et al., 2012). IBU was present in the mixture but could not be detected at 21.64 g O_3/g DOC due to analytical errors associated with the limit of detection of IBU. The major improvement in PAC-catalyzed ozonation was observed for 2 MPs in group IV: POFA and PFOS that showed almost no removal by single ozonation which was aligned with their expected reactivity (Table 5.2).

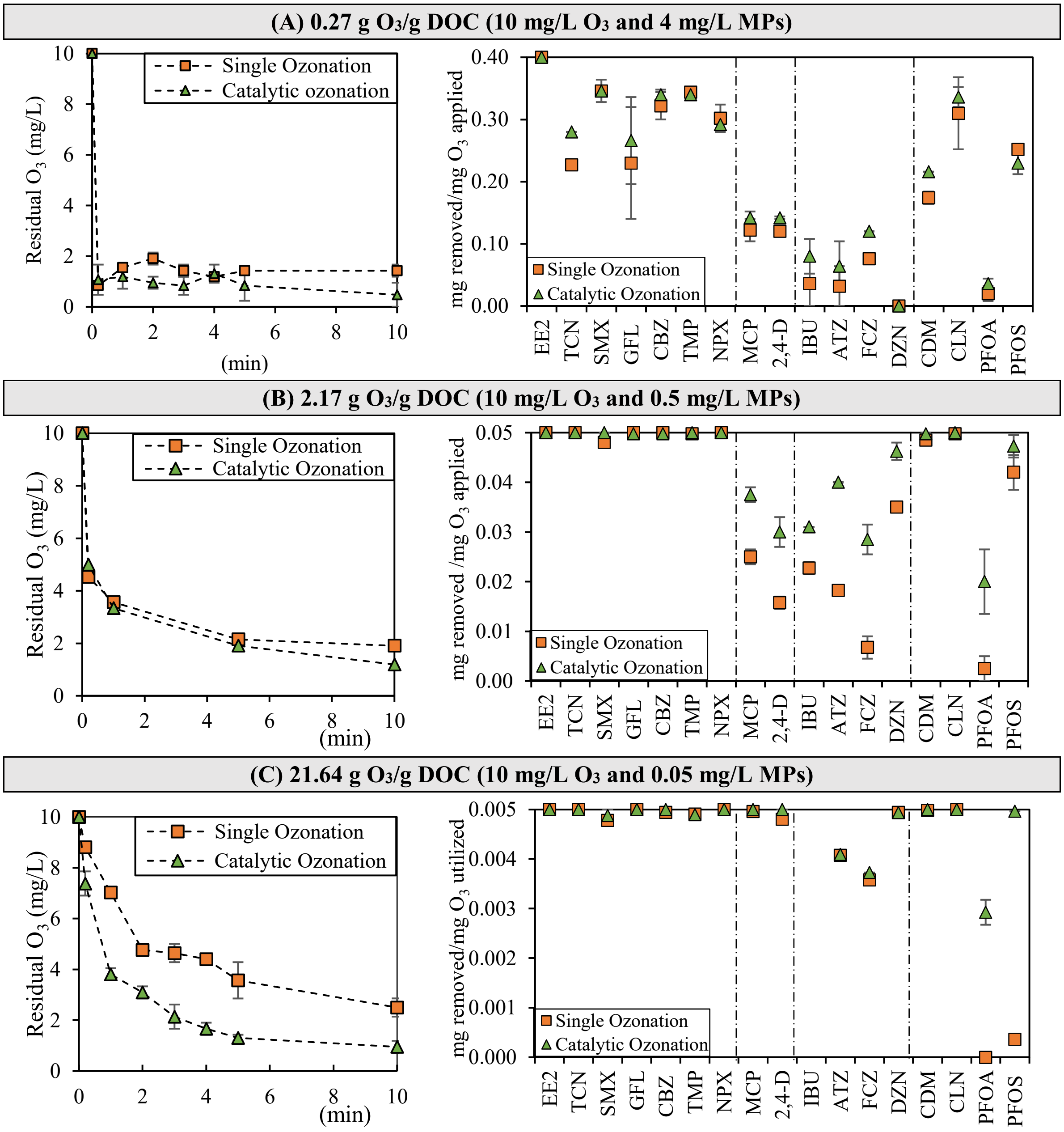


Figure 5.2 Residual O₃ and MPs specific degradation rates (mg MP removed after 1 minute/mg O_3 applied) in single and PAC catalyzed ozonation with different O_3 specific doses: Mixture of MPs at 0.05 mg/L, Mixture of MPs at 0.5 mg/L, Mixture of MPs at 4 mg/L each in borate buffer; O_3 dose: 10 mg/L, PAC dose: 100 mg/L, specific O_3 doses: **(A)** 0.27g O_3/g DOC; **(B)** 2.17 g O_3/g DOC; **(C)** 21.64 g O_3/g DOC

5.3.3. Benchmarking the removal of MPs by single and PAC-catalyzed ozonation

Along with the single and PAC-catalyzed ozonation experiments that were performed, adsorption experiments using 100 mg/L of PAC were also carried out as a control with mixtures of MPs at different concentrations. Figure 5.3 presents a comparison between the three treatments for the removal of MPs in the mixture during 10 minutes reaction time with data on all removals plotted and compared. At low O_3 specific dose (0.27 g O_3/g DOC), removals were generally low and concentrated around 0 implying minimal removal. Still, most MPs showed higher affinity for removal by catalytic ozonation than by single ozonation or adsorption. At higher O_3 specific dose (2.17g O_3/g DOC), the removal of MPs in the mixture revealed a wider spread and was mostly favoured by catalytic ozonation rather than by single ozonation or adsorption. MPs from groups II and III still showed less removal compared to other groups. At the highest O_3 specific dose (21.64 g O_3/g DOC) most MPs revealed higher affinity for removal by catalytic ozonation than by single ozonation. It was also remarkable that MPs belonging to groups III and IV were comparably or slightly better removed by adsorption on PAC.

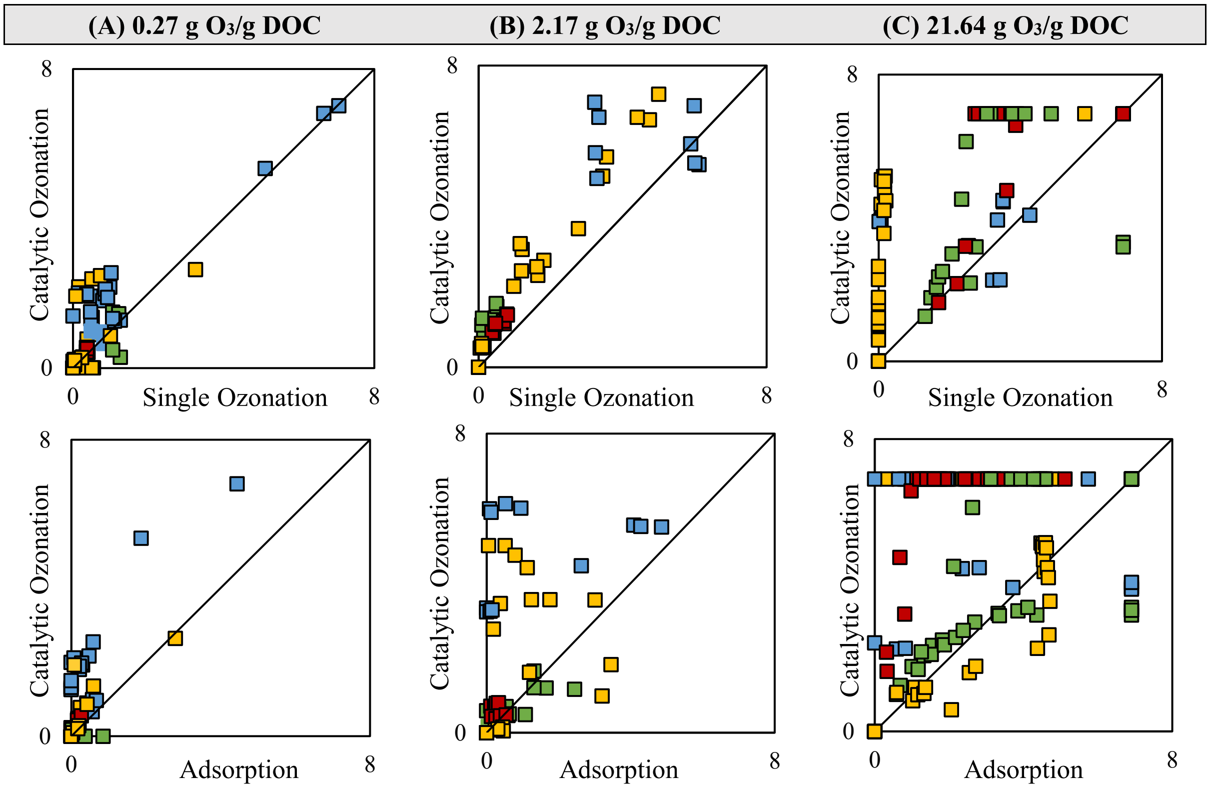
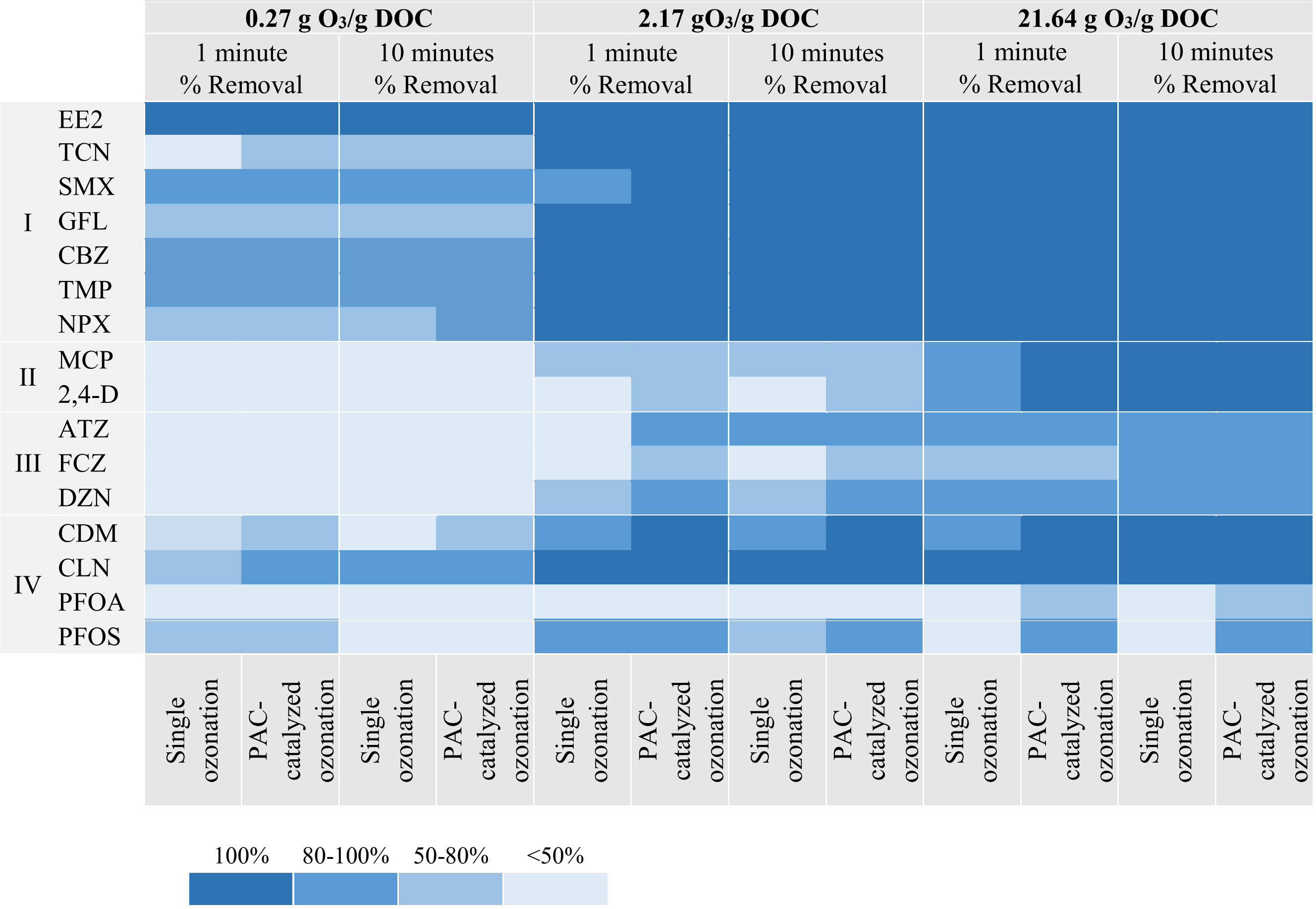


Figure 5.3 Comparison between the removal as Ln C_0/C by single ozonation, catalytic ozonation and adsorption for the different categories of MPs at three O_3 specific doses: **(A)** 0.27 g O_3/g DOC; **(B)** 2.17 g O_3/g DOC, and **(C)** 21.64 g O_3/g DOC during a 10 minutes reaction time: blue: *Group I*, red: *Group II*, *green: Group III, y*ellow: *Group IV*.

Table 5.3 provides a benchmark for the removal of MPs at different O_3 specific doses. Removals were classified in accordance with the classification in Table 5.2 in four categories: <50%; between 50-80%, between 80-100%; and 100%. Results showed that the removal categories for most MPs were similar at 1 minute and 10 minutes which meant that the reactions were almost complete within the first 1 minute of exposure to O_3 and PAC. Also, increasing the O_3 specific dose shifted the percent removal of most MPs to at least the next higher level. An almost ten times increase in O_3 specific dose guaranteed complete degradation of fast reacting MPs (group I) by single or PAC–catalyzed ozonation. Yet, for MPs with limited reactivity with O_3 (groups II and III) that increase was only efficient in PAC-catalyzed ozonation. So, in order to enhance the degradation of diverse MPs, an increase in the O_3 dose was not enough. It was the addition of PAC to catalyze the ozonation process that prompted significant improvements in the removal of recalcitrant organic compounds. Since IBU could not be detected at 21.64 g O_3/g DOC as mentioned in section 5.3.2, it was not included in this table; yet, it is worth mentioning that its removal remained less than 50% and was shifted to 50-80% with 1 minute PAC-catalyzed ozonation and 10 minutes single or PAC-catalyzed ozonation at lower dose. The removal of PFOS was remarkably high and disagreed with the expected low removal in Table 5.2. A possible explanation was provided by Dai et al. (2019a) who claimed that the hydrophobic PFOS tends to adsorb onto the foam that results from the mixing process. The foaming phenomenon was clearly noted in our experiments and could be the reason behind its overestimated removal.

Table 5.3 Heatmap of MPs' removal by single and PAC catalyzed ozonation at 1 minute and 10 minutes of treatment and different O_3 specific doses.



		0.27 g O_3/g DOC				**2.17 gO_3/g DOC**				**21.64 g O_3/g DOC**			
		1 minute % Removal		10 minutes % Removal		1 minute % Removal		10 minutes % Removal		1 minute % Removal		10 minutes % Removal	
		Single ozonation	PAC-catalyzed ozonation	Single ozonation	PAC-catalyzed ozonation	Single ozonation	PAC-catalyzed ozonation	Single ozonation	PAC-catalyzed ozonation	Single ozonation	PAC-catalyzed ozonation	Single ozonation	PAC-catalyzed ozonation
I	EE2	█	█	█	█	█	█	█	█	█	█	█	█
	TCN	░	▒	▒	▒	█	█	█	█	█	█	█	█
	SMX	▓	▓	▓	▓	▓	█	█	█	█	█	█	█
	GFL	▒	▒	▒	▒	█	█	█	█	█	█	█	█
	CBZ	▓	▓	▓	▓	█	█	█	█	█	█	█	█
	TMP	▓	▓	▓	▓	█	█	█	█	█	█	█	█
	NPX	▒	▒	▒	▓	█	█	█	█	█	█	█	█
II	MCP	░	░	░	░	▒	▒	▒	▒	▓	█	█	█
	2,4-D	░	░	░	░	░	▒	░	▒	▓	█	█	█
III	ATZ	░	░	░	░	░	▓	▓	▓	▓	▓	▓	▓
	FCZ	░	░	░	░	░	▒	░	▒	▒	▒	▓	▓
	DZN	░	░	░	░	▒	▓	▒	▓	▓	▓	▓	▓
IV	CDM	░	▒	░	▒	▓	█	▓	█	▓	█	█	█
	CLN	▒	▓	▓	▓	█	█	█	█	█	█	█	█
	PFOA	░	░	░	░	░	░	░	░	░	▒	░	▒
	PFOS	▒	▒	░	░	▓	▓	▒	▓	░	▓	░	▓

100%	80-100%	50-80%	<50%
█	▓	▒	░

Classifying MPs according to their reactivity with O_3 established a general understanding of their response to single and PAC-catalyzed ozonation in a mixture. However, estimating their removal still requires the identification of appropriate surrogates to validate the treatment. Several studies attempted to correlate the removal of MPs with other parameters that can be easily monitored. For instance, the ultraviolet absorbance at 254 nm (UVA_{254}) was appraised in different studies for its ability to predict the removal of some MPs in real time. Differential total phosphorus was also correlated with MPs (Zhang et al., 2015). In this study, correlations between the removals of MPs were attempted to identify surrogate compounds on the basis of their degradation in single (Figure 5.4) and PAC-catalyzed ozonation (Figure 5.5). The illustrated correlations correspond to the O_3 specific dose 2.17 g O_3/g DOC. Actually, there was a clear discrepancy between the different O_3 specific doses analyzed in most of the correlations where the data for all O_3 specific doses did not follow the same trend and deviated remarkably between low and high doses. This is possibly explained by the high level of DOC that occurred at the low O_3 specific dose and implied high IOD and not enough residual O_3 to react with the MPs. This also explained the low removals and the clear deviation from the data obtained at higher O_3 specific dose. This deviation was actually eased in PAC-catalyzed ozonation with some exceptions. It was thus determined that CBZ could serve as a surrogate for MPs that are highly reactive with O_3 while ATZ could serve as a surrogate for MPs that are less reactive with O_3 or with unknown reactivity.

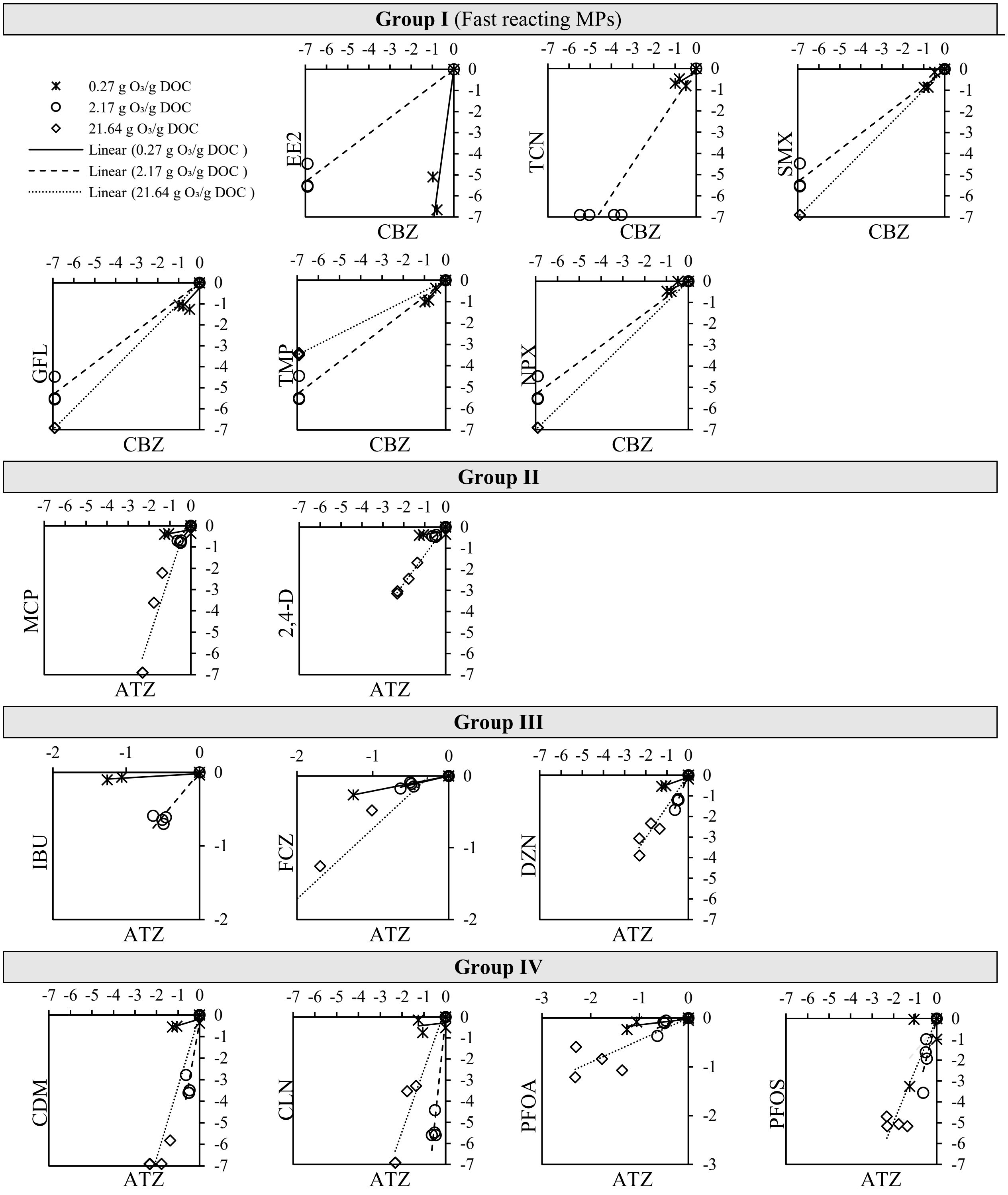


Figure 5.4 Correlation between the removal (Ln C/C_0) of CBZ and the removal of MPs in group I, the removal of ATZ and the removal of MPs in groups II, III and IV under three different O_3 specific doses during single ozonation.

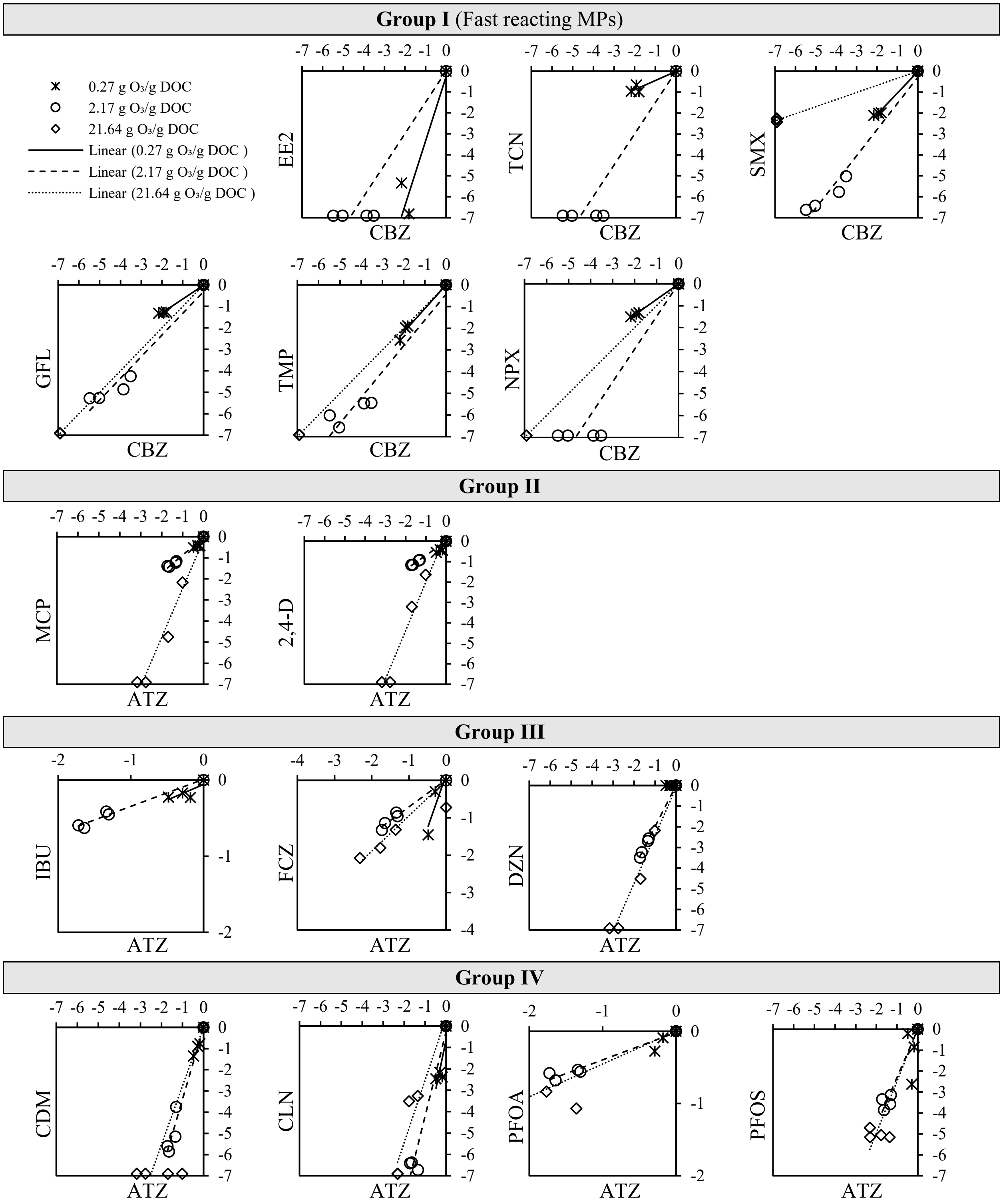


Figure 5.5 Correlation between the removal (Ln C/C_0) of CBZ and the removal of MPs in group I, the removal of ATZ and the removal of MPs in groups II, III and IV under three different O_3 specific doses during catalytic ozonation.

5.3.4. Kinetics of MPs removal in a mixture by single and catalytic ozonation

Under the different O_3 specific doses compared in this study during single and PAC-catalyzed ozonation, the reaction seemed to be very fast in the first 1 minute where most of the degradation occurred, after which there was a minimal degradation if any. In order to confirm this observation, the predicted half-lives of MPs were calculated under the different O_3 specific doses based on the assumption that the overall reaction between the MP and O_3 or between MP and $^{\bullet}OH$ are bimolecular and follow second order rate kinetics Equation 5.1 (Metcalf & Eddy, 2014). The time required to degrade half the initial concentration of the MPs otherwise known as the half-life, was obtained from Equations 5.1 and 5.2 and calculated according to Equation 5.3.

$$-\frac{dC}{dt} = k_{[MP]}[MP][O_3] \qquad \textit{Equation 5.1}$$

$$k' = k_{[MP]}[O_3] \times \frac{[MP]}{[MP]_t} \qquad \textit{Equation 5.2}$$

$$t_{1/2} = \frac{ln2}{k'} \qquad \textit{Equation 5.3}$$

Where $k_{[MP]}$ is the second order rate constant for the degradation of MP by O_3 in $M^{-1}s^{-1}$; [MP] is the concentration of the MP in M, $[O_3]$ is the concentration of O_3 in M; k' is the first order rate constant in s^{-1}; $t_{1/2}$ is the half-life of the MP, and $[MP]_t$ is the total molar concentration of all MPs in the mixture. k' was corrected to account for the relative concentration of the MP to all MPs in the mixture assuming that 1 M of O_3 would react with 1 M of MP and knowing that the MPs are present at different molar concentrations in the mixture. So, the overall reaction rate depends on the molar concentration of the oxidant as well as that of the target compound. On the other hand, the half-life depended on the oxidant's concentration provided that the oxidant is reacting strictly with the MP. Similarly, the half-lives for the reactions between MPs and $^{\bullet}OH$ only were calculated following the same assumptions made for O_3 and assuming that one molar of O_3 in water decomposes into one molar of $^{\bullet}OH$. Details of the first order rate constants and half-lives are presented in Tables A.1 and A.2 in the Appendix.

It was remarkable that the predicted half-lives of MPs were longer when treated in a mixture compared to when treated individually and that the O_3 specific dose did not reveal any significant effect on the time predicted for the removal of MPs. Jin et al. (2012) tested and summarized three methods for measuring the rate constants for MPs with molecular O_3 depending on their reactivity. Those methods are: 1) Competition kinetics for fast reacting MPs, performed in the presence of the target compound and a reference compound (with known rate constant with O_3) at the same molar concentration, and $^{\bullet}OH$ scavenger (typically tertiary butanol TBA); 2) Compound monitoring for slow reacting MPs, performed in the presence of the target MP and O_3 at ten times the concentration of MP in addition to TBA; and 3) O_3 monitoring method for low solubility MPs, performed in the presence of the target MP at five times the concentration of O_3 and with TBA, the concentration of O_3 is monitored with time and used to calculate the rate constant. The rate constants for the MPs with O_3 reported in literature are thus obtained from the reaction between the target compound and molecular O_3 only generally in clean matrix and under known experimental conditions such as pH and temperature. It was also assumed that major radicals contributing to the reaction are scavenged. DOC is one main factor known to affect the reaction rate constant with O_3 in two possible manners: the reaction between DOC and molecular O_3 generates radicals that contribute to the oxidation of MPs; or the reaction between DOC and molecular O_3 consumes the oxidant and reduces its availability to degrade MPs (Uslu et al., 2015). In this study, since DOC was the only factor that changed, it can be presumed that the concentration of MPs expressed as DOC was controlling the removal kinetics as discussed below.

Overall, only 3 MPs in the mixture presented removal trends as illustrated in Figures 5.6 used to compute the overall rate constants. 2,4-D (group II) was better removed than ATZ and FCZ (group III) in both single and catalytic ozonation.

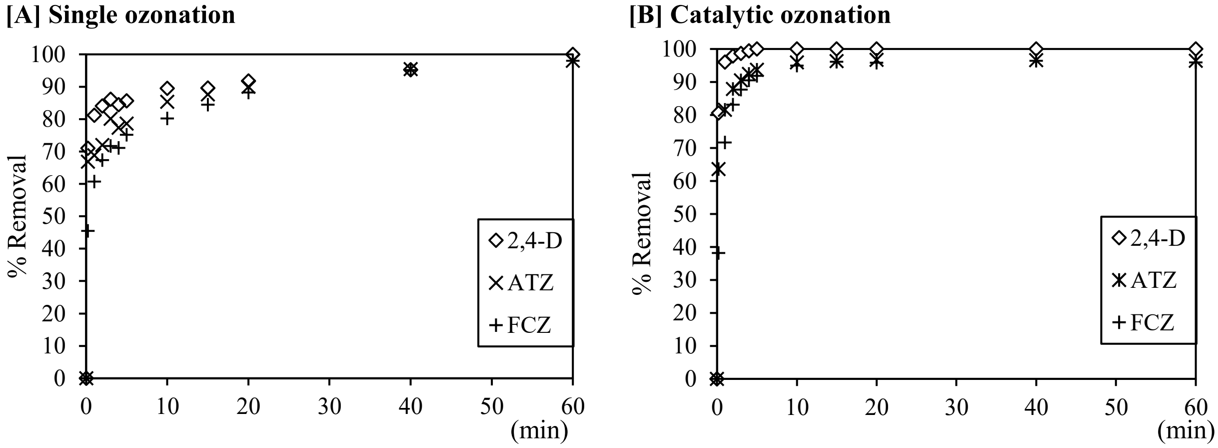


Figure 5.6 Removal of 2,4-D, ATZ and FCZ by **(A)** Single ozonation and **(B)** Catalytic ozonation as a function of time.

Generally, the apparent rate constants were in agreement with the reactivity of those compounds with O_3 (Table 5.2). In single ozonation, the degradation of MPs could be divided into three zones. In zone 1 including the first 12 seconds, the removal of MPs was very fast with all three MPs dropping by more than 50%. The removal started slowing down in zone 2 that extends between 12 seconds and 5 minutes before starting in zone 3 that lasted until 60 minutes. In zone 1, the measured first order rate constants in single ozonation (Figure 5.7) were comparable to those in catalytic ozonation (Figure 5.8). However, in zone 2, the reactions were faster in catalytic ozonation than in single ozonation whereby the rate constants in the former case were 6.7×10^{-2} s^{-1}, 5.7×10^{-3} s^{-1}, 6.7×10^{-3} s^{-1} for 2,4-D, ATZ and FCZ respectively compared to 3.7×10^{-3} s^{-1}, $1.6x10^{-3}$ s^{-1}, 2.4×10^{-3} s^{-1} in single ozonation. Zone 3 in single ozonation was obviously the slowest. It is also worth noting that the obtained rate constants are higher than those estimated for the reaction with molecular O_3 in Table 5.4 and significantly lower than those for the reaction with $^{\bullet}OH$ predicted in Table 5.5. Therefore, the overall kinetics in single and PAC-catalyzed ozonation were closer to the degradation kinetics under the effect of molecular O_3 only which ties with the competition between the different MPs in the mixture and their preferential degradation pathways. Also, when measured in real matrix, those rates are expected to decrease (Rozas et al., 2017; Shu et al., 2016). Guo et al. (2018) raised the issue of incomplete mixing that can occur in batch systems resulting in an overestimation of the O_3 degradation and accordingly the degradation of MPs with limited reactivity with O_3. Thus, the use of stopped-flow systems was recommended to better estimate the O_3 degradation and MPs' removal.

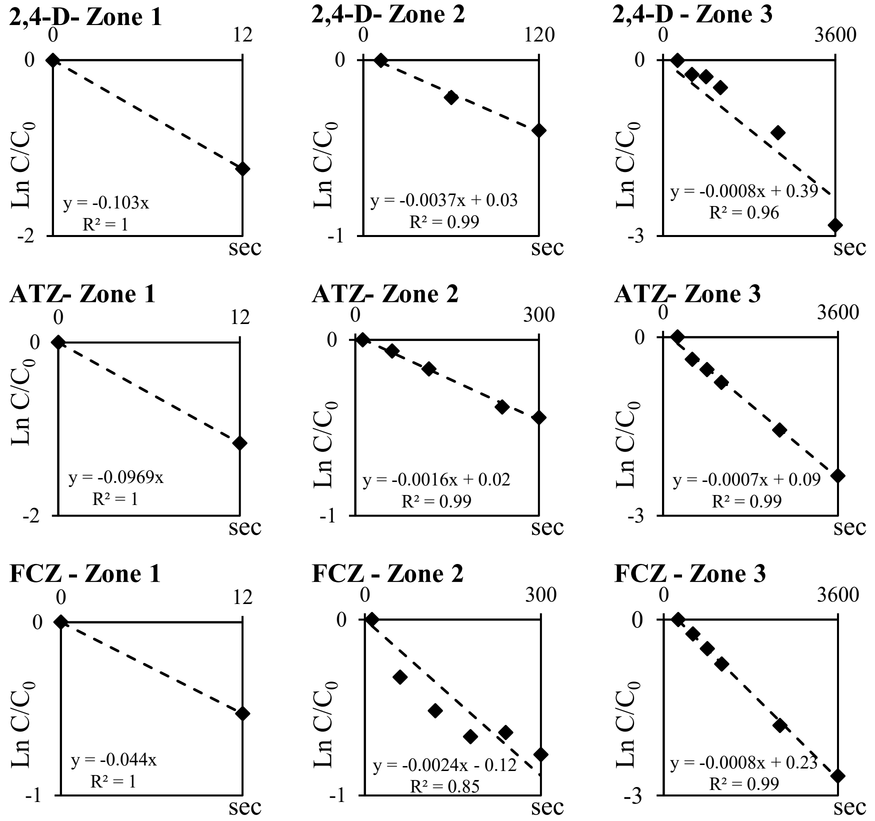


Figure 5.7 Degradation kinetics of MPs by single ozonation (Mixture of MPs at 0.05 mg/L each, borate buffer: 4 mM, O_3 dose: 10 mg/L).

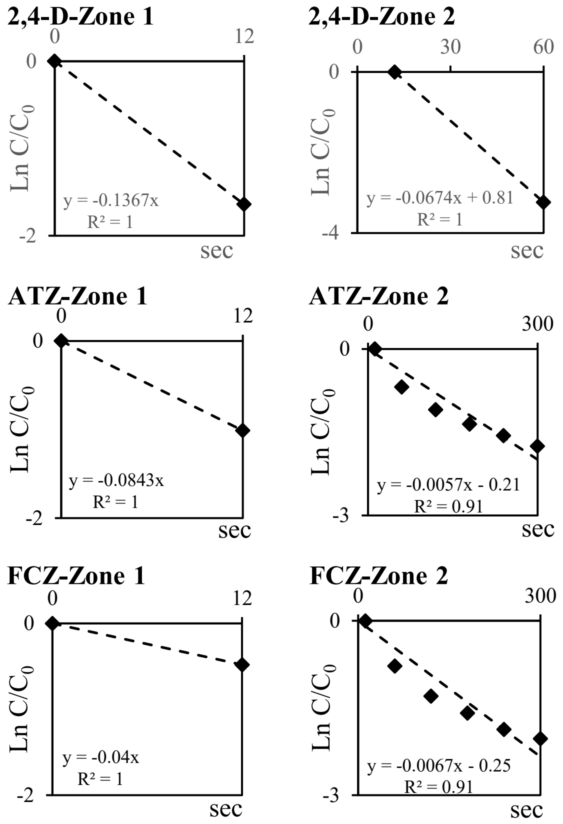


Figure 5.8 Degradation kinetics of MPs by catalytic ozonation divided into three different zones (Mixture of MPs at 0.05 mg/L each, borate buffer: 4 mM, O_3 dose: 10 mg/L, PAC: 100 mg/L).

5.3.5. Formation of intermediates in single and PAC-catalyzed ozonation.

Literature was surveyed for the common intermediates that form during the oxidation of each of the 17 MPs present in the mixture (Table A.3 in the Appendix). To the best of our knowledge, the oxidation mechanisms of seven MPs in the mixture GFL, MCP, FCZ, DZN, CLN, PFOA and PFOS have not been studied yet. The thirteen intermediate compounds provided in Table 5.4, were detected after 10 minutes of single ozonation using 0.27 g O_3/g DOC, among which 11 compounds were also detected in catalytic ozonation.

Glutaric acid was identified during single ozonation only and it is reportedly an intermediate in the ozonation of EE2 that is generated at later stages before complete mineralization into carbon dioxide (Zhang et al., 2006). *p*-Benzoquinone was likewise formed in single and catalytic ozonation of SMX as an intermediate. In fact, oxamic, oxalic, maleic and pyruvic acids have been reported in literature as the last ozonation products that form prior to the complete mineralization and formation of carbon dioxide and inorganic ions (Goncalves et al., 2012; Zhang et al., 2006). Multiple intermediates have been identified for CBZ with $C_{13}H_9NO$ detected in single ozonation only. The mechanism of CBZ ozonation suggested by Hubner et al. (2014) comprises $C_{13}H_9NO$ that is formed via both direct pathway, by reaction with molecular O_3, and indirect pathway by reaction with hydroxyl radicals ($^{\bullet}OH$) and it does not undergo further transformations. $C_{15}H_{10}N_2O_3$ could also be generated through both direct and indirect pathways and transformed by reaction with O_3 into $C_{15}H_{10}N_2O_4$. Similarly, the study implied that $C_{15}H_{12}N_2O_3$ is formed through the indirect pathway and doesn't proceed through further reactions. $C_{10}H_{10}O_3$ and $C_9H_{10}O_2$ identified in this study have also been detected as intermediates in the 60 minutes single and catalytic ozonation of NPX in presence of nickel oxide (Aguilar et al., 2019). It was suggested that direct pathway is responsible for the degradation of NPX and indirect pathway might contribute to the removal of the intermediates. $C_8H_{15}N_5O$ was reported as an intermediate in the single ozonation of ATZ where it is formed though the substitution of Cl by OH (Li & Zhou, 2019). It was claimed that it can undergo other transformations in ozonation catalyzed by zero valent iron. $C_7H_6N_2$ and $C_6H_8N_2$ that were identified here can be potentially associated with the ozonation of CDM since they were also reported as by-products of the photodegradation of CDM by UV irradiation (Kiss & Virág, 2009b).

It is therefore possible that the different oxidation mechanisms occurring in single and PAC-catalyzed discussed in Chapter 4, in addition to the possible adsorption onto PAC resulted in the formation of more intermediates in single ozonation.

Table 5.4 Oxidation intermediates and by-products identified in the mixture with 0.27 g O_3/g DOC at 10 minutes by single and catalytic ozonation: compounds in bold were identified in single ozonation only

MP	**Oxidation intermediates/by-products**		**Mass (m/z)**	**Reference**
EE2	**$C_5H_8O_4$**	**Glutaric acid**	**133.0501**	(Zhang et al., 2006)
SMX	$C_6H_4O_2$	p-Benzoquinone	109.029	(Goncalves et al., 2012)
CBZ	$C_8H_6N_2O_2$	1-(2-benzoic acid)- (1H,3H)-quinazoline-2,4-dione	163.0508	(McDowell et al., 2005)
	$C_{14}H_9NO_2$	2-Nitroanthracene or 9-Nitroanthracene	224.0710	(Hubner et al., 2014)
	$C_{15}H_{10}N_2O_4$	Phencomycin	283.0725	
	$C_{15}H_{12}N_2O_3$	Hydrofuramide	269.0933	
	$C_{15}H_{10}N_2O_3$	Carbmazepine-o-quinone	267.0770	
	$C_{13}H_9NO$	Acridone	196.0767	
NPX	$C_{10}H_{10}O_3$	2-(4-(2-Hydroxyvinyl) phenyl) acetic acid	177.0554	(Aguilar et al., 2019)
	$C_9H_{10}O_2$	2-(*p*-Tolyl) acetic acid	149.0592	
ATZ	$C_8H_{15}N_5O$	2-Hydroxy-4-ethylamino-6-isopropylamino-1,3,5-triazine	198.1355	(Li & Zhou, 2019)
CDM	**$C_7H_6N_2$**	**Benzimidazole**	**119.0609**	(Kiss & Virág, 2009b)
	$C_6H_8N_2$	1,2-diaminobenzene	109.0766	

For a better understanding of the differences between intermediate compounds formed in single ozonation and those formed in catalytic ozonation, the corresponding peaks were integrated and their areas were reported and plotted in Figure 5.9. Assuming proportionality between the peak area and the compound's concentration, it can be noted that most of the intermediate compounds were more abundantly generated in single ozonation than in catalytic ozonation. Similar results were obtained in other studies (Goncalves et al., 2012; Gonçalves et al., 2013a; Rozas et al., 2017). Such findings were associated with the greater ability of catalytic ozonation for the mineralization of target compound(s). In this case, where ozonation was catalyzed by carbon material, the enhanced mineralization could be due to either the catalytic effect or the adsorptive capacity of the catalyst or both combined.

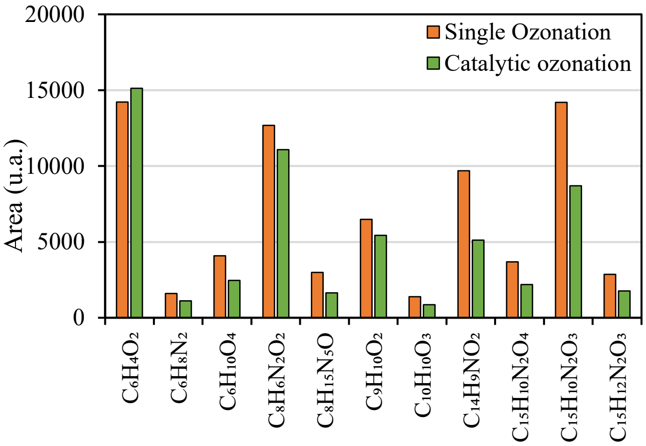


Figure 5.9 Comparison between the peak areas corresponding to the detected intermediates in single ozonation and in PAC-catalyzed ozonation at 10 minutes reaction time.

5.4. Conclusions

In this study, the effect of single and PAC-catalyzed ozonation were compared under different O_3 specific doses using a diverse mixture of MPs from different categories and different classes of reactivity. Overall, most MPs showed higher affinity for the removal by PAC-catalyzed ozonation which was mainly observed at higher O_3 specific dose. Under this condition more than 50% removal could be achieved for the less reactive MPs. CBZ and ATZ were determined good surrogate MPs for fast and slow reacting MPs, respectively. The removal kinetics were affected by the level of DOC and its capacity to consume the applied O_3 dose and exert an instantaneous demand. Still faster kinetics were obtained in PAC-catalyzed ozonation leaning more towards the removal kinetics with molecular O_3. Also, in this case, less intermediate compounds were formed possibly because the removal occurs through different pathways in single and PAC-catalyzed ozonation. Further studies are required for a better understanding of the degradation mechanisms of MPs in individual treatments in comparison with treatments in a mixture.

Acknowledgments

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CHAPTER 6: Advancing the Treatment of Primary Influent and Effluent Wastewater during Wet Weather Flow by Single versus Powdered Activated Carbon-catalyzed Ozonation for Micropollutants removal, Disinfection and Toxicity Abatement[4]

6.1. Introduction

Combined sewer overflows (CSO) contain storm water runoffs along with domestic and industrial wastewater and toxic materials and debris (USEPA, 2018). Their direct release to the environment promotes a cumulative increase in *Escherichia coli* (*E.coli*) in the aquatic system by up to 2 log (Madoux-Humery et al., 2016). There have also been several studies on the contribution of CSO to the release of micropollutants (MPs) into receiving waters (Evans et al., 2016; Gasperi et al., 2008; Madoux-Humery et al., 2016; Phillips et al., 2012). While these problems persist, several treatment options surfaced in order to prevent the discharge of untreated wastewater during wet weather conditions. In a first step, the enhanced primary treatment consisting of coagulation/ flocculation/ sedimentation has been investigated (Alameddine et al., 2020). Then, different solutions for disinfection have been explored including: ultraviolet irradiation (UV) (Tondera et al., 2015; Wojtenko et al., 2001a), performic acid (Chhetri et al., 2015; Chhetri et al., 2014; Tondera et al., 2016), peracetic acid (Chhetri et al., 2016; Chhetri et al., 2014; Coyle et al., 2014) and ozone (O_3) (Tondera et al., 2015; Wojtenko et al., 2001b). In comparison, studies on the removal of MPs from the primary influent (PI) during wet weather have been relatively scarce (Jung et al., 2015; Pongmala et al., 2015). Therefore, there is a need for an efficient treatment that can address both disinfection and MPs removal and partake in the enhanced primary treatment of PI during wet weather conditions.

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[4] A version of this chapter will be submitted jointly with a version of chapter 5 to Journal of Hazardous Materials.

Ozonation is one widely recognized technique for its capacity to both disinfect and oxidize (Altmann et al., 2014). The application of ozone (O_3) is often favored because O_3 has strong and fast disinfection abilities that cover a wide range of microorganisms, and tends to form less regulated disinfection by-products (DBPs) (Cho et al., 2002 ; Rodayan et al., 2014). In the literature, ozonation was widely applied following secondary treatment, and was deemed efficient for the removal of a variety of MPs such as triclosan, gemfibrozil, atenolol, sulfamethoxazole, diclofenac, carbamazepine, among others (Altmann et al., 2014; Can & Çakır, 2010; Huber et al., 2005; Ikehata et al., 2008; Jin et al., 2016; Lee et al., 2013; Lee et al., 2014b; Nothe et al., 2009; Wildhaber et al., 2015; Zhou et al., 2015). Ozonation was also previously tested on CSO samples after settling where it achieved good pathogens removal and significant reductions in quality parameters such as turbidity, dissolved organic carbon (DOC), total organic carbon (TOC) and total suspended solids (TSS), but there was no data reported on its effect on MPs removal from CSO (Tondera et al., 2015). The common ranges of applied O_3 doses for the treatment of secondary effluent were reported as O_3 concentrations: 5 - 15 mg O_3/L (Nothe et al., 2009) or O_3 specific doses: 0.21 - 1.53 mg O_3/mg DOC (Song et al., 2017; Zimmermann et al., 2011). Doses outside that range such as 2.24 mg O_3/mg DOC were also studied (Jin et al., 2016). It was alleged that ozonation exhibits better energy efficiency and higher capacity to target even the most recalcitrant compounds compared to other techniques such as UV or UV/H_2O_2 (Kovalova et al., 2013; von Sonntag & von Gunten, 2012). Nevertheless, there are several concerns commonly brought forward when discussing O_3 for the treatment of wastewater in general and CSO in particular. In real life applications, ozonation is associated with several limitations pertaining to its low stability and the need to manufacture it *in-situ* and therefore safety concerns and maintenance costs that can be entailed (Wojtenko et al., 2001a). Moreover, the complexity of a wastewater matrix entails the presence of O_3 sinks such as: nitrites, nitrates, sulphites, iron and manganese that can hinder the O_3 available for disinfection and oxidation (Lee et al., 2013). Similarly, the higher the content of CSO in TSS, COD and TOC, the higher the O_3 demand. Natural organic matter (NOM), pH and temperature can also affect the O_3 decomposition rate (Wojtenko et al., 2001b). These factors are thus to be accounted for when adjusting the O_3 dosage. Likewise, ozonation affects the chemical structure and composition of wastewater, and can promote the formation of by-products and intermediates (carboxylic acids, aldehydes, bromates, ketone, peroxides) that might be more toxic than the parent compound (Jin et al., 2016; Wojtenko et al., 2001a).

In order to mitigate these limitations, recent trends in O_3-based advanced oxidation processes (AOPs) suggest the application of catalysts to improve the generation of radicals and thus the removal of compounds that are less reactive with molecular O_3. Single ozonation and other AOPs are likely applied as pre-treatments to partially oxidize organic compounds and hence improve their biodegradation, and most commonly as tertiary treatments on low organics matrices (Ikehata et al., 2006). Among the various types of catalysts, carbon-based catalysts can be the most practical in wastewater treatment because they can be used for adsorption, they are relatively affordable, and do not leave metal residues in the treated media. There is a variety of carbon-based catalysts including multi-walled carbon nanotubes (Fan et al., 2014; Gonçalves et al., 2010; Gonçalves et al., 2013b; Liu et al., 2011; Oulton et al., 2015; Restivo et al., 2012), carbon nanofibers (Restivo et al., 2013), and activated carbon (AC). The latter whether in powdered or granular form (as powdered activated carbon PAC or granular activated carbon GAC), has the advantage of very high adsorption capacity due to its small particle size. Therefore, applying it as a catalyst in the wastewater treatment industry can secure dual roles: catalyzing the oxidation of target compounds and removing them and/or their by-products by adsorption. Since the oxidation process entails the chemical transformation of one compound into another, while adsorption involves their physical removal, the synergy between the two processes can be promising for enhanced removal and lowered toxicity. However, the role of PAC in catalytic ozonation can be deterred by the dissolved organic matter (DOM) which compete with target pollutants for the adsorption site on PAC affecting the reaction with molecular O_3 and the radicals, which results in the need for increasing its concentration (Margot et al., 2013). In secondary treatment, the common specific PAC dose range is 2 – 3 g PAC/g DOC (Rizzo et al., 2019). To the best of our knowledge, PAC-catalyzed ozonation has not been studied yet for the treatment of PI during wet weather conditions.

This study aimed primarily to test the applicability of single and PAC-catalyzed ozonation to the treatment PI during wet weather through two possible treatment trains. A dose screening was initially performed followed by an evaluation of the impact of both treatment trains on conventional contaminants, micropollutants, and disinfection. The safety of the discharge of the effluent was appraised through acute toxicity, genotoxicity and Yeast Estrogen Screen (YES) bioassays. Finally a detailed cost analysis was performed to predict the applicability of the proposed ozonation processes.

6.2. Material and methods

6.2.1. Sample collection and preparation

During the first stage of this study, samples of PI were collected from a wastewater treatment plant in Alberta over a six months period, extending between April and November 2018. Those samples were acquired before the primary clarifier, after grit removal and were used for screening the effect of adsorption and single ozonation on the removal of major contaminants. During the second stage, another sampling campaign was conducted in March 2020 where three types of wastewater samples were acquired: PI, secondary effluent before UV treatment and final effluent after UV treatment. They were used to compare the effect of PAC-catalyzed ozonation for the treatment of PI during wet weather. All samples were collected in plastic pails that were soaked in

20% bleach overnight and then thoroughly rinsed with deionized water. Samples were transferred to the laboratory and characterized for pH, *E. coli* and DOC on the same day and PI samples were immediately used in the ozonation experiments. It is worth noting that in order to emulate wet weather conditions, the acquired PI samples were uniformly diluted to 50% either with deionized (DI) water (to represent untreated PI during wet weather) or directly in the reactor during treatment (with DI water and O_3 stock solution) as described later in the experimental procedure. All samples were stored at 4 ºC in the dark until analysis completion.

6.2.2. Experimental procedures

Initially, a set of ozonation experiments was performed on samples of diluted PI at different O_3 specific doses to determine the optimum dose to be applied in the proposed treatment trains. Another set of adsorption experiments with different PAC doses was also conducted as a control to screen the effect of PAC on the removal of DOC and COD.

During the second stage of the study, two types of experiments were performed at bench scale level to simulate two possible options for applying ozonation during the enhanced treatment of the PI during wet weather conditions (Figure 6.1). The first option, hereafter referred to as simultaneous treatment (ST), consisted of applying single ozonation (SO) or catalytic ozonation (CO) during the coagulation/ flocculation/ sedimentation (CFS) process that takes place in the primary clarifier. In order to address this treatment option, jar tests were carried in a B-KER^2 Jar Test apparatus with 3-inch wide Phipps & Bird stirrers. In each jar, 75 mg/L of the coagulant aluminum sulfate was simultaneously added with O_3 stock solution with or without PAC such as the volume of O_3 stock solution added did not exceed 30% of the total volume. One minute of rapid mixing was initiated at 150 rotations per minute (rpm) (equivalent to a Gt value of 9300) while all jars were covered with aluminum foil to minimize the volatilization of O_3. Slow mixing followed for 10 minutes at 15 rpm (equivalent to a Gt value of 6000) after which the stirrers were carefully removed to avoid any media disturbance. Settling was then allowed for 1 hour after which the supernatant was carefully collected with a syringe immersed at 2 inches below the surface. The acquired samples had no residual O_3 and were immediately tested for *E. coli* and then stored at 4 °C in the dark for further analysis. All experiments were performed in duplicates at room temperature (20 °C).

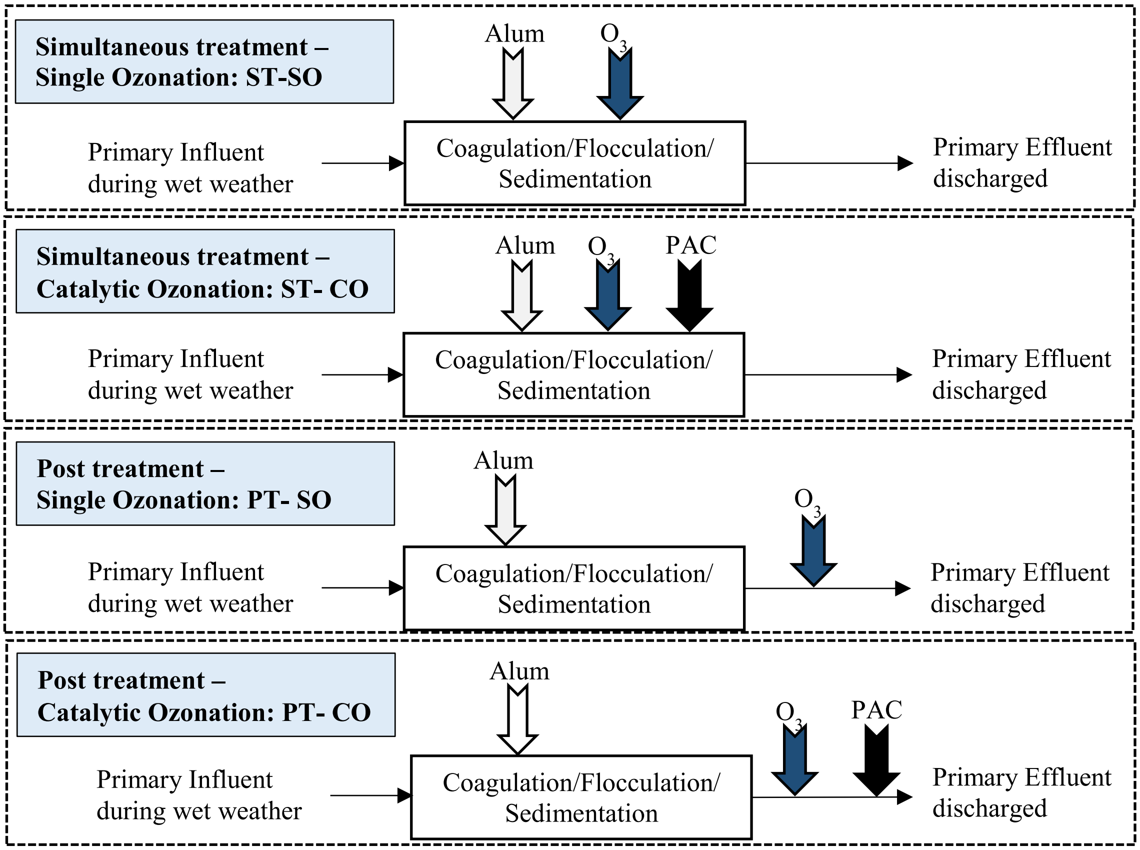


Figure 6.1 Schematic representation of the performed single and catalytic ozonation experiments as simultaneous and post treatments.

The second option entailed applying single or catalytic ozonation on the CFS effluent before discharge into the river. Although such treatment is conventionally performed in a contact chamber, having this addition to a wastewater treatment plant might not be always feasible. This is not only because of space and cost limitations, but also because it will result in an increase in the overall retention time which does not coincide with the high influent flow rates, a major characteristic of the CSO. Instead, ozonation is suggested as a treatment in the pipe for the CFS effluent to improve its quality before discharge. This treatment will be referred to as post treatment (PT). At bench-scale level, PT was performed following a full jar test using 75 mg/L of aluminum sulfate with rapid mixing (1 minute at 150 rpm), slow mixing (10 minute at 15 rpm) and settling (1 hour). The supernatant was then collected and the required volume was transferred to a 250 mL round bottom flask reactor. O_3 and PAC were added from their respective saturated stock solutions and the reactor was immediately capped with no free headspace. The reactor was stirred with a magnetic stirrer over a multi-position stir plate. After 1 minute, residual O_3 was measured and sodium thiosulfate (2mM) was added to the reactor to stop any reaction with residual O_3. All experiments were performed in duplicates, at room temperature (20 °C). A short exposure time to the oxidant and catalyst was selected in order to emulate an in-pipe treatment whereby the travel time between the primary clarifier and the point of discharge was estimated between 0.6 and 3 minutes for a flow rate ranging between 600 mega liters per day (MLD) and 100 MLD.

6.2.3. Wastewater spiking with MPs

A similar set of simultaneous and post experiments was conducted after spiking the PI that was diluted to emulate wet weather conditions with carbamazepine (CBZ) and atrazine (ATZ) to achieve a final concentration of 2 mg/L of each MP. These experiments were performed to validate the efficiency of single and PAC-catalyzed ozonation for the degradation of different types of MPs when applied for the chemical treatment of PI during wet weather. CBZ and ATZ were selected to represent organic MPs that are highly reactive with O_3 and those with low reactivity: CBZ is rapidly degraded by molecular O_3 ($k_{O3/CBZ}= 3\times10^5\ M^{-1}s^{-1}$, (Huber et al., 2003)) while ATZ is not

($k_{O3/ATZ} = 6\ M^{-1}s^{-1}$, (Acero et al., 2000)). Also, those MPs were determined good surrogates for other MPs as discussed in section 5.3.2, Chapter 5. Both MPs were weighed and dissolved directly in a small volume of PI before transferring them to the dedicated PI sample.

6.2.4. Chemicals

All the used chemicals, including sodium indigo trisulfonate, sodium thiosulfate, CBZ and ATZ were acquired from Sigma Aldrich, Canada. O_3 was generated from dry oxygen using the O_3 Generator Model GSO-30. It was bubbled into O_3 demand-free water (ODFW) in an ice bath to obtain a saturated stock solution. Commercial PAC WPX with a particle size of 45 µm was acquired from Calgon Carbon. It has a measured surface area of 632 $m^2g^{-1}$and its full characterization is available in section 4.3.1, Chapter 4. PAC was added from a stock solution of 6 g/L in ODFW. Microtox® reagents were purchased from MODERNWATER. SOS ChromoTest test kit for genotoxicity was obtained from Environmental Bio-detection Products Inc. Canada. XenoScreen XL YES test kit for YES bioassays was procured by XENOMETRIX, Switzerland.

6.2.5. Analytical methods

pH and turbidity were determined using Accumet Research AR20 pH/conductivity meter (Fischer-Scientific) and T-100 handheld Oakton Turbidity meter, respectively. UV absorbance (UVA) was measured at 254 nm using Thermo Scientific GENESYS 10S UV-Vis Spectrophotometer in 1-cm path length quartz cells using samples that were filtered with 0.45 µm nylon syringe filters. The %UV Transmittance (%UVT) was calculated using Equation 6.1.

$\%UVT = 100 \times 10^{-UVA}$ *Equation 6.1*

DOC was measured using a high temperature combustion TOC analyzer (TOC-L analyzers, Shimadzu), as per Standard Method 5310-B (APHA, 2017). In the first stage of the study, the total COD was measured for unfiltered samples following the Standard Method 5220D; and *E. coli* was analyzed using the Membrane Filter Technique, Standard Method 9222 and reported as CFUs/100 mL (colony forming units). During the second stage, COD was measured in filtered samples with 0.45 μm nylon filtered and analyzed as COD dissolved COD_d using HACH method 8000. *E. coli* was quantified based on the most probable number as MPN/100 mL using Colilert-18 method from IDEXX to better accommodate for a prompt analysis of the different samples of treated and untreated wastewater. It should be noted that 1 MPN/100 mL is equivalent to 1 CFU/100 mL according to IDEXX official website (Leonard, 2020). Phosphate anions were quantified using Dionex ICS Ion Chromatography.

MPs were analyzed using ultra-performance liquid chromatography – quadrupole time-of-flight mass spectrometry (Xevo G2-S, Waters), operated in positive mode. Chromatographic separation was achieved using ACQUITY UPLC BEH C18, 50×2.1 mm column, at 50 °C with an injection volume of 10 μL. The mobile phase consisted of water with 0.1 % formic acid (solvent A) and acetonitrile with 0.1 % formic acid (solvent B).

The instantaneous O_3 demand (IOD) for untreated and coagulated PI during wet weather was measured using Standard Method 2350 D (APHA, 2017). The residual O_3 in all single and catalytic ozonation experiments was measured following the Indigo method (Bader & Hoigne, 1981).

6.2.6. Toxicity tests

The acute toxicity of untreated and treated wastewater samples was assessed via standard Microtox® assays with the bacterial reagent *Vibrio fischeri.* Bioluminescence inhibition tests were undertook in duplicates in 96-well plates. Samples were transferred to the wells and an adequate volume of osmotic adjustment solution was added to adjust their salinity. In another 96-well plate equal amounts of bacterial solutions were transferred into each well and the luminescence was measured using Synergy Microplate reader. Samples were added to the bacteria-containing 96-well plate, which was then incubated at 15 °C for 5 minutes after which the luminescence was measured again. The inhibition of light emission was then calculated.

The potential carcinogenic effect of wastewater samples was evaluated through SOS-ChromoTest, a colorimetric method used to measure the relative strength of a potential genotoxic compound. Upon exposure to a genotoxic agent, *E. coli* PQ37, a modified strain of *E. coli* uses SOS gene repair complex to repair the DNA damage and synthesizes β-galactosidase, an enzyme that reacts with blue chromogen. In 96-well plates, different serial dilutions were prepared for each tested sample with dimethyl sulfoxide (DMSO). *E. coli* PQ37 was then added to each well and the plates were incubated at 37 ºC for 2 hours after which blue chromogen was added. The absorbance was measured at 420 nm and 600 nm using Synergy Microplate reader. The plates were incubated again at 37 ºC for 90 minutes and the final absorbance was measured at 420 nm and 600 nm. The cytotoxic effect of the samples was calculated through the bacteria survival rate in Equation 6.2. The genotoxic effect was calculated using the growth factor G in Equation 6.3, the β-galactosidase activity β-gal in Equation 6.4, and the induction ratio IF in Equation 6.5 (SOS-ChromoTest, 2019). IF ≥1.2 was the criteria used to declare a sample genotoxic (Kocak, 2015).

$$\% \text{ Survival rate} = 100 \times \frac{\mathrm{OD}_{420}}{\mathrm{OD}_{420\,c}}$$ *Equation 6.2*

$$G = \frac{A_{420} - A_{420\,b}}{A_{420\,c} - A_{420\,b}}$$ *Equation 6.3*

$$\beta - \mathrm{gal} = \frac{A_{600} - A_{600\,b}}{A_{600\,c} - A_{600\,b}}$$ *Equation 6.4*

$$\mathrm{IF} = \frac{\beta - \mathrm{gal}}{G}$$ *Equation 6.5*

Where: OD_{420} and $\mathrm{OD}_{420\,c}$ represent the optical density at 420 nm of the sample and negative control respectively; A_{420}, $A_{420\,b}$ $A_{420\,c}$ represent the absorbance at 420 nm of the sample, blank and negative control, respectively; A_{600}, $A_{600\,b}$ $A_{600\,c}$ represent the absorbance at 600 nm of the sample, blank and negative control, respectively.

YES bioassays were also conducted on all samples to measure their hormonal activity on estrogen receptors. The Yeast cell contains an estrogen receptor gene that binds to estrogen and gets activated. Then it binds to an estrogen responsive element that contains a reporter gene responsible for the synthesis of β-galactosidase. The latter enzyme turns the yellow chlorophenol red β-D-galactopyranoside into purple or red. A 96 well assay plate was prepared with samples and controls added and serial dilutions performed using DMSO, Yeast culture was prepared and diluted according to its measured OD_{690} and then distributed to the sample plate and incubated at 31 ºC and 100 rpm for 18 hours after which the OD_{690} was measured again. A known volume was then transferred to a fresh plate containing lysis buffer. The fresh plate was then incubated at 31 ºC and 100 rpm for up to 1 hour after which OD_{690} and OD_{570} were measured and used to calculate the % induction and growth factor. 10% Induction was the criteria used to declare the samples as exhibiting an estrogenic toxicity.

6.3. Results and discussion

6.3.1. Wastewater characterization and IOD

Table 6.1 summarizes the characteristics of the PI samples used to screen the effect of O_3 and PAC specific doses on the removal of conventional contaminants. IOD was measured for the PI before and after coagulation with 30 seconds exposure time in order to assess the minimum required O_3 dose for the treatment. With 15 mg/L O_3 and 14 mg/L O_3 as applied O_3 doses, the IOD was 9.69 ±1.19 mg O_3/L for raw PI during wet weather and it dropped by around 36% to 6.21 ±0.68 mg O_3/L after CFS. It is crucial to note that this IOD is dose specific, may not be extrapolated to other doses, and is expected to vary as the quality of PI varies (APHA, 2017). However, it can still provide an estimate for the O_3 doses required in ST and PT.

Table 6.1 Average characteristics of primary influent samples used in the first stage of the study, after dilution with deionized water (50:50) to simulate primary influent during wet weather conditions.

Measured Parameter	PI during wet weather flow* (± STDEV)	
pH	7.3	(±0.1)
Turbidity (NTU)	66.87	(±3.62)
%UVT	52	(±9)
COD_{total} (mg O/L)	219.3	(±37.4)
DOC (mg C/L)	25.10	(±5.91)
***E. coli* (CFUs/100 mL)**	2.16×10^6	$(\pm 0.47 \times 10^6)$

*Average of five sampling campaigns

Table 6.2 describes the characteristics of the PI acquired for the second set of experiments and used in the performance assessment of single and catalytic ozonation in ST and PT. It also shows the effect of spiking the PI during wet weather with CBZ and ATZ in terms of increase in COD_d and DOC. Table 6.2 also compares PI during wet weather to secondary and final effluents in a conventional treatment train. Secondary and tertiary treatments removed 94% of COD_t and 80% and 82% of the DOC, respectively.

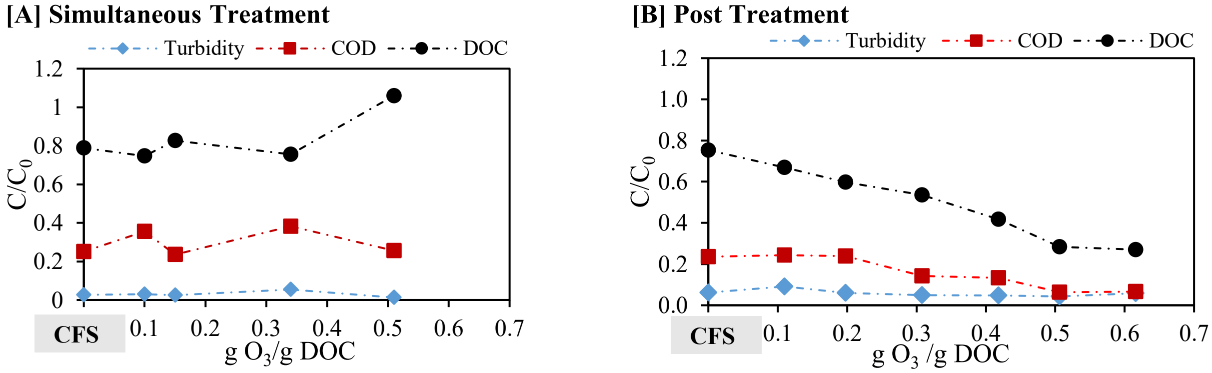
Table 6.2 Characteristics of the primary influent (PI) used in the performance assessment of single and PAC-catalyzed ozonation as simultaneous or post treatments in comparison with the characteristics of secondary and final effluents.

Measured Parameter	**PI during wet weather flow**		**Secondary Effluent**	**Final Effluent**
	Before spiking	**After spiking with CBZ and ATZ**	**Before UV treatment**	**After UV treatment**
pH	7.1 (±0.1)	7.2 (±0 .0)	7.1	7.1
Turbidity (NTU)	88.75 (±2.85)	93.20 (±5.80)	0.60	1.44
%UVT	63 (±0.5)	52 (±0.3)	64	64
$COD_{dissolved}$ (mg O/L)	56 (±2)	76 (±0)	N.M.*	N.M.
COD_{total} (mg O/L)	219	N.M.	27 (±4)	29 (±1)
DOC (mg C/L)	24.52	27.63	10.09	8.87
Phosphate (mg PO_4^{3-}/L)	6.37 (±0.01)	6.37 (±0.01)	<0.05	<0.05
***E.coli* (MPN/100 mL)**	87 ×10^4	87 ×10^4	24.2 ×10^4	0

* N.M = Not measured; CBZ: carbamazepine; ATZ: atrazine.

6.3.2. Dose screening for O_3 and PAC

An initial screening of the effect of O_3 and PAC doses on the removal of conventional macropollutants was conducted on samples of diluted PI to simulate PI during wet weather, during CFS (i.e. ST) and after CFS (i.e. PT). Only low O_3 specific doses were tested in order to explore the effect of minimizing the chemical addition. In simultaneous treatment (Figure 6.2A), the small increment in the O_3 specific dose did not show any significant effect on the removal of turbidity and total COD and on the %UVT beyond the effect of CFS only. However, a negative effect was observed on DOC removal as 0.5 mg O_3/mg DOC increased the final DOC compared to CFS. Similar results were found elsewhere (Tondera et al., 2015) where increasing the O_3 dose to 10 mg/L increased the DOC concentration by 27% and a higher O_3 dose of 15 mg/L increased it further by 41% compared to the influent untreated wastewater (7.8 ±5.4 mg/L COD). In fact, Chandrakanth and Amy (1996) alleged that it is possible that O_3 oxidized NOM that is adsorbed onto the suspended colloids, increasing the acidic functional groups and rendering them more hydrophilic. As a result, NOM desorbed into the aqueous phase and was measured as DOC. It is also possible that O_3 oxidized NOM in the aqueous phase into a lower molecular weight matter resulting in an increased affinity for adsorption onto the colloids. The authors observed that at lower O_3 doses, the adsorption of aqueous NOM onto the colloid either balanced or exceeded its desorption; while at higher O_3 doses, which was the case observed in Figure 6.2A desorption exceeded adsorption. In PT (Figure 6.2B), the O_3 specific dose showed a similar effect on turbidity and total COD; however, there was a substantial improvement in the removal of DOC and an increase in the %UVT. As such 0.5 mg O_3/mg DOC achieved 72% removal of DOC when applied after CFS, which was almost 60% improvement from CFS only. Accordingly, the effect of the O_3 specific dose on DOC removal in PT opposed that in ST because of the dissimilarities between the two targeted media. In PT, O_3 was applied after the removal of suspended matter which means that the applied O_3 was not utilized to breakdown large particles instead it targeted the oxidation of dissolved matter. This enhancement in DOC removal was aligned with an increase in %UVT since the latter is an indicator of the matrix content in organic matter and more specifically in aromatic carbon C=C. Those compounds absorb UV light at 254 nm in a proportional manner to their concentration (APHA, 2017; Chow et al., 2008). An O_3 specific dose of 0.5 g O_3/g DOC was thus selected for further investigation.


[A] Simultaneous Treatment

[B] Post Treatment

Figure 6.2 Effect of O_3 dose on the removal of turbidity, COD and DOC after 30 minutes of single ozonation as **(A)** Simultaneous Treatment, and **(B)** Post Treatment (a dose of 0 g O_3/g DOC corresponds to CFS only).

Similarly, PAC doses up to 500 mg/L were tested in simultaneous and post-treatments for the removal of COD and DOC where they showed no significant effect, except some improvement in DOC removal at higher PAC doses (Figure 6.3) after 30 minutes. Actually, a typical contact time for PAC application ranges between 18 minutes and 3 hours (Rizzo et al., 2019). It is possible that when PAC is added at low concentrations in ST, it aggregates with alum and thus loses its efficiency, while at higher doses it acted as coagulant aid (Szlachta & Adamsk, 2009; USEPA, 2020). A dose of 100 mg/L was chosen to catalyze the ozonation in the next set of experiments because this dose did not have the effect of coagulant aid and was proven to catalyze the degradation of O_3 and improve removals when applied with O_3 specific doses between 0.2 and 2.2 g O_3/g DOC (Chapter 5). Also, this dose matches the common specific PAC dose range, which is 2 – 3 g PAC/g DOC as reported in literature for application in secondary treatment (Rizzo et al., 2019), and it did not increase the final TSS to more than 30 mg/L, the desired value for primary effluent discharge.

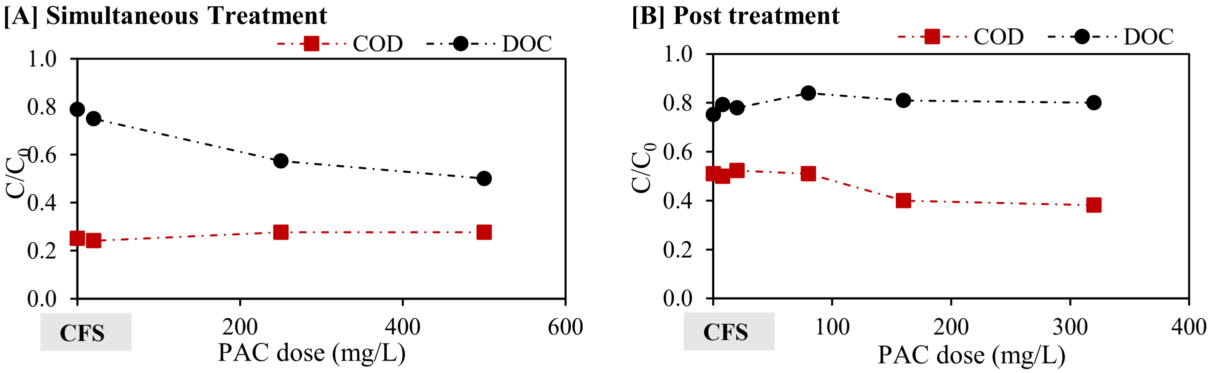


Figure 6.3 Effect of PAC dose on the removal of COD and DOC after 30 minutes of adsorption as a control in **(A)** Simultaneous Treatment and **(B)** Post Treatment (a dose of 0 mg/L PAC corresponds to CFS only).

6.3.3. Simultaneous versus post treatment of PI during wet weather by single and PAC-catalyzed ozonation

A fixed O_3 specific dose of 0.5 mg O_3/mg DOC was selected to assess the performance of single and catalytic ozonation with 100 mg/L PAC. 0.5 mg O_3/mg DOC corresponded to 14 mg O_3/L in ST and 5.5 mg O_3/L in PT. In the former case, there was no residual O_3 at the time of sample collection (i.e. after 1 hour and 11 minutes). However, in the latter case, where the contact time was set to 1 minute only to simulate an in-pipe treatment, the residual O_3 was 2.98 ± 0.12 mg/L O_3 that corresponded to almost 45% of the applied O_3 dose.

Figure 6.4 summarizes the effect of each treatment on the removal of key wastewater quality monitoring parameters. In ST, single ozonation unveiled a negative impact on the removal of turbidity, COD and DOC while catalytic ozonation did not entail any significant effect past the removal by CFS. This result can be associated with the mechanism of oxidation of the organic matter in wastewater by O_3. Whereby O_3 targets specific sites in the hydrophobic fraction of the wastewater through substitution or oxidation-reduction, leading to their cleavage into less hydrophobic compounds (Jin et al., 2016) thus an increase in turbidity and in the soluble portion of the organic material measured by DOC. These observations were slightly attenuated in the presence of PAC by virtue of its role as adsorbent and catalyst. Our results showed that even a PAC dose as high as 250 mg/L did not increase the TSS past the desirable limit in the primary effluent (30 mg/L), probably because PAC was expected to settle during the 1 hour settling time. It is possible that the observed improvement in %UVT upon treatment was due to the mechanism of oxidation through cycloaddition where the electrophilic site in the O_3 molecule reacted with the unsaturated target molecules and broke the double bond C=C, thus decreasing the UV absorbance at 254 nm (Beltran, 2004; Chow et al., 2008). Nevertheless, despite the effect on COD_d and DOC, the main benefit from applying single or catalytic ozonation in ST resides in the improved disinfection to almost 3 log removal of *E. coli*.

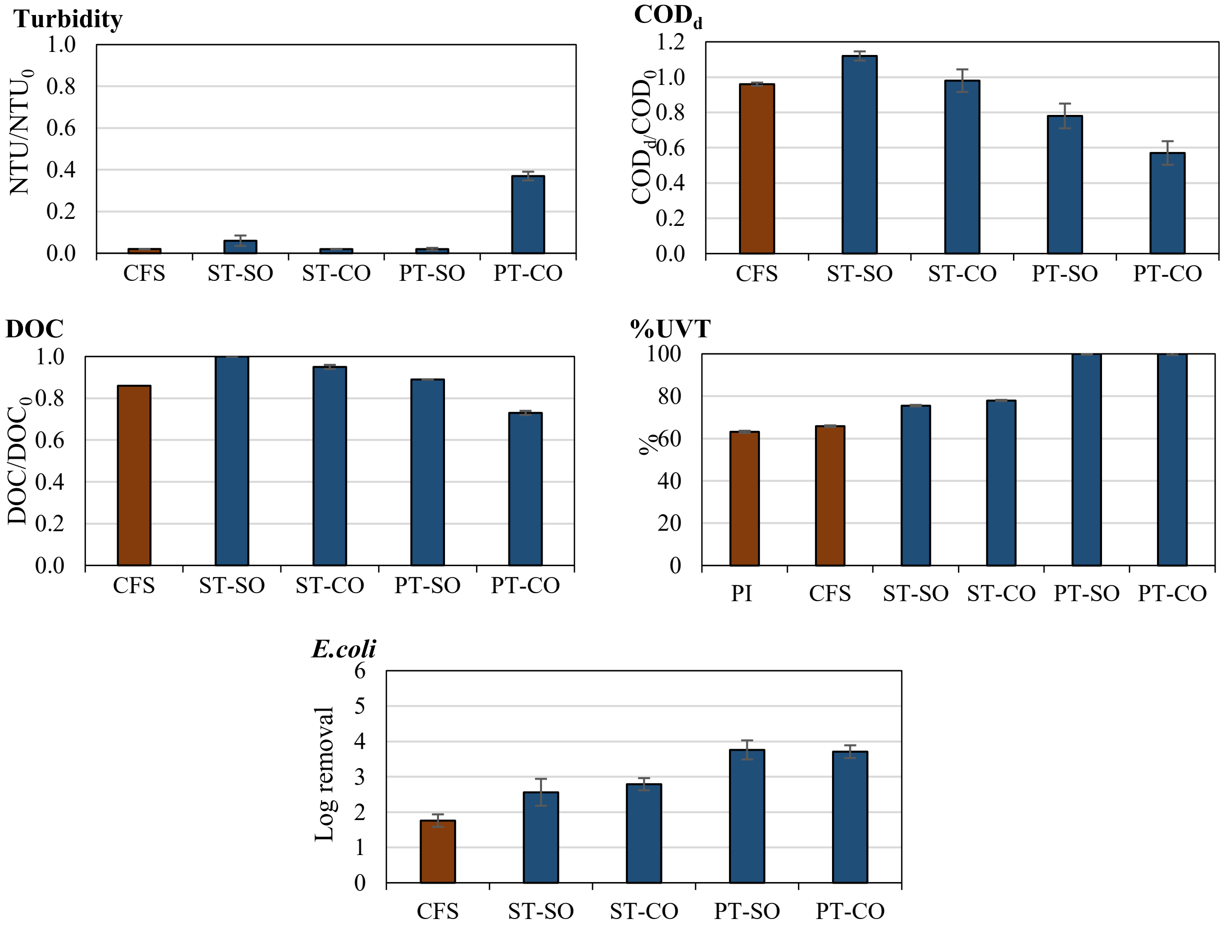


Figure 6.4 Comparison between Simultaneous and Post treatments for the removal of turbidity, COD_d, DOC, *E. coli* and enhancement of %UVT during the treatment of PI during wet weather flow (O_3 specific dose: 0.5 g O_3/g DOC; PAC dose: 100 mg/L). Results correspond to samples collected after 1 hour settling in ST and 1 minute treatment in PT.

In PT, PAC-catalyzed ozonation increased the turbidity significantly which was expected as one disadvantage for suspending PAC in the CFS effluent. It was, however, more efficient for the removal of COD_d and DOC compared to single ozonation which indicated that PAC-catalyzed ozonation enhanced the degree of mineralization. The role of PAC as a strong adsorbent could also be contributing to these results. As such, single ozonation removed 22% and 11% of COD_d and DOC, respectively, while catalytic ozonation removed 43% of COD_d and 27% of DOC. These results are better than those reported by Lei et al. (2007) who combined O_3 and granular activated carbon (GAC) for the treatment of industrial wastewater from a pharmacy plant. O_3 was continuously bubbled in a column reactor to which GAC (60 g/L) and wastewater with adjusted pH were added. Under basic conditions (pH 10), after 1 minute of treatment, there were almost 31% and 0% COD removal by O_3+GAC and O_3 only, respectively; while after 1 hour treatment, the COD removal attained 91% with O_3+GAC and 29% O_3 only. Moreover, there was at least 99% removal of phosphate by CFS only, which eliminates the risk of eutrophication in the receiving natural water (Yamashita & Yamamoto-Ikemoto, 2014).

In PT, both single and PAC-catalyzed ozonation were capable of enhancing the disinfection realizing up to 4 log removal. The initial *E. coli* concentration was in agreement with ranges reported in the literature: 1×10^5 – 1×10^7 (Tondera et al., 2015), 1×10^6 – 8×10^6 MPN/100 mL (Tondera et al., 2013), 2×10^3 – 1×10^7 MPN/100 mL (Christoffels et al., 2014). However, it is interesting that within 1 minute only of PT, single and catalytic ozonation achieved 4 log removal of *E. coli*. In fact, knowing that within this contact time 55% of the applied O_3 dose was utilized, it is anticipated that a longer exposure time could achieve even better disinfection. In comparison, Tondera et al. (2015) achieved 3.4 log removal with O_3 doses between 8.4-12.1 mg/L O_3 (equivalent to 1.08 -1.55 g O_3/g DOC) and 15 minutes exposure time. Also, some suggested that a 2 minutes O_3 exposure time is enough to achieve efficient removal of fecal coliform from wastewater (Xu et al., 2002). It was reported that due to the specificity of this wastewater in terms of its high volume and flow rate, an improved disinfection can be achieved using higher disinfectant dose and/or mixing intensity (Wojtenko et al., 2001b). Overall, the quality of the PT effluent was better than that of the secondary effluent for E.coli and comparable for DOC and phosphate.

The removal of selected MPs by single and catalytic ozonation in both treatment options is displayed in Figure 6.5. The CFS removed 5% and 10% of CBZ and ATZ, respectively. This low removal by CFS can be anticipated since both MPs exhibit some hydrophobic character, (logKow = 2.45 and 2.61, respectively) and thus are expected to persist after CFS (Reungoat et al., 2010). The O_3 specific dose of 0.5 mg O_3/mg DOC was sufficient to completely remove CBZ by single or catalytic ozonation in any treatment form. Single ozonation only was not efficient for the removal of ATZ (11% in ST and 15% in PT) which was expected as ATZ has low reactivity with O_3. However, the removal of ATZ significantly improved when catalytic ozonation was applied reaching 97% in ST after the complete one hour treatment and 75% in PT after 1 minute treatment. Our results are comparable to those reported in the literature for CBZ and slightly lower for ATZ. Kovalova et al. (2013), attained complete removal of CBZ from secondary effluent using an O_3 specific dose of 0.64 mg O_3/mg DOC or by adsorption only with 23 mg/L PAC. Margot et al. (2013) reported more than 90% removal of CBZ using 0.8 mg O_3/mg DOC or 12 mg/L PAC. Altmann et al. (2014) achieved comparable results with 0.5 mg O_3/mg DOC or 20 mg/L PAC. Also, Lee et al. (2013) tested different O_3 specific doses ranging between 0.25 and 1.5 g O_3/g DOC and reported roughly between 20 and 50% removal of ATZ from spiked secondary effluent originating from different WWTPs. Parallel to the removal of MPs, the removal of DOC in spiked PI hinted to the attained degree of mineralization by each of the applied treatments. As such, SO did not affect DOC in ST and decreased it by 11% in PT. In contrast, CO decreased DOC by 5% and 27% in ST and PT, respectively. Thus, the highest degree of mineralization was achieved in PT-CO despite the fact that less ATZ was removed in this case. It is possible that since the primary effluent carried a lower load of particles, PT targeted via oxidation and adsorption the dissolved organics that could have been otherwise hindered by the presence of larger particles in ST.

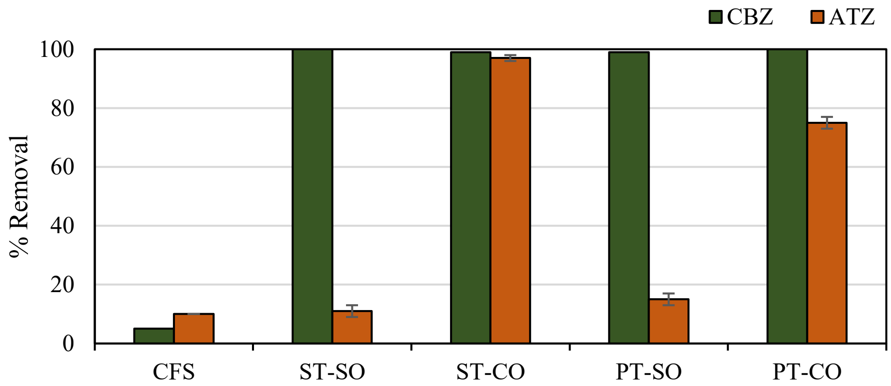


Figure 6.5 Effect of the treatment on the removal of CBZ, ATZ and DOC in PI during wet weather that was spiked with 2 mg/L CBZ and 2 mg/L ATZ. Results correspond to samples collected after 1 hour settling in ST and 1 minute treatment in PT.

6.3.4. Toxicity assays and fate of PAC

Figure 6.6A depicts the different treatments' effects on the toxicity of PI during wet weather assessed using *V. fischeri.* All treatments reduced the acute toxicity of the PI to different extents. In general, ST increased the wastewater's acute toxicity in comparison with CFS alone. Particularly single ozonation turned out more toxic than catalytic ozonation which goes along with the increase in DOC illustrated in Figure 6.5. As discussed in section 6.3.3, ozonation contributes to the breaking down of non-polar compounds into smaller polar compounds. Reungoat et al. (2010), claimed that toxicity is related to the level of hydrophobicity: more hydrophobic compounds are more toxic. It is then possible that the cleavage of the parent compound in single ozonation generated several less hydrophobic products that collectively maintained a more toxic effect. This was less pronounced in PAC-catalyzed ozonation due to either removal of those hydrophobic compounds by adsorption, or to an enhanced oxidation process that shifted the reaction further towards the generation of more hydrophilic products. In PT, single and catalytic ozonation maintained the same acute toxicity level as CFS, and did not impose any negative effect.

Results of the genotoxicity test are summarized in Figure 6.6B. The survival rate in all samples exceeded 80% which, according to the test's supplier, validates the test results proving that the samples were not cytotoxic to the test bacteria. Also, all the tested samples resulted in IF values lower than the threshold IF value of 1.2. This signifies that neither the untreated nor the treated samples were genotoxic, or contained gentoxic substances. Yet, it was remarkable that the IF was significantly lower in samples from the PT process train (both SO and CO). Therefore, wastewater after CFS only or ST showed the same genetic toxicity as the PI, while PT further reduced the genetic toxicity of the effluent. Similarly, YES bioassays (Figure 6.6C) conducted on all samples revealed that none of them showed an estrogenic toxicity since the % induction was below 10%. However, it was observed that the estrogenic activity was reduced in wastewater samples pertaining to the PT train.

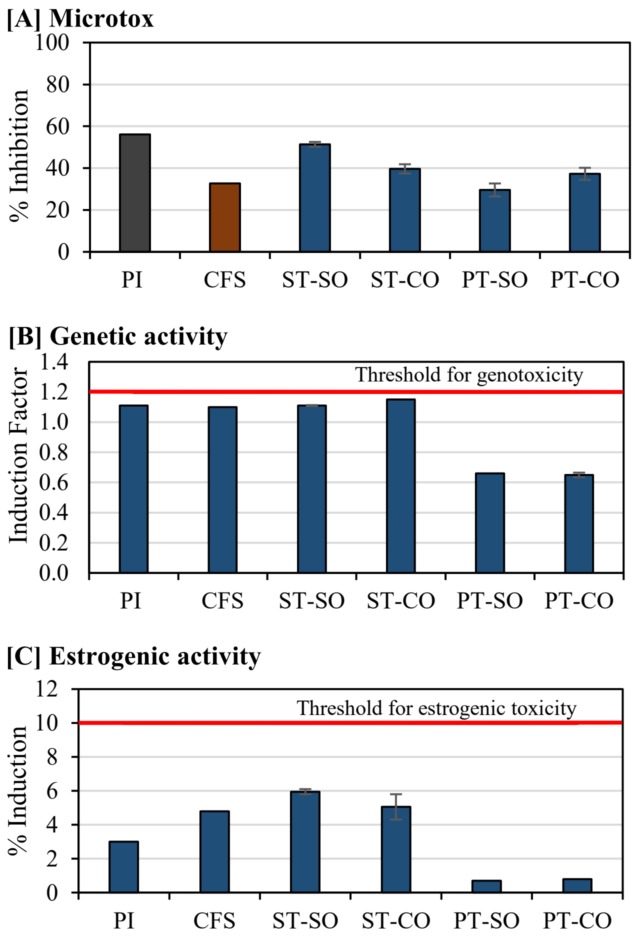


Figure 6.6 Effect of the treatment on the acute toxicity and genotoxicity of the primary effluent: **(A)** Results of the Microtox® bioassay after 5 minutes exposure time; **(B)** Results of the SOS Chromotest for genotoxicity (Induction Factor ≥ 1.2 = genotoxic); **(C)** Results of the YES assay for the estrogenic activity (% Induction > 10% = estrogenic toxicity).

While sludge analysis was out of this study's scope, it was noticeable that applying PAC during ST would entail disposal of the used PAC with the primary sludge according to the conventional operations of the WWTP. However, applying PAC during PT could result in its build up in the pipe, before flushing it through the outfall to the receiving water. As such, PAC can end up as sediments in the river and its actual impact was out of the scope of this study.

6.3.5. Cost Analysis

While it is universally approved that O_3 is highly competent for pathogens reduction, and despite all the knowledge regarding its high capacity for oxidizing organic matter; it is still argued that applying it in CSO treatment in particular, might not be a cost-effective option. As a matter of fact, as the CSO quality is prone to changes due to weather conditions, higher O_3 doses can be required for mitigation and hence the expanding costs of treatment (Wojtenko et al., 2001b). Therefore, and due to concerns with its high capital cost, the USEPA (2018) did not endorse its application for CSO disinfection. Wojtenko et al. (2001b) reported that in a disinfection project in Philadelphia, USA, the ozonation capital cost for a 2 minutes contact time and oxygen-fed generator, was 8.6 times and 7.7 times higher than other disinfection processes (hypochlorite and conventional chlorination, respectively).

In this study, cost calculations were made based on the assumptions in Table 6.3. It was estimated that the expected range of flow rates during wet weather conditions 100-600 MLD corresponded to a retention time ranging between 52-310 minutes in ST, and 0.56 to 3.34 minutes in PT. The costs were projected for the different treatment options based on assumptions made for service life (15 years) and interest rate (6%), and O_3 dose (approximate doses based on a specific O_3 dose of 0.5 g O_3/g DOC). The cost of PAC was estimated at 2.53$/kg (Yang et al., 2010). Moreover, as the suggested treatment options are applied seasonally for the treatment of PI during wet weather, the smallest possible footprint is usually favoured. In this study, none of the suggested treatments required the addition of a contact chamber which resulted in waiving the corresponding costs. The operation was also presumed at a maximum of 100 days per year according to which the operation costs were corrected. It should be noted that the operation and maintenance costs associated with PAC application in PAC-catalyzed ozonation consist of PAC supply as well as disposal. In ST-CO those costs are waived since PAC is removed with the sludge. Yet in PT-CO, they are to be accounted for especially if it is deemed that the river sediments require remediation, which was not considered in this research and was excluded from the calculations.

Table 6.3 Assumptions for the cost estimates.

Parameter	**Value**
Flow rate during wet weather conditions, MLD	100 - 600
Residence time in the clarifier, min	52 - 310
Residence time in effluent channel before discharge, min	0.56 - 3.34
Service life, yr	15
Days of operation per year	100
O_3 dose in simultaneous treatment, mg/L	14
O_3 dose in post treatment, mg/L	5.5
PAC dose, mg/L	100
Price of PAC, $/kg	2.53
Interest rate	6%

The estimated costs for all four proposed treatments are detailed in Table 6.4. In general, the cost of ST was 15 to 30 times higher than that of PT. This renders the former a cost-prohibitive alternative. Moreover, in ST, the addition of PAC did not result in considerable cost increase as the cost of SO and CO were relatively close. However, in PT, PAC addition led to at least doubling the estimated cost for high flow rate (0.32 and 0.63 $/m^3 in ST and PT, respectively). Reungoat et al. (2010) reported a comparable ozonation cost of 0.16 €/m^3 equivalent to 0.21 $/m^3 (based on 2010 exchange rate of 1.33) for an average O_3 dose of 5.7 mg O_3/L applied to a secondary effluent.

Table 6.4 CapEx[a] and OpEx[b] analyses for the different treatment options with single and PAC-catalyzed ozonation, assuming the total period of operation is 15 years.

	Simultaneous Treatment		**Post Treatment**	
	SO [c]	**CO [d]**	**SO [c]**	**CO [d]**
Estimated CapEx, $	94,368,072	94,956,893	3,004,090	3.592,911
Estimated OpEx, $/yr	1.220,459 - 3,878,902	10,454,959 - 59,285,902	529,883 - 2,476,115	9,764,383 -57,886,115
Corrected OpEx, $/yr	334,372 - 1,062,713	2,864,372 -16,242,713	145,173 - 678,388	2,675,173 - 15,858,388
Total annual cost, $/yr	94,702,444 - 95,430,785	97,821,265 - 111,199,606	3,149,263 - 3,682,478	6,268,084 - 19,451,299
Estimated cost per volume of PI during wet weather, $\$/\text{m}^3$	1.59 – 9.47	1.85 – 9.78	0.06 – 0.32	0.32 – 0.63

[a] CapEx: capital expenditures.

[b] OpEx: operational and maintenance expenditures. Both CapEx and OpEx values are present worth (PW) in the year 2016, adjusted with Engineering News Record (ENR) index.

[c] Estimated with cost equations for ozonation systems by Sharma et al. (2013). Reference: Sharma, J.R.,Najafi M., and Qasim S.R., Preliminary cost estimation models for construction, operation, and maintenance of water treatment plants. Journal of Infrastructure Systems, 2013. 19(4): p. 451-464.

[d] Estimated with CapEx for a PAC dry feed system obtained from McGivney and Kawamura, 2008, while the OpEx cost was estimated from the cost of chemical addition obtained from (Yang et al., 2010), added to the OpEx of single ozonation. References: McGivney W.T. and Kawamura S. (2008) Cost estimating manual for water treatment facilities, John Wiley & Sons, Inc.; Yang, W., Paetkau, M., & Cicek, N. (2010). Improving the performance of membrane bioreactors by powdered activated carbon dosing with cost considerations *Water Science and Technology, 62*(1), 172-179. doi: https://doi.org/10.2166/wst.2010.276

6.3.6. Overall performance assessment

The overall performance of each suggested CSO treatment option was summarized in Table 6.5. Each treatment was rated based on its effect on wastewater quality parameters and toxicity, as well as operational limitations and costs. As such, a ST whether through single or PAC-catalyzed ozonation was unfavourable since it had a negative effect on the wastewater content of organic matter and its toxicity. It also implied higher additional cost compared to PT. The latter was only favoured with single ozonation because PAC-catalyzed ozonation incurred major financial and environmental concerns associated with the disposal of PAC. Consequently, single ozonation applied in the pipe after a complete EPT is a promising treatment to improve the quality of the primary effluent before final disposal.

Table 6.5 Color-coded performance assessment of the different treatment options in comparison with primary treatment (CFS) only.

	Simultaneous Treatment		**Post Treatment**	
	O_3	**O_3+PAC**	**O_3**	**O_3+PAC**
pH	🟩	🟩	🟩	🟩
Turbidity removal	🟩	🟩	🟩	🟥
COD removal	🟥	🟧	🟩	🟩
DOC removal	🟥	🟥	🟧	🟨
E.coli removal	🟩	🟩	🟩	🟩
Removal of highly reactive MPs	🟩	🟩	🟩	🟩
Removal of less reactive MPs	🟧	🟩	🟧	🟨
Toxicity to *V. fisheri*	🟥	🟥	🟩	🟩
Genetic and Estrogenic toxicity	🟩	🟩	🟩	🟩
Problem with PAC disposal	🟩	🟩	🟩	🟥
Cost	🟥	🟥	🟩	🟩

🟩 Significant Improvement / No issue or concern
🟨 Improvement
🟧 No Improvement
🟥 Decline / Potential issue or concern

6.4. Conclusions

This study showed that a post treatment approach consisting of coagulation/ flocculation/ sedimentation followed by an ozonation process is a more viable option for the treatment of primary influent during wet weather conditions. In fact, under this treatment train, and 1 minute exposure time, both single and PAC-catalyzed ozonation were satisfactory for disinfection, achieving 4 log removal of *E. coli.* Complete removal of MPs that are highly reactive with O_3 was also attained, and none of the treatment approaches left any concerns about the effluent's acute, genetic or estrogenic toxicity. However, PAC-catalyzed ozonation proved more effective for the elimination of MPs that are less reactive with O_3 and subsequently DOC and COD removal. Therefore, if disinfection is the only concern, single ozonation in the pipe is a reasonable solution at an average cost 0.19 $/m^3. Yet, if disinfection along with the removal of a wider range of MPs are to be attained, PAC-catalyzed ozonation can be a promising solution with a higher average cost of 0.48 $/m^3. Further studies exploring options for PAC removal and disposal as well as cost optimization are needed.

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CHAPTER 7: Conclusions and Recommendations

7.1. Thesis overview

Combined sewer overflows (CSOs) are characterized by their high level of suspended solids, pathogens and orthophosphate. It is undeniable that the release of raw untreated CSO into environmental waters distresses the environmental and public health. However, its treatment remains very challenging. In practicality, CSO is equivalent to municipal wastewater that was diluted with storm water and snow melts. It occurs seasonally and at high flow rates which triggers a prompt and effective treatment with minimal cost and footprint taking into consideration the complex matrix composition. A primary treatment consisting of coagulation/ flocculation and sedimentation is inevitable to remove conventional contaminants, yet the choice of chemicals remains critical for the treatment success. Those chemicals usually added to aggregate and remove suspended matter, cannot compete with oxidation techniques aimed at disinfection and removal of organic compounds. Ozonation is one such technique that has been studied to disinfect and remove organic compounds and has been recently upgraded with the use of a catalyst to further enhance its efficiency. Catalytic ozonation has been therefore competing with other processes although its fundamental catalytic mechanisms are arguable and not very well understood. In real life application, carbon-based catalysts such as PAC can be used to catalyze the ozonation of wastewater for enhanced disinfection and removal of micropollutants. However, little is known about the catalytic mechanisms involved, the efficiency and overall performance of PAC catalyzed ozonation, especially with the high adsorption capacity of PAC.

To shed the light on a basic treatment method that mitigates for the direct discharge of CSO, enhanced primary treatment was investigated through a comprehensive approach from bench to full scale presented in Chapter 3. The study tested and compared three metal-based coagulants and investigated the additional effect of polymer to aid the flocculation and improve the removal of colloidal matters. Chapter 4 delivered a detailed examination of the fundamentals of the catalytic mechanisms involved in PAC-catalyzed ozonation. It paved the road for a better understanding of the role of PAC-catalyzed ozonation in the treatment of different types of MPs. The study was performed using a mixture of different MPs including pharmaceuticals, herbicides and perfluorinated compounds known for their diverse affinities towards ozone. Several of those MPs were studied for the first time in a PAC and ozone system at near environmental concentrations. Chapter 5 proceeded with a comparison between the O_3 specific doses and their effect on the removal of MPs by single and PAC-catalyzed ozonation. It suggested that some MPs can serve as surrogates to help predict the removal of other MPs. In this chapter there was an attempt to study the overall removal kinetics of MPs in a mixture treated by O_3 only and by O_3 and PAC, as well as an overview of the intermediate products that form in each process. Chapter 6 resumed with the application of PAC-catalyzed ozonation for the treatment of primary influent (PI) during wet weather conditions. It evaluated several options for an all-inclusive treatment by considering coagulation/ flocculation/ sedimentation for the removal of suspended solids, as well as single and catalytic ozonation for the removal of MPs, disinfection and toxicity reduction.

7.2. Conclusions

To sum up, the research presented in this thesis focused on two solutions for the treatment of the PI during wet weather conditions in response to the issue of CSO discharge. The thesis answered questions related to practical, fundamental and theoretical aspects of the PI treatment in a cohesive manner aspiring to optimize the quality of the effluent and ultimately preserve the environment and public health. There was a special emphasis on PAC-catalyzed ozonation and its fundamentals being an emerging technique with excessive potentials. The key conclusions are recapped below.

Chapter 3: EPT of PI during wet weather conditions

- Alum outperformed other metal-based coagulants in the primary treatment of PI during wet weather flow: 1 mg of Al added as alum with low mixing conditions was able to remove 22 NTUs, 19 mg chemical oxygen demand (COD) and 0.8 mg orthophosphate (ortho-P).
- Three-factor ANOVA indicated that TSS removal depended mostly on rapid mixing while COD and ortho-P removals depended on slow mixing and coagulant dose.
- The addition of polymer did not lead to any pronounced improvements in the quality of the treated wastewater neither in bench-scale nor in full scale operations.
- Turbidity and percentage UV transmission showed good correlation with total suspended solid and ortho-P. Therefore, they can be used as surrogates for estimating micropollutants' (MPs) removal and online process control.

Chapter 4: Fundamentals of the catalytic mechanisms in PAC-catalyzed ozonation

- PAC-catalyzed ozonation improved the removal of MPs that are resistant to ozonation by up to 27% and promoted faster specific degradation rates.
- Radical probing experiments showed that scavenging hydroxyl radical ($^{\bullet}$OH) did not have any significant impact on the removal of MPs, while scavenging other reactive oxygen species, namely singlet oxygen $^1O_2$, was more influential.
- Electron Paramagnetic Resonance spectroscopy ascertained that the decomposition of O_3 in presence of PAC at neutral pH did not boost the generation of free $^{\bullet}$OH.
- Free $^{\bullet}$OH did not play any significant role in PAC-catalyzed ozonation.

- It is likely that the catalytic effect was expressed at the surface of the catalyst and in the interface between PAC and the bulk solution.
- It is likely that the catalytic decomposition of O_3 by PAC produced adsorbed $^{\bullet}OH$ as $PAC^{\bullet}$–HO and other strong oxidizing species like $[^1O_2 + PAC]$.

Chapter 5: Effect of O_3 specific dose on MPs' removal by single and PAC-catalyzed ozonation

- In a diverse mixture of MPs, most compounds showed higher affinity for the removal by PAC-catalyzed ozonation which was mainly observed at higher O_3 specific dose. Under this condition more than 50% removal could be achieved for the less reactive MPs.
- Carbamazepine and atrazine can serve as surrogate MPs for fast and slow reacting compounds, respectively.
- The removal kinetics were affected by the level of dissolved organic carbon (DOC) available to consume O_3.
- Faster kinetics were obtained in PAC-catalyzed ozonation leaning more towards the removal kinetics with molecular O_3.
- Less intermediate compounds were formed in PAC-catalyzed ozonation possibly because the removal occurs through different pathways in single and PAC-catalyzed ozonation, in addition to the combined role of catalysis and adsorption.

Chapter 6: Applicability of PAC-catalyzed ozonation for the treatment of PI during wet weather

- Post treatment approach consisting of coagulation/ flocculation/ sedimentation followed by ozonation processes is a viable option for the treatment of PI during wet weather conditions.
- Single and PAC-catalyzed ozonation applied as post-treatment were satisfactory for disinfection and removal of MPs that are highly reactive with O_3 without any concerns about the effluent's acute, genetic or estrogenic toxicity.

- PAC-catalyzed ozonation proved more effective for the removal of MPs that are less reactive with O_3 and subsequently DOC and COD.
- If disinfection is the only concern, single ozonation in the pipe is a reasonable solution at an average cost 0.19 $\$/m^3$.
- If removal of a wider range of MPs are to be attained, PAC-catalyzed ozonation is a promising solution at an average cost of 0.48 $\$/m^3$.

7.3. Recommendations

The above-mentioned conclusions can lay the ground for further investigations. We therefore propose the recommendations summarized below to be addressed in future works.

- Bench-scale experiments performed for the optimization of coagulant dose suggested the use of turbidity and UVA_{245} for online process control. This requires validation through bench-scale coagulation and ozonation experiments that account for the varying PI quality through different dilutions and different temperatures. Moreover, there is a need to confirm their use as surrogates for MPs removal after coagulation and single or catalytic ozonation processes with and without spiking.
- Since testing the addition of polymer during the primary treatment of PI revealed some improvements only at full scale operation, further experiments that investigate the effect of slow mixing and retention time during bench scale are recommended.
- The confusion between the role of PAC as catalyst or initiator/ promoter of O_3 decomposition and its role as adsorbent has been behind the reluctance in its application in catalytic ozonation. With all the difficulties that arise when demonstrating the exact removal mechanism during PAC-catalyzed ozonation, mainly because of its strong adsorbing nature, there is still no clear evidence of the exact species that are involved. Also, knowing that there

are different types of activated carbon, any suggested mechanism for one carbon-based catalyst might not essentially apply to all other carbon-based catalysts. This eventually blurs the fundamentals of ozonation catalyzed by carbon materials despite carbon catalysts being more preferred in environmental applications. The challenge remains in the identification of reliable and targeted radical probes and scavengers that do not adsorb onto PAC and can provide strong exact answers with high certainty pertaining to the species involved in the mechanisms.

- The attempt to study the degradation kinetics of the mixture of MPs by single and PAC-catalyzed ozonation did not prove very successful in a batch system since only three of the less O_3-reactive MPs could be monitored. Semi-batch or stopped flow systems deserve a try where continuous supply of O_3 is required in order to mitigate for the fast O_3 decomposition in batch systems and thus securing enough oxidant to carry on the reaction for a longer time and allowing for a better representation of the compounds decay over time.
- Out of the seventeen studied MPs, the pathways of the oxidation of five MPs have not been investigated before. Detailed studies investigating the oxidation mechanisms of fluconazole, diazinon, clindamycin, mecoprop and gemfibrozil individually are needed. Moreover, a comparison between the intermediates formed when MPs are studied individually and those formed in a mixture can give a better insight into the matrix effect on the catalytic and non-catalytic mechanisms.
- Bench-scale experiments performed in the ozonation study for PI mainly portrayed batch reactors that do not represent the suggested full-scale applications in the pipe. Therefore, another experimental setup that can model in-pipe treatment with plug flow reactors and direct O_3 bubbling is recommended to better elucidate and validate the removal of organics and *E.coli*. A fluidized bed reactor could represent another possible configuration. The effect

of other environmental conditions, namely temperature, is also worth the investigation knowing that O_3 is more stable at lower temperatures and that the studied PI occurs in spring and summer seasons due to snow melts and rains.

- Upgrading the treatment of PI during wet weather conditions through the addition of PAC-catalyzed ozonation after primary treatment delivered several advantages regarding the quality of the effluent. A major drawback of the process is associated with the disposal of utilized PAC when the treatment is suggested in the pipe. Further studies that explore options for PAC removal, such as end of pipe settling tanks, and disposal as well as cost optimization are needed.
- The O_3 and PAC doses that were tested in this research for the treatment of PI during wet weather flow were justified. Yet, further optimization of the doses and exposure time is beneficial to account for the fluctuating quality of the PI during wet weather conditions.
- Studying the effect of single and PAC-catalyzed ozonation on the removal of pre-existing MPs in the PI would provide data pertaining to a broad range of MPs. Solid phase extraction (SPE) could be applied to wastewater samples before and after the suggested treatments to acquire the exact MPs' degradation information. This can confirm the validity of the proposed surrogates and process control parameters as well as the treatment's compliance with target values or projected guidelines whenever they are implemented.
- Although PAC has numerous advantages, being an affordable and excellent adsorbent that is commonly used in the water and wastewater treatment industries, it is worth exploring other types of carbon-based catalysts. For instance, adsorbents that can be prepared from the sludge generated in primary or secondary clarifiers or anaerobic digesters, also referred to as biochar, can also be evaluated for their capacity to catalyze the ozonation process.

- In this study we evaluated the treatment of PI during wet weather flow with two approaches coagulation/ flocculation/ sedimentation and oxidation. Since, the former is compulsory for the removal of suspended solids, the latter is an additional polishing step that showed great potential for disinfection and removal of micropollutants. Still, other processes that can compete with single or catalytic ozonation can be tested and compared in terms of effluent quality, feasibility and cost assessment. UV disinfection, ferrate addition, chlorination and membrane filtration could possibly be good candidates.
- While the work presented in this study targeted the treatment of PI during wet weather flow, it could lay the ground for engineered green approaches for CSO treatment. As such, in areas with split sewers, the installation of porous pavement and manholes through which storm water and snowmelts can infiltrate, can provide a route for the removal of trace organics through adsorption and oxidation in presence of dissolved oxygen.

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APPENDIX

1. Supplementary Tables and Figures

Table A.1 Predicted half-lives of MPs in a reaction with molecular O_3 only under different O_3 specific doses.

		Individually treated		**In mixture 0.27 g O_3/g DOC**			**In mixture 2.17 g O_3/g DOC**			**In mixture 21.64 g O_3/g DOC**		
MP	**k_{O3} ($M^{-1}s^{-1}$)***	**k' (s^{-1})**	**$t_{1/2}$ (s)**	**Molar conc. (µM)**	**k' (s^{-1})****	**$t_{1/2}$ (s)*****	**Molar conc. (µM)**	**k' (s^{-1})**	**$t_{1/2}$ (s)**	**Molar conc. (µM)**	**k' (s^{-1})**	**$t_{1/2}$ (s)**
EE2	7.00E+09	1.46E+06	4.75E-07	13.50	7.77E+04	8.92E-06	1.69	7.71E+04	8.99E-06	0.17	7.71E+04	8.99E-06
TCN	3.80E+07	7.92E+03	8.76E-05	13.82	4.32E+02	1.60E-03	1.73	4.29E+02	1.62E-03	0.17	4.29E+02	1.62E-03
SMX	5.70E+05	1.19E+02	5.84E-03	15.81	7.41E+00	9.35E-02	1.98	7.36E+00	9.42E-02	0.20	7.36E+00	9.42E-02
GFL	4.90E+05	1.02E+02	6.79E-03	15.98	6.44E+00	1.08E-01	2.00	6.39E+00	1.08E-01	0.20	6.39E+00	1.08E-01
CBZ	3.00E+05	6.25E+01	1.11E-02	16.93	4.18E+00	1.66E-01	2.12	4.15E+00	1.67E-01	0.21	4.15E+00	1.67E-01
TMP	2.70E+05	5.63E+01	1.23E-02	13.78	3.06E+00	2.26E-01	1.72	3.03E+00	2.29E-01	0.17	3.03E+00	2.29E-01
NPX	2.00E+05	4.17E+01	1.66E-02	17.38	2.86E+00	2.42E-01	2.17	2.83E+00	2.45E-01	0.22	2.83E+00	2.45E-01
MCP	101	2.10E-02	3.29E+01	16.34	1.36E-03	5.11E+02	2.33	1.53E-03	4.52E+02	0.23	1.53E-03	4.52E+02
2,4-D	29.1	6.06E-03	1.14E+02	18.10	4.33E-04	1.60E+03	2.26	4.29E-04	1.62E+03	0.23	4.29E-04	1.62E+03
IBU	9.6	2.00E-03	3.47E+02	19.39	1.53E-04	4.53E+03	2.42	1.51E-04	4.58E+03	0.24	1.51E-04	4.58E+03
ATZ	6	1.25E-03	5.55E+02	18.56	9.16E-05	7.57E+03	2.32	9.08E-05	7.64E+03	0.23	9.08E-05	7.64E+03
FCZ	1	2.08E-04	3.33E+03	13.07	1.08E-05	6.45E+04	1.63	1.06E-05	6.52E+04	0.16	1.06E-05	6.52E+04
DZN	N/A	1.70E-03	4.08E+02	13.14	8.82E-05	7.86E+03	1.64	8.73E-05	7.94E+03	0.16	8.73E-05	7.94E+03
CDM	N/A			20.92			2.62			0.26		
CLN	N/A			9.43			1.18			0.12		
PFOA	N/A			9.66			1.21			0.12		
PFOS	N/A			7.43			0.93			0.09		
Total Molar conc. of MPs $[MP]_t$				253.24			31.95			3.19		
Total Equiv. DOC				36.93			4.62			0.46		

Notes:

N/A = Not available

*Obtained from literature

** $k^1(s^{-1}) = k_{O_3}(M^{-1}s^{-1}) \times [O_3](M) \times \frac{[MP]}{[MP]_t}$

*** $t_{1/2} = \frac{Ln2}{k'(s^{-1})}$

Table A.2 Predicted half-lives of MPs in a reaction with hydroxyl radicals $^{\bullet}OH$ only under different O_3 specific doses.

		Individually treated		**In mixture 0.27 g O_3/g DOC**			**In mixture 2.17 g O_3/g DOC**			**In mixture 21.64 g O_3/g DOC**		
MP	**$K_{\bullet OH}$ ($M^{-1}s^{-1}$)***	**k' (s^{-1})**	**$t_{1/2}$ (s)**	**Molar conc. (µM)**	**k' (s^{-1})****	**$t_{1/2}$ (s)*****	**Molar conc. (µM)**	**k' (s^{-1})**	**$t_{1/2}$ (s)**	**Molar conc. (µM)**	**k' (s^{-1})**	**$t_{1/2}$ (s)**
EE2	9.80E+09	2.04E+06	3.40E-07	13.5	1.09E+05	6.37E-06	1.69	1.08E+05	6.42E-06	0.17	1.08E+05	6.42E-06
TCN	9.60E+09	2.00E+06	3.47E-07	13.82	1.09E+05	6.35E-06	1.73	1.08E+05	6.40E-06	0.17	1.08E+05	6.40E-06
SMX	5.50E+09	1.15E+06	6.05E-07	15.81	7.15E+04	9.69E-06	1.98	7.10E+04	9.76E-06	0.20	7.10E+04	9.76E-06
GFL	7.10E+09	1.48E+06	4.69E-07	15.98	9.33E+04	7.43E-06	2	9.26E+04	7.49E-06	0.20	9.26E+04	7.49E-06
CBZ	8.80E+09	1.83E+06	3.78E-07	16.93	1.23E+05	5.66E-06	2.12	1.22E+05	5.70E-06	0.21	1.22E+05	5.70E-06
TMP	6.90E+09	1.44E+06	4.82E-07	13.78	7.82E+04	8.86E-06	1.72	7.74E+04	8.96E-06	0.17	7.74E+04	8.96E-06
NPX	9.60E+09	2.00E+06	3.47E-07	17.38	1.37E+05	5.05E-06	2.17	1.36E+05	5.10E-06	0.22	1.36E+05	5.10E-06
MCP	1.9E+09	3.96E+05	1.75E-06	16.34	2.55E+04	2.71E-05	2.33	2.89E+04	2.40E-05	0.23	2.89E+04	2.40E-05
2,4-D	N/A			18.1			2.26			0.23		
IBU	7.4E+09	1.54E+06	4.50E-07	19.39	1.18E+05	5.87E-06	2.42	1.17E+05	5.94E-06	0.24	1.17E+05	5.94E-06
ATZ	3.0E+09	6.25E+05	1.11E-06	18.56	4.58E+04	1.51E-05	2.32	4.54E+04	1.53E-05	0.23	4.54E+04	1.53E-05
FCZ	N/A			13.07	0.00E+00		1.63			0.16		
DZN	8.40E+09	1.75E+06	3.96E-07	13.14	9.08E+04	7.63E-06	1.64	8.98E+04	7.72E-06	0.16	8.98E+04	7.72E-06
CDM	N/A			20.92			2.62			0.26		
CLN	N/A			9.43			1.18			0.12		
PFOA	3.00E+07	6250	1.11E-04	9.66	2.38E+02	2.91E-03	1.21	2.37E+02	2.93E-03	0.12	2.37E+02	2.93E-03
PFOS	3.00E+07	6250	1.11E-04	7.43	1.83E+02	3.78E-03	0.93	1.82E+02	3.81E-03	0.09	1.82E+02	3.81E-03
Total Molar conc. of MPs $[MP]_t$				253.24			31.95			3.19		
Total Equiv. DOC				36.93			4.62			0.46		

Notes:

N/A = Not available

*Obtained from literature

** $k^1(s^{-1}) = k\,\cdot_{OH}(M^{-1}s^{-1}) \times [\,^{\bullet}OH](M) \times \frac{[MP]}{[MP]_t}$

*** $t_{1/2} = \frac{Ln2}{k'(s^{-1})}$

Table A.3 Oxidation intermediates and by-products for the 17 studied MPs reported in literature.

MP	Oxidation intermediates/by-products		Mass (m/z)	Reference
EE2	$C_6H_{10}O_3$		129	(Huber et al., 2004)
	$C_6H_{11}O_4$		145	
	$C_{14}H_{20}O_5$		267	
	$C_{15}H_{22}O_7$		313	
	$C_{16}H_{21}O_8$		341	
	$C_{14}H_{20}O_4$		251	
	$C_{16}H_{22}O_7$		325	
	$C_2H_2O_4$	Oxalic acid	91.0031	(Zhang et al., 2006)
	$C_3H_4O_4$	Malonic acid	105.0188	
	$C_4H_6O_4$	Succinic acid	119.0344	
	$C_6H_{10}O_4$	Adipic acid	147.0657	
	$C_5H_8O_4$	Glutaric acid	133.0501	
TCN	$C_6H_4Cl_2O$	2,4-Dichlorophenol	162.9717	(Chen et al., 2012)
	$C_6H_5ClO_2$	4-Chlorocatechol	143.9978	
SMX	$C_4H_6N_2O$	3-Amino-5-methylisoxazole	99.0558	(Goncalves et al., 2012)
	$C_6H_4O_2$	p-Benzoquinone	109.029	
	$C_2H_3NO_3$	Oxamic acid	90.0191	
	$C_3H_4O_3$	Pyruvic acid		
	$C_2H_2O_4$	Oxalic acid	91.0031	
	$C_4H_4O_4$	Maleic acid	117.0188	
GFL	N/A			
CBZ	$C_{15}H_{10}N_2O_2$	1-(2-benzaldehyde)-4-hydro-(1H,3H)-quinazoline-2-one	251.082	(McDowell et al., 2005)
	$C_{15}H_{10}N_2O_3$	1-(2-benzaldehyde)-(1H,3H)-quinazoline-2,4-dione	267.077	
	$C_8H_6N_2O_2$	1-(2-benzoic acid)- (1H,3H)-quinazoline-2,4-dione	163.0508	
	$C_{14}H_9NO_2$	2-Nitroanthracene or 9-Nitroanthracene	224.0710	(Hubner et al., 2014)
	$C_{15}H_{14}N_2O_3$		309.0645	
	$C_{15}H_{10}N_2O$		267.0775	
	$C_{15}H_{10}N_2O_4$	Phencomycin	283.0725	
	$C_{15}H_{12}N_2O_2$		253.0980	
	$C_{15}H_{12}N_2O_3$	Hydrofuramide	269.0933	
	$C_{15}H_{10}N_2O_2$		269.0933	
	$C_{15}H_{12}N_2O_2$		253.0980	
	$C_{15}H_{10}N_2O_3$	Carbmazepine-o-quinone	267.0770	
	$C_{14}H_9NO_2$		224.0709	
	$C_{13}H_9NO$	Acridone	196.0767	
	$C_{14}H_{11}NO_4$		258.0761	
	$C_{14}H_{11}NO_4$		208.0760	
TMP	$C_{14}H_{19}N_4O_3$		291.1441	(Kuang et al., 2013)
	$C_{13}H_{19}N_4O_4$		295.1391	
	$C_{14}H_{19}N_4O_5$		323.1335	
	$C_{14}H_{21}N_4O_5$		325.1503	
	$C_{14}H_{19}N_4O_6$		339.1309	
	$C_{14}H_{17}N_4O_3$		277.1216	
	$C_{13}H_{16}N_3O_4$		278.1156	
	$C_{12}H_{17}N_4O_4$		281.1220	
	$C_{14}H_{19}N_2O_6$		311.1195	
	$C_{14}H_{19}N_4O_7$		355.1224	
	$C_{14}H_{21}N_4O_7$		357.1369	
	$C_{11}H_{14}N_3O_3$		236.0939	
	$C_{14}H_{19}N_4O_4$		307.1197	
	$C_{11}H_{17}N_4O_7$		317.1183	
	$C_5H_6N_4O$		139.062	

MP	Oxidation intermediates/by-products		Mass (m/z)	Reference
	$C_5H_8N_4O$		141.0776	
NPX	$C_{13}H_{18}O_4$	2-(4-(2-Mmethoxyethyl)-3-methylphenyl) propanoic acid	239.1283	(Aguilar et al., 2019)
	$C_{13}H_{14}O_3$	1-(6-Methoxynaphthalene-2-yl) ethylhydroperoxide	219.1021	
	$C_{12}H_{14}O_3$	2-(4-(2-Hydroxyvinyl)phenyl) acetic acid	207.1021	
	$C_{10}H_{10}O_3$	2-(4-(2-Hydroxyvinyl)phenyl) acetic acid	177.0554	
	$C_9H_{10}O_2$	2-(*p*-Tolyl)acetic acid	149.0592	
	$C_2H_2O_4$	Oxalic acid	91.0031	
	CH_2O_2		47.0133	
MCP	N/A			
2,4-D	$C_6H_4Cl_2O$	2,4-Dichlorophenol	162.9717	(Ying-hui et al., 2006)
	$C_6H_5ClO_2$	Chlorohydroxyquinone	143.9978	
	$C_6H_5ClO_2$	4-chlorocatechol	143.9978	
	$C_6H_4Cl_2O_2$	3,5-Dichlorocatechole	178.9667	
	$C_2H_2O_4$	Oxalic acid	91.0031	
	$C_2H_4O_2$	Acetic acid	61.029	
IBU	C_9H_9O		133.0653	(Huang et al., 2015)
	$C_{12}H_{15}O_5$		239.0919	
	$C_{12}H_{17}O$		177.1279	
	$C_{12}H_{17}O$		176.1279	
	$C_{12}H_{15}O$		175.1123	
	$C_{13}H_{17}O_3$		221.1178	
	$C_{26}H_{33}O_8$		473.2175	
	$C_{13}H_{17}O_2$		205.1229	
ATZ	$C_8H_{13}ClN_6O$	N-(4-chloro-6-(isopropylamino)-1,3,5-triazin-2-yl)		(Li & Zhou, 2019)
	$C_8H_{15}N_5O$	2-Hydroxy-4-ethylamino-6-isopropylamino-1,3,5-triazine	198.1355	
	$C_8H_{14}Cl_{15}NN_4$	2-Chloro-4-amino-6-isoproylamino-1,3,5-triazine		
	$C_3H_3ClN_5$	2-Chloro-4,6-diamino-1,3,5-triazine	145.0155	
	$C_3H_5N_5O$	2-Hydroxyl-4,6-diamino-1,3,5-triazine		
FCZ	N/A			
DZN	N/A			
CDM	$C_8H_7N_3O_2$	benzimidazole-2-ylcarbamic-acide		(Kiss & Virág, 2009a)
	$C_7H_7N_3$	2-amino-benzimidazole	134.0718	
	$C_7H_6N_2$	Benzimidazole	**119.0609**	
	$C_7H_{11}N_3$	2-methyl-amino-aniline	138.1031	
	$C_6H_8N_2$	1,2-diaminobenzene	109.0766	
	C_6H_5OH	benzene		
	C_6H_5OH	Phenol		
	$C_6H_5NH_2$	Aniline		
CLN	N/A			
PFOA	N/A			
PFOS	N/A			

Note: N/A = Not available

Table A.4 Cost analysis for single and PAC-catalyzed ozonation as ST and as PT

		Simultaneous Treatment		**Post Treatment**		**Unit**
		Max flow 600 MLD	**Min Flow 100 MLD**	**Max flow 600 MLD**	**Min Flow 100 MLD**	
Flow rate		600,000	100,000	600,000	100,000	m^3/d
Service life		15	15	15	15	yr
Interest rate		6	6	6	6	%
Present worth (PW) factor		9.712	9.712	9.712	9.712	-
ENR index (May 2011)		9,027.23	9,027.23	9,027.23	9,027.23	-
ENR index (March 2016)		10,279.94	10,279.94	10,279.94	10,279.94	-
Adjustment factor		1.1	1.1	1.1	1.1	-
Ozone dose		14.0	14.0	5.5	5.5	mg/L
		0.014	0.014	0.006	0.006	kg/m^3
Ozone generation capacity		8400.0	1400.0	3300.0	550.0	kg/d
		18480	**3080**	**7260**	**1210**	lb/d
Contact time		52	310	0.56	3.34	min
Contact chamber volume		-	-	-	-	ft^3
CC*	**Ozone generation**	804,818,004.6	804,818,004.6	25,620,375.8	25,620,375.8	$
	Ozone contact chamber	0.0	0.0	0.0	0.0	$
	Adjusted annual CC	94,368,071.9	94,368,071.9	3,004,089.7	3,004,089.7	$
O&M	**Ozone generation**	3,406,220.2	1,071,734.2	2,174,376.4	465,311.9	$
	Adjusted value	3,878,901.9	1,220,458.9	2,476,114.9	529,883.3	$

<u>Note:</u>

In CC:

Ozone generation = $0.0002x^3-1.5794x^2 + 4{,}424.4x + 214{,}180$; where x = ozone generation capacity (lb/day)

Adjusted annual CC = (Ozone generation + Ozone contact chamber)/FW factor) * Adjustment factor

In O&M:

Ozone generation = (-0.01*x^2) + 367.19*x + 35653; where x = ozone generation capacity (lb/day)

Adjusted value = Ozone generation * Adjustment factor

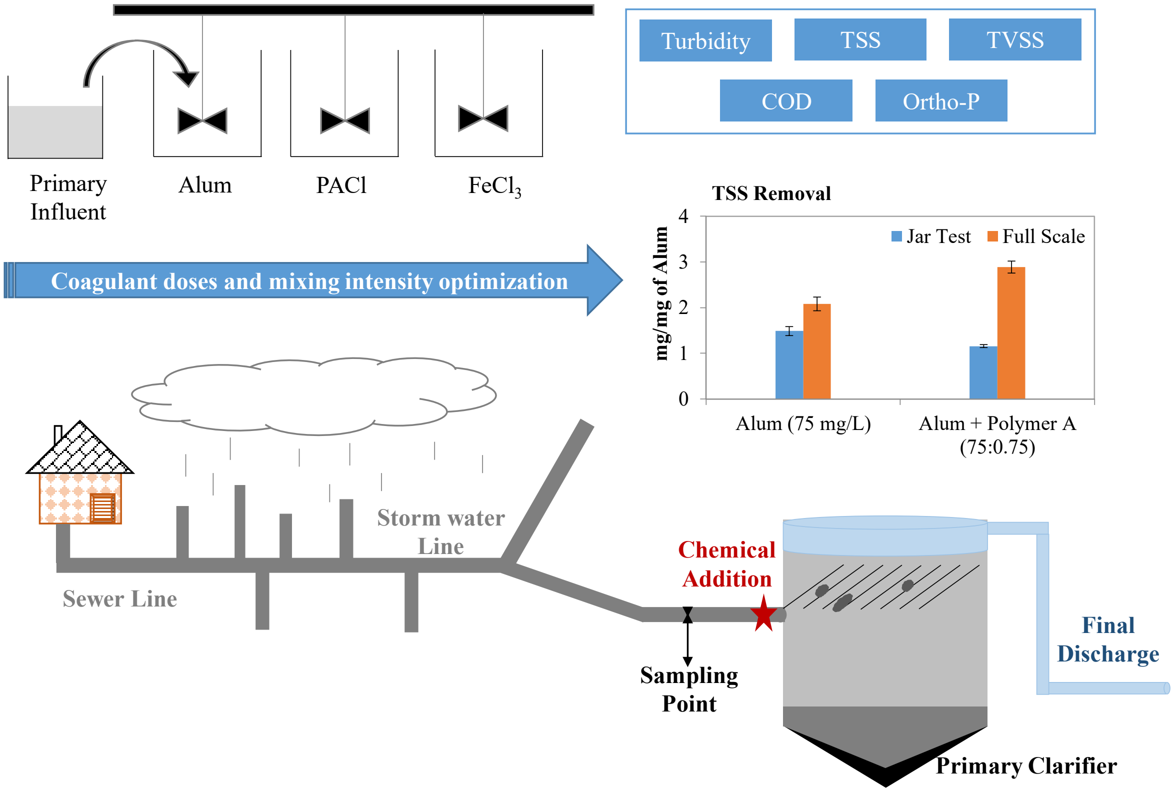

Figure A.1 Graphical summary of Chapter 3.

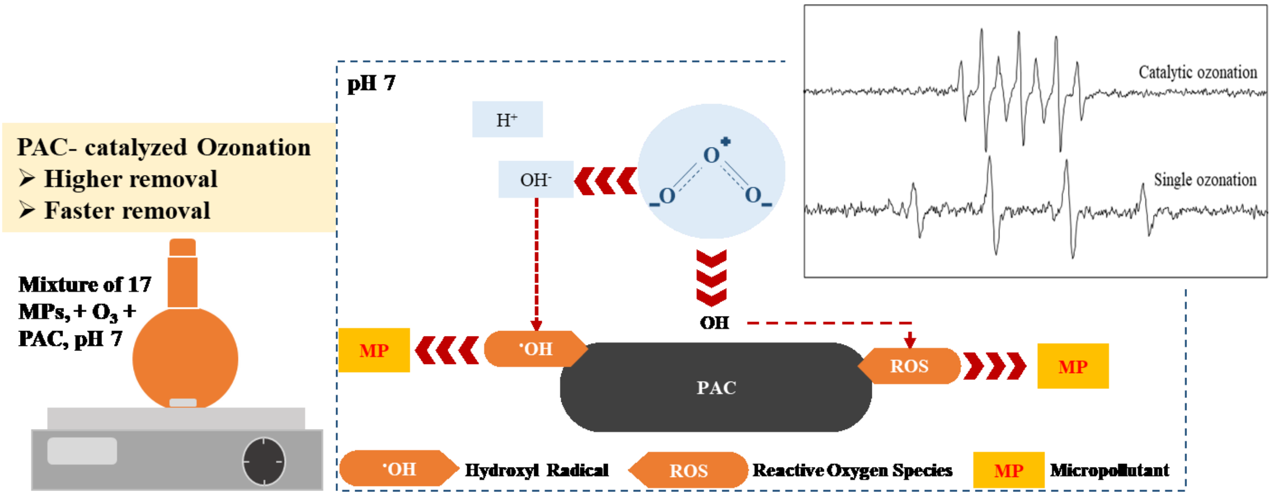

Figure A.2 Graphical summary of Chapter 4.

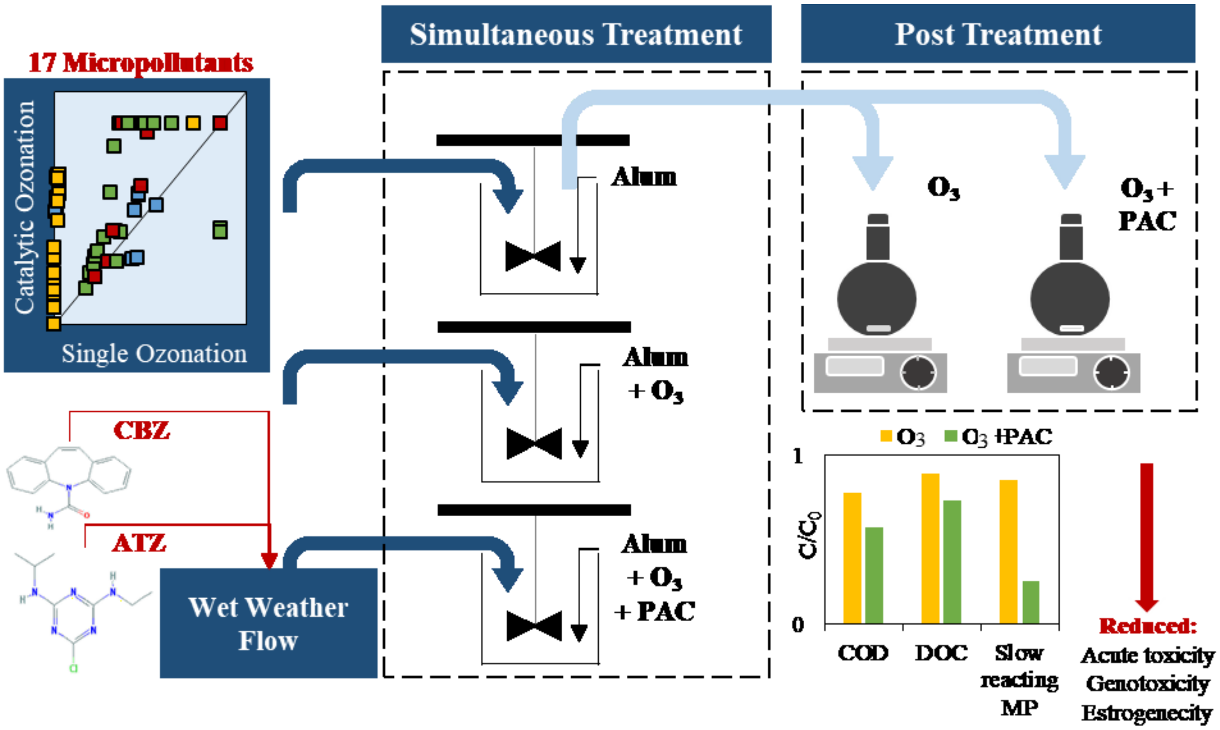

Figure A.3 Graphical summary of Chapters 5 and 6.

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   8.4. No amendment or waiver of any terms is binding unless set forth in writing and signed by the parties. The Rightsholder and CCC hereby object to any terms contained in any writing prepared by the User or its principals, employees, agents or affiliates and purporting to govern or otherwise relate to the licensing transaction described in the Order Confirmation, which terms are in any way inconsistent with any terms set forth in the Order Confirmation and/or in these terms and conditions or CCC's standard operating procedures, whether such writing is prepared prior to, simultaneously with or subsequent to the Order Confirmation, and whether such writing appears on a copy of the Order Confirmation or in a separate instrument.

   8.5. The licensing transaction described in the Order Confirmation document shall be governed by and construed under the law of the State of New York, USA, without regard to the principles thereof of conflicts of law. Any case, controversy, suit, action, or proceeding arising out of, in connection with, or related to such licensing transaction shall be brought, at CCC's sole discretion, in any federal or state court located in the County of New York, State of New York, USA, or in any federal or state court whose geographical jurisdiction covers the location of the Rightsholder set forth in the Order Confirmation. The parties expressly submit to the personal jurisdiction and venue of each such federal or state court.If you have any comments or questions about the Service or Copyright Clearance Center, please contact us at 978-750-8400 or send an e-mail to support@copyright.com.

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