THE ROLE OF OZONATION IN POTABLE REUSE TREATMENT TRAINS

by

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ABSTRACT

Dramatic population growth along with climate change has caused water shortage in regions where an estimated 2.1 billion people live. As a result of dwindling conventional water supplies, potable reuse of municipal wastewater has been considered as an imperative component of water resource management. The implementation of potable reuse projects has mainly employed multiple purification steps to provide effective removal of aquatic pathogens as well as organic and inorganic contaminants. Typically, conventional potable reuse treatment trains employ reverse osmosis (RO) as their main purification barrier that is able to provide substantial contaminant removal. However, limitations associated with RO such as high capital and operation costs, concentrate disposal, and challenging requirements for influent water quality (i.e., removing suspended solids and organic matter content to reduce membrane fouling) has raised interest for alternative designs in potable reuse applications.

Ozonation followed by biologically active filtration (BAF) is an effective treatment technology for eliminating organic matter from a variety of wastewater effluent streams through a multibarrier solution (oxidation, biological and physical filtration) and has been considered as an non-membrane-based alternative technology to RO for low salinity source waters or locations with bleeding capacity for their finished water. The main objective of this research was to optimize the O_3-BAF treatment train approach by enhancing the oxidation strength of the ozonation process as well as develop a novel approach for the BAF acclimation or start-up process. The pilot-scale performance of O_3-BAF was evaluated by investigating the removal of refractory organic contaminants as well as disinfection byproducts formation potential.

Moreover, among membrane-based technologies in potable reuse applications, nanofiltration (NF) can be a potential alternative to RO due to its relatively lower energy consumption. A bench-scale study was conducted to evaluate the impact of pre-ozonation at relatively low O_3 doses on the reduction of NF fouling and provided an insight on the feasibility of this treatment during potable reuse of municipal wastewater effluent.

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LIST OF ABBREVIATION

AOP	Advanced Oxidation Process
ATP	Adenosine Triphosphate
BAA	Bromoacetic Acid
BAF	Biologically Active Filtration
BCAA	Bromochloroacetic Acid
BCAM	Bromochloroacetamide
BCAN	Bromochloroacetonitrile
BDCAA	Bromodichloroacetic Acid
BDCAL	Bromodichloroacetaldehyde
BDCM	Bromodichloromethane
BET	Brunauer-Emmet-Teller
CAA	Chloroacetic Acid
COD	Chemical Oxygen Demand
DBAA	Dibromoacetic Acid
DBAM	Dibromoacetamide
DBAN	Dibromoacetonitrile
DBCAA	Dibromochloroacetic Acid
DBCAL	Dibromochloroacetaldehyde
DBCM	Dibromochloromethane
DBP	Disinfection Byproduct
DCAA	Dichloroacetic Acid
DCAM	Dichloroacetamide
DCAN	Dichloroacetonitrile
DEET	N, N-Diethyl-m-Toluamide
DI	Deionized Water
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter

EBCT	Empty Bed Contact Time
EDC	Endocrine-Disruptive Compound
EDS/EDX	Energy Dispersive X-Ray Spectroscopy
EEMs	Excitation-Emission Matrix
EfOM	Effluent Organic Matter
EQS	Environmental Quality Standard
ESEM	Environmental Scanning Electron Microscopy
ESI	Electroscopy Ionization
FAT	Fully Advanced Treatment
FTIR	Fourier Transform Infrared Spectroscopy
GAC	Granular Activated Carbon
GC-MS	Gas Chromatography Mass Spectrometry
HAA	Haloacetic Acid
HLB	Hydrophilic-Lipophilic Balance
IAA	Iodoacetic Acid
IARC	International Agency for Research on Cancer
IC	Ion Chromatography
IOA	International Ozone Association
IOD	Instantaneous Ozone Demand
LC-MS	Liquid Chromatography- Mass Spectrometry
LFB	Laboratory-Fortified Blank
LMW	Low Molecular Weight
LRB	Laboratory-Reagent Blank
MCL	Maximum Concentration Level
MDL	Method Detection Limit
MF	Microfiltration
MP	Micropollutant
MRM	Multiple Reaction Monitoring
MTBE	Methyl Tert-Butyl Ether
MWCO	Molecular Weight Cut Off
NAMS	North American Membrane Society

NDBA	N-Nitrosodi-n-Butylamine
NDEA	N-Nitrosodiethylamine
NDMA	N-Nitrosodimethylamine
NDPA	N-Nitrosodi-n-Propylamine
NDPhA	N-Nitrosodiphenylamine
NF	Nanofiltration
NMEA	N-Nitrosomethylamine
NMOR	N-Nitrosomorpholine
NPIP	N-Nitrosopiperidine
NPYR	N-Nitrosopyrrolidine
NSF	National Science Foundation
NTU	Nephelometric Turbidity Unit
O&M	Operation and Maintenance
PCP	Personal Care Product
PVC	Polyvinyl Chloride
PVDF	Polyvinylidene Fluoride
QSAR	Quantitative Structure-Activity Relationships
RO	Reverse Osmosis
RPD	Relative Percent Difference
SAT	Soil Aquifer Treatment
SBMBR	Sequencing Batch Membrane Bioreactor
SCADA	Supervisory Control and Data Acquisition
SI	Supporting Information
SIM	Select Ion Monitoring
SPE	Solid Phase Extraction
TBAA	Tribromoacetic Acid
TBAL	Tribromoacetaldehyde
TBM	Tribromomethane
TCAA	Trichloroacetic Acid
TCAL	Trichloroacetaldehyde
TCAM	Trichloroacetamide

TCAN	Trichloroacetonitrile
TCEP	Tris(2-Carboxyethyl) Phosphine
TCF	Temperature Correction Factor
TCM	Trichloromethane
TCNM	Chloropicrin
TDS	Total Dissolved Solid
THM	Trihalomethanes
TMP	Transmembrane Pressure
TN	Total Nitrogen
TOC	Total Organic Carbon
U.S. EPA	United States Environmental Protection Agency
UF	Ultrafiltration
UFC	Uniform Formation Condition
UV	Ultraviolet
WHO	World Health Organization
WWTP	Wastewater Treatment Plant
XPS	X-ray Photoelectron Spectroscopy

“The ideal society we have desired can never grow into a reality or see a light of day, and there will be no end to the troubles of states, or indeed of humanity itself, until philosophers become kings in this world, or until those we now call kings and rulers really and truly become philosophers.”

−Plato, The Republic (381 BC)

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It is an inevitable fact that majority of the events, incidents, and occurrences are subject to being forgotten as a function of time. Most of us, willingly or not willingly, have been put in a situation in which we are forced to do our everyday ordinary tasks that ultimately increases the kinetics of the forgetting process. However, there are certain moments or time frames that cannot be easily forgotten, no matter how much time passes. My journey to Colorado for pursuing my Ph.D. is and will be one of them. In the early stage of my life, I looked at "time" as something that never ends, but over time I realized that for every begin, there is an end waiting. And yet, my Ph.D. train has arrived at its last station. This is, indeed, one of the ends among many others I am going to face during this lifespan. So, it is my pleasure to use this opportunity and express my sincere appreciation to people who have helped me during my Ph.D. at the Colorado School of Mines.

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CHAPTER 1
INTRODUCTION

1.1 Problem statement and significance

The decline of available conventional water resources as a result of population growth, increased urbanization, and climate change has made potable reuse of municipal wastewater effluent an important aspect of water resource management [1]. The presence of micropollutants (MPs) (including pharmaceuticals, personal care products (PCPs), endocrine-disrupting compounds (EDCs), etc.) along with pathogens in aquatic environments are the main challenges surrounding water reuse applications in many countries. In 2012, approximately 143,000 MPs were registered in the European market and the majority of them would enter aquatic systems at some point of their life cycle [2]. The design and implementation of conventional wastewater treatment plants (WWTPs) has been mainly focusing on reducing the level of carbon, nutrients, and suspended solids from the aquatic environment along with removal of harmful pathogens [3]. Therefore, WWTP effluents have become one of the major pathways for continuous input of numerous MPs that are poorly removed due to their recalcitrance and polarity [3, 4]. Despite MP's low concentrations in WWTP effluent, ranging from ng/L up to several µg/L, they may cause harmful impacts including estrogenicity, genotoxicity, and mutagenicity on drinking water resources [2, 5]. The diversity of MPs has made their monitoring cumbersome and the behavior of the majority of MPs in the wastewater matrix is also largely unknown [6]. Moreover, it is important to note that the majority of investigated MPs, especially pharmaceuticals, accounted only for <1% of nonspecific toxicity based on bioassay measurements, and the concentration of other contaminants such as oxidation byproducts has been found to be much closer to toxicity level of potential human health concern [7]. Among oxidation/disinfection by-products, some of them such as bromate (BrO_3^-) and nitrosamines, e.g., N-nitrosodimethylamine (NDMA), are reported as (possible) human carcinogens and therefore, minimization of their formation during ozonation is of great importance [8, 9]. In drinking water applications, a guideline concentration of 10 µg/L was set for bromate [9-11], while the chronic environmental quality standard (EQS) of 50 µg/L was set for bromate from Ecotox Center Eawag-EPFL [12]. In terms of NDMA, the World Health Organization (WHO) set a guideline concentration of 100 ng/L for drinking water [13] while other

countries such as the United States (U.S.) and Germany have proposed a lower value of 10 ng/L [14-16]. The United States Environmental Protection Agency (U.S. EPA) has set a maximum concentration level (MCL) of 80 µg/L for the sum of four of trihalomethanes (i.e., THFusFM4) (chloroform, bromodichloromethane, dibromochloromethane, and tribromomethane), and 60 µg/L for the sum of five haloacetic acids (i.e.,HAA5) (monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, bromoacetic acid, and dibromoacetic acid) [17, 18].

The implementation of potable reuse projects has employed multiple purification barriers to efficiently remove pathogens and organic contaminants. In the U.S., reverse osmosis (RO) has been predominantly employed for potable reuse applications as the main purification step. Among potable reuse schemes in the U.S. (located in California, Arizona, Colorado, New Mexico, Florida, and Georgia) [19], the majority of the schemes (in the coastal regions of the U.S.) employ RO as their main treatment step for organic removal, while some use granular activated carbon (GAC), and several others implement soil aquifer treatment (SAT), although the implementation of SAT often depends on site constraints and geological conditions, which has limited its applicability [20]. For instance, the full advanced treatment (FAT) approach, considered as a potential standard for potable reuse in the U.S., is known for providing acceptable performance in removing bulk organic matter, regulated and unregulated MPs, and bio-toxicity through membrane treatment processes followed by advanced oxidation processes (AOPs) [21, 22]. FAT is most commonly achieved by employing microfiltration (MF) followed by RO, and AOPs, which is typically the combination of ultraviolet (UV) and an oxidant (e.g., hydrogen peroxide, sodium hypochlorite, etc.) [22]. However, challenges with RO treatment, including intensive energy consumption, limited concentrate disposal options (non-coastal regions), and sensitivity to influent water quality (i.e., organic matter content and suspended solids), have caused several utilities to consider alternative treatment technologies for their potable reuse applications [6, 23-25]. Another imperative factor affecting the selection of treatment schemes in potable reuse is the regulations affiliated with the location the reuse is applied. Even though potable reuse has been employed since 1960s, no uniform regulation has been developed in many countries and even in counties such as U.S. and Australia with a potable reuse guideline, no Federal regulations currently exist [20]. However, several states with substantial potable reuse applications such as California and Florida have developed comprehensive potable reuse regulations while some other states such as Georgia and Texas allow the practice on a case-by-case basis with project-specific permits [19].

The focus of most regulations and guidelines has been mainly on pathogen, organic compound, and nitrogen removal [26]. In the U.S. and Australia, multiple barrier advanced treatment is required to achieve significant log removal of viruses, protozoa, and bacteria due to existing limitations in achieving validated log reduction across just one treatment process. In terms of total organic carbon (TOC), the state of California has set the strictest limit of 0.5 mg/L in case of complete injection of reused water (with no dilution) while the state of Florida as well as U.S. EPA set their TOC limit at 3 mg/L and 2 mg/L respectively [20]. This considerable difference in TOC limits has led to different treatment trains applied between these locations because achieving the California TOC limit is usually only possible when RO is applied. In terms of total dissolved solids (TDS), according to Thompson et al. [27], between 200-400 mg/L of salt from different sources such as human excretion, gray water, water softeners, and industrial contributions is entering to the nation's wastewater stream. As a result, the U.S. EPA has set a secondary maximum contaminant level (MCL) for TDS at a concentration of 500 mg/L due to aesthetic reasons for water customers [27]. Hence, geographic locations for TDS concentration as well as the capacity of blending the treated water with other potable water supplies in case of elevated TDS concentration are the important factors for the consideration of non-membrane-based treatment technologies in potable reuse.

The combination of ozonation followed by biologically active filtration (BAF) recently has been considered as an alternative technology to FAT providing a multibarrier solution (oxidation, biological and physical filtration) for low salinity source waters or locations with blending capacity for their finished water. Ozone (O_3) is a selective oxidant that can react rapidly with electron rich moieties (i.e., tertiary amines, thioethers, olefins, and activated aromatics) [8, 28]. The decomposition of O_3 due to its reaction with electron rich moieties in wastewater [29-31] can lead to the formation of more powerful, non-selective hydroxyl radical ($^{\cdot}OH$) that can further react with alkanes, amides, and non-activated aromatic compound [32]. The oxidation of MPs in water and wastewater treatment mainly depends on the reactivity of O_3 and $^{\cdot}OH$ towards targeted MPs and towards dissolved organic matter (DOM) present in the water matrix [28]. The second-order rate constants of contaminants with O_3 and $^{\cdot}OH$ are physical-chemical rate constants that indicate their level of reactivity with MPs while the exposure of O_3 and $^{\cdot}OH$ reflect their stability in a water matrix [33]. The independence of rate constant parameters from the exposure parameters shows that second-order rate constant can be determined independent of the water matrix through either

laboratory experiments in well-defined system, estimated based on quantitative structure-activity relationships (QSARs), or by quantum chemical calculation [33].

The oxidation via O_3 molecules and $^{\cdot}OH$ has shown the ability to degrade a variety of MPs with the second-order rate constant of O_3: 1 to 10^{10} [$M^{-1}s^{-1}$], and of $^{\cdot}OH$: 10^8-10^{10}[$M^{-1}s^{-1}$] [34-36]. Generally, the efficiency of ozonation for MP removal depends on four factors including: (1) the level of O_3 and OH^* reactivity with the targeted MP; (2) O_3 dose and the stability of O_3 and OH^* in water/wastewater matrices; (3) removal of undesirable effects such as biological activities of MP after ozonation; and (4) the biodegradability of transformed MPs for post-treatment processes such as biofiltration [33]. One main challenge associated with ozonation during reuse of municipal wastewater effluent is the limitation of O_3 for abatement of refractory MPs [37] (i.e., compounds with a low second-order degradation rate constant with O_3). Due to their inactivated aromatic structure, O_3-refractory MPs cannot be oxidized efficiently by O_3 [35]. Therefore, enhancement in production and/or formation $^{\cdot}OH$ during ozonation, has received attention in the past two decades [28] because $^{\cdot}OH$ as a non-selective secondary oxidant has a higher oxidation power than O_3, enabling it to overcome the limitations of O_3 for efficient abatement of refractory MPs.

In recent years, BAF has drawn new attention as an ozonation post-treatment process due to its synergetic benefits for removing dissolved organic carbon (DOC), biodegradable organic matter, and the attenuation of certain toxic oxidation byproducts [38, 39]. In BAF applications, filter media is used to supply high surface area for the microbial cell attachment [40]. Among different filter media, granular activated carbon (GAC) has shown higher adsorption capacity and bioactivity compared to non-adsorptive media such as sand and anthracite [40-45]. Slightly electro-positively charged GAC with its high surface area (>1000 m^2/g) can be efficient for removing electro-negatively charged water contaminants such as DOM [46]. GAC can initially remove a wide range of contaminants through adsorption [40]. Over time, GAC loses its adsorption capacity, eventually becomes exhausted and during this phase, microorganisms colonize on the rough porous surface of activated carbon media using dissolved oxygen as the electron accepter and organic matter on the surface as an electron donor to establish biomass or a biofilm [46-48]. After establishment of a biofilm, the physically exhausted activated carbon can be defined as a BAF that can remove DOC and other organic contaminants present in the water through biodegradation [40, 46, 49, 50]. The effectiveness of biodegradation improves with the increasing effectiveness of the GAC to adsorb and retain the organic matter [24, 40]. The application of O_3

prior to BAF breaks down a portion of the recalcitrant organic compounds into smaller biodegradable fragments [46, 48, 51]. As a result, pre-ozonation of water prior to BAF and increasing the biological activity of the biofilm can extend the media's operation life during BAF treatment [51-54]. Both O_3 and BAF are well established for wastewater and drinking water treatment, and the combination of ozonation with biological post-treatment is well known to the international water reuse community.

Among membrane-based treatment processes in reuse applications of municipal wastewater effluents, nanofiltration (NF) can be considered as a potential membrane-based alternative for RO due to its relatively lower energy requirements. Moreover, NF produces a less concentrated reject stream related to TDS compared to RO. NF is able to retain small molecular weight organic compounds (>200 Daltons) [55-59] and a wide range of micropollutants such as pesticides, endocrine disrupting compounds, and pharmaceuticals providing high quality water for potable reuse applications [57, 58, 60-63]. Numerous NF membrane systems have already been implemented in the drinking water industry [64-70]. While NF's retention performance cannot achieve the DOC effluent requirement of some states such as California, the implementation of NF is possible through dilution with drinking water, and applications in other states may be possible.

1.2. Objectives and scope of work

This research focused primarily on promoting the oxidation power during ozonation of municipal wastewater effluent for enhanced removal of O_3 refractory MPs. To meet this objective, the presence of GAC during ozonation (O_3/GAC) followed by BAF ((O_3/GAC)-BAF) was compared to conventional O_3-BAF for the removal of O_3-refractory MPs during treatment of municipal wastewater effluent. To assess the balance between oxidative abatement and formation of oxidation by-products, this study also compared the efficacy of conventional O_3-BAF with (O_3/GAC)-BAF, regarding the removal of precursors for 35 halogenated disinfection by-products (DBPs) and bromate during post chloramination. In addition, work conducted investigated the impact of pre-ozonation of municipal wastewater effluent on the reduction of NF fouling, and identifying the optimum specific ozone dose for efficient fouling abatement while not forming low molecular weight contaminants with the ability to pass through a NF membrane.

1.3. Structure of dissertation

This research is the product of bench- and pilot-scale studies conducted at the AQWATEC laboratory of the Colorado School of Mines (Golden, CO) in collaboration with Stanford University (Palo Alto, CA) as well as a pilot-scale study conducted at Southern Nevada Water Authority (Las Vegas, NV). This dissertation is the collection of three journal articles that were prepared over the course of this doctoral research. Chapter 2 includes a journal article, described in Section 1.3.1, and is under review by *Environmental Science and Technology* for publication. Chapter 3 is a manuscript described in Section 1.3.2 that is under review by *Chemosphere* for publication. Chapter 4, that is summarized below in Section 1.3.3, has been adapted and reprinted from the published manuscript in *Separation and Purification Technology* (copyright permission is not required). An additional project on the removal of per- and polyfluoroalkyl substances using super-fine activated carbon and ceramic membrane was also conducted and published in *Journal of Hazardous Material* (in which I am the second author) and is not included in this dissertation. The release agreements from all co-authors are included in the appendix of this doctoral dissertation.

1.3.1. Evaluation of enhanced O_3-BAF for the removal of 1,4-dioxane and DBP precursors from wastewater effluent

As discussed above, O_3-BAF treatment has become an attractive alternative to RO treatment for wastewater effluent reuse applications due to the ability to produce a high-quality effluent while reducing brine/concentrate production and disposal. Chapter 2 of this dissertation summarize a study to evaluate the presence of GAC during ozonation (O_3/GAC) followed by BAF, compared to conventional O_3-BAF for the removal of 1,4-dioxane during treatment of municipal wastewater effluent. As a polar heterocyclic O_3-refractory compound, 1,4-dioxane is a highly soluble MP that has been frequently detected in ground water, surface water, and wastewater streams and therefore was used as a model compound to evaluate the performance of O_3/GAC in this study. Effluent from a sequencing batch membrane bioreactor (SBMBR) system that received raw wastewater from a 250-unit student apartment complex at the Colorado School of Mines was further treated by O_3-BAF at three specific ozone doses (0.5, 0.7, and 1.0 mg O_3/mg DOC) and different empty bed contact times (EBCT; 15-45 min). The reaction of O_3 with GAC (O_3/GAC) to promote the formation of hydroxyl radicals ($^{\cdot}OH$) was then evaluated at 1.0 mg O_3/mg DOC and

0.5 g GAC/L followed by BAF at 15-45 min EBCT. The efficacy of these techniques was compared for the removal of O_3 refractory 1,4-dioxane. In addition, a novel acclimation process of a BAF systems was introduced its performance was evaluated. The second objective of this study was to compare the efficacy of conventional O_3-BAF with O_3/GAC-BAF, regarding the removal of precursors for 35 halogenated DBPs, NDMA, and bromate.

1.3.2. Robustness of O_3-GAC for removal of MPs during reuse of municipal wastewater effluent

Work detailed in Chapter 2 was expanded upon by performing long-term O_3/GAC experiments to evaluate the robustness of the process to remove 13 different environmentally relevant MP's. The main goal of work presented in Chapter 3 was to evaluate O_3/GAC for the treatment of tertiary wastewater effluent from Clark County Water Reclamation District (Las Vegas, NV) for the removal of 13 environmentally relevant MPs. While results presented in Chapter 2 were based on short-term experiments, a major objective of Chapter 3 was to systematically evaluate the robustness of O_3/GAC during long-term experiments. In addition, the effect of varying O_3 dose and GAC dose was assessed to optimize operating conditions. The effect of O_3 on GAC chemical and physical properties and its impact on removal of MPs during O_3/GAC is also detailed in Chapter 3.

1.3.3. Effect of pre-ozonation on NF membrane fouling reduction during reuse of municipal wastewater effluent

While the works performed in Chapter 2 and 3 focused on evaluation of non-membrane-based treatment processes, research conducted in Chapter 4 assessed NF as a membrane-based alternative treatment process for RO during reuse application. In the study described in Chapter 4 of this dissertation, a fully automated high-pressure bench-scale membrane system was employed to evaluate the effect of pre-ozonation on fouling behavior of NF when treating SBMBR wastewater effluent for potable reuse applications and the potential to improve membrane treatment. For this purpose, the fouling propensity of an NF membrane (NF90) at two different O_3 doses (0.2 and 0.4 mg O_3/mg DOC) was investigated. In addition to membrane characterization, the correlation between fouling mitigation and organic carbon removal performance of the membrane was also examined.

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CHAPTER 2

EVALUATION OF ENHANCED OZONE-BIOLOGICALLY ACTIVE FILTRATION TREATMENT FOR THE REMOVAL OF 1,4-DIOXANE AND DISINFECTION BYPRODUCT PRECURSORS FROM WASTEWATER EFFLUENT

Modified from a paper submitted for possible publication in *Environmental Science and Technology*[1]

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2.1. Abstract

Ozonation followed by biologically active filtration (BAF) (O_3-BAF) treatment has become an alternative to reverse osmosis in potable wastewater reuse applications due to the ability to produce a high-quality effluent while reducing brine production and disposal. In this study, effluent from a sequencing batch membrane bioreactor (SBMBR) was treated by O_3-BAF at three specific ozone doses (0.5, 0.7, and 1.0 mg O_3/mg DOC) and different empty bed contact times (EBCT; 15-45 min). The reaction of O_3 with granular activated carbon (GAC) (O_3/GAC) to promote the formation of hydroxyl radicals ($^{\cdot}OH$) was evaluated at 1.0 mg O_3/mg DOC followed by BAF at 15-45 min EBCT. The efficacy of these techniques was compared for the removal of O_3 refractory 1,4-dioxane, and the reduction in the formation of bromate and 35 regulated and unregulated halogenated disinfection byproducts (DBPs) and 8 *N*-nitrosamines after chloramination. Conventional ozonation (without presence of GAC during ozonation) removed 6-11 % of 1,4-dioxane, while BAF increased the removal to ~25%. O_3/GAC improved the removal of 1,4-dioxane to ~ 40%, while BAF increased the removal to ~50%. No bromate was detected during conventional ozonation.

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Although O_3/GAC formed 12.5 µg/L bromate, this concentration was reduced during BAF treatment to < 6.8 µg/L. Even though conventional ozonation was more effective than O_3/GAC for the reduction in chloramine-reactive *N*-nitrosodimethylamine (NDMA) precursors, BAF treatment after either conventional or enhanced ozonation reduced NDMA formation during chloramination to < 10 ng/L. O_3/GAC was more effective at reducing halogenated DBP formation during post-chloramination. Regardless, the reduction in halogenated DBP formation during post-chloramination achieved by BAF treatment was ~ 90% relative to the formation in the SBMBR effluent after either conventional or enhanced ozonation. The reduction of haloacetic acid (HAA) formation improved moderately with increasing BAF EBCT. Both O_3-BAF and O_3/GAC-BAF met regulatory levels for trihalomethanes (THMs), HAAs, NDMA, and bromate.

2.2. Introduction

With dwindling conventional water supplies in the Unites States and many regions worldwide, potable reuse of municipal wastewater effluent has become an important component of water resource management [1, 2]. Typical conventional potable reuse applications employ 'full advanced treatment (FAT)" consisting of microfiltration (MF), reverse osmosis (RO), and advanced oxidation processes (AOPs: mainly using ultraviolet (UV) with hydrogen peroxide (H_2O_2) treatment) that provide acceptable performance in removing bulk organic matter, micropollutants (MPs), pathogens, and bio-toxicity [3, 4]. Limitations of RO-based FAT include high capital and operation costs, concentrate disposal, membrane fouling, and strict requirements for influent water quality (i.e., organic matter content and suspended solids), which have caused several utilities to consider more sustainable alternative treatment technologies [5-7]. Implementation of an alternative reuse process that consists of ozonation followed by BAF has gained considerable attention especially for waters with low salinity.

Ozone (O_3) is an effective oxidant that has been widely used in water reuse applications for disinfection and oxidative abatement of MPs [8]. The performance of O_3 in degrading a variety of MPs (e.g., pharmaceuticals and pesticides) has been investigated in numerous studies [9-16]. One of the main challenges associated with O_3 treatment during reuse of municipal wastewater effluent is the insufficient abatement of O_3-refractory MPs [17]. To overcome this limitation, research on the AOP for enhanced degradation of recalcitrant contaminants has received great attention in the past decades [8, 18]. There are numerous types of AOPs (O_3 based, cavitation

based, sulfate based, etc.) [18-20]. In water reuse applications, several studies have evaluated O_3 associated AOPs such as O_3/H_2O_2, O_3/UV [8, 21], and catalytic ozonation (metal based [22-28], and carbon based [29-33]). Among existing techniques, recent studies [34-38] have demonstrated that the presence of AC during ozonation promotes the oxidation performance through decomposition of O_3 into $^{\cdot}OH$. BAF after ozonation is an important treatment step for the removal of by-products and biodegradable organic carbon formed during ozonation, thus achieving higher dissolved organic carbon (DOC) removal rates and improved water quality [37, 39]. Previous studies have shown that the abatement of MPs and bulk parameters such as DOC in municipal wastewater effluent through ozonation and BAF depends on the second-order rate constant of each compound, the specific O_3 dose (mg O_3/mg DOC), and EBCT of the BAF [8]. During the O_3-BAF process, most of the DOC removal (~20-70%) is achieved by BAF treatment with EBCTs ranging from 15 to 30 min, and minimal increase in performance at higher EBCTs has been reported [16, 40-42]. Reungoat et al.[42] reported that the combination of ozonation and BAF using wastewater effluent as a source water was able to remove 90% of investigated MPs, 70% of non-specific toxicity, and 95% of estrogenicity.

There are concerns regarding unspecific toxicity of unknown by-products from wastewater ozonation [43]. Oxidation by-products may be formed by reaction of O_3 and/or $^{\cdot}OH$ with different components of wastewater effluent [8]. While increasing the O_3 dose increases the capacity to oxidize MPs by both direct O_3 and indirect $^{\cdot}OH$ pathways, it may increase the formation of oxidation by-products. Among oxidation by-products, compounds such as bromate (BrO_3^-) (in bromide (Br^-) containing waters) and nitrosamines, particularly NDMA, are reported as probable/possible human carcinogens. Therefore, minimization of NDMA and bromate formation during ozonation is of great importance [44, 45]. In addition, it has been reported that ozonation may enhance the formation of certain unregulated DBPs such as haloacetaldehydes and halonitromethanes after chlorine/chloramine disinfection [41, 46, 47]. However, minimal research has been conducted to determine if BAF can provide adequate DBP precursor removal, particularly precursors produced through an ozonation process [41]. While numerous studies have evaluated DBP precursor removal by O_3-BAF from surface water [48-53], limited studies have investigated O_3-BAF treatment of wastewater effluents [41, 54-56]. Moreover, it is important to highlight that the fate of the majority of the previously investigated compounds, especially pharmaceuticals, account for <1% of the nonspecific toxicity measured by bioassays [16, 41]. These bioassays

typically do not capture the volatile DBPs of current research interest, because they are typically lost during the extraction and concentration procedures used to prepare the samples [57, 58]. Nevertheless, the concentrations of DBPs in advanced treatment water effluents are considerably closer to the levels of potential human health concern than those of pharmaceuticals [1].

Chuang et al. [41] employed a laboratory bench-scale O_3-BAF (GAC filter media system) to investigate the removal of DBP precursors from two nitrified wastewater effluents and reported significant removal at 0.35 mg O_3/mg DOC and 15 min BAF EBCT. Despite additional removal at 0.7 mg O_3/mg DOC, increasing the O_3 dose did not show any significant improvement. In another study, Farre et al. [55] investigated removal of DBP precursors (NDMA, the four regulated trihalomethanes (THM4), and the five regulated haloacetic acids (HAA5)) from wastewater effluent by introducing 5 mg/L of O_3 followed by BAF (GAC filter media) with an EBCT of 60 min. The formation potential of regulated THM4 and HAA5 was reduced by approximately 41% and 48%, respectively. In addition, substantial NDMA removal by the BAF unit even in the absence of ozonation, was observed. In another study, Zeng et al. [56] measured DBP removal across a full-scale O_3-BAF system and observed partial removal of halogenated DBPs by BAF employing GAC as filter media. Zeng et al. also reported that after an increase in NDMA concentration from 2 to 21 ng/L caused by ozonation, the BAF reduced the concentration back to less than 2 ng/L.

Also known as diethylene dioxide, 1,4-dioxane is a synthetic polar heterocyclic compound that is widely used as a solvent stabilizer for chlorinated solvents to prevent hydrolysis, and is also a common byproduct of chemical processes involving ethylene glycol or ethylene oxide [59, 60]. Due to its high aqueous solubility (4.31×10^5 mg/L), 1,4-dioxane is frequently detected in ground water, surface water, and wastewater streams [61-64]. The U.S. Environmental Protection Agency (EPA) and the International Agency for Research on Cancer (IARC) classified 1,4-dioxane as a probable human carcinogen (group B2) and hence, a priority MP [65]. 1,4-dioxane and NDMA have been used as model compounds to validate the performance of UV-based AOPs within potable reuse trains in California [66]. The relatively low second order rate constant of 1,4-dioxane with O_3[8] has made this contaminant difficult to remove during ozonation.

The first objective of this study was to investigate the removal of 1,4-dioxane in the presence of GAC during ozonation (O_3/GAC) followed by BAF compared to conventional O_3-BAF during treatment of municipal wastewater effluent. The second objective of this study was to compare the

efficacy of conventional O_3-BAF with O_3/GAC-BAF, regarding the removal of precursors for 35 halogenated DBPs, including unregulated iodinated THMs, HAAs, haloacetaldehydes, haloacetamides, haloacetonitriles, and trichloronitromethane (TCNM) in addition to regulated DBPs including THM4, HAA5, and bromate. Because the contribution of DBPs to water toxicity is known to be a function of both concentration and toxic potencies [41], DBP concentrations were weighted by measured toxic potency to provide an estimate of DBP associated toxicity for both conventional O_3-BAF and O_3/GAC-BAF. In addition, a novel approach for the acclimation of BAF systems was developed and its characteristics and performance were evaluated.

2.3. Material and methods

2.3.1. Ozone-BAF system design and experimental set-up

During this study, the O_3-BAF system was continuously fed with effluent from a 30 m^3/d (8,000 gal/day) pilot-scale SBMBR system that received raw wastewater from a 250-unit student apartment complex at the Colorado School of Mines (Golden, Colorado). The SBMBR was operated with a total suspended solids concentration of 5.1 g/L, and solid retention time of 25 days. A complete description of the SBMBR system is provided elsewhere [67]. A schematic flow diagram of the pilot-scale treatment system including the investigated O_3-BAF is depicted in Figure 2.1.

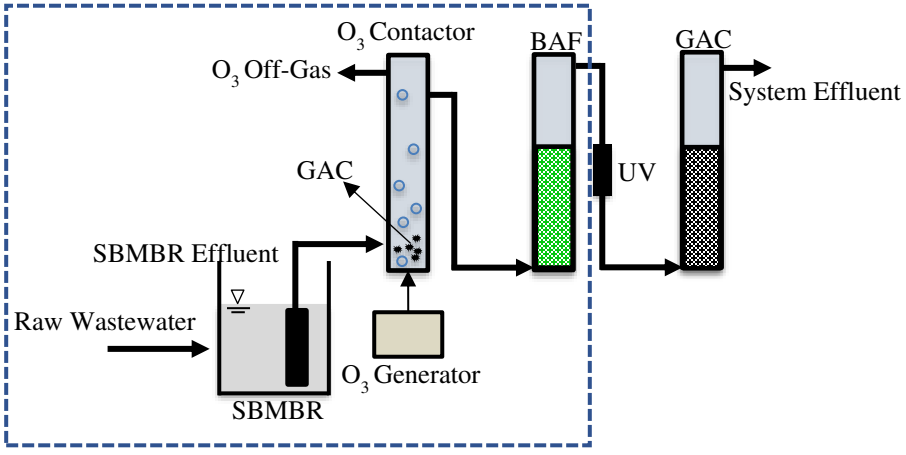

Figure 2.1. Process flow diagram of pilot-scale ozonation system (not to scale)

2.3.2. Ozonation

The ozonation process was carried out in a polycarbonate column (height: 130 cm; diameter: 5.1 cm) operated in concurrent flow mode. An O_3 mass balance was used to calculate the transferred O_3 dose (TOD), Appendix A. The specific O_3 ratio is defined as the mass-based TOD normalized to DOC ratio (mg O_3/mg DOC) and was subsequently nitrite-corrected (equation 6.2), Appendix A, because nitrite consumes ozone quickly with a 1:1 molar stoichiometry without generating $^{\cdot}OH$ [68].

2.3.3. Enhanced ozonation

The presence of GAC during ozonation was used to promote O_3 transformation into $^{\cdot}OH$ for enhanced contaminant abatement. Coal-based Filtrasorb 400 (F400) (Calgon Carbon Corp., Pittsburg, PA) GAC was rinsed with DI water and baked for 24 hours at 120 ºC. A GAC dose of 0.5 g GAC/L (volume of ozone chamber) was added into the O_3 contactor as the minimum concentration capable of increasing the rate of O_3 transformation into $^{\cdot}OH$ for the O_3/GAC process as reported elsewhere [37]. A specific ozone dose of 1.0 mg O_3/mg DOC (0.25 mol O_3/mol C) was also chosen based on previous findings of Sanchez-Polo et al. who observed enhanced transformation of O_3 to $^{\cdot}OH$ around this selected specific ozone dose [69].

2.3.4. Operational condition and sample collection

A series of experiments were designed to investigate the efficiency of conventional ozonation as well as O_3/GAC followed by BAF for removal of 1,4-dioxane and DBP precursors as a function of the specific O_3 dose (mg O_3/mg DOC) and EBCT of the BAF column. 1,4-dioxane was spiked (30 µg/L) in-line into the pilot system to evaluate the removal performance of O_3/BAF as well as (O_3/GAC)-BAF and ended before DBPs experiment started in order to avoid any interference. During conventional ozonation, O_3 was introduced into the system at three different nitrite corrected specific O_3 doses of 0.5, 0.7, and 1.0 mg O_3/mg DO (0.12, 0.17, 0.25 mol O_3/mol C) (to simplify the reading of the paper, the unit of mg O_3/mg DOC was used in the manuscript). The effect of O_3/GAC was investigated by adding 0.5 g (GAC F400)/L in the O_3 contactor and operating the pilot system at an O_3 dose of 1.0 [mgO_3/mg DOC]. The impact of EBCT was evaluated at 15, 30, and 45 min. Throughout the experiments, prior to each sample collection, the

first four bed volumes of BAF were discarded. O_3 effluent samples for each condition were collected after four hours of stable operation.

2.3.5. Characterization and acclimation of BAF

BAF using GAC as filter media (also known as biological activated carbon (BAC)) is becoming more common for the removal of MPs, and DBP precursors. The process of contaminant removal in the BAF system mainly occurs through adsorption into the GAC pore structure and/or biodegradation performed by attached biofilms on the GAC. In general, distinguishing between these two removal pathways is a difficult task. Numerous approaches have been used to distinguish the role of biodegradation from sorption in BAF such as measuring the concentration of microorganisms present in GAC, the oxygen consumption throughout the BAF, [70, 71] heterotrophic plate counts [72, 73], total direct cell counts [74], adenosine triphosphate (ATP) concentration [75], environmental scanning electron microscopy with an attached X-ray energy dispersive system (ESEM-EDS) [76, 77], phospholipids [78], the uptake of labeled substrates [79], and the reduction of 2-(p-iodo-phenyl)-3(p-nitrophenyl)-3 phenyl tetrazolium chloride (INT) [80]. ESEM-EDS has been used to visualize the biomass and the spatial distribution of elements in the biofilm [76, 77]. However, arduous analytical methods, complex nature of biomass, and difficulties in interpretation of data from some of these techniques have raised discussions on the reliability of their results [81]. For instance, oxygen uptake by GAC itself can interfere with the use of oxygen uptake rates as a surrogate for biological activity and the substantial percentage of viable but uncultivable microorganisms may influence the use of heterotrophic plate counts to measure total cell mass [75]. Thus, a conclusive explanation of variable removal performance in different BAF applications is not possible. In this study, a novel approach for BAF acclimation was introduced. In this procedure, fresh GAC was acclimated by a mixture of activated sludge and SMBR effluent over a period of 3 months in up-flow mode at an EBCT of 60 min. A detailed description of the BAF acclimation process is provided in the SI (Appendix A). For evaluation of the acclimation process, ATP was measured for viable biomass, the Brunauer, Emmett, and Teller (BET) isotherm method was used for surface characterization, and ESEM-EDS was employed to visualize the biofilm acclimation process (Appendix A).

2.3.6. Analytical methods

2.3.6.1. 1,4-Dioxane

1,4-dioxane samples were analyzed immediately after collection to avoid the addition of preservatives and loss of analyte. Samples were extracted in triplicate using liquid-liquid extraction and analyzed by GC-MS in SIM mode using modified U.S. EPA method 522 [82]. Spiked samples (100, 500 µg/L) recovery from the sample matrix ranged from 96-110% ± 1-2%. Additionally, check standards analyzed after every 15 samples were within 100 ± 30% of the established concentration. Additional analytical details and method validation procedures are provided in the SI (Appendix A).

2.3.6.2. Chloramination conditions and DBP analysis

Collected samples were stored at 4 ºC for less than one week prior to chloramine addition and analysis. DBP precursors were measured using uniform formation condition (UFC) tests. In brief, chloramine stocks (50 mM, 1:1.2 chlorine: nitrogen molar ratio) were prepared daily by slowly adding sodium hypochlorite to ammonium chloride solution (Fischer Scientific), and standardized spectrophotometrically at 245 nm and 295 nm, as described in detail elsewhere.[83] Samples were dosed with the chloramine solution to a final concentration of 5 mg/L as Cl_2, and stored headspace free at 20 ºC (± 2 ºC) in the dark. After 72 hours, the chloramine residual was quenched with 33 mg/L ascorbic acid, and samples were analyzed in duplicate for nitrosamines, and in triplicate for halogenated DBPs.

Eight *N*-nitrosamines were extracted using a modified version of the USEPA method 521 (500mL per sample)[84]. Seven classes of DBPs were analyzed using a modified version of USEPA Method 551.3[85] including four regulated THMs, four haloacetonitriles (HANs), six iodinated THMs, four haloacetamides (HAMs), four haloacetaldehydes (HALs), two haloketones (HKs), and one halonitromethane (HNM). Ten HAAs were measured using a modified version of USEPA Method 552.3 (50 mL per sample). Extracts were analyzed by GC-MS, with method reporting limits between 0.05-0.20 µg/L for halogenated DBPs, and 2 ng/L for *N*-nitrosamines. Analytical methods details were described previously [56, 86]. Individual DBPs and their acronyms) as well as quantification methods for bromide and bromate are provided in the SI (Appendix A).

2.3.6.3. Calculation of DBP-associated toxicity

The contribution of a DBP to the toxicity of disinfected water depends on both its concentration and its toxic potency. Halogenated DBP-associated toxicity in the investigated O_3-BAF and (O_3/GAC)-BAF systems was calculated by weighting measured concentrations by cytotoxicity LC_{50} (lethal concentration, 50%) values as a metric of toxic potency (Table A.5, and 6.6, Appendix A). Briefly, in this study, an LC_{50} value is an analyte concentration that results in a 50% reduction in growth of Chinese hamster ovary (CHO) cells compared to negative (untreated) controls. All the LC_{50} values for DBPs were measured previously by the same research group, which warrants comparability [47, 86-92]. Measured DBP concentrations were divided by LC_{50} values. For certain regulated DBPs (e.g., NDMA), both LC_{50} and $LECR_{50}$ (life excess cancer risk, 50%) are available where $LECR_{50}$ values are lower. Since the analysis showed a lower contribution to toxicity from regulated DBPs, $LECR_{50}$ values were used. The sum of the toxicity-weighted DBP concentrations was compared for different treatments to evaluate the evolution in DBP-associated toxicity achieved by the treatments assuming toxicity is additive [41, 93, 94]. Zeng et al. [56] employed the same approach to estimate DBP associated toxicity in FAT potable reuse trains while Chuang et al. [41] applied this approach to evaluate the DBP-associated toxicity of two nitrified wastewater effluents after treatment by O_3-BAF at laboratory scale. Reungoat et al.[42] also weighted concentrations by metric of toxic potency to estimate the contribution of pharmaceuticals to the non-specific toxicity of wastewater effluents.

2.4. Results and discussion

2.4.1. Ozone-BAF influent water quality characteristics

The concentrations of key O_3-BAF feed water parameters measured in the SBMBR effluent during all experiments are provided in the (Table A.1, Appendix A).

2.4.2. BAF performance characterization

The BAF column was acclimated for 90 days (see section 2.3.5), after which ATP measurements were initiated on a monthly basis. Pre-ozonation was applied starting 4 months after ATP measurements commenced. Experiments with 1,4-dioxane and DBPs were conducted during the 12^{th} and 13^{th} months after the commencement of ATP measurements. Thus, acclimation of the biofilm occurred over 15 months prior to initiating the experiments, with pre-ozonation occurring

over 8 of these months. Figure 2.2 provides the results of monthly measurements of ATP in samples taken from the middle and bottom of the BAF column.

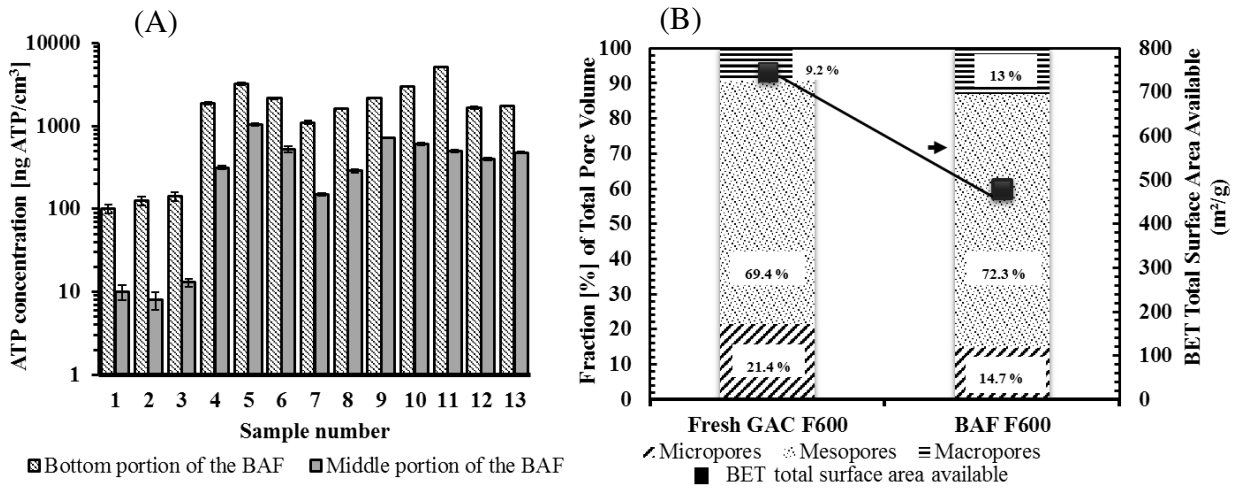

Figure 2.2. (A) ATP concentrations measured on a monthly basis starting 90 days after initiating the acclimation process. The error bars represent the standard deviation of triplicate experiment. (B) BET total available surface area and fraction of the total pore volume

ATP concentrations increased sharply after the fourth month of sampling, coinciding with the initiation of pre-ozonation treatment. Thereafter ATP concentrations stabilized. When experiments with 1,4-dioxane and DBPs were conducted (month 12 and 13 in Figure 2A), ATP concentrations measured in the bottom and middle portion of the column were 1706 ± 58 and 440 ± 57 ng ATP/cm^3 GAC, respectively. According to Pharand et al. [81], an ATP concentration of 10^2 – 10^3 ng ATP/cm^3 GAC indicates an active and acclimated BAF, which suggests the predominance of biodegradation in the removal of effluent organic matter. Relative to the 745 m^2/g BET surface area measured on fresh GAC, the BET surface area decreased to 479 m^2/g (~ 35% decline) after acclimation. The total pore volume for the fresh GAC was dominated by mesopores (69.4%) followed by micropores (21.4%) and macropores (9.2%). For the acclimated BAF, the fraction of micropores declined from 21.4 % to 14.7 %, indicating that the majority of the loss in total available surface area involved micropores. In addition to ATP analysis and surface characterization, BAF DOC removal was monitored for 76 days. During this time, the acclimated BAF achieved a relatively constant DOC removal of approximately 65% (Figure A.1 Appendix A). The consistent DOC removal during this timeframe indicates that biodegradation was dominant over adsorption as the adsorption performance should decline over time. This

observation is consistent with previous research from Farre et al. [55] and Corwin et al.[95]. However, it is possible that adsorption still had a minor contribution to the removal process.

To provide visual evidence for biofilm development on the GAC surface, and to compare the elemental content between fresh GAC and GAC after the acclimation process, ESEM-EDS imaging at 274× and 6000× magnification was employed. While the fresh GAC exhibited a porous surface at both magnifications, the acclimated GAC shows a covered/blocked surface (Figure 2.3). Figure A.2 (Appendix A) compares the elemental content as measured by EDS on the fresh and acclimated GAC surfaces.

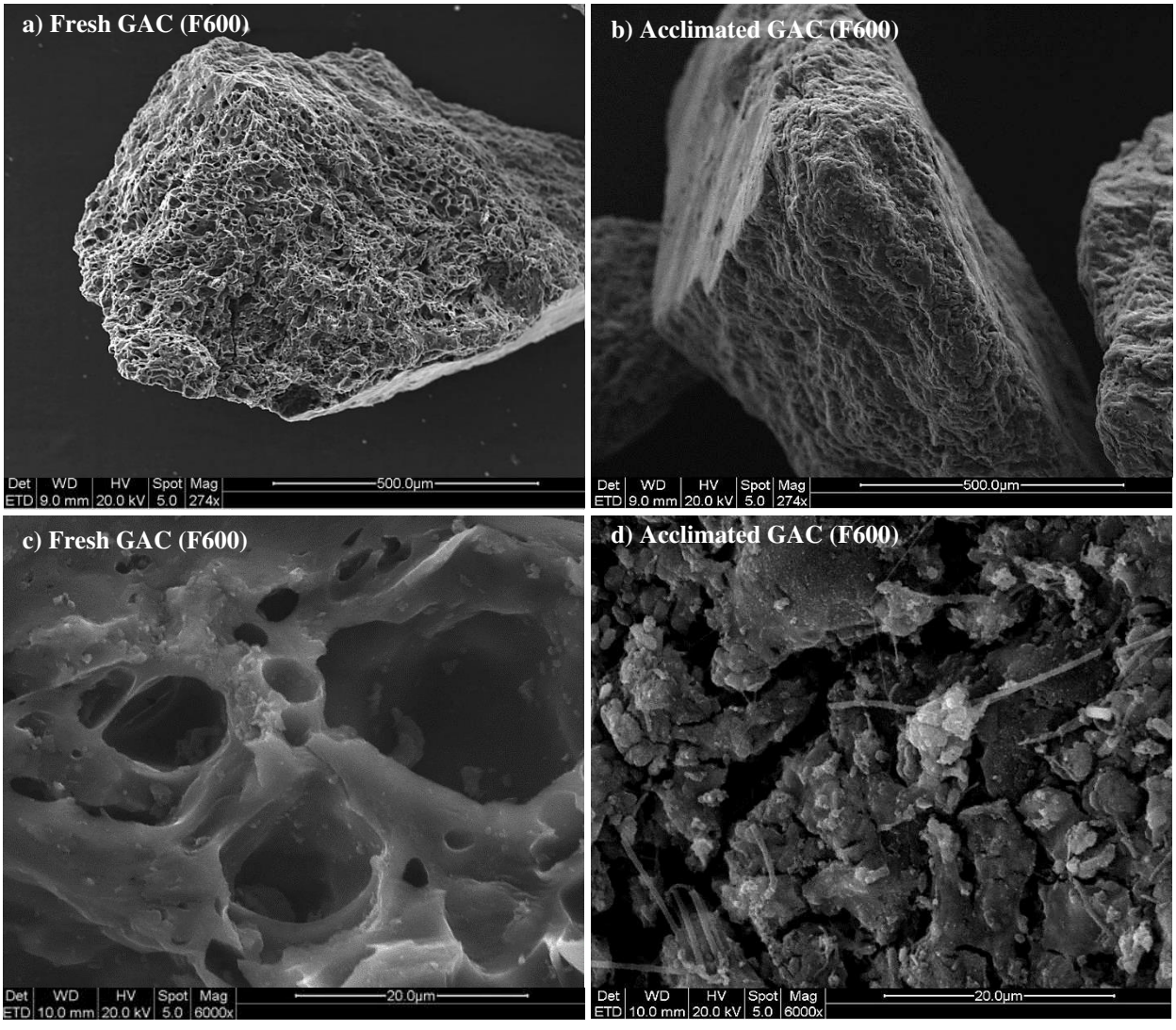

Figure 2.3. ESEM image of fresh GAC at (A) 274× and (C) 6000× magnification and of acclimated GAC at (B) 274× and (D) 6000× magnification

2.4.3. Evaluation of (O_3/GAC)-BAF vs O_3-BAF for removal of 1,4-dioxane

As discussed previously, the presence of GAC during ozonation leads to enhanced O_3 transformation into ·OH that could potentially target and transform ozone-refractory MPs. It is important to note that GAC is also an effective adsorbent for organic contaminants. 1,4-dioxane served as an ideal probe compound to evaluate the O_3/GAC process due to its low sorption affinity (log K_{OW} = - 0.27) and low reaction rate constant with ozone (0.32 $M^{-1}s^{-1}$) [8]. Moreover, 1,4-dioxane's strong heterocyclic ether bonding makes it relatively resistant to biodegradation [62, 96, 97].

The efficiency of 1,4-dioxane and DOC degradation by BAF only (in the absence of ozonation) was first evaluated at different EBCTs (15, 30, and 45 min). The results presented in Figure 4 indicate low and similar 1,4-dioxane removal efficiencies by BAF at all three EBCTs (approximately 15% removal). The findings are in agreement with previous studies [62, 96-99] indicating the resistance of 1,4-dioxane to biodegradation. During the experiment, approximately 66% DOC removal was observed for all EBCTs (Figure 2.4) and varying the EBCT did not impact the BAF performance. Thus, subsequent experiments were performed at the shortest BAF EBCT of 15 min. However, other parameters such as shorter EBCT or dissolved oxygen concentration may be limiting factors [42].

1,4-dioxane removal efficiency was evaluated for conventional O_3/BAF at three specific ozone doses (0.5, 0.7, 1.0 mg O_3/mg DOC), and (O_3/GAC)-BAF was compared to the conventional O_3/BAF at 1.0 mg O_3/mg DOC. ATP measurements of the GAC in the O_3 chamber taken during O_3/GAC experiments did not show the presence of microbial communities on the GAC surface before and after ozonation. Figure 2.5 presents the results of 1,4-dioxane abatement. 1,4-dioxane removal in the presence of GAC without O_3 demonstrated that sorption was negligible. During conventional ozonation, increasing the specific ozone dose led to a marginal increase in 1,4-dioxane removal (6-11%, at 0.5-1.0 mg O_3/mg DOC). However, the addition of GAC to the O_3 chamber significantly increased the 1,4-dioxane abatement efficiency across the ozonation unit to 40%. This increase in oxidation is likely a result of enhanced/accelerated ·OH formation due to the presence of GAC during ozonation and/or a removal of ·OH scavengers by adsorption on the added GAC. It has been reported that during ozonation of surface water, electron-donating residues of GAC, especially nitrogen-containing functional groups (e.g. pyrrole groups), are responsible for ·OH production and the effectiveness of O_3/GAC decreases when these sources are exhausted [37].

Moreover, the sorption capacity of the GAC towards ·OH scavengers should also decline over time. Thus, long-term experiments are suggested to further evaluate the capacity of different types and doses of GAC during O_3/GAC treatment of wastewater effluent. The BAF removal efficiency for 1,4-dioxane at 15 min EBCT for conventional O_3-BAF was similar to the previous experiments conducted without pre-ozonation (Figure 2.4). However, the BAF removal efficacy of 1,4-dioxane after O_3/GAC slightly decreased. This subtle decrease may be due to a decrease in the initial 1,4-dioxane concentration as a result of enhanced removal through O_3/GAC. This observation is consistent with a previous study by Suh et al. [100] that evaluated the impact of 1,4-dioxane concentrations on biodegradability. Suh et al. [100] reported that a higher concentration of 1,4-dioxane results in an increase in biochemical oxygen demand (BOD)/chemical oxygen demand (COD) which leads to increased biodegradation. However, information on the kinetics of 1,4-dioxane oxidation and biodegradability is very limited, and therefore more research in this area is needed. In sum, the 1,4-dioxane removal efficiency from the combination of O_3/GAC followed by BAF reached 50%.

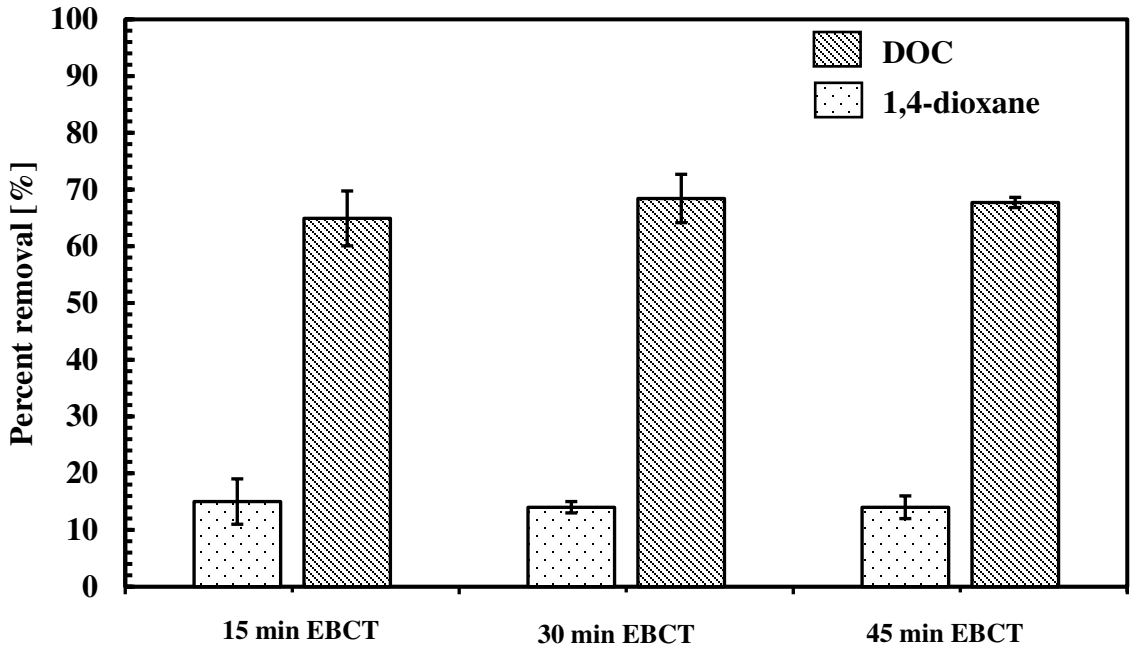

Figure 2.4. Removal of 1,4-dioxane and DOC through BAF. Error bars represent the standard deviation of triplicate experiments.

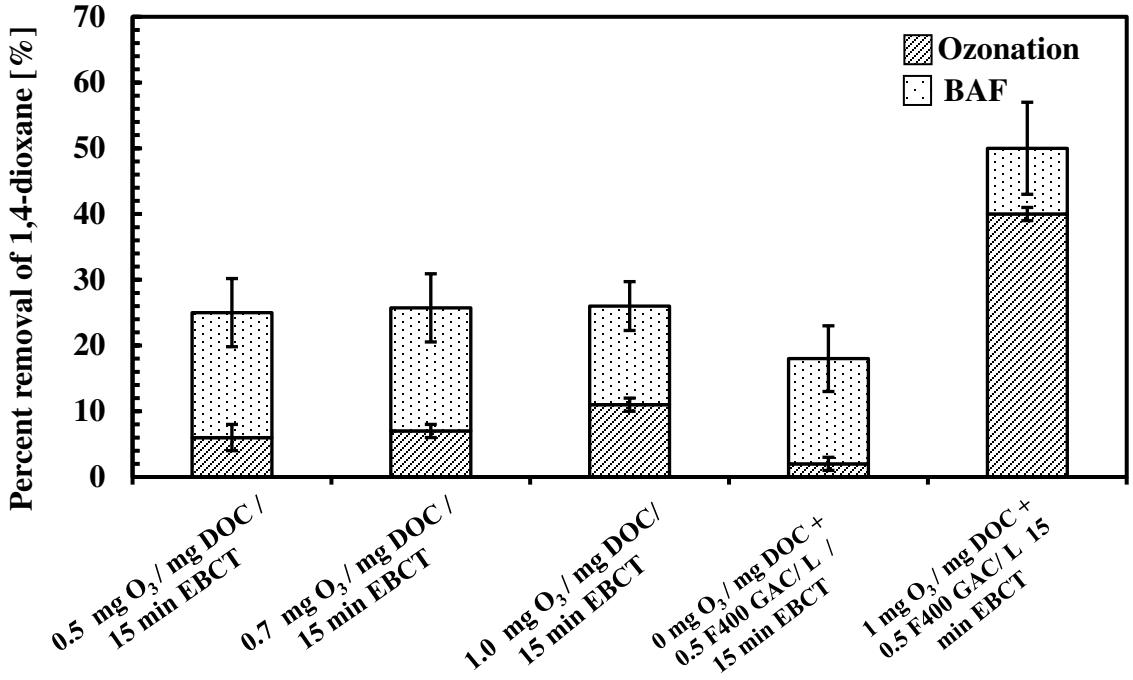

Figure 2.5.Removal of 1,4-dioxane during conventional O3-BAF and (O3/GAC)-BAF. Error bars represent the standard deviation of triplicate experiments.

2.4.4. DBP formation after chloramination in the samples from conventional and enhanced ozonation followed by BAF

DBP formation after chloramine UFC treatment was characterized on a mass and toxicity-weighted basis for conventional ozonation at three specific ozone doses (0.5, 0.7, and 1.0 mg O_3/mg DOC) and O_3/GAC at 1.0 mg O_3/mg DOC, each in combination with BAF operated at three EBCTs (15, 30, and 45 min). The sum of the measured halogenated DBP concentrations formed after chloramine UFC treatment of the SBMBR effluent serving as the influent to the ozonation unit ranged from approximately 220-280 nM (Figure 2.6). These DBPs were dominated by chlorinated and brominated HAAs (range 158-173 nM), followed by haloacetamides (HAMs; ~15-90 nM), and the four regulated trihalomethanes (THM4; ~10-24 nM). These three DBP classes together constituted >90% of the DBPs formed on a mass basis. Iodinated THMs (I-THMs) were not detected. Haloacetic acids, haloacetonitriles (HANs) and haloacetamides dominated on a toxicity-weighted basis.

Conventional ozonation at all three doses marginally increased the formation of DBPs. This subtle increase was mainly driven by the formation of haloacetamides (HAMs) during ozonation at 0.5 and 0.7 mg O_3/mg DOC, while the slight increase at 1.0 mg O_3/mg DOC was primarily caused by HAAs (~ 11%). An increase in haloacetamides had been reported by Chuang et al. [41] during treatment of two nitrified wastewaters with 0.7 mg O_3/mg DOC and chloramination. No significant reduction in the sum on the toxicity-weighted DBP concentrations was observed after ozonation. Unlike conventional ozonation at 1.0 mg O_3/mg DOC, a substantial decrease in the formation of DBPs could be observed after treatment with O_3/GAC at the same specific ozone dose. On a mass basis, this decrease was predominantly driven by ~84% reduction in THM4, ~51% reduction in haloacetamides and ~31% reduction in haloacetic acids formation. A control in the absence of ozonation demonstrated that sorption to the GAC (during O_3/GAC) did not significantly remove DBP precursors (no significant DOC removal was observed during the adsorption control test) indicating that enhanced formation of $^{\cdot}OH$ during O_3/GAC contributed to the reduction of DBP precursors. The sum of the toxicity-weighted DBP concentrations also declined by ~40%. The contribution of haloacetamides and haloacetonitriles to the DBP-associated toxicity was nearly eliminated, leaving haloacetic acids as the main contributor to the DBP-associated toxicity.

For all of the conventional ozone and O_3/GAC experimental conditions, BAF treatment played the major role for the reduction of DBP precursors after ozonation. Formation of haloacetaldehydes, haloketones and chloropicrin (a halonitromethane (HNM)) was eliminated. On both a mass and toxicity-weighted basis, haloacetic acids dominated DBP formation after chloramination of the BAF effluents. With the exception of conventional ozonation at 1.0 mg O_3/mg DOC, increasing the EBCT led to a moderate decline in HAA formation. On either a mass concentration or toxicity-weighted basis, DBP formation after chloramination of BAF effluents was similar between conventional and enhanced ozonation.

NDMA formation following chloramination of the SBMBR effluent ranged from ~176-340 ng/L (Figure 2.6). Both conventional ozonation and O_3/GAC decreased NDMA formation during post-chloramination to ~15-109 ng/L (Figure 2.6), which may be due to the oxidation of NDMA precursors during both conventional and O_3/GAC treatment. The reduction in NDMA formation was lowest for conventional ozonation at 0.5 mg O_3/mg DOC and for the O_3/GAC at 1.0 mg O_3/mg DOC. Overall, conventional ozonation was more effective in removing NDMA

precursors compared to O_3/GAC. Oxidation of NDMA precursors in drinking waters by conventional or enhanced ozonation was observed previously by Lee et al. [101], Krasner [102], and Shah et al. [103] BAF reduced NDMA formation to less than the 10 ng/L notification level in California [104] for all conditions. With the exception of 0.5 mg O_3/mg DOC, the reduction in NDMA formation slightly increased with increasing the EBCT.

With bromide concentrations of 63.0 ± 1.8 µg/L present in the SBMBR effluent throughout the experiments, bromate was not detected during conventional ozonation, while 12.5 ± 0.3 µg/L was measured after O_3/GAC treatment indicating increased oxidation power and less $\cdot OH$ scavenging. This concentration exceeds the 10 µg/L Maximum Contaminant Level (MCL) in drinking water [105]. However, the bromate formed during O_3/GAC treatment was reduced by BAF treatment to < 6.8 µg/L (Table A.7, Appendix A). Limited studies [106, 107] have investigated the bromate removal pathway during BAF treatment with GAC as filter media. Bromate removal might be caused by different mechanisms such as chemical reduction in anoxic/anaerobic zones along the depth of the BAF (likely caused by inhomogeneous flow) or sorption of bromate onto GAC via either ionic bonding to the GAC surface or diffusion into the biofilm and/or GAC surface.

2.5. Conclusion

The main objective of this study was to evaluate the process of O_3-BAF to simultaneously achieve efficient removal of O_3 refractory compounds, e.g., 1,4-dioxane, while meeting regulatory limits on DBPs as well as investigating the formation of unregulated DBPs. In addition, a novel approach for BAF acclimation process was introduced and evaluated. The results of the pilot experiments suggest that addition of GAC (in small doses) to the ozone chamber enhances the removal of 1,4-dioxane while at the same time does not lead to greater DBP formation compared to ozonation alone. The effect of BAF treatment on the removal of DBPs precursors and their associated additive toxicity was effective at the lowest investigated EBCT and increasing the EBCT showed marginal improvement. This was consistent with the results reported from Chuang et al. [41]. Conventional ozonation was more effective than O_3/GAC regarding the reduction of chloramine-reactive NDMA, while O_3/GAC was more effective at reducing halogenated DBP formation during post-chloramination

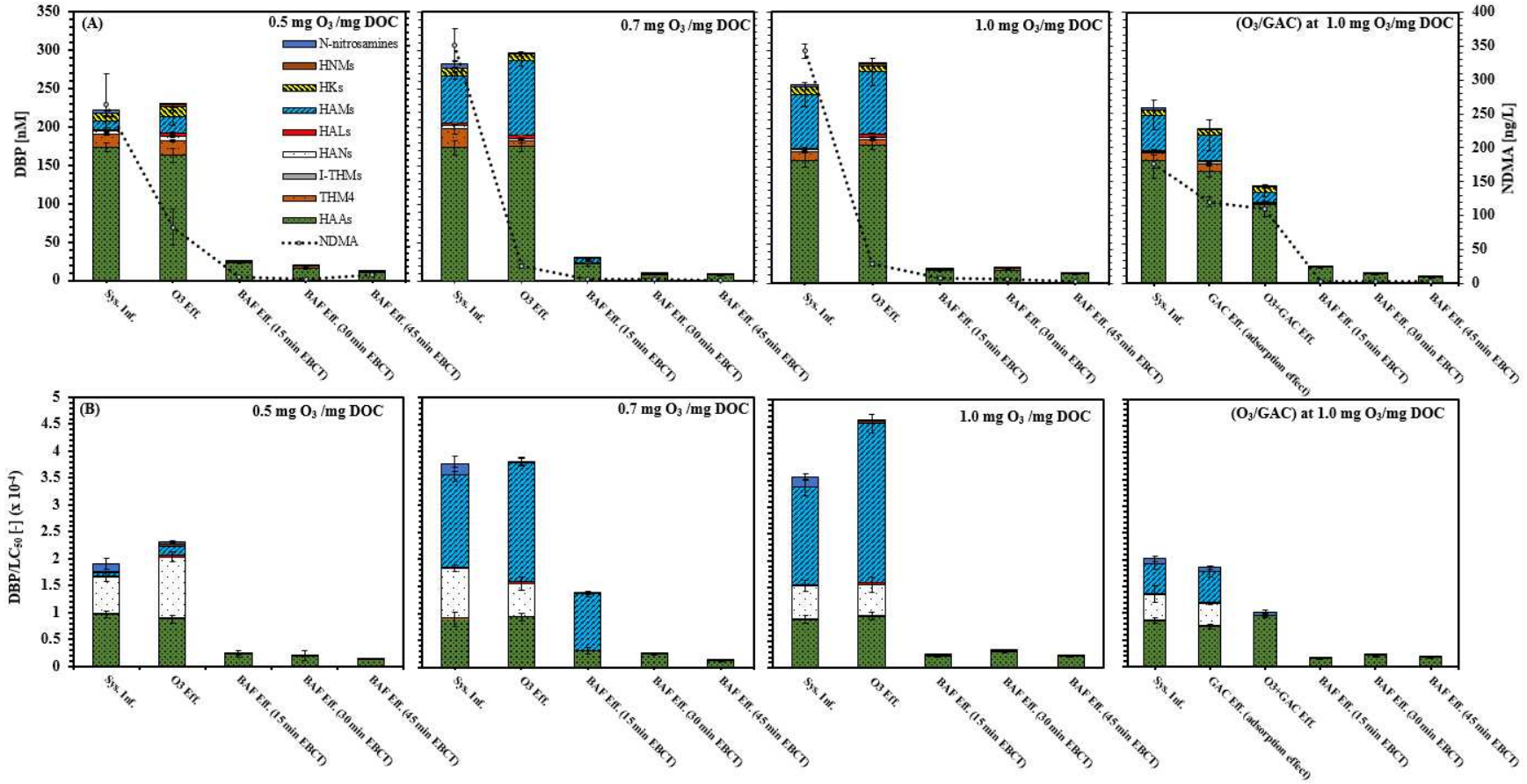

Figure 2.6. DBP formation after chloramine UFC treatment of SBMBR effluent, conventional and enhanced ozonation followed by BAF treatment on a (A) mass concentration basis and (B) toxicity-weighted basis. Error bars represent the standard deviation of duplicates for nitrosamines, and triplicates for halogenated DBPs.

Overall, both O_3-BAF and O_3/GAC-BAF met regulatory levels for trihalomethanes (THMs), haloacetic acids (HAAs), and bromate. Reduction of DBP precursors and bromate is important for the implementation of practical alternatives (e.g., O_3-BAF and (O_3/GAC)-BAF) to FAT of wastewater effluent that meet current and future regulatory frameworks.

The findings of this research, as a proof of concept, are being used for an ongoing investigation assessing the optimization and implications of using different types of GAC as the key component of removing different categories of O_3 refractory micropollutants during water reuse applications such as large-scale municipal wastewater effluent. In a lab-scale study on ozonation of Lake Zurich water, Sanchez-Polo et al. observed that electron-donating residues within GAC, specifically its nitrogen containing functional groups were responsible for $^{\cdot}OH$ production and the exhaustion of this source caused a decrease in $^{\cdot}OH$ production [37]. However, investigating with the synergistic effect of GAC to transform the aqueous O_3 to $^{\cdot}OH$ along with its capacity to adsorb O_3 and $^{\cdot}OH$ scavengers, in addition to finding the optimized dose and renewal process, is essential for progress in removal of adsorbable and non-adsorbable O_3 refractory micropollutants in water reuse applications. In addition, robustness of O_3-BAF as the core treatment step of RO-free potable reuse treatment trains in low saline regions is an area with limited research. Lack of a uniform acclimation process in BAF within utilities along with episodic release of industrial pollutants in municipal wastewater stream in some regions has been target of discussion about the performance of BAF when facing unexpected industrial micropollutants (e.g., methylene chloride). Yet, the findings of this study suggest that despite a wider range of molecular weight and higher DOC concentrations in O_3-BAF effluent compared to RO effluent, O_3-BAF is able to provide a high-quality effluent with respect to investigated contaminants.

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CHAPTER 3

SIMULTANEOUS OZONE AND GRANULAR ACTIVATED CARBON TREATMENT OF MICROPOLLUTANTS DURING POTABLE RESUE OF MUNICIPAL WASTEWATER EFFLUENT

Modified from a paper submitted for possible publication in *Chemosphere*[1]

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3.1. Abstract

The main objective of this study was to evaluate the efficacy of the simultaneous utilization of ozone (O_3) alone, and O_3 with granular activated carbon (GAC) (O_3/GAC) at pilot-scale for the enhanced removal of micropollutants (MPs) in potable reuse. The results revealed enhanced removal of tris-(2-carboxylethyl) phosphine (TCEP), sucralose, and meprobamate during the O_3/GAC treatment compared to their sum of removal during isolated ozonation and GAC adsorption experiments. The long-term O_3/GAC experiment showed the promotive effect of GAC substantially decreased after 20 hours of O_3 exposure. This decreased performance correlates with changes to GAC surface properties caused by O_3. After 6 hours of operation, O_3 initially led to an increase in Brunauer-Emmett-Teller (BET) surface area on the GAC improving the elimination level of investigated MPs (except N-nitrosomorpholine (NMOR)). However, after 20 hours of exposure, O_3 ultimately caused structural damages to the GAC surface, decreased the BET surface area in the final stages of the experiment, and a 4-fold increase in O_{1s}:C_{1s} ratio on the GAC surface was observed due to an increase in surface acidic functional groups caused by O_3.

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3.2. Introduction

It is estimated that 1.2 billion people live in regions with water scarcity problems [1]. This problem is further being exacerbated by climate change, dramatic population growth, and increasing competition for water resources between industry and agricultural sectors leading to an increased gap between water demand and supply [2-5]. As a result, potable reuse of municipal wastewater effluent has become an important component of water resource management [6].

In water and wastewater applications, O_3 is an effective oxidant that has been primarily applied as a disinfectant, and in recent years has also been employed for oxidative abatement of certain classes of micropollutants (MPs) [7-9]. Typically, molecular O_3 can react as a dipole, an electrophile or a nucleophile that selectively undergoes oxidative reactions with unsaturated aromatic and aliphatic compounds [10-12]. However, one main challenge associated with ozonation during reuse of municipal wastewater effluent is the limitation of O_3 for abatement of refractory MPs [13]. Due to their inactivated aromatic structure, O_3-refractory MPs cannot be oxidized efficiently by molecular O_3 [10]. Therefore, production and/or formation of hydroxyl radicals ($^{\cdot}OH$) during ozonation, known as advanced oxidation process (AOP), has gained attention in the past two decades [14]. As a non-selective secondary oxidant, $^{\cdot}OH$ has a higher oxidation power than O_3, enabling it to overcome the limitations of O_3 for efficient abatement of O_3-resistant MPs [15, 16]. For the sake of simplicity, the majority of mechanistic research studies on MPs oxidation are usually performed in ultrapure water batch experiments [7]. However, it is important to note that in a wastewater matrix, the main fraction of O_3 is usually consumed by dissolved organic matter (DOM), predominantly due to oxidation of phenolic moieties in DOM present in wastewater matrix [7, 17-19]. Therefore, conducting experiments under realistic conditions is essential for a proper evaluation of MP abatement in potable reuse of municipal wastewater effluents. Although the ozonation of municipal wastewater effluent can be considered an AOP due to transformation of O_3 into $^{\cdot}OH$ during reaction with certain types of DOM [20], the presence of radical scavengers (e.g., carbonate, bicarbonate, and certain organic matter) highlights the importance of finding a technology that improves $^{\cdot}OH$ formation and/or production to promote the destruction of O_3-refractory MPs [21].

Numerous studies have investigated O_3 associated AOPs such as O_3/H_2O_2 and O_3/ultraviolet (UV) to enhance $^{\cdot}OH$ formation [10, 14], as well as catalytic ozonation including

metal-based [11, 22-28] and carbon-based [29-33]. Among these technologies, the presence of activated carbon (AC i.e., granular activated carbon (GAC), powder activated carbon) during ozonation (O_3/AC) has been reported to improve oxidation performance through enhanced transformation of O_3 to $^{\cdot}OH$ [29, 34-40]. This technique not only provides the advantage of high sorption capacity of activated carbon (due to its high surface area ranging from 500 to 1500 m^2g^{-1} [36]) for removal of MPs and O_3 and $^{\cdot}OH$ scavengers, but also serves as an initiator/promoter in a radical-type chain reaction of O_3 decomposition that enhances the formation of $^{\cdot}OH$ [41, 42].

Existing research [43-45] indicates that nitrogen and oxygen functional groups along with the high surface area of AC are the main components of its promotive effect on decomposing O_3 into $^{\cdot}OH$. While nitrogen functional groups increase electron density, resulting in acceleration of O_3 decomposition to $^{\cdot}OH$ [15, 43], oxygen functional groups initiate a chain reaction mechanism [42] and provide adsorption sites for surface reactions [45, 46]. Despite the agreement on the effect of AC in the decomposition of aqueous O_3 into $^{\cdot}OH$, its role as a catalyst, promoter, or initiator is still a subject of debate [39]. For instance, while Jans & Hoigné [40] reported the reaction of O_3 with AC to be a catalytic reaction, a more detailed study by Sánchez-Polo et al. [43] showed that AC during ozonation acts more as a conventional initiator or promoter and when electron-donating residues within AC are exhausted, $^{\cdot}OH$ production stops [14]. It is important to highlight that overall effectiveness of O_3/AC is strongly dependent on both AC properties and the water matrix [37]. The authors of this study are aware of only two previous studies [41, 47] that addressed the effect of O_3/AC on removal of refractory MPs from municipal wastewater effluent at the bench-scale; yet, no investigation has been conducted at pilot- and/or full-scale investigating the MPs that were selected in this study. The main goal of this study was to evaluate the effectiveness of simultaneous ozonation and GAC treatment (O_3/GAC) on the removal of 16 environmentally relevant MPs from a reclaimed wastewater effluent. While two previous studies provided results based on short-term (1-3 hours) experiments, one objective of this study was to systematically evaluate the robustness of O_3/GAC over a long-term experiment (up to 20 hours). To achieve this goal, the effect of varying O_3 dose and GAC dose was assessed to achieve optimized operating conditions. In addition, the effect of ozonation on chemical and physical properties of GAC and its impact on the removal of MPs during the O_3/GAC was investigated.

3.3. Materials and methods

The description of chemicals, reagents, and stock solutions used during experimental procedure are provided in Appendix B.

3.3.1. Pilot-scale system setup

The constructed pilot-scale O_3/GAC system consisted of a 6-inch (15.24 cm) diameter, 13-foot (396.24 cm) long polyvinyl chloride (PVC) clear contactor with a removable GAC cell unit at the bottom of the column (enabling GAC replacement) where O_3 was introduced to fluidized GAC. The tertiary-filtered wastewater effluent (before disinfection) from a reclamation facility located in Nevada, U.S., served as the influent for the designed pilot-scale O_3/GAC system. In this full-scale facility, the raw municipal wastewater is treated through primary treatment (bar screen, ferric chloride coagulant, grit removal, anionic polymer, primary clarification), followed by secondary treatment (modified Johannesburg process for biological removal of nitrogen and phosphorous), and biologically active filtration using dual-media filtration (anthracite and sand). The system influent was continuously fed into a 264 gallon (1000 L) influent tank, from which the water was pumped into the O_3 contactor at the rate of 5 L/min. O_3 was generated by passing compressed air through an O_3 generator (SGC 21, Pacific Ozone, CA) that continuously fed the O_3 contactor through a 4-inch (10.2 cm) 20-micron 316 L grade stainless steel diffuser. The process flow diagram of the pilot-scale system is illustrated in Figure 3.1.

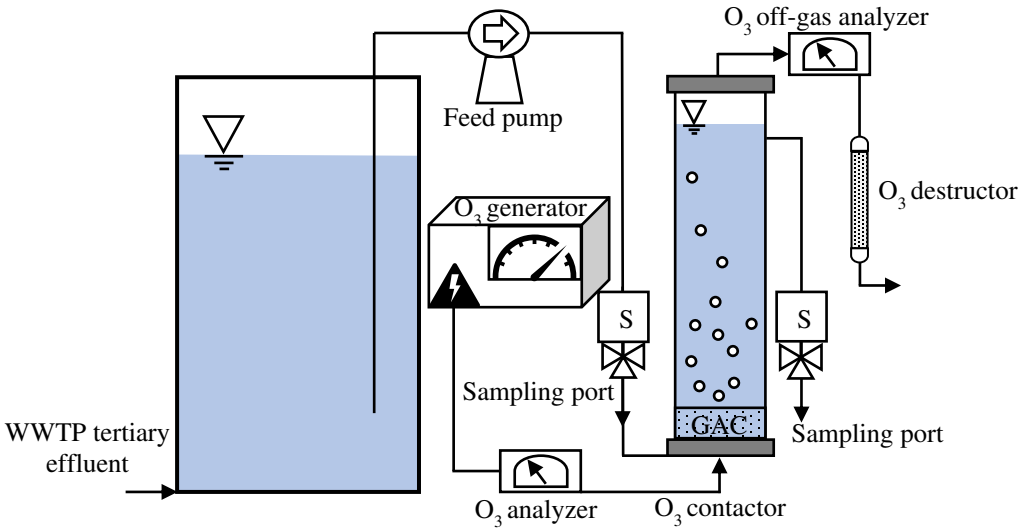

Figure 3.1. Process flow diagram of pilot-scale ozonation system (not to scale)

The O_3 in-gas and off-gas concentrations during pilot-scale testing were determined using a Mini-HiCon with the SC-010-R sample conditioning system (IN USA, MA) and was continuously monitored. An O_3 mass balance was used to calculate transferred O_3 dose (TOD: O_3 consumed by the wastewater matrix) as defined in equation 3.1:

$$TOD = \frac{Q_{gas}}{Q_{water}} ([O_3]_{gas-in} - [O_3]_{off-gas}) \quad (3.1)$$

where Q_{gas} and Q_{water} are the volumetric gas and water flowrates, respectively, $[O_3]_{gas\text{-}in}$ is the O_3 concentration in the inlet, and $[O_3]_{off\text{-}gas}$ is the O_3 off-gas concentration. The specific O_3 ratio was defined as the mass-based TOD normalized to DOC ratio (mg O_3/mg DOC) and was subsequently nitrite-corrected (equation 3.2) (nitrite concentration was between 0.03 - 0.05 mg/L during experiments), since nitrite consumes O_3 quickly with a 1:1 molar stoichiometry without generating $^{\cdot}OH$ [48]:

$$\frac{gO_3}{gDOC} = \frac{gO_3}{gDOC} - (\frac{46}{14})(g(NO_2 - N)/gDOC) \quad (3.2)$$

3.3.2. Enhanced ozonation procedure

Simultaneous use of O_3 and GAC (O_3/GAC) was employed to evaluate its promotive effect for removal of O_3-refractory MPs. Due to the low dose of GAC (0.5– 2.0 g GAC/L) and the operational method (i.e. fluidized), no head loss was observed. To perform comparative analysis, the results of O_3/GAC experiments were then compared to those of ozonation-only and adsorption-only experiments. All three treatment approaches (ozonation-only, adsorption-only, and O_3/GAC) were conducted under identical operational conditions, in which the samples were taken 30 min after the start of the experiment (discarding 3 bed volumes (156 L) of the contactor before sampling). Ozonation-only was performed at three different doses (0.3, 0.5, and 0.85 mg O_3/mg DOC). The selection of O_3 dosing during the experiment was based on previous studies [43, 49], as well as the consideration of bromide concentration in the influent, which ultimately dictated the maximum allowable O_3 dose to minimize bromate formation. The adsorption-only treatment process was conducted at two different GAC doses of 0.5 and 2.0 g GAC/L (volume of O_3 contactor). The selection of GAC doses was based on a previous study [43]. O_3/GAC experiments

were performed at O_3 doses of 0.3, and 0.5 mg O_3/mg DOC and two GAC doses of 0.5 and 2.0 g GAC/L.

To assess the robustness of the O_3/GAC treatment process over time, the reduction level of refractory MPs during O_3/GAC at 0.5 mg O_3/mg DOC and 2.0 g GAC/L was evaluated over 20 hours of experimental runtime.

3.3.3. GAC characterization

A commercial coal based GAC from Filtrasorb 400 (F400) (Calgon Carbon Corporation, PA) was selected and used in this study. The GAC was prepared by extensive rinsing with deionized water (DI) followed by drying for 24 hours at 120 ºC prior to each experiment. The surface morphology and structure of F400 GAC before and after ozonation was characterized by employing environmental scanning electron microscopy (ESEM) (Quaanta 600, FEI Company, Hillsboro, OR) in vacuum mode. The F400 GAC samples were also analyzed for surface area characterization and pore analysis employing a Micromeritics Tristar 3020 instrument (Micromeritics – Norcross, GA). Samples were dried and degassed with nitrogen gas for 6 hours prior to undergoing nitrogen physical adsorption (physisorption) analysis to evaluate the specific surface area using the Brunauer-Emmett-Teller (BET) [50] and the Barrett-Joyner-Halenda (BJH) equations [51] to determine pore volume and pore-size distribution, respectively. The surface speciation of the GAC before and after the O_3/GAC experiment was evaluated using an X-ray photoelectron spectroscopy (XPS) HiPP-III Scienta-Omicron photoelectron spectrometer operating in swift mode. Pass energy analyzer slit width for surveys was 500 eV and 4 mm and for core level scans was 200 eV and 1.0 mm. An 800 µm aperture was fixed on the analyzer entrance. Monochromatic Al Kα X-rays were used to generate the photoelectron signal. A single point calibration was performed using Au $4f_{7/2}$ at 83.98 eV. Analysis was performed using CASA XPS.

3.3.4. Analytical methods for target micropollutants

Samples collected during experiments were analyzed for select MPs (Table B.7, Appendix B) at the Southern Nevada Water Authority laboratory. Samples were collected in 1 L trace-clean amber Boston round glass bottles. Sample bottles were preserved with 1 g/L sodium azide to prevent microbial degradation and 50 mg/L ascorbic acid to quench any chlorine or O_3 residual.

Sample bottles were maintained at 4 ºC during transport to the analytical facility, where they were stored at 4 ºC. Samples were extracted within 14 days of collection. The analytical method used for NMOR is described in the SI.

3.3.4.1. Solid-phase extraction

Analytes were extracted from aqueous samples in batches of six using 6-mL, 200 mg hydrophilic-lipophilic balance (HLB) cartridges from Waters Corporation (Milford, MA). Extractions were performed on an AutoTrace™ automated solid-phase extraction (SPE) system (Thermo Fischer Scientific, Waltham, MA). The SPE cartridges were sequentially preconditioned with 5 mL of MTBE, 5 mL of methanol, and 5 mL of reagent water. Each sample was loaded onto a cartridge at 15 mL/min. Cartridges were rinsed with 5 mL of reagent water and then dried under a nitrogen stream for 30 minutes. Each cartridge was eluted with 5 mL methanol followed by 5 mL of 10/90 (v/v) methanol/MTBE, and both fractions were collected in a single 15 mL calibrated centrifuge tube. The resulting extract was concentrated with a gentle stream of nitrogen to a volume just below 500 µL, and then brought to a final volume of 500 µL using methanol.

3.3.4.2. Instrumental analysis

An Agilent (Palo Alto, CA) G1312A binary pump and an HTC-PAL autosampler (CTC Analytics, Zwingen, Switzerland) were used for all analyses. All analytes were separated using a 50 x 4.6 mm Kinetex 2.6µm C18 column (Phenomenex, Torrance, CA). Chromatographic separation was accomplished using a binary gradient of 5 mM ammonium acetate (v/v) in water (A) and 100% methanol (B) at a flow rate of 800 µL/min. An injection volume of 2 µL was used for all analyses. Tandem mass spectrometry was performed using an API 4000 triple-quadrupole mass spectrometer (Applied Biosystems, Foster City, CA). Analytes were grouped into negative electrospray ionization (ESI) or positive ESI based on sensitivity and selectivity for each compound. Once established, the optimal compound-dependent parameters were determined, and source-dependent parameters were optimized for each compound group. Data were collected in scheduled multiple reaction monitoring (MRM) mode for ESI negative and ESI positive compounds for each transition monitored (Table B.2, Appendix B).

An isotopically labeled version of each analyte was added to each calibration point to generate a relative response ratio. Recoveries of the isotopes in samples were compared with the

relative response ratio and a concentration of the unlabeled analyte was calculated. Linear or quadratic regression with 1/x weighting was used and regression coefficients typically exceeded 0.995. Calibration curve verifications were analyzed at least every six samples and were generally between 80 and 120% of the expected concentration. Sample extracts with compound concentrations greater than the calibration range were diluted and reanalyzed. All reported aqueous values accounted for sample-specific dilution or concentration. Method detection limits (MDLs) were calculated from (n=7) analysis of reagent water fortified with unlabeled analytes near expected MDLs and containing isotopically labeled standards in concentrations matching the calibrators. MDLs were calculated by multiplying the standard deviation of replicate measurements by the appropriate student's T value for n - 1 degrees of freedom. Reporting limits were set conservatively for each analyte from calculated MDLs and to account for variable loss during sample preparation as observed from internal standard peak areas (Table B.3, Appendix B).

3.3.4.3. Quality control

A laboratory-reagent blank (LRB) and a laboratory-fortified blank (LFB) were incorporated at a SPE step for validation of extraction. Values below detection were set at <1/3 signal intensity of the lowest calibrator for each analyte and recovery limits of +/- 20% for LFBs were adopted. A sample duplicate and a fortified matrix sample were extracted at a frequency of one per batch of six, and relative percent difference (RPD) limits of 20% and recovery limits of +/- 20% of true value set for each, respectively. Calibration curve verification standards were analyzed at least every six samples and acceptance limits were set at +/-20% of expected concentration. Secondary transitions during MS/MS analysis were monitored for each target analyte and were used for positive confirmation of values, while peak area counts of internal standards were required to be at least 10% of average peak signal of calibrators, at same concentration, for reporting. Data failing to meet quality control criteria was not reported. Finally, data where target-isotope response ratios did not match those from calibration were not reported.

3.4. Results and discussion

3.4.1. Characterization of wastewater treatment plant effluent

Tertiary effluent served as the feed water of all experiments in this study. Water quality parameters of tertiary effluent are summarized in Table B.5 (Appendix B). The concentrations of

MPs in the tertiary effluent are summarized in Table B.6 (Appendix B). The investigated MPs classified into three groups based on their second-order rate constant with O_3 and $^{\cdot}OH$ and are summarized in Table B.7 (Appendix B). In general, compounds with an O_3 and $^{\cdot}OH$ second-order rate of $K_{O3,\ pH\ 7} \geq 1\times10^5$ and $K_{^{\cdot}OH} > 5\times10^9$ $M^{-1}s^{-1}$ respectively, (Group I) show a high reactivity with O_3 and $^{\cdot}OH$. For compounds with an O_3 second-order rate between $10 \leq K_{O3,\ pH\ 7} < 1\times10^5$ $M^{-1}s^{-1}$ (e.g. gemfibrozil; Group II) a moderate reactivity with O_3 can be expected. Compounds with an O_3 second-order rate bellow $K_{O3,\ pH\ 7} < 10$ $M^{-1}s^{-1}$ (Group III, IV) have low reactivity with O_3 and their removal is mainly controlled by the magnitude of their $^{\cdot}OH$ second-order rate constant [52].

3.4.2. Comparison of the O_3/GAC efficiency with ozonation-only and adsorption-only; effect of operation parameters

The efficiency of simultaneous ozonation and adsorption onto GAC in the O_3/GAC treatment process was investigated and compared to ozonation-only (O_3 in the absence of GAC) and adsorption-only (GAC in absence of O_3) for removal of selected MPs.

3.4.2.1. Ozonation analysis of MPs removal

Figure 3.2 shows the percent removal of selected MPs by ozonation-only treatment at three specific O_3 doses of 0.3, 0.5, and 0.85 mg O_3/mg DOC. The removal of the Group I MPs (triclosan, sulfamethoxazole, carbamazepine, trimethoprim, and naproxen) at all three specific O_3 doses was efficient (above 96% at 0.3 mg O_3/mg DOC, and above 98% for 0.5, and 0.85 mg O_3/mg DOC), which can be attributed to their relatively high reactivity with O_3. The elimination rates of Group I MPs are similar to those reported by Lee et al. and Dickenson et al. [52, 53]. The removal rate of carbamazepine is consistent with the results reported by Bourgin et al. [54].

The removal efficiency of gemfibrozil and fluoxetine from Group II was lower compared to those of Group I MPs. The average removal for gemfibrozil and fluoxetine at 0.3 mg O_3/mg DOC were 83 ± 1.8% and 76 ± 1.9%, respectively. Increasing the specific O_3 dose to 0.5 mg O_3/mg DOC improved the elimination of gemfibrozil and fluoxetine to 89 ± 1.0% and 94 ± 1.2%, respectively. These MP elimination levels at 0.85 mg O_3/mg DOC were above 98%. Ozonation of the Group III MPs (DEET, primidone, sucralose, meprobamate, and NMOR) resulted in a lower elimination than that of Group I and II, which is consistent with their lower second-order reaction rate constant with O_3 ($K_{O3,\ pH\ 7}$) (<10 $M^{-1}s^{-1}$). The removal of NMOR during ozonation at 0.85 mg

O_3/mg DOC was not evaluated. The removal of DEET and sucralose are similar to the results reported by Bourgin et al. [54]. Having similar $K_{O3, pH\ 7}$ and $K_{\cdot OH}$, removal of DEET and primidone were comparable to each other during ozonation-only (average elimination of 56 ± 3%, 74 ± 4%, and 88 ± 1% at 0.3, 0.5, and 0.85 mg O_3/mg DOC, respectively). Sucralose and meprobamate showed a similar elimination level at 0.3 mg O_3/mg DOC (~ 22%). However, meprobamate showed higher removal at both 0.5 and 0.85 mg O_3/mg DOC compared to sucralose. Since both compounds have a similar $K_{O3, pH\ 7}$, this difference in elimination level at 0.5 and 0.85 mg O_3/mg DOC may be due to the higher $K_{\cdot OH}$ (2-fold) of meprobamate, indicating that the removal rate was likely controlled through oxidation by $\cdot$OH. As a halogen-containing aliphatic contaminant, TCEP showed a poor removal during all applied O_3 doses (< 20%). The removal rate from TCEP are in similar to those reported by Dickenson et al. [53] During O_3 treatment at 0.3 and 0.5 mg O_3/mg DOC, bromate concentrations remained below the 10 µg/L maximum contaminant level (MCL) for drinking water set by the USEPA [55]. However, increasing the O_3 dose to 0.85 mg O_3/mg DOC led to bromate formation of 11.1 µg/L. Therefore, subsequent O_3/GAC experiments focused on lower O_3 doses (0.3 and 0.5 mg O_3/mg DOC).

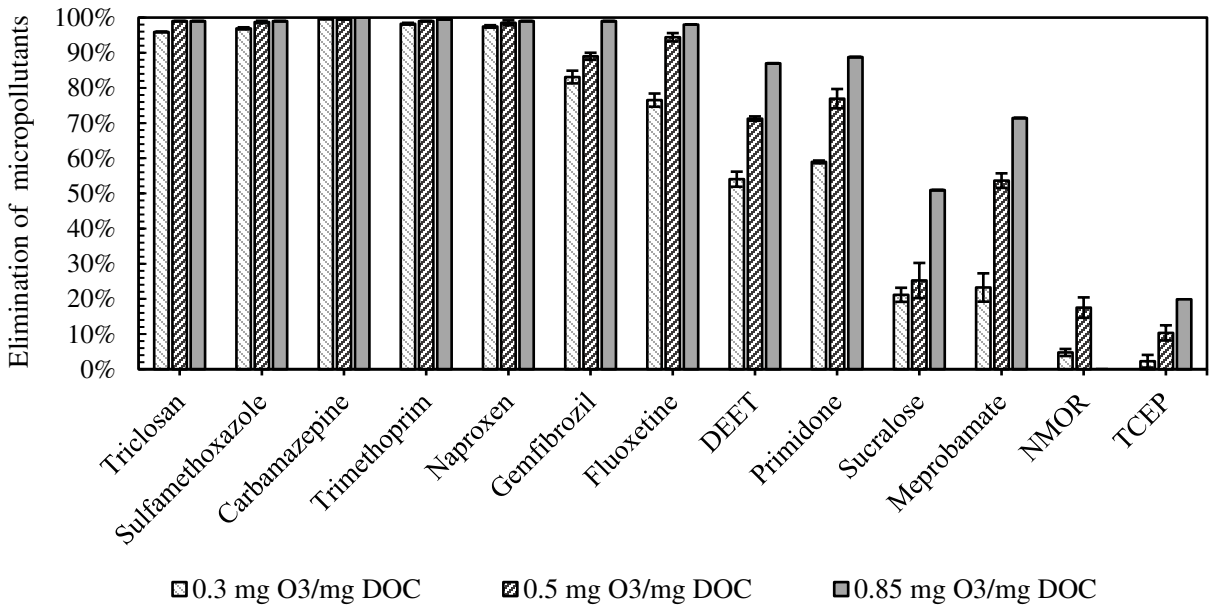

Figure 3.2. Elimination of selected micropollutants by ozonation-only as a function of specific O_3 dose (0.3, 0.5, and 0.85 mg O_3/mg DOC): triclosan, sulfamethoxazole, carbamazepine, trimethoprim, naproxen (Group I), gemfibrozil and fluoxetine (Group II), DEET, primidone, sucralose, meprobamate, and NMOR (Group IV), and TCEP (Group V). The error bars represent the average deviation of replicated experiments.

3.4.2.2. Adsorption analysis of MPs removal with GAC

To determine the extent of MP removal by adsorption during O_3/GAC, adsorption-only experiments were carried out. Figure 3.3 displays the removal values of selected MPs onto GAC at two doses of 0.5 and 2.0 g GAC/L (volume of O_3 contactor) in a fluidized bed GAC chamber (Figure 3.1). During adsorption-only experiments at 0.5 g GAC/L, the majority of MPs (except gemfibrozil) showed a removal rate of ~3-12%. The adsorption of gemfibrozil at 0.5 g GAC/L showed the highest removal among the investigated MPs (~40%) while NMOR, with ~3% removal, exhibited the lowest removal rate. The increase of the GAC dose to 2.0 g GAC/L led to a moderate increase in adsorption rate for all MPs. The highest removal rate was observed for naproxen, trimethoprim, and gemfibrozil (43, 50, and 56%, respectively) while sucralose, TCEP, and NMOR showed the least removal rates with 13, 18, and 19%, respectively.

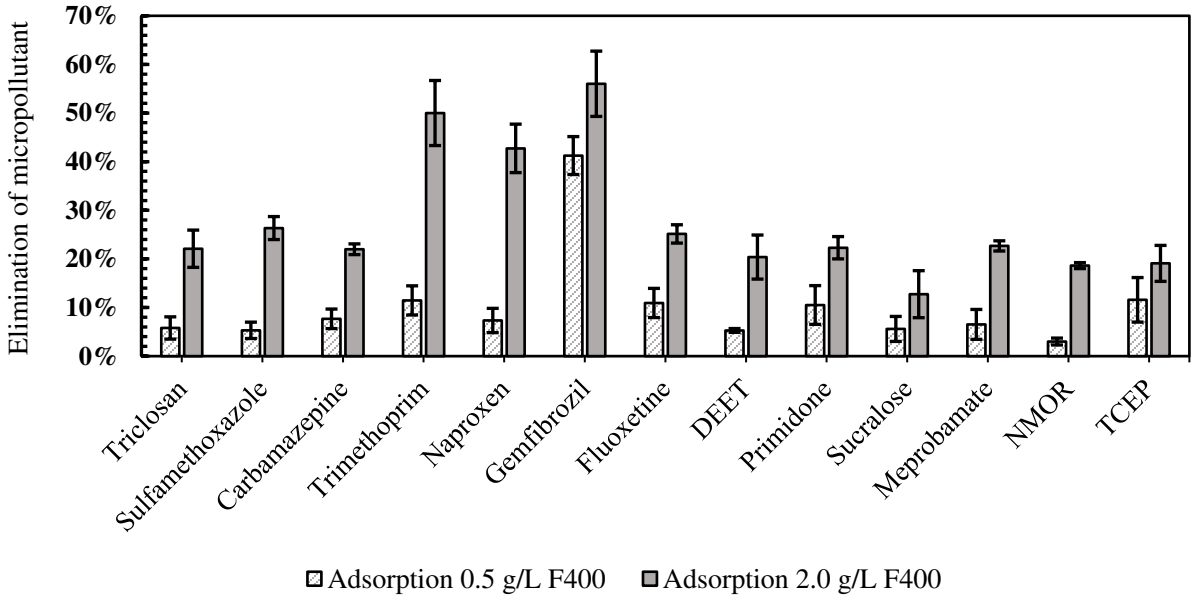

Figure 3.3. Elimination of selected micropollutants by adsorption-only treatment process at 0.5, and 2.0 g GAC/L (volume of O_3 contactor) in a fluidized bed GAC chamber (Fig. 1). The error bars represent the average deviation of replicated experiments.

3.4.2.3. Enhanced ozonation (O_3/GAC) performance

To investigate the applicability of the simultaneous use of O_3 and GAC for treatment of municipal wastewater effluent, O_3/GAC experiments were carried out at specific O_3 doses of 0.3 and 0.5 mg O_3/mg DOC and GAC doses of 0.5 and 2.0 g GAC/L. Figure 3.4shows the elimination level obtained from O_3/GAC for O_3-refractory MPs in Group III and IV. Grab samples were taken

30 min after the start of each experiment. In all O_3/GAC experiments, no bromate formation was observed and its concentration remained below detection limit (1 µg/L). NMOR was not analyzed during this phase of O_3/GAC testing. Among the MPs in Group III, the removal of DEET (58-82%) and primidone (61-87%) during the O_3/GAC treatment process showed an increase compared to their respective elimination during ozonation-only (Figure 3.2: DEET 54-71% and primidone 59-77%). However, the comparison between O_3/GAC (Figure 3.4) and the sum of the corresponding ozonation-only (Figure 3.2) and adsorption (Figure 3.3) removal did not show any additional removal for DEET and primidone during O_3/GAC. This behavior may indicate that adsorption and ozonation-only were responsible for the higher efficacy of the combined system. The results of meprobamate during O_3/GAC showed a slight increase (~5%) at 0.3 mg O_3/mg DOC, 0.5 g GAC/L and a 14 % increase at 0.5 mg O_3/mg DOC, 2.0 g GAC/L compared to the sum of respective ozonation-only and adsorption. Increasing the O_3 dose, however, did not lead to any additional meprobamate removal during O_3/GAC, compared to the sum of ozonation-only and adsorption.

The O_3/GAC experiment for sucralose at 0.3 mg O_3/mg DOC and 0.5 g GAC/L showed an additional removal of 10% compared to the sum of ozonation-only and adsorption-only. Increasing the GAC dose to 2.0 g GAC/L at 0.3 mg O_3/mg DOC resulted in similar removal. However, increasing the O_3 dose while maintaining the GAC dose (0.5 mg O_3/mg DOC, 0.5 g GAC/L) led to an additional increase of 18% compared to the sum of respective ozonation-only and adsorption-only. An additional removal of 27% was achieved for sucralose during O_3/GAC at 0.5 mg O_3/mg DOC, 2.0 g GAC/L compared to sum of ozonation-only and adsorption-only.

For Group IV, TCEP removal during O_3/GAC showed an additional removal of 21% at 0.3 mg O_3/mg DOC, 2.0 g GAC/L and 17% at 0.5 mg O_3/mg DOC, 2.0 g GAC/L compared to the sum of their respective ozonation-only and adsorption results. O_3/GAC at 0.5 g GAC/L for both 0.3 and 0.5 mg O_3/mg DOC did not lead to an additional removal of TCEP compared to the sum of ozonation-only and adsorption.

Overall, the results showed that the operational conditions in which O_3/GAC demonstrate an additional removal efficiency compared to the sum of ozonation-only and adsorption-only could be attributed to several factors, including: (i) decomposition of O_3 to $^{\cdot}OH$ as a result of the reaction between O_3 and GAC, leading to enhanced oxidation of certain MPs; (ii) reaction between O_3 and

adsorbed DOM on the GAC surface resulting in ·OH formation; (iii) adsorption of O_3 and ·OH scavengers onto GAC that enables a longer O_3 and ·OH exposure, enhancing the oxidative abatement of MPs; and (iv) increasing GAC surface area during the initial phase of the O_3/GAC process (discussed in next section) In general, the level of O_3 and ·OH contribution in oxidative abatement of a MP can be measured and predicted in a controlled laboratory batch experiment; however, the complexity of these predictions is exacerbated when adding a wastewater effluent to the matrix. It is important to note that in real case scenarios, in which continuous wastewater effluent enters the system, O_3 and ·OH exposures cannot be predicted or simply quantified because they are functions of several operational and environmental conditions that are constantly changing in the wastewater stream (e.g., scavenging capacity of wastewater matrix, pH, DOM) [14, 56].

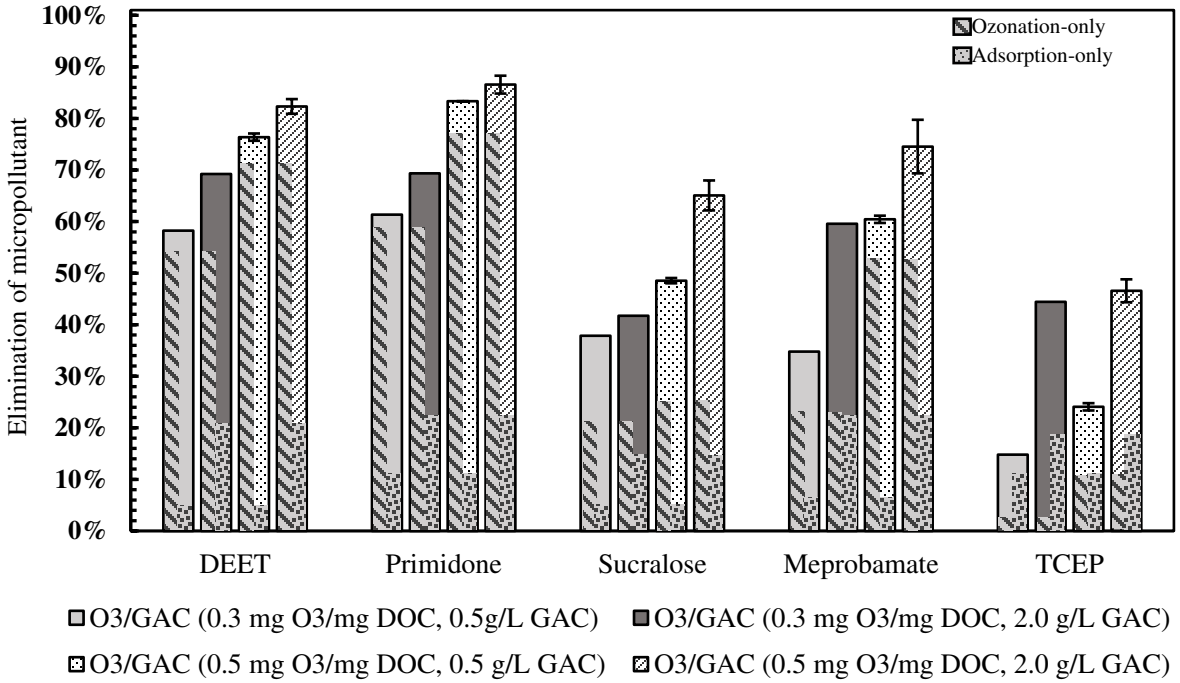

Figure 3.4. Elimination of Group III (except NMOR) and Group IV of micropollutants during O_3/GAC treatment process at four different conditions: (a) 0.3 mg O_3/mg DOC, 0.5 g GAC/L, (b) 0.3 mg O_3/mg DOC, 2.0 g GAC/L, (c) 0.5 mg O_3/mg DOC, 0.5 g GAC/L, and (d) 0.5 mg O_3/mg DOC, 2.0 g GAC/L. The error bars for conditions (c) and (d) represent the average deviation of replicated experiments.

3.4.3. Robustness of the O_3/GAC treatment process

In this phase of the study, the robustness of O_3/GAC treatment as a function of operating time for removal of O_3 refractory MPs was investigated. The key advantage of this experiment was the concurrent assessment of the GAC efficacy for enhanced ozonation as well as evaluating

the GAC adsorption capacity throughout the O_3/GAC treatment process. To achieve this goal, O_3/GAC experiments were carried out at 0.5 mg O_3/mg DOC, 2.0 g GAC/L for 20 hours. Figure 3.5. summarizes the results of MPs (Group III and IV) removal during the O_3/GAC robustness experiment. The O_3/GAC effluent samples were collected after 0.5, 2.0, 6.0, and 20 hours of operation (Figure 3.5: labeled as *O_3/GAC*). After each O_3/GAC sampling, the O_3 generator was turned off, three bed volumes of O_3 contactor were discarded, and adsorption effluent samples were collected (Figure 3.5: labeled as *Adsorption-only during O_3/GAC*). Ozonation-only (in absence of GAC) samples were taken prior to O_3/GAC to demonstrate the elimination level through ozonation (Figure 3.5: labeled as *Ozonation-only*). Multiple influent samples were taken throughout the experiment.

The experimental results revealed an overall decrease in removal performance of O_3/GAC after 20 hours of operation for all investigated compounds (Figure 3.5, O_3/GAC) indicating that the GAC did not serve as a catalyst and its promotive effect decreased over time. This finding is in agreement with the previous study from Sanchez-polo et al. [43]. The removal efficacy of O_3/GAC for DEET, meprobamate, and primidone decreased to the level of ozonation-only after 20 hours of operation while the elimination of sucralose, TCEP, and NMOR was still slightly higher (~10%) compared to ozonation-only. Moreover, it is important to highlight that O_3/GAC initially led to an increase in adsorptive removal of investigated MPs (except NMOR; see Figure 3.5 adsorption during O_3/GAC), before ultimately decreasing in the final stages of the experiment. These results confirm the GAC surface characteristics described in Section 3.4.4. This behavior can be the consequences of: (i) changes of polarity and functionality of the GAC surfaces and/or, (ii) textural alteration of the GAC during the experiments.

DEET, the compound with the highest log K_{ow} (log K_{ow}=2.18), exhibited good adsorption as expected. Both sucralose (log K_{ow}= -1.0) and primidone (log K_{ow}=0.91) on the other hand, exhibited high adsorption while having a low log K_{ow}. This may be due to the particular spatial distribution of the different hydrophobic and hydrophilic functional groups within the structure of a given MP. For instance, primidone has a benzene ring that serves as an anchor for adsorption and it has an aliphatic chain that shields a ketone group. Sucralose has two chlorine atoms that are readily accessible for adsorption, while many oxygen atoms are situated at the center of the molecule.

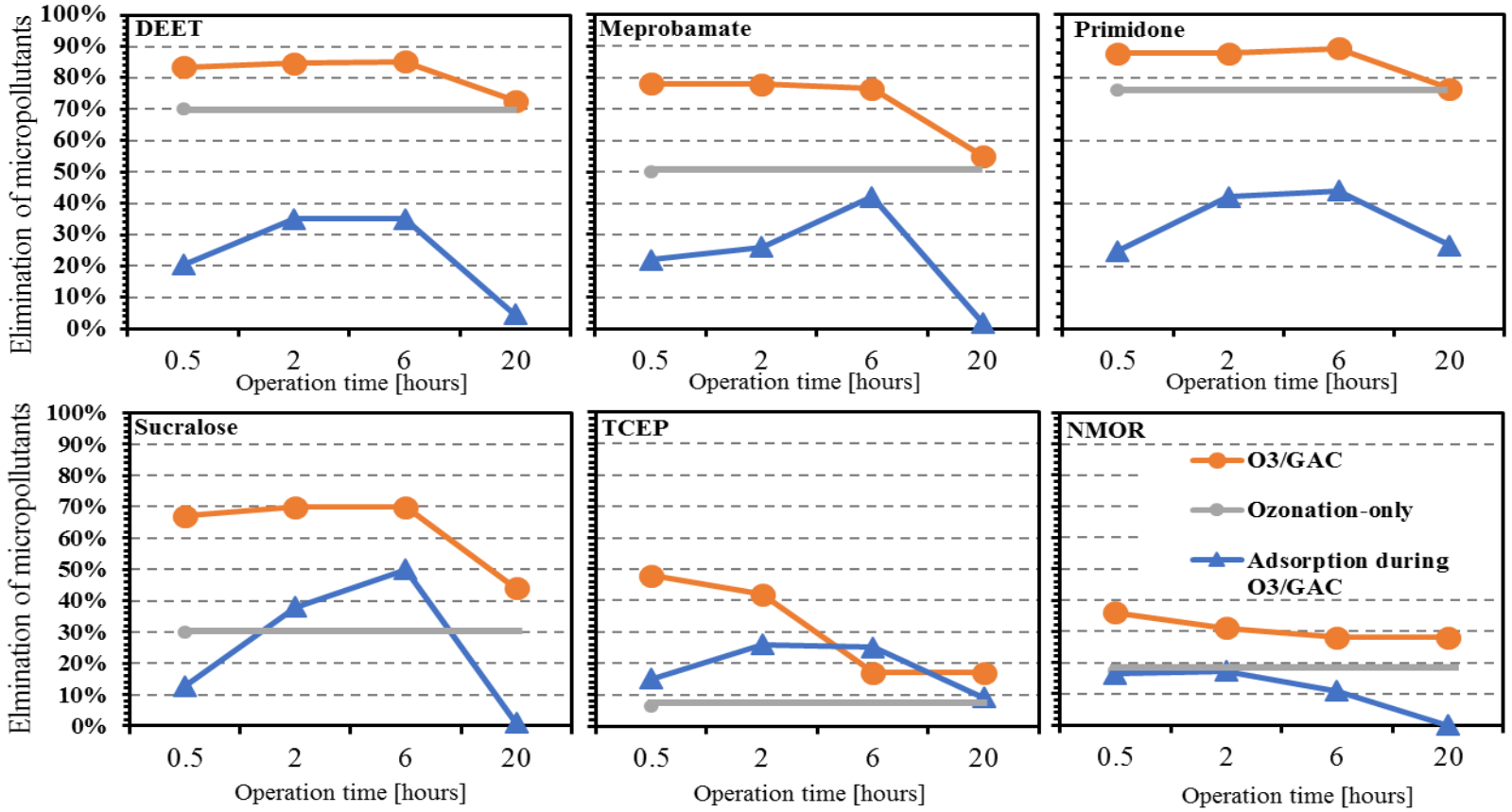

Figure 3.5. Robustness of O3/GAC treatment process for Group III and IV of MPs at 0.5 mg O3/mg DOC, 2.0 g GAC/L over 20 hours operation

3.4.4. GAC surface characterization during O_3/GAC

Physical and chemical surface characteristic of GAC before and after O_3/GAC treatment were investigated to better understand the impact of O_3 on GAC and its relationship to the observed removal of MPs.

3.4.4.1. ESEM

To provide visual evidence of the GAC surface structure change during the O_3/GAC treatment process, ESEM images at 1155× magnification were employed. Figure 3.6 depicts ESEM micrographs of three GAC samples: (A) fresh F400 GAC, (B) F400 GAC after 6 hours of O_3/GAC operation, and (C) F400 GAC after 20 hours of O_3/GAC operation. Operational conditions for both (B) and (C) were at 0.5 mg O_3/mg DOC with a GAC dose of 2 g/L. Comparison of the micrographs demonstrates that morphological changes on the GAC surface occurred during the O_3/GAC treatment process. In the first 6 hours of the O_3/GAC treatment process, an increase in the porosity is likely due to the visible observation of the formation of new micropores. However, the micrograph of the GAC sample after 20 hours operation exhibited less micropores and a likely decrease in the porosity of the GAC surface, compared to both fresh GAC and that of GAC after 6 hours operation. These structural alterations are probably the result of the direct exposure of the GAC to O_3.

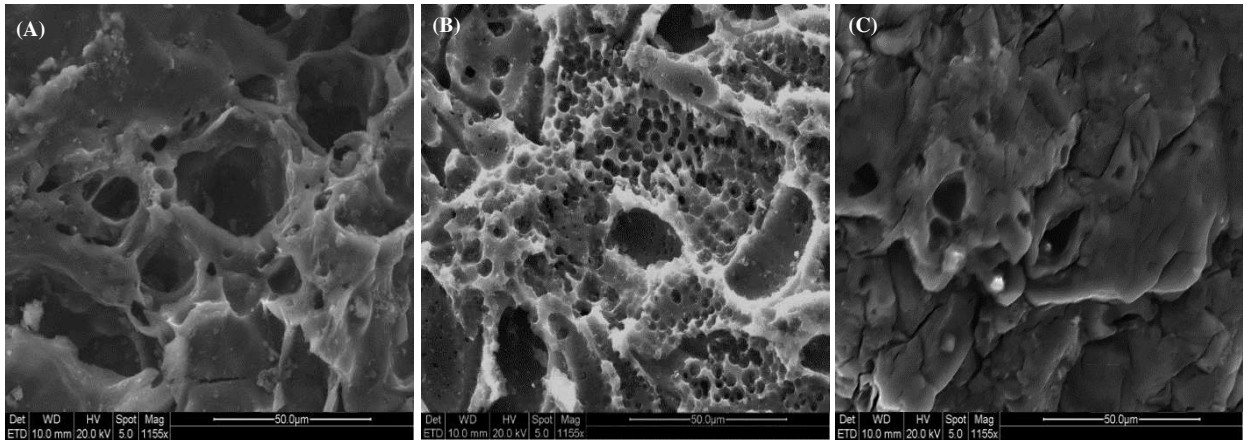

Figure 3.6. ESEM micrographs of (A) fresh F400 GAC, (B) F400 GAC after 6 hours of the O3/GAC treatment process, and (C) F400 GAC after 20 hours of the O3/GAC treatment process at 1155× magnification

The ESEM observations were be confirmed with the results of BET surface area analysis that are shown in Figure 3.7. Relative to the 834 m^2/g BET surface area measured on fresh GAC, the BET

surface area increased to 897 m^2/g (~ 8% increase) after 6 hours of O_3/GAC operation. The fraction of micropores also increased from 12.6 % to 20.1 %, while both fractions of meso- and macropores slightly decreased compared to the fresh GAC. These results indicate that the increase in BET surface area was mainly attributed to the increase in micropores. The textural alteration of the GAC after 6 hours of O_3/GAC operation is consistent with previous studies [57-59] that reported an increase of surface area at low doses of O_3 exposure due to carbon gasification.

The BET surface area of F400 GAC after 20 hours of operation decreased to 753 m^2/g (~ 10% decline compared to the fresh GAC and ~ 15% decline compared to the GAC after 6 hours of operation). This decrease in BET surface area could be a consequence of two factors: (a) destruction of the pore structure and possible blockage of the pores entry and/or (b) sorption of contaminants into pores. In all three GAC samples, the total pore volume was dominated by mesopores, followed by micropores, and macropores. Overall, the results showed that the GAC surface physical destruction during O_3/GAC increased with the exposure time in the first 6 hours of operation. While the impact of O_3 during the O_3/GAC process at 0.5 mg O_3/mg DOC initially led to an increase in BET surface area, the effect of continuous exposure of O_3 to the GAC for 20 hours resulted in a decrease in BET surface area and destruction of its structure.

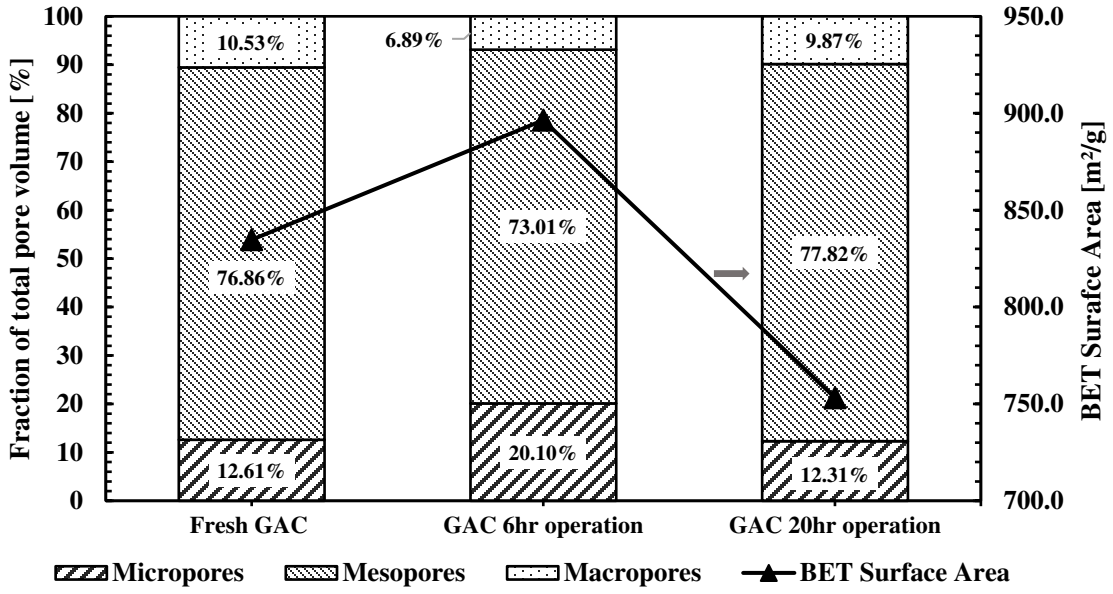

Figure 3.7. Fractions of the total available surface area and pore volume constituted by micropores, mesopores, and macropores

3.4.4.2. XPS analysis

Figure 3.8 shows the survey scan spectra of GAC used during the O_3/GAC experiment. A 4-fold increase of the O_{1s}:C_{1s} ratio in GAC after 20 hours of O_3/GAC compared to the fresh GAC was found. This increase indicated the impact of ozonation on the GAC surface and is consistent with the findings of Kawamoto et al. [60] and Park et al. [58]. Table 3.1 summarizes the O_{1s} and C_{1s} core level spectra for fresh GAC as well as GAC after 20 hours of O_3/GAC operation (Figure S2) [57, 61-63]. These results showed an increase in carboxylic acid functional groups accounting for approximately 50% of acidic sites on the GAC surface after 20 hours of O_3/GAC operation in agreement with previous reports [57, 58, 64]. Moreover, the O_3/GAC treatment process also led to an increase in ether functional groups on the GAC surface. These changes of the GAC surface functional groups may have an important impact on the polarity of the surface and consequently, on the GAC's adsorption behavior leading to selective adsorption of certain MPs [58, 65, 66]. Franz et al. [67] reported that surface oxygen groups, particularly carboxylic functional groups, initiated the formation of water clusters via H-bonding that can lead to a reduction of adsorption capacity.

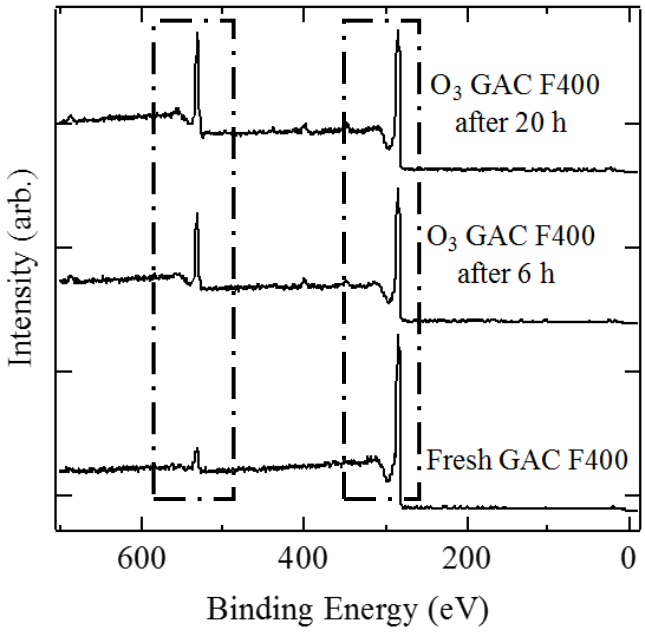

Figure 3.8. Survey spectra of: fresh F400 GAC, GAC after 6 hours of O3/GAC operation, and GAC after 20 hours of O3/GAC operation showing increasing O_{1s} signal for increased exposure time.

Table 3.1. XPS results of O1s and C1s for fresh F400 GAC and F400 GAC after 20 hours of O3/GAC operation

Functional groups	Element	Binding energy [eV]	Fresh F400 GAC [% atomic]	O_3/GAC after 20h [% atomic]
C=O (carbonyl, quinone)	O(1s)	530.7	6.20	1.11
C−OH, C−O−C (hydroxyl, ethers)	O(1s)	532.1	23.8	47.9
R−COOH (carboxylic acids, anhydride, lactone)	O(1s)	533.3	37.5	48.1
C−C (graphitic, aromatic)	C(1s)	284.6	56.4	45.3
C−OH (C in hydroxyl)	C(1s)	286.0	23.4	24.9
C−O (ethers)	C(1s)	286.4	5.10	11.1
C=O (C in carbonyl)	C(1s)	287.3	3.64	5.31
R=H or alkyl (C in R−COO)	C(1s)	288.6	4.20	9.56
Л − Л* (transitions in aromatic)	C(1s)	291.0	7.20	3.85

3.5. Conclusion

The simultaneous utilization of O_3 and GAC (O_3/GAC) for the removal of MPs in municipal wastewater treatment was investigated. Experimental results revealed that O_3/GAC improved the abatement of selected MPs compared to ozonation-only. Among the investigated MPs, TCEP, sucralose, and meprobamate exhibited an enhanced removal compared to their sum of ozonation-only and adsorption-only. However, the overall effectiveness of O_3/GAC substantially decreased after extended O_3 exposure, indicating that GAC did not contribute as a catalyst and its promotive effect came to a halt for most of MPs (with exception of sucralose and NMOR) after 20 hours of operation.

O_3/GAC initially led to an increase in BET surface area (mainly micropores) that had an impact on the improvement in adsorption removal of investigated MPs (except NMOR). However, continuous exposure of O_3 ultimately caused structural damage to the GAC surface and led to a decrease in BET surface area in the final stages of the experiment. A 4-fold increase of O_{1s}:C_{1s} ratio was observed on the GAC surface after 20 hours of O_3/GAC operation, in comparison to the fresh GAC. This increase in oxygen containing functional groups, particularly carboxylic functional groups, could hinder the sorption of MPs into the GAC. Overall, the experimental data suggests that the combination of O_3 and GAC at optimum operational conditions (based on the wastewater matrix) has the potential for removing O_3-refractory MPs with different adsorption capacity in a single treatment step during potable reuse applications. An automation step of renewing the GAC in the O_3 contactor could improve the treatment process to maintain its highest performance.

3.6. References

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CHAPTER 4

EFFECT OF PRE-OZONATION ON NANOFILTRATION MEMBRANE FOULING DURING WATER REUSE APPLICATIONS

Modified from a paper published in the Journal *Separation and Purification Technology*[1]

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4.1. Abstract

The selection of appropriate purification technologies for the potable reuse of municipal wastewater effluent is an important component of water resource management. In this study, a fully automated high-pressure bench-scale membrane system was used to investigate the impact of pre-ozonation of wastewater effluent on nanofiltration (NF) fouling during reuse applications. A commercial polyamide NF membrane was employed to evaluate the impact of pre-ozonation on fouling and determine an effective specific ozone dose. The results indicate that pre-ozonation of sequencing batch reactor membrane bioreactor (SBMBR) effluent with a relatively low specific ozone dose (0.2 mg O_3/mg DOC) effectively mitigated a significant portion of fouling on the membrane compared to filtration without pre-ozonation. However, increasing the specific ozone dose to 0.4 mg O_3/mg DOC did not provide a significant additional benefit. The dissolved organic carbon removal performance of the NF membrane did not show a substantial change when pre-ozonation was applied and remained relatively constant which may be due to the relatively low applied specific ozone dose. Organic fouling was suspected to be the main fouling mechanism during SBMBR filtration with NF membrane.

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4.2. Introduction

Population growth and climate change has placed significant stress on finite conventional water resources across the globe [1]. Development of cost-effective and robust purification technologies with the capability of treating lower quality waters such as municipal wastewater treatment plant (WWTP) effluent for reuse applications is becoming an important component of water resource management [2]. Membrane filtration technologies are well established and generally sufficient in removing a variety of contaminants during the reclamation of unconventional water resources. Nanofiltration (NF) is able to retain small molecular weight organic compounds (> 200 Daltons) [3-7] and a wide range of micropollutants such as pesticides, endocrine disrupting compounds, and pharmaceuticals, providing high quality water for potable reuse applications [5, 6, 8-11]. Numerous NF membrane systems have already been implemented in the drinking water industry [12-18]. However, despite NF's efficient retention performance, membrane fouling is still a major impediment leading to a reduction in membrane permeability and causing a substantial increase in operation and maintenance (O&M) costs. Membrane fouling is a complex process in which organic and inorganic foulants accumulate on the membrane surface and form a cake or gel layer causing a significant increase in hydraulic resistance [19-21]. Moreover, the deposition of foulants on the membrane surface along with subsequent cleaning processes over time leads to deterioration of membrane materials which instigates a decline in effluent quality and ultimately shortens the membrane lifetime [22]. Effluent organic matter (EfOM) and natural organic matter (NOM) have proven to be the major source of fouling during operation of high-pressure membrane processes such as reverse osmosis (RO) and NF during reuse applications [23-26].

The main approaches taken to mitigate membrane fouling are typically pretreatment processes, and modification of membrane materials and/or feed water chemistry. Application of ozone (O_3) as pretreatment is one of the potential technologies to minimize membrane fouling. O_3 is a strong oxidant that represents a hybrid structure with two possible resonances [27]. While the positive charge on the central oxygen atom counts for the electrophilic nature of the O_3 molecule, the negative charges on the terminal atoms imparts its nucleophilic behavior [5, 28]. According to von Gunten [29], the electrophilic property of O_3 is mainly responsible for its rapid reaction with unsaturated bonds that transforms them into oxygenated saturated functional groups including aldehydes, ketones, and particularly, hydrophilic reaction products such as carboxylic acids. These

hydrophilic reaction products hypothetically have a lower tendency to adsorb on the membrane surfaces which accounts for one of the main factors for organic fouling mitigation [5]. Numerous studies at the bench and pilot scale have evaluated the effect of pre-ozonation on the flux performance of microfiltration [30-36] ultrafiltration (UF) [37-45], and NF [8, 14, 46-51] with different feed waters. While some studies have assessed pre-ozonation as an efficient method to mitigate membrane fouling, other studies showed no significant fouling mitigation by employing pre-ozonation, which could be due to difference in membrane type (polymeric versus ceramic), pore size (MF, UF, or NF), feed water chemistry, O_3 dose, and surface chemistry of the membrane [8]. The authors are not aware of any study evaluating the effect of pre-ozonation to downstream NF for treating WWTP effluent for potable reuse applications.

In terms of total dissolved solid (TDS), according to Thompson et al. [52], between 200-400 mg/L of salt from different sources such as human excretion, gray water, water softeners, and industrial contributions is entering to wastewater streams. The United States Environmental Protection Agency (U.S. EPA) has set a secondary maximum contaminant level (MCL) for TDS at a concentration of 500 mg/L due to aesthetic reasons for consumers [52]. Hence, geographic variations of TDS concentrations as well as the capacity of blending the treated water with other potable water supplies in case of elevated TDS concentrations are also important factors for the application of lower-pressure NF membranes for potable reuse. However, Bellona et al. [53] reported a NaCl rejection range of 85-95% for the NF90 (feed water with 2000 mg/L NaCl) as well as 97.7% for $MgSO_4$ (feed water with 2000 mg/L $MgSO_4$). Therefore, the NF90 membrane provides an adequate rejection of TDS that would allow its application in potable reuse applications with a wide variety of source water salinity.

The main objective of this study was to evaluate the effect of pre-ozonation on fouling behavior of NF when treating wastewater effluent for potable reuse applications and the potential to improve membrane treatment. For this purpose, the fouling propensity of an NF membrane (NF90) at two different O_3 doses was investigated using a fully automated high-pressure bench-scale membrane system. In addition to membrane characterization, the correlation between fouling mitigation and organic carbon removal performance of the membrane was investigated.

4.3. Material and methods

4.3.1. Feed water quality and analysis

Feed water used for membrane testing was collected from an 8,000 gallons per day (30 m^3/d) pilot scale sequencing batch membrane bioreactor (SBMBR) system that receives raw wastewater from a 250-unit student apartment complex at Colorado School of Mines (Golden, Colorado). A complete description of the SBMBR system is provided elsewhere [54]. The concentration of key feed water quality parameters is summarized in Table 4.1. Feed water samples were analyzed for dissolved organic matter (DOC) using a carbon analyzer (Shimadzu ion TOC-L, Columbia, MD). Prior to each analysis, samples were filtered with 0.45 µm PVDF syringe filter (VWR, Radnor, PA). Chemical oxygen demand (COD) was analyzed using a Hach DR 6000 (Loveland, CO). For measurement of anions, ion chromatography (IC; ICS-900, Dionex, Sunnyvale, Ca), was employed, while cations/metals were analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES; optima 5300 DV, PerkinElmer, Fremont, CA). Prior to metal analysis, samples (10 mL) were fortified with 2 mL of 50% (v/v) HNO_3 (Fischer scientific). Conductivity was determined using a Cole Parmer EC Meter (model 1481-91) employing Standard Method 2510. pH measurements were taken with a Beckman 260 portable pH meter (Beckman, Fullerton, CA).

Table 4.1. Summary of main chemical institutes in the influent water

Analytes	Unit	Concentration
DOC	[mg/L]	5.7±0.20
COD	[mg/L]	17.16± 0.27
Total N	[mg/L]	1.78± 0.04
$NO3^-$- N	[mg/L]	0.68 ± 0.01
NO_2^--N	[mg/L]	0.12 ± 0.01
Br^-	[µg/L]	62.7 ±2.51
PO_4^{3-}	[mg/L]	10.51± 0.20
SO_4^{2-}	[mg/L]	90± 0.52
Cl^-	[mg/L]	75.98
F^-	[mg/L]	n.a.
Ca^{2+}	[mg/L]	43.50±1.9
Fe^{2+}	[mg/L]	0.1±0.1
Na^+	[mg/L]	57.8±0.4
Mg^{2+}	[mg/L]	9.85±0.12
pH	-	7.03±0.1

n.a: not available

Table 4.1. continued

Analytes	Unit	Concentration
Conductivity	µS/cm	608±2.08
Turbidity	NTU	0.04±0.01

4.3.2. Bench-scale system setup

A bench-scale high-pressure cross-flow membrane filtration system was used to evaluate fouling behavior of an NF membrane under different operational conditions. The membrane cell unit consisted of two rectangular plates with the dimension of 14.6 cm x 9.5 cm x 0.86 cm for channel length, width, and height, respectively. The membrane cell provided an active area of 139 cm^2 as well as cross-sectional flow area of 0.82 cm^2 with a 34-mil spacer on the feed side and a tricot spacer on the permeate side. To minimize adsorption of any contaminants, the system was mainly constructed with stainless-steel components. The filtration experiments were performed in recirculation mode during which both reject and permeate flow were returned to the stainless-steel feed tank. During experiments, permeate flow rate and reject flow were monitored with inline flowmeters (Atrato, series 700 and (JLC, series 800 respectively). Control of the membrane flux was achieved using a control valve (HASS, EPV-SS-6L) and transmembrane pressure (TMP) was monitored using a pressure transducer (OMEGA, PX-309) while recovery experiments were conducted by discharging the permeate and calculating the recovery throughout the entire recovery experiments. All experiments were conducted under controlled temperature using an automated valve on a heat exchanger with building cooling fluid, coupled with a temperature probe. The total dissolved solid (TDS) rejection performance of the membrane during experiments was measured using a conductivity probe (Cole-Palmer, GH19500). To enable stable operating conditions and automatic control/monitoring of the discussed bulk quality parameters, a supervisory control and data acquisition (SCADA) was used. The process flow diagram of the bench-scale system is illustrated in Figure 4.1.

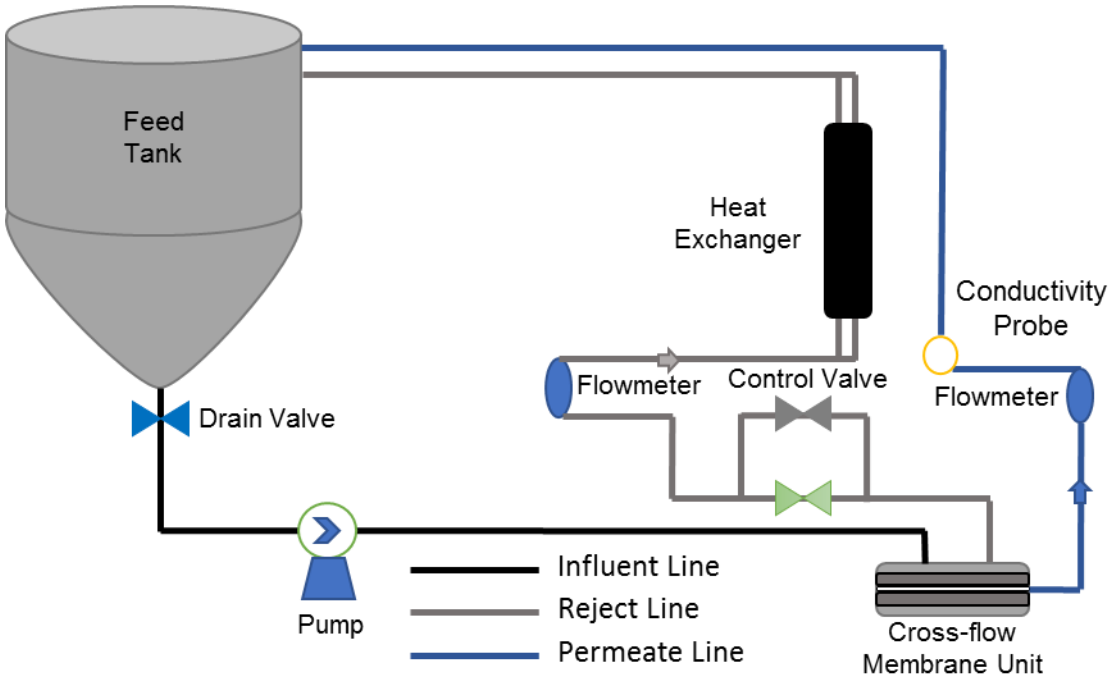

Figure 4.1. Process flow diagram of bench-scale high-pressure membrane system (not to scale)

4.3.3. Membrane fouling propensity test

A commonly used nanofiltration membrane, NF 90 (DOW Filmtec, Midland MI) was selected to evaluate the fouling behavior under different experimental conditions. The properties of the virgin NF90 membrane are summarized in Table 4.2. Prior to each membrane filtration experiment, virgin NF90 specimens were soaked in DI water and stored at 4 ºC for minimum of 24 hours. The DI water in the soaking tank was changed periodically. Before starting the fouling experiment, NF90 membrane specimens were compacted using DI water for 24 hours at the same pressure applied at the beginning of the fouling experiments. For fouling and rejection experiments, the feed tank was filled with 10 L of SBMBR effluent. The feed flow was set and maintained at 2 L/min equaling a nominal cross-flow velocity of 0.4 m/s. Using the automated cooling system, the temperature was set and maintained approximately at 20 ± 0.5 ºC. An aggressive permeate flux of 30 $Lm^{-2}h^{-1}$ was evaluated to investigate whether pre-ozonation could potentially allow NF operation at elevated flux. All fouling experiments were conducted in triplicate for at least 36 h to ensure that each membrane reached an apparent steady-state condition. In order to quantify the fouling extent of NF90, the normalized specific flux was employed. Equation 4.1 was used to calculate the specific flux, J_s ($L.m^2.h^{-1}.kPa^{-1}$). The normalized specific

flux, J´, was then calculated by dividing J/ΔP by the clean membrane specific flux as is shown in Equation 4.2.

$$J_S = \frac{J}{\Delta P} \tag{4.1}$$

$$J'_S = \frac{\left(\frac{J}{\Delta P}\right)}{\left(\frac{J}{\Delta P}\right)_0} \tag{4.2}$$

where: J_s = specific flux ($L.m^2.h^{-1}.\ kPa^{-1}$)

ΔP= transmembrane differential pressure (kPa)

Due to the deviation of the set temperature (20 ± 0.5 ºC), the temperature correction factor using Equation 4.3 [55] was employed to normalize the specific flux to 20 ºC.

$$TCF = \exp[\ U\ \times (\frac{1}{T+273} - \frac{1}{298})] \tag{4.3}$$

where: TCF = temperature correction factor (dimensionless

T = water temperature (ºC)

U = membrane-specific manufacture-supplied constant (1/K) = 3020 (Filmtec membrane).

4.3.4. Calculation of scaling tendency

OLI stream analyzer (OLI systems Inc., Cedar Knolls, NJ) was used to estimate the scaling tendency of the SBMBR effluent. Generally, scaling tendency is defined as the ratio of the activity product (Q) of a solution to the solubility product and can be determined with Equation 4.4. [56].

$$Scaling\ tendency = \frac{Q}{K_{SP}} \tag{4.4}$$

where: K_{SP} = solubility product

Q = activity product.

It is estimated that when Q/K_{SP} >1.0 the scaling of the solid on the membrane is possible and in case of $Q/K_{SP} \leq 1.0$, there is small tendency for scaling on the membrane [57]. The results of OLI software scaling tendency are described in the supporting information (SI).

4.3.5. Membrane characterization

4.3.5.1. Fourier transform infrared spectrometer

Characterization of functional group on the virgin and fouled NF90 membrane were conducted using a Nicolet Nexus 870 Fourier transform infrared (FTIR) spectrometer (Nicolet 4700 FTIR, Thermo Electron Corporation, Madison, WI). By adapting the attenuated total reflection (ATR) method, the spectra were recorded with 500 scans and a wave number resolution of 2.0 cm^{-1}. Virgin and fouled NF90 membrane specimens were dried in a desiccator for 24 hours prior to FTIR testing.

4.3.5.2. Environmental scanning electron microscopy

The surface morphology and structure of the NF 90 membranes was characterized by employing environmental scanning electron microscopy (ESEM) (Quaanta 600, FEI Compony, Hillsboro, OR) in vacuum mode. A semi-quantitative elemental composition of virgin and fouled membranes integrated from ESEM was conducted by energy dispersive spectroscopy (EDS).

Table 4.2. Properties of the NF90 membrane [8, 58]

Properties of NF 90	
Material	Polyamide, TFC
Molecular weight cut-off [g/mol]	200-300
Maximum pressure [MPa]	4.1
Maximum temperature [ºC]	45
pH	3-10
Hydraulic resistance [m^{-1}], 10^{13}	4.0-7.7
Contact angle	63.2 º

4.3.5.3. Three-dimensional fluorescence spectroscopy

To further investigate the characteristics of effluent organic matter (EfOM) fractions throughout the pre-ozonation treatment, excitation emission matrix (EEM) fluorescence spectroscopy tests using Aqualog spectra fluorescence (Horiba, Edinson, NJ) for different water samples were performed. To avoid quenching of fluorescence, generated samples were diluted

with Milli-Q to adjust the DOC concentration to less than 2 mg/L and filtered with 0.45 µm PVDF syringe filter (VWR, Radnor, PA). Consequently, the results were multiplied by their respective dilution factors. Upon each fluorescence measurement, a blank sample containing Milli-Q water was run under identical conditions to eliminate the effect of Raman scattering. After the correction for inner filter effects and Rayleigh scattering, the recorded EEMs were normalized to Raman Units (RU) to enable the comparison of fluorescence intensities across different samples. The range of excitation wavelength was set from 240 to 450 nm covering an emission range of 250 to 600 nm with 2.33 nm (4 pixel) increments. A detailed analytical procedure is described elsewhere [59].

4.3.6. Pre-ozonation setup

Ozonation of the feed water was achieved through addition of an ozonated stock solution. The O_3 stock solution was generated by passing oxygen gas (93±3 %) (DeVilbiss oxygen concentrator) through an O_3 generator (Trigen LAB2B, East Kilbride, Scotland) and diffusing O_3 gas into a 0.6 m long and 0.05 m diameter polycarbonate column filled with DI water at temperature of approximately 2 ºC. The O_3 concentration of the stock solution was measured continuously using a UV based photometric dissolved O_3 meter (CHEMetric, I-2019). To this end, an appropriate amount of concentrated O_3 stock solution was added to the feed tank.

4.4. Results and discussion

4.4.1. Justification of optimum ozone dose

In general, the consumption of O_3 in water can be classified in two different stages of reactions, the instantaneous O_3 demand (IOD) (0-20 seconds: typically the time required for the first measurement of O_3 concentration) and the slow decay stage that can be expressed as a pseudo first order reaction [60]. The presence of residual O_3 concentration in feed water can damage polyamide membranes resulting in membrane failure within a short amount of time [61, 62]. In order to prevent the contact of the O_3 molecule with the polyamide membrane, some water and wastewater facilities employ oxidant quenching agents such as sodium metabisulfite which increases O&M cost and consequently is not an attractive approach [63]. For this reason, finding the optimum ozone dose that is instantaneously consumed in the feed water while providing sufficient efficacy for fouling mitigation can be considered as a cost effective option [63]. In this

study, an O_3 decay test was performed to determine the optimum specific O_3 dose for fouling mitigation experiments. The IOD was chosen to be the threshold of selected specific ozone dose. The residual concentration of different specific O_3 dose was measured every 20 seconds for two minutes. As a result, specific O_3 dose of 0.4 mg O_3/mg DOC was found to be the closest value to the IOD which is similar to the value found by Park et al. [63]. From the lower values (0-0.4 mg O_3/mg DOC), the middle specific O_3 dose of 0.2 mg O_3/mg DOC was also selected for fouling experiments.

It is important to note that oxidation by-products may be formed by reaction of O_3 and/or hydroxyl radical (OH^*) with different components of wastewater effluent [27]. Among oxidation by-products, some of them such as bromate (BrO_3^-) and nitrosamines, e.g., N-nitrosodimethylamine (NDMA) are reported as (possible) human carcinogens and therefore, minimization of their formation during ozonation is of great importance [64, 65]. Bromate formation in bromide (Br^-) containing waters along with NDMA formation when NDMA precursors such as hydrazine and sulfamides are present, are the main concerns for ozone applications [27, 29, 64, 66]. For drinking water, a guideline/standard concentration of 10µg/L was set for bromate [65, 67, 68], while the acute and chronic environmental quality standard (EQS) of 50 µg/L was set for bromate from Ecotox Center Eawag-EPFL [69]. For NDMA, World Health Organization set a guideline concentration of 100 ng/L for drinking water [70] while other countries such as USA and Germany proposed a lower value of 10 ng/L [71-73]. Several studies reported that for specific ozone doses of $\leq$ 0.45 mg O_3/mg DOC, the O_3 and OH^* exposure shows a very low value which leads to a low bromate yield (<1%, w/w) [64, 74, 75]. Myllykanags et al. [76] reported that bromate formation exceeded the 10 µg/L only when the initial bromide ion concentration was greater than 100 µg/L while von Gunten et al. [77]. stated that exceeding bromate concentration of 25 µg/L will be only in waters with high bromide concentration (> 200 µg/L). In this study the measured bromide concentration in the SBMBR effluent was 62.7 ± 2.51 µg/L which was under both reported threshold values from Myllykanags and von Gunten et al. [76, 77]. In addition, all applied specific ozone doses in this study were below 0.45 mg O_3/mg DOC that as discussed, assure a low bromate yield (<1%, w/w). Previous research indicated that NDMA formation potential in MBR effluent with ozone pretreatment was low (data not shown) however; NDMA formation potential is site specific and should be evaluated prior to pre-ozonation applications.

4.4.2. Impact of pre-ozonation on membrane fouling and DOC rejection

The feasibility of fouling mitigation via pre-ozonation during the filtration of SBMBR effluent was investigated during bench-scale NF filtration experiments. The trends of normalized specific flux behavior during filtration (a) without pre-ozonation; (b) with pre-ozonation at 0.2 mg O_3/mg DOC; and (c) with pre-ozonation at 0.4 mg O_3/mg DOC are presented in Figure 2. All measurements were conducted in triplicate for at least 36 hours under constant cross-flow velocity, flux, and temperature. The standard deviation is shown in gray and the intersection of different conditions is illustrated in dark gray. During filtration without pre-ozonation, the normalized specific flux decreased sharply from 1 to approximately 0.73 during the first 17 hours and then gradually decreased to about 0.7. By comparing filtration with pre-ozonation, pre-ozonation led to a distinct fouling decrease. The specific ozone dose of 0.2 mg O_3/mg DOC was able to mitigate the fouling and increase the normalized specific flux significantly compared to filtration without pre-ozonation. A slight fouling alleviation was observed when the specific ozone dose was increased to 0.4 mg O_3/mg DOC indicating that doubling the specific ozone dose did not result in a significant fouling reduction.

Potable reuse installations and practitioners often use DOC as a surrogate for contaminant removal and thus, achieving high DOC removal is typically a priority for potable reuse applications [78]. The reaction of O_3 with organic compounds results in the formation of low-molecular weight compounds [79] and, increasing the specific ozone dose generally increases the amount of low-molecular weight compounds that can lead to a decline in total DOC removal by membranes [27]. However, previous studies have demonstrated variable data in terms of DOC removal [40] that may be due to differences in water type as well as specific ozone dose. To assess the impact of pre-ozonation on DOC removal, as well as prediction of membrane's behavior in larger scale application, rejection experiments were performed as a function of permeate flux and water recovery.

The impact of pre-ozonation on DOC removal by NF90 as a function of flux (10-60 L/m^{2}h) and recovery (10-80%) is depicted in Figure 4.3. The rejection of DOC did not follow a close relationship with flux and recovery and remained constant (approximately 94%) for all experimental conditions. This behavior may be due to the low specific ozone dose that did not lead to substantial formation of low-molecular weight compounds.

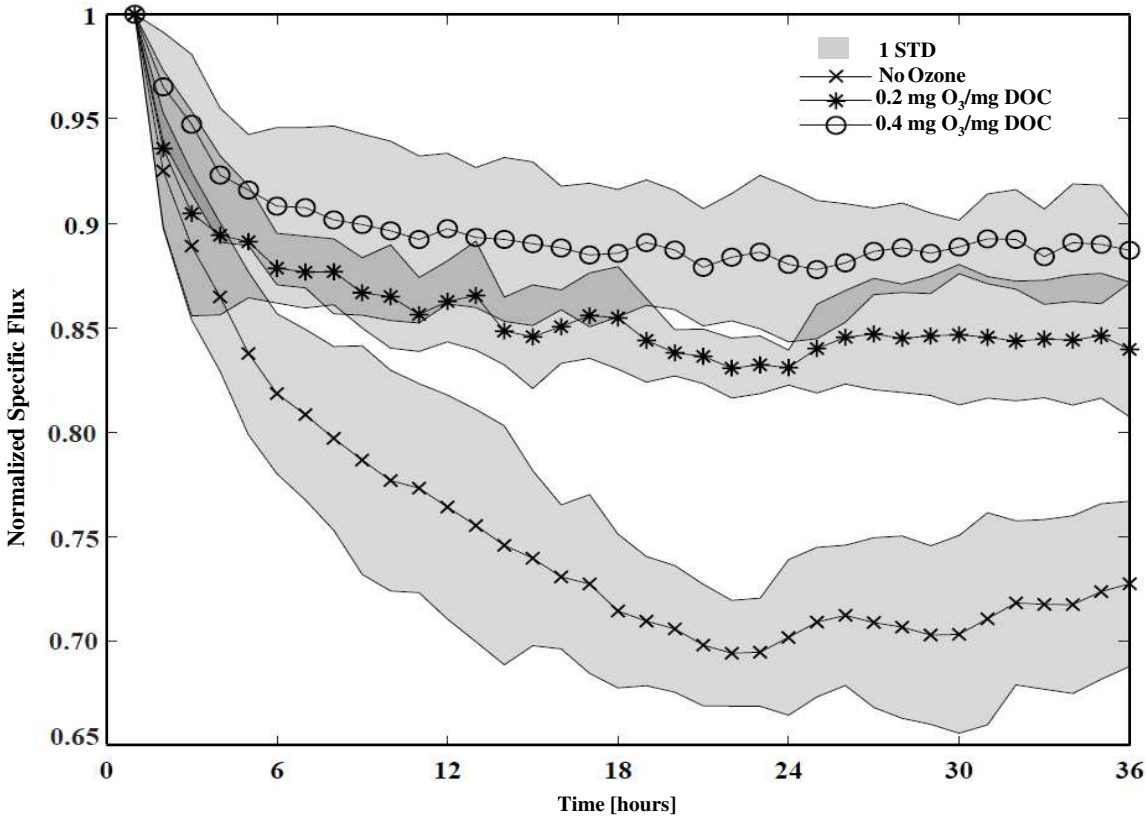

Figure 4.2. Normalized specific flux during filtration of SBMBR effluent with and without pre-ozonation. All measurements were conducted under constant flux (30 L/m2h), temperature (20ºC), and pH (7.1± 0.1)

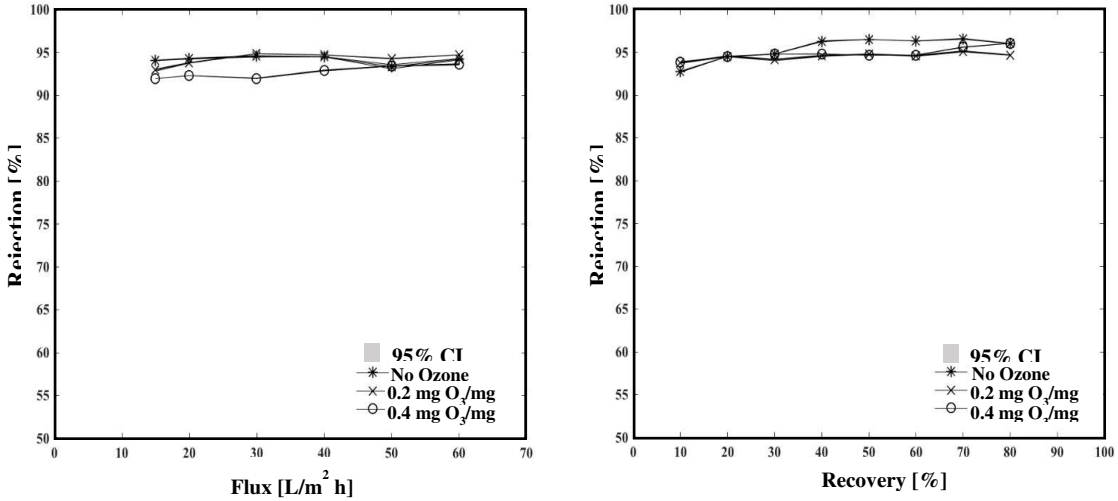

Figure 4.3. Observed rejection of DOC with and without pre-ozonation at different fluxes (left) and recoveries (right)

4.4.3. Foulant characterization

In addition to organic fouling, the implementation of NF for water reuse at different scales (from bench to full-scale) can face the challenge of inorganic scaling depending on the feed water characteristics and system operation (i.e., recovery). In general, inorganic scaling is a limiting factor to achieving high recovery in high-pressure membrane process including NF [63, 80]. Therefore, the tendency of scaling for the selected SBMBR effluent as a function of recovery, temperature, and pressure (data shown in Appendix C) was investigated. To this end, the results of analysis for cation and anions concentration in SBMBR effluent were used as the input data for the OLI software for prediction and theoretical quantification of scaling tendency. In addition, ESEM-EDS measurement of samples was employed to compare the elemental content between fouled and virgin membrane. The results of OLI software and ESEM-EDS indicates that inorganic scaling during fouling experiments was minimal and that organic matter fouling dominated.

4.4.4. Impact of organic fouling on membrane characteristics

Virgin and fouled NF90 membrane specimens were analyzed with FTIR to characterize functional groups and surface chemistry changes caused by organic fouling. By comparing FTIR spectra between the virgin and fouled membranes (Figure 4.4), it could be observed that the virgin NF90 membrane had peaks at a wave number of 679 cm^{-1}, reflecting possible aromatic functional groups, and 1400-1500 cm^{-1} reflecting possible aliphatic moieties, were weakened when the fouling layer was present [81]. On the fouled membrane with no pre-ozonation, aliphatic methylene groups [82] exhibited a peak at wave number near 2920-2930 cm^{-1} while this peak could not be observed for the fouled membranes with pre-ozonation as well as the virgin membrane. For both fouled membrane with pre-ozonation, the peak at a wavelength around 1700 cm^{-1} was strengthened compared to virgin and without pre-ozonation indicating that the major component of foulants were possibly saturated aliphatic ketone and carboxylic acids [81]. Overall results of FTIR showed the existence of organic fouling. ESEM micrographs of virgin and fouled NF90 membrane specimens with and without pre-ozonation are shown in Figure 4.5. Comparing the surface of virgin NF90 (a) and fouled membrane without pre-ozonation (b) provide visual evidence that organic fouling led to a change of membrane surface structure. However, the micrographs of pre-ozonated membranes were similar and did not show a substantial difference to the virgin NF90 membrane.

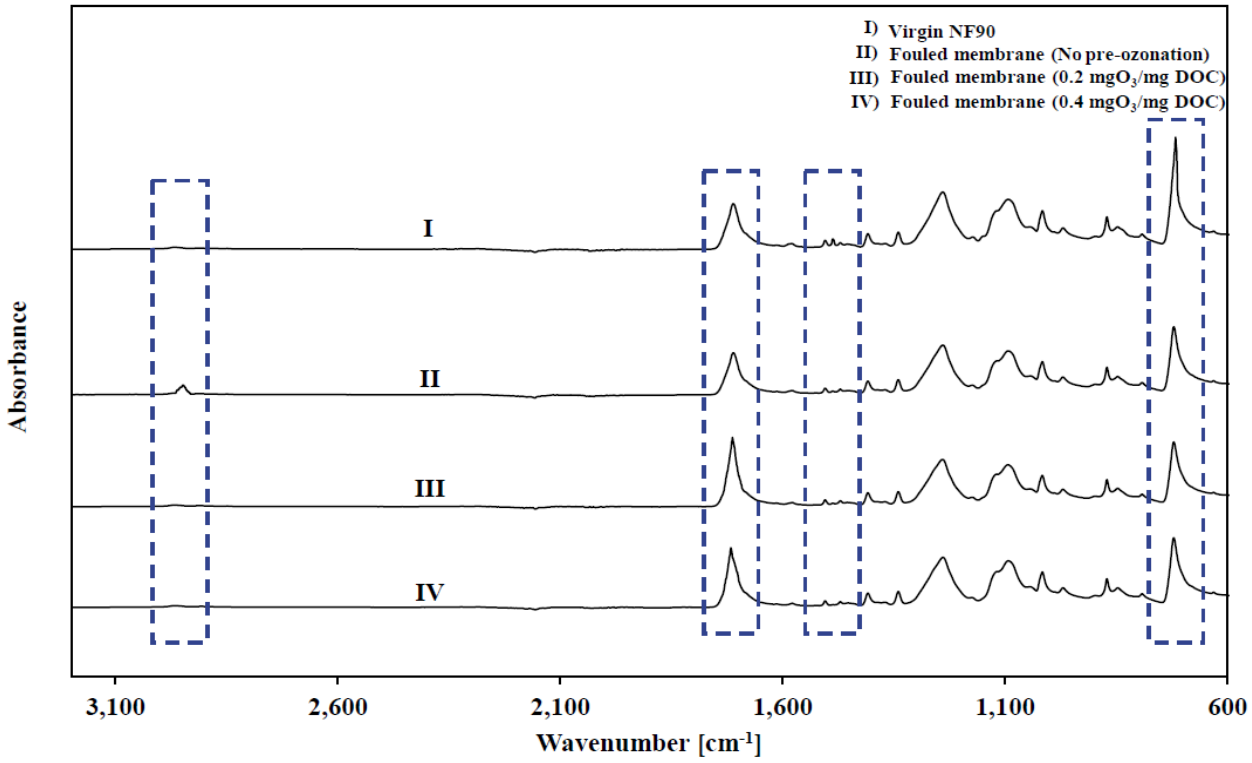

Figure 4.4. Spectra of FTIR of virgin and fouled NF90 membrane specimens

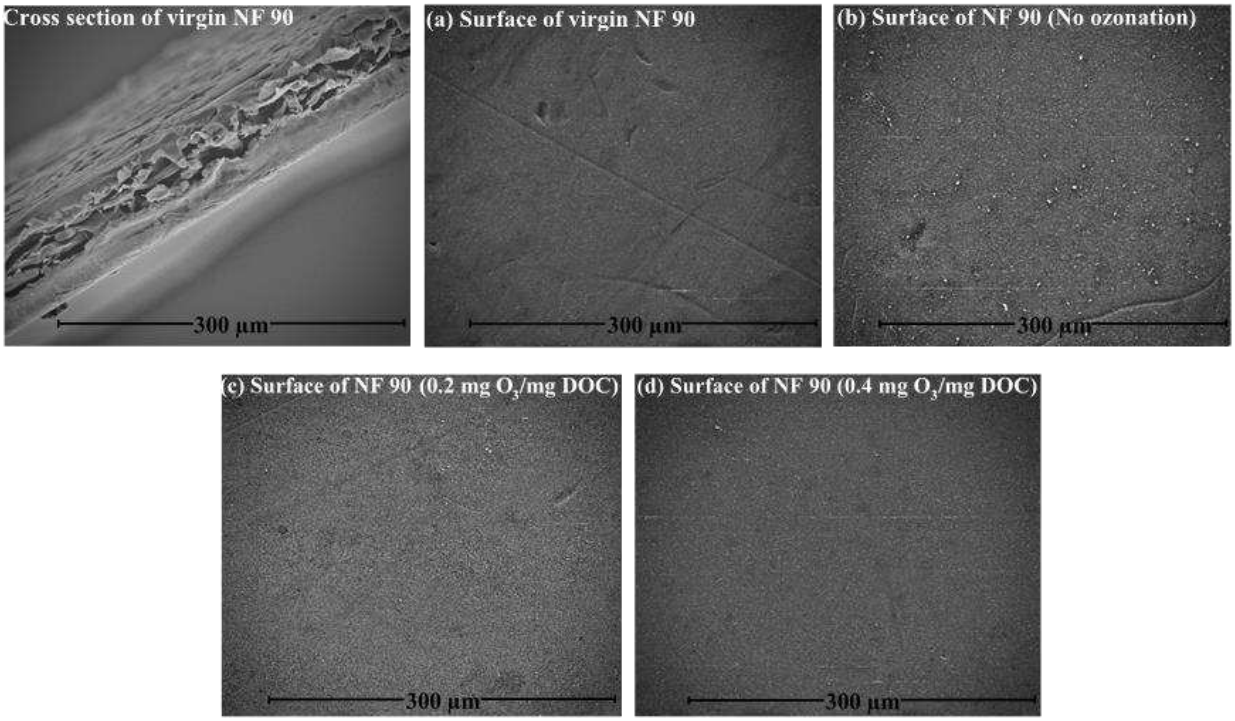

Figure 4.5. ESEM micrographs of cross section and surface of virgin NF90 and fouling layers of fouled membranes

4.4.5. The alteration of effluent organic matter characterization through pre-ozonation

As discussed previously, the electrophilic property of O_3 in general, leads to rapid reactions with electron rich aromatic moieties [83] and transform them mainly to hydrophilic reaction products that have a lower tendency to adsorb on the relatively hydrophobic NF90 membrane. Based on past studies, the hydrophobic interaction between the NF90 membrane and foulants is considered to be the major fouling mechanism [63, 84]. A semi-quantitative assessment of the NOM/EfOM composition in SBMBR effluent through pre-ozonation was conducted using 3D-EEM fluorescence measurement. For each sample, 3D-humic

EEM fluorescence spectroscopy scanned the fluorescence signals at different emission and excitation wavelength and were normalized to the daily measured integral of the Raman water peak area in order to obtain the fluorescence intensity of the original sample [59, 85, 86] which generated a 3D grid (excitation x emission x intensity) in RU. The measurement tool can be used to classify fluorophores based on characteristic excitation and emission properties [87]. EEM scans generated from samples collected during filtration are shown in Figure 4.6. According to past research [88], fluorescence intensity in EEM scans can be classified into five regions associated with different fractions of EfOM; aromatic protein including tyrosine-like (region I) and tryptophan-like (region II); fulvic acid-like compounds (region III); soluble microbial byproduct-like (region IV); and humic acid-like compounds (region V).

The EEM spectra from SMBR effluent (Figure 4.6.a) shows three primary peaks in the II, III, and IV regions with the maximum intensity of 2.7 RU. After pre-ozonation with 0.2 mg O_3/mg DOC (Figure 4.6.b), the EEM spectra displays an overall attenuation in intensity. This trend continues with increasing specific ozone dose to 0.4 mg O_3/mg DOC (Figure 4.6.c) indicating that the introduction of O_3 led mainly to the decomposition of hydrophobic humic-like substances. After filtration with NF90, maximum fluorescence intensity declined from 2.7 to 0.2 RU. When comparing the EEM spectra of effluent samples, a relatively similar EfOM fraction in region I, II, II, and IV could be observed in effluent samples with no pre-ozonation (Figure 4.6.d) and effluent samples with 0.2 mg O_3/mg DOC pre-ozonation (Figure 4.6.e). Increasing the specific ozone dose (Figure 4.6.f) weakened the fluorescence intensity of region III. The relative fluorescence (%) of system influents in each described EEM wavelength region along with the trend of normalized total fluorescence calculated from the sum of integration of volume under EEM divided by DOC is summarized in Figure 4.7. The normalized total fluorescence calculated from EEM scans has

been reported as an indicator of hydrophobicity of organic matter content [63, 88]. A comparison of total fluorescence in Figure 4.7 shows a substantial decline after the pre-ozonation of SBMBR effluent indicating a decomposition of hydrophilic substance that is in agreement with the observed fouling mitigation (Figure 4.2) as well as substantial decline in specific UV absorbance which is defined as UV absorbance at 254 nm normalized by DOC concentration (specific UV absorbance (SUVA)) (data provided in SI). Increasing the specific ozone dose further decreased the total fluorescence. Region V associated with humic acid-like along with region III corresponding to fulvic-like compounds were the most difficult NOM/EfOM fraction to reduce at both applied specific ozone doses. It is important to note that 3D-EEM fluorescence spectroscopy, provided a semi-quantitative assessment on decomposition of groups of hydrophobic compounds to support a better understanding of fouling reduction through pre-ozonation, and did characterize the entire EfOM composition in its scans. A critical analysis of EEM to characterize dissolved organic matter is discussed elsewhere [89].

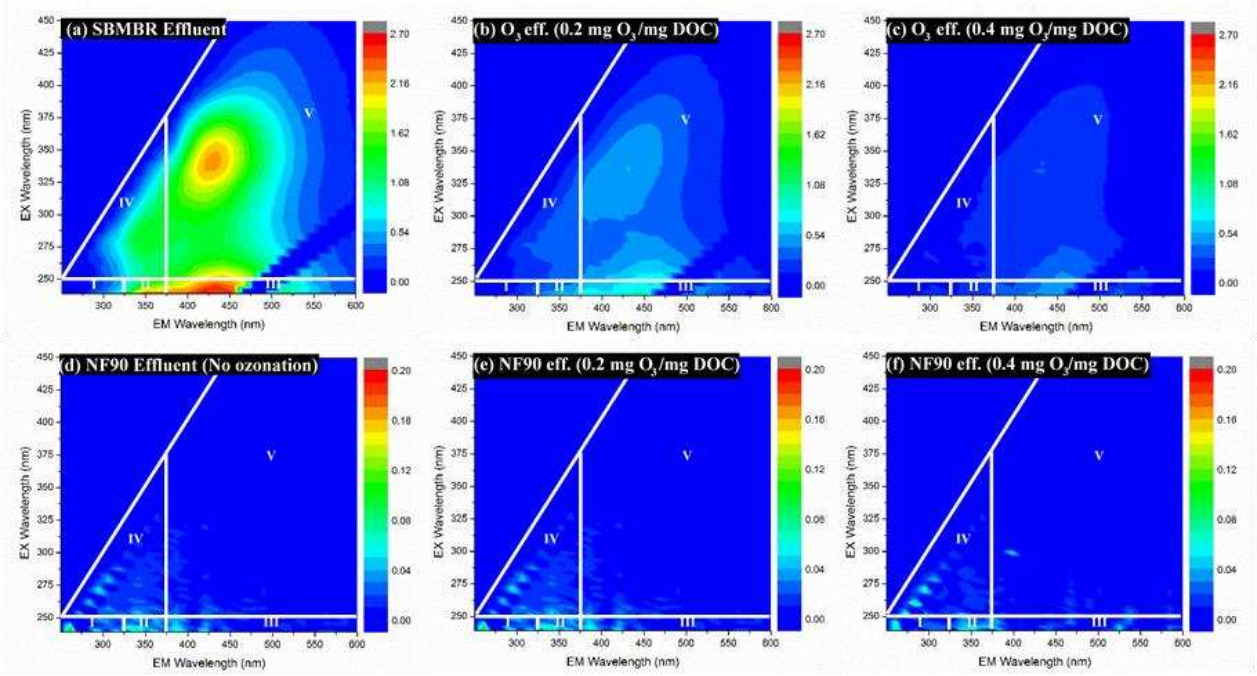

Figure 4.6. Excitation/Emission Matrices (EEM) throughout the treatment, classifying dissolved organic matter of (a) SBMBR effluent, (b) O_3 effluent of 0.2 mg O_3/mg DOC, (c) O_3 effluent of 0.4 mg O_3/mg DOC (d)NF90 effluent with no pre-ozonation, (e) NF90 effluent of 0.2 mg O_3/mg DOC, and (f) NF90 effluent of 0.4 mg O_3/mg DOC fraction into 5 regions: aromatic protein (I and II), fulvic acid-like compounds (region III), soluble microbial byproduct-like (region IV), and humic acid-like compounds (region V).

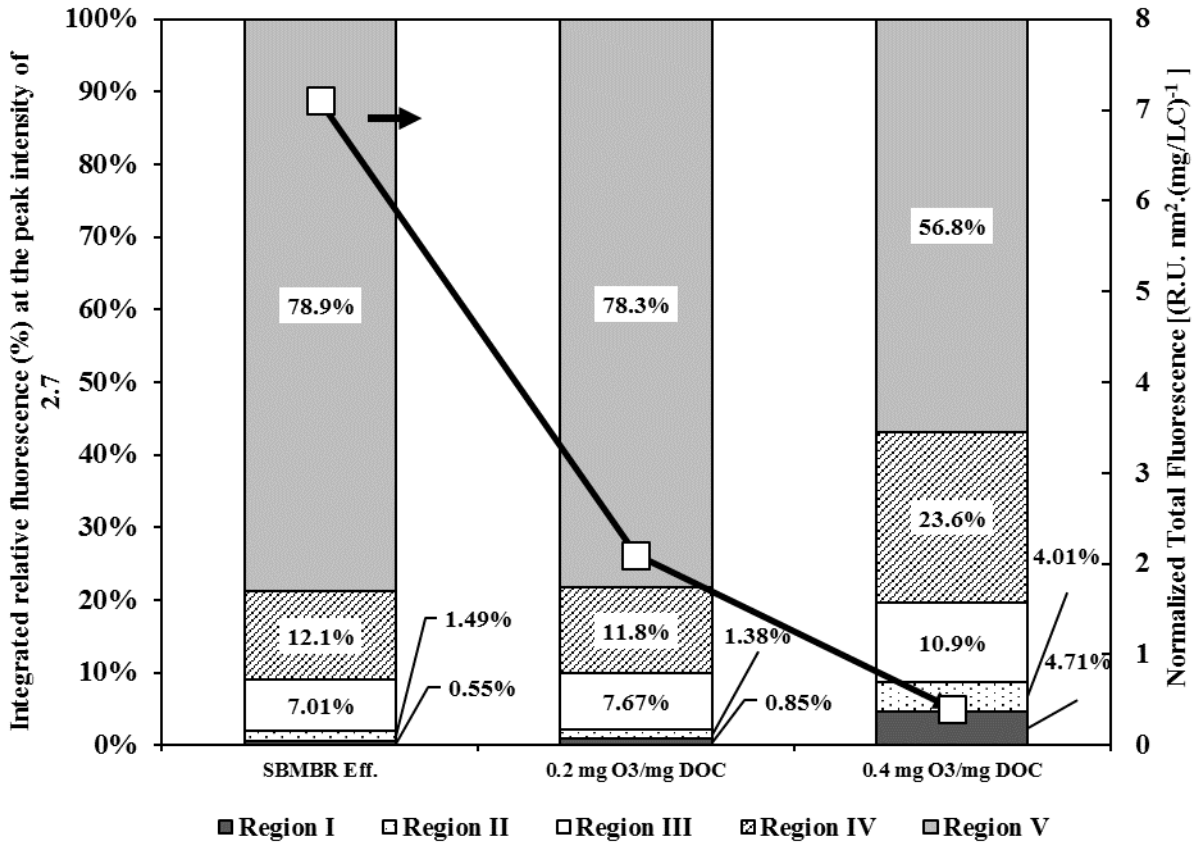

Figure 4.7. Total fluorescence and relative fluorescence (%) integrated in each defined region

4.5. Conclusion

With the objective of improving treatment technologies used during potable water reuse applications, this study examined the effect of ozonation as a pre-treatment process for reduction of polyamide NF membrane fouling when treating wastewater effluent (SBMBR, DOC: 5.7± 0.20). Fouling propensity of the NF90 membrane specimens at two different specific ozone doses (0.2 and 0.4 mg O_3/mg) was investigated using a fully automated high-pressure bench-scale membrane system. The results of pre-ozonation at a specific ozone dose of 0.2 mg O_3/mg DOC showed a significant reduction in fouling compared to the filtration with no pre-ozonation. However, increasing the specific ozone dose to 0.4 mg O_3/mg DOC did not provide a significant additional reduction in fouling. Moreover, it was found that pre-ozonation led to a reduction of total fluorescence indicating a decrease in hydrophobicity of the organic matter present in the feed water. The performance of the NF90 in rejecting DOC did not change after pre-ozonation and remained mainly constant among the conditions tested. In addition, DOC rejection by the NF90

membrane did not show a clear relationship with flux and recovery and had near constant rejection (approximately 94%) for all experimental conditions. This behavior may be due to the relatively low applied specific ozone doses, which did not lead to a substantial transformation of high-molecular weight compounds into low-molecular weight organic compounds. This research determined that using pre-ozonation during filtration of SBMBR effluent could be considered an option to improve operation of the NF90 membrane for potable reuse applications. Comparing the performance and costs associated with membrane cleaning versus pre-ozonation for fouling mitigation is suggested as a possible future area of research. A detailed evaluation on formation of bromate and NDMA is also suggested for future studies.

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CHAPTER 5
CONCLUSION

5.1. Research synopsis

A collection of three full-length research articles that comprehensively evaluated the role of O_3 in alternative treatment trains treating municipal wastewater effluent is presented in this dissertation. These investigations include: (a) a pilot-scale study that evaluated the O_3/GAC followed by BAF compared to conventional O_3-BAF for the removal of 1,4-dioxane and formation potential of DBPs during treatment of municipal wastewater effluent; (b) a pilot-scale assessment of O_3/GAC for the enhanced removal of different MPs in municipal wastewater effluent as well as the effect of O_3 on the physical and chemical properties of GAC during the O_3/GAC process; and (c) a benchmark evaluation of pre-ozonation on fouling behavior of NF when treating wastewater effluent for potable reuse applications to improve membrane treatment.

5.1.1. Summary of O_3/GAC-BAF for the removal of 1,4-dioxane and DBP precursors

The O_3-BAF pilot-scale system was investigated for the treatment of municipal wastewater effluent at three specific ozone doses (0.5, 0.7, and 1.0 mg O_3/mg DOC) and different empty bed contact times (EBCT; 15-45 min). The application of O_3/GAC to enhance the formation of $^{\cdot}OH$ was assessed at 1.0 mg O_3/mg DOC followed by BAF at 15-45 min EBCT. The effectiveness of selected treatment parameters was evaluated by comparing the removal of 1,4-dioxane, and the reduction of the formation of bromate, 35 DBPs, and 8 *N*-nitrosamines in post chloramination. A novel approach for the acclimation of the BAF process using fresh F400 GAC was developed and its performance was investigated using several methods including ATP measurements, ESEM, and BET analysis. Conventional ozonation removed 6-11 % of 1,4-dioxane, while BAF increased the removal to ~25%. O_3/GAC enhanced the removal efficacy of 1,4-dioxane to ~ 40%, while BAF increased the removal to ~50%. The findings of this study suggest that the presence of GAC during the ozonation treatment process used in potable reuse applications leads to an enhancement of the removal of refractory MPs while decreasing the formation of DBPs.

5.1.2. Summary of evaluation of O_3/GAC robustness and process optimization

Based on the successful performance of O_3/GAC for the abatement of 1,4-dioxane in the previous study, the research conducted in this portion of the study aimed to evaluate the efficiency of O_3/GAC at different O_3 and GAC doses for the enhanced removal of 13 different MPs in municipal wastewater effluent. The work conducted in this study also examined the robustness of O_3/GAC promotive effect as a function of time. The effect of O_3 on the properties of GAC surface during the O_3/GAC was investigated. Results from this study suggest an enhanced removal of TCEP, sucralose, and meprobamate compared to their sum of removal by ozonation-only and adsorption-only. The results of robustness experiments indicated that despite the enhanced removal during the initial phase of the O_3/GAC process, the overall effectiveness of the O_3/GAC substantially decreased after extended O_3 exposure. These findings suggest that the promotive effect of the GAC after 20 hours of operation substantially decreased. The impact of O_3 on the GAC surface led to an increase in BET surface area (mainly micropores) that resulted to an improvement in adsorption removal of the majority of investigated MPs. The automation of renewing GAC during O_3/GAC process can provide an optimum abatement of O_3-refractory MPs with low and high adsorption capacity within one treatment step during potable reuse applications.

5.1.3. Summary of impact of pre-ozonation of NF membrane fouling

While the findings from the work presented in the first two main chapters of this dissertation demonstrated the potential of non-membrane-based treatment processes for potable reuse applications, this portion of the study was designed to improve membrane-based treatment technologies used for potable water reuse applications. To this end, the impact of pre-ozonation of wastewater effluent on the operation (specifically fouling) of an NF membrane (NF90, Dow/Filmtec) was evaluated. Evaluation of NF90 fouling propensity indicated that pre-ozonation of SBMBR effluent at the relatively low specific O_3 dose of 0.2 mg O_3/mg DOC could effectively reduce a substantial portion of NF membrane fouling in comparison to NF filtration without pre-ozonation. Increasing the specific O_3 dose to 0.4 O_3/mg DOC during pre-ozonation did not show a significant additional reduction in fouling. Moreover, pre-ozonation did not affect the performance of the NF90 in rejecting DOC. This finding indicates that the relatively low applied specific O_3 doses did not lead to a substantial transformation of high-molecular weight compounds into low-molecular weight organic compounds with ability to pass through NF90.

5.2. Future work

Increasing water scarcity along with dramatic population growth and climate change has raised the gap between potable water supply and demand. In addition, despite the substantial progress in purification technologies in potable reuse applications, lack of fundamental understanding about how to approach and implicate the proper engineering solutions and poor decision-making process, has aggravated this growing challenge. As a result, fourteen of the world's 20 biggest cities are currently facing water scarcity or drought conditions [1]. For these reasons, the fundamental rethinking of how to approach the engineering problems in potable reuse of municipal wastewater is the first essential step that needs to be taken.

As a non-membrane-based treatment technology, O_3-BAF has the potential to be an alternative treatment step for RO for regions that do not have the capacity to implement RO as their main purification treatment process. Despite noticeable advantage of O_3-BAF, some obstacles remain. Future research should focus on employing a unanimous inoculation process of BAF system for reuse application. This could enable a more valid comparison between different BAF systems and helps for further optimization and improvement of BAF. Increasing the oxidation power through simultaneous use of O_3 and GAC can be an effective process for removal of hydrophobic and hydrophilic MPs in one treatment step. Finding the optimum dose of GAC and O_3 along with automatization of GAC renewal during the operation may allow the O_3/GAC process to maintain its enhanced removal performance.

For membrane there is likely e-based treatment, using pre-ozonation during filtration of wastewater effluent could be considered an option to improve operation of the NF90 membrane for potable reuse applications. Further investigations should focus on the comparison between different pre-treatments (i.e. pre-ozonation versus membrane cleaning) as well as cost analysis. Moreover, further evaluation of oxidation byproducts such as bromate and NDMA is also suggested for optimization of the O_3 dose.

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APPENDIX A

SUPPLEMENTARY INFORMATION FOR: EVALUATION OF ENHANCED OZONE-BIOLOGICALLY ACTIVE FILTRATION TREATMENT FOR THE REMOVAL OF 1,4-DIOXANE AND DISINFECTION BYPRODUCT PRECURSORS FROM WASTEWATER EFFLUENT

Modified from a paper submitted for possible publication in *Environmental Science and Technology*[1]

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Bulk quality parameters

Water samples were analyzed for dissolved organic matter (DOC) using a carbon analyzer (Shimadzu ion TOC-L, Columbia, MD). Prior to each analysis, samples were filtered with 0.45 µm PVDF syringe filter (VWR, Radnor, PA). Chemical oxygen demand (COD) was analyzed using a Hach DR 6000 (Loveland, CO). For measurement of anions, ion chromatography (IC; ICS-900, Dionex, Sunnyvale, Ca), was employed, while cations/metals were analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES; optima 5300 DV, PerkinElmer, Fremont, CA). Prior to metal analysis, samples (10 mL each) were fortified with 2 mL of 50% (v/v) HNO_3 (Fischer scientific). Conductivity was determined using a Cole Parmer EC Meter (model 1481-91) employing Standard Method 2510. pH measurements were taken with a Beckman 260 portable pH meter (Beckman, Fullerton, CA).

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Table A.1. Basic water quality analysis

Sample	pH	Chloride [mg/L]	Bromide [µg/L]	Iodine [µg/L]	NH_4^+ [mg/l as N]	DOC [mg/L]	UV_{254nm} [cm^{-1}]	$SUVA_{254nm}$ [L $mg^{-1}m^{-1}$]
Cond. I Sys. Inf.	**6.9**	**96.6**	**67.0**	**<MDL**	**0.05**	**5.90±0.1**	**0.109**	**1.84**
Cond. I O_3 Eff. (0.5 mg O_3/mg DOC)	**6.9**	**95.4**	**68.0**	**<MDL**	**0.05**	**5.7±0.1**	**0.075**	**1.33**
Cond. I BAF Eff. (EBCT 15 min)	**6.9**	**95.4**	**66.0**	**<MDL**	**<MDL**	**2.1±0.1**	**0.014**	**0.65**
Cond. I BAF Eff. (EBCT 30 min)	**7.0**	**93.7**	**66.0**	**<MDL**	**<MDL**	**1.9±0.2**	**0.010**	**0.52**
Cond. I BAF Eff. (EBCT 45 min)	**7.0**	**95.9**	**70**	**<MDL**	**<MDL**	**1.8±0.1**	**0.008**	**0.44**
Cond. II Sys. Inf.	**6.9**	**89.1**	**63.0**	**<MDL**	**0.03**	**5.3±0.5**	**0.107**	**1.87**
Cond. II O_3 Eff. (0.7mg O_3/mg DOC)	**7.0**	**88.8**	**68.0**	**<MDL**	**0.04**	**5.2±0.4**	**0.065**	**1.16**
Cond. II BAF Eff. (EBCT 15 min)	**7.0**	**89.3**	**66.0**	**<MDL**	**<MDL**	**1.80±0.1**	**0.013**	**0.72**
Cond. II BAF Eff. (EBCT 30 min)	**7.0**	**90.2**	**65.0**	**<MDL**	**<MDL**	**1.5±0.2**	**0.008**	**0.53**
Cond. II BAF Eff. (EBCT 45 min)	**7.0**	**88.1**	**70.0**	**<MDL**	**<MDL**	**1.3±0.2**	**0.007**	**0.53**
Cond. III Sys. Inf.	**6.9**	**87.7**	**61.0**	**<MDL**	**0.02**	**5.7±0.4**	**0.107**	**2.01**
Cond. III O_3 Eff. (1 mg O_3/mg DOC)	**7.1**	**87.8**	**71.0**	**<MDL**	**0.04**	**5.3±0.5**	**0.057**	**1.09**
Cond. III BAF Eff. (EBCT 15 min)	**7.0**	**87.9**	**67.0**	**<MDL**	**<MDL**	**1.9±0.1**	**0.012**	**0.63**
Cond. III BAF Eff. (EBCT 30 min)	**7.0**	**88.5**	**69.0**	**<MDL**	**<MDL**	**1.9±0.3**	**0.009**	**0.47**
Cond. III BAF Eff. (EBCT 45 min)	**7.0**	**87.7**	**73.0**	**<MDL**	**<MDL**	**1.9±0.1**	**0.008**	**0.42**

Table A.1. continued

Sample	pH	Chloride [mg/L]	Bromide [µg/L]	Iodine [µg/L]	NH_4^+ [mg/l as N]	DOC [mg/L]	UV_{254nm} [cm^{-1}]	$SUVA_{254nm}$ [L $mg^{-1}m^{-1}$]
Cond. IV Sys. Inf.	**6.9**	**86.8**	**63.3**	**<MDL**	**0.03**	**5.8±0.1**	**0.112**	**1.93**
Cond. IV O_3/GAC Eff. (0 mg O_3/mg DOC) adsorption effect of GAC in ozone chamber	**6.9**	**85.0**	**64.0**	**<MDL**	**0.04**	**5.6±0.1**	**0.109**	**1.96**
Cond. IV O_3/GAC Eff. (1 mg O_3/mg DOC)	**7.0**	**86.8**	**63.0**	**<MDL**	**0.07**	**4.5±0.4**	**0.041**	**0.83**
Cond. IV BAF Eff. (EBCT 15 min)	**7.0**	**86.6**	**62.0**	**<MDL**	**<MDL**	**1.9±0.1**	**0.010**	**0.53**
Cond. II BAF Eff. (EBCT 30 min)	**7.0**	**87.0**	**61.0**	**<MDL**	**<MDL**	**1.9±0.2**	**0.008**	**0.42**
Cond. II BAF Eff. (EBCT 45 min)	**6.9**	**87.4**	**64.0**	**<MDL**	**<MDL**	**1.9±0.1**	**0.006**	**0.31**

Ozonation process

The O_3 gas was generated by passing oxygen gas (93±3 %) from a DeVilbiss oxygen concentrator through an O_3 generator (Trigen LAB2B, East Kilbride, Scotland) that continuously fed the O_3 contactor through an 80 µm ceramic diffusor. The O_3 concentration from in-gas and off-gas was measured using a Model 454 H ozone monitor (Teledyne API, San Diego, CA) while the dissolved O_3 concentration in the ozonation column was determined with a Q46H/64 dissolved ozone sensor (Teledyne API, San Diego, CA). An O_3 mass balance was used to calculate transferred O_3 dose (TOD) as defined in equation A.1.

$$TOD = \frac{Q_{gas}}{Q_{water}} ([O_3]_{gas-in} - [O_3]_{off-gas}) \quad \text{(A.1)}$$

where Q_{gas} and Q_{water} are the gas and water flowrates, respectively, $[O_3]_{gas\text{-}in}$ is the O_3 concentration in the gas phase prior entering the O_3 contactor, and $[O_3]_{off\text{-}gas}$ is the O_3 off-gas concentration. The specific O_3 ratio is defined as the mass-based TOD normalized to DOC ratio (mg O_3/mg DOC) and was subsequently nitrite-corrected (equation A2) since nitrite consumes ozone quickly with a 1:1 molar stoichiometry without generating ·OH [1]:

$$\frac{gO_3}{gDOC} = \frac{gO_3}{gDOC} - (\frac{46}{14})(gNO_2 - N/gDOC) \quad \text{(A.2)}$$

Throughout all experiments a 100% O_3 transfer efficiency have been achieved.

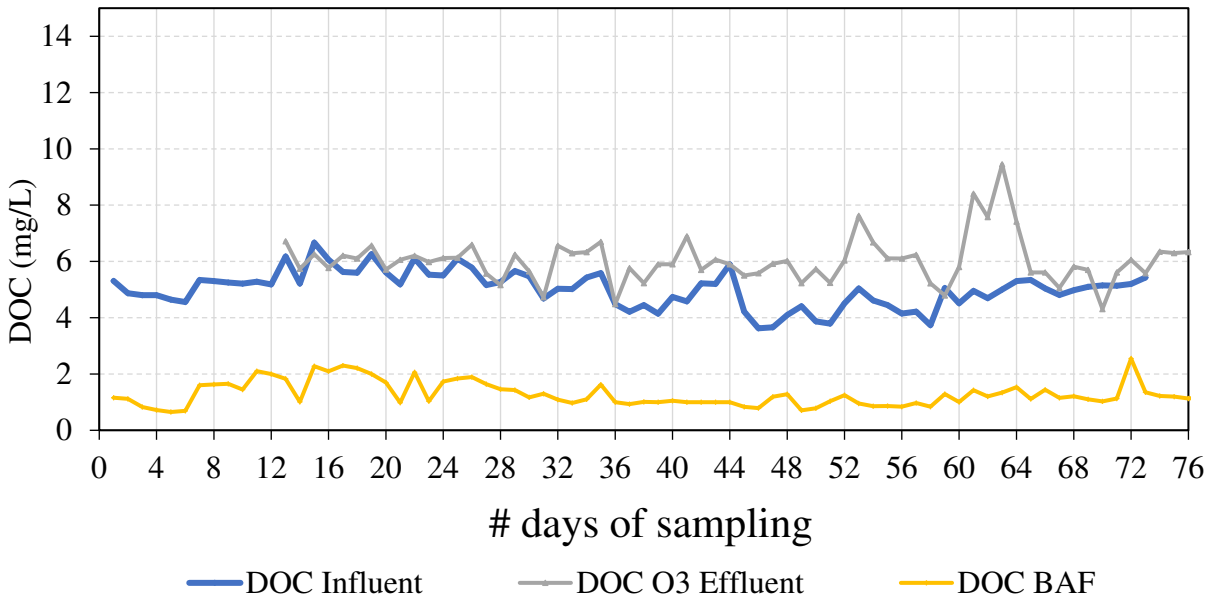

Figure A.1. DOC Removal throughout the O_3-BAF system

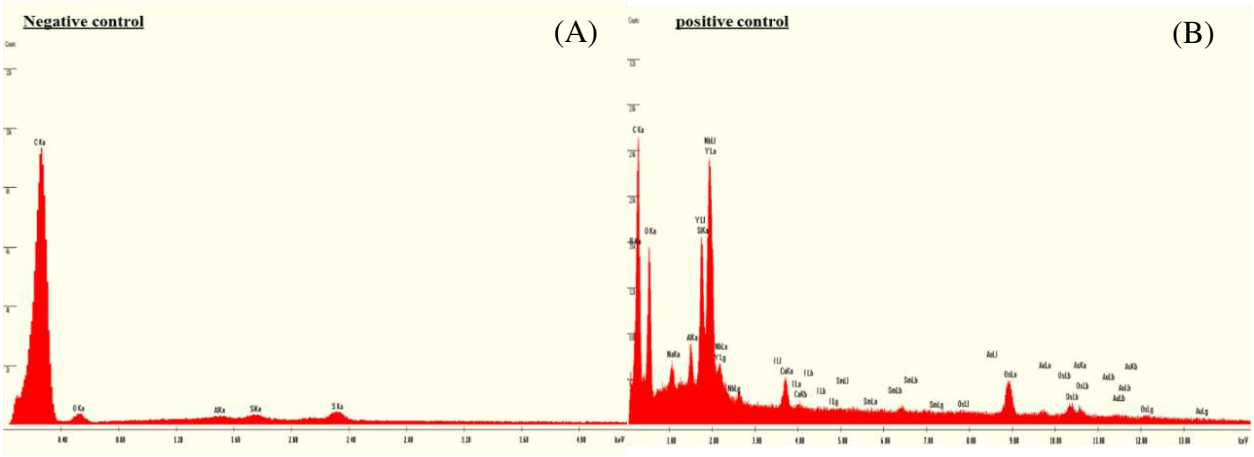

Figure A.2. ESEM-EDS of (A) negative and (B) positive control of GAC. Positive control samples exhibited carbon and oxygen peaks on biofilm scan as compared to only carbon in negative controls

Brunauer, Emmett, and Teller (BET) isotherm method [2] was used to measure the specific surface area of the GAC F400 (Table A.2.) used in enhanced ozonation.

Table A.2. Characteristics of F400 [3]

Type of GAC	Surface Area [m^2/g]	Iodine Number [mg/g]	Apparent bed density [g/cm^3]	Effective Size [mm]
F400	1075	>1000	0.47	0.55-0.75

Biologically active filtration acclimation process

For the BAF, fresh F600 GAC was placed in a 6 inch by 48-inch polyvinyl chloride (PVC) column and acclimated by activated sludge diluted with SMBR effluent for a period of 3 months in up-flow mode at an EBCT of 60 min. The dilution rate started with 90% activated sludge and 10% SMBR effluent and over the period of three month the ratio got to 90% SMBR effluent and 10% activated sludge. 2 weeks prior to start the experiments; the BAF was fed by 100% SMBR effluent. During the acclimation process, the BAF column was aerated with an airflow of (0.5 L/min). The bed was fluidized with air and back flow every 7 days in order to prevent any clogging or headloss. No clogging was observed throughout the entire acclimation process. Throughout the entire study establishment of microbial communities and biofilm development on the GAC surface was evaluated. Adenosine triphosphate (ATP) tests were used to determine the concentration of active microbial biomass in the GAC. The ATP tests were conducted based on release of suspended cells with nucleotide-releasing buffer and measuring the intensity of the emitted light in a luminometer (Celsis Advance).[4] Environmental scanning electron microscopy with an attached X-ray energy dispersive system (ESEM-EDS) (Quaanta 600, FEI Compony, Hillsboro, OR) was also employed to provide a visual presentation of biofilm development on the GAC surface as well as to comparing the elemental content between fresh GAC and the GAC after the acclimation process. The GAC samples were also analyzed for surface area characterization and pore analysis employing a Micromeritics Tristar 3020 instrument (Micromeritics – Norcross, GA).

Fresh coal-based GAC Filtrasorb 600 (F600) was rinsed numerous times with DI water and packed into a polyvinyl chloride column (130 cm in height and 10.2 cm diameter) after baking at 120 ºC for 24 hours. Throughout the entire experiment (including acclimation process), the system

Table A.3. Textural characteristic of F600

Type of GAC	Surface Area [m^2/g]	Iodine Number [mg/g]	Apparent bed density [g/cm^3]	Effective Size [mm]
F600	860	850	0.63	0.3-1.3

The GAC samples were also analyzed for surface area characterization and pore analysis employing a Micromeritics Tristar 3020 instrument (Micromeritics – Norcross, GA). To this end, samples were dried out and degassed with nitrogen gas for 6 hours prior undergoing nitrogen physical adsorption (physisorption) analysis to evaluate the specific surface area using the Brunauer-Emmett-Teller (BET) equation [2] as well as the Barrett-Joyner-Halenda (BJH) equations [5] to determine pore volume and pore-size distribution.

1,4-Dioxane

The World Health Organization (WHO) has recommended a concentration level of 50 ng/L as its maximum contaminant level [6]. The EPA has also set a maximum limit of 30 µg/L for wastewater treatment plants discharge [7]. 1,4-dioxane has a low reaction kinetic of second order rate constant with O_3 (0.32 M^{-1} s^{-1}) and is also relatively reluctant to biodegradation under conventional biotreatment technologies [8, 9]. In 2017, the EPA ranked 1,4-dioxane as one of the most mobile organic contaminants which is not readily biodegradable in water and soil [10]. However, enhanced oxidation processes involving increased concentration of $^{\cdot}OH$ may be efficient options to remove 1,4-dioxane due to its relatively high reaction rate constant with $^{\cdot}OH$ (2.28 x 10^8 M^{-1} s^{-1}).[7, 11-13]

Certified grade 1,4-dioxane, 1,4-dioxane-d_8, and methyl tert-butyl ether (MTBE) were purchased from Sigma-Aldrich (St. Louis, MO). Reagent grade sodium sulfate was obtained from Fischer Scientific (Hampton, NH) and baked at 100 ºC for 24 hours. Water samples were filtered by a 0.45 µm PVDF syringe filter (VWR, Radnor, PA) and were collected in triplicate. 1,4-dioxane-d_8 was used as the internal standard. Samples were pre-treated and concentrated using salt-assisted liquid-liquid extraction (LLE). Low recovery of 1,4-dioxane due to its high miscibility in water as well as its low octanol-water partition coefficient (K_{OW}) was addressed by selecting a sample to solvent ration of 3 to 1. Extractions were carried out by adding a 30 mL sample aliquot

in a 60-mL vial followed by the addition of 50 µL of 20 µg/mL in MTBE 1,4-dioxane-d_8 (isotopically-labeled standard) and 10 ml of MTBE. To increase the extraction efficiency, 10 g of sodium sulfate was added in the solution and samples were thereafter shaken vigorously for 2 minutes. Samples were let sit for 3 minutes to allow the phases to separate. The organic layer was transferred to a 15 mL conical vial where 1 g sodium sulfate was added to the extract to eliminate residual water. Extracts were evaporated to a final volume of 500 µL under a gentle nitrogen stream at ambient conditions using an N-EVAP 112 nitrogen evaporation unit (Organomation Associates Inc., Berlin, MA). Eluate was transferred into 2 mL amber GC vials and stored below -5 ºC prior to analysis (less than 7 days). Samples were analyzed for 1,4-dioxane using a 7890B Agilent gas chromatography system and a 5977B Mass spectrometry detector (MSD) (Agilent technologies, Santa Clara, CA) with a DB-5MS (30 m x 0.25 mm x 0.25um, Agilent Technologies) capillary column. The system was operated with ultra-high purity helium as the carrier gas with a constant flowrate of 1 mL/min. The oven temperature program was as follows: 35°C held for 4 minutes, then ramped to 70°C at a rate of 5°C/min then ramped to a final temperature of 280°C at 20°C/min and held for 2 minutes. A 1µL injection was made using a 7693 autosampler (Agilent Technologies) in splitless mode at an injector temperature of 280°C. The transferline and ion source were kept at constant temperatures of 250 °C and 150 °C, respectively. The MSD was operated in selected ion monitoring (SIM) and electron ionization (EI) mode (70 eV) with a solvent delay of 3.5 minutes.

Mass spectra was obtained from analytical standards in full scan (m/z 50-500). Identification of 1,4-dioxane and 1,4-dioxane-d_8 was achieved by comparison of mass spectra from analytical standards and the NIST library (version 2.2) at established retention times. Analytical parameters for analysis of 1,4-dioxane are summarized in Table A4. 1,4-dioxane was quantified using isotope-dilution method with 1,4-dioxane-d_8. Samples were analyzed in SIM mode scanning for quantifier and confirming ions at time window around the established retention times. At least 7 calibration standards were prepared in MTBE for quantitation. Data was processed using Mass Hunter Workstation Software (Agilent, version B.08.00). Established concentrations of 1,4-dioxane were normalized to C/C_o ratios by dividing the influent 1,4-dioxane concentration (C_o) by the effluent concentration (C). The MDL was calculated using Equation A3 [14].

$$MDL = 3S_a/b \quad \text{(A.3)}$$

where S_a is the standard deviation of the response and b is the slope of the calibration curve. Alternative methods dedicated to determination of oxygenated volatile organic compounds are reported by Boczkaj et al. [15].

Table A.4. Analytical parameters of 1,4-dioxane and its corresponding analogue

Compound	Formula	MW [g/mol]	RT [min]	Quant. ion[a] (Qual. ion) [m/z]	MDL [µg/L]
1,4-dioxane	$C_4H_8O_2$	88.1	4.19	88.1 (57.1)	0.01
1,4-dioxane-d_8	$C_4D_8O_2$	96.2	4.07	96.2 (62.1)	n.a.

[a]Confirmation ion provided in parentheses
Abbreviations: MW- molecular weight; RT-Retention time; MDL-method detection

Bromate analysis

For drinking water, a guideline/standard concentration of 10µg/L has been set for bromate [16-18] while the acute and chronic environmental quality standard (EQS) of 50 µg/L was set for bromate from Ecotox Center Eawag-EPFL. [19] For NDMA, WHO set a guideline concentration of 100 ng/L for drinking water [20] while other countries such as the USA and Germany proposed a lower value of 10 ng/L [21-23].

Br^- and BrO_3^- sample preparation consisted of 1 mL of each sample filtered with 0.45 µm PVDF syringe filter (VWR, Radnor, PA) and stored at 4 ºC prior to analysis. Br^- and BrO_3^- were analyzed by Capillary-HPIC (High Performance Ion Chromatography) with MS-MS-detection equipped with a AS19-4µ 0.4 * 250 mm column. A gradient of 5-150 mM KOH at 10µL/min was applied to separate the ions. The quantification limits were 1 µg/l and Br^- 5 µg/l for BrO_3^- and Br^-, respectively.

Table A.5. N-Nitrosamines and halogenated DBP risk level

Chinese hamster ovary cell comparative cytotoxicity of target halogenated DBPs		
	LC_{50} (M)	Reference
THMs		
TCM	9.17×10^{-3}	Plewa and Wagner [24]
BDCM	1.15×10^{-2}	Plewa and Wagner [24]
DBCM	5.36×10^{-3}	Plewa and Wagner [24]
TBM	3.96×10^{-3}	Plewa and Wagner [24]
HAAs		
CAA	8.48×10^{-4}	Plewa and Wagner [25]
BAA	9.60×10^{-6}	Plewa and Wagner [25]
DCAA	7.30×10^{-3}	Plewa and Wagner [25]
TCAA	2.40×10^{-3}	Plewa and Wagner [25]
BCAA	7.78×10^{-4}	Plewa and Wagner [25]
DBAA	5.21×10^{-4}	Plewa and Wagner [25]
BDCAA	6.85×10^{-4}	Plewa and Wagner [25]
DBCAA	2.00×10^{-4}	Plewa and Wagner [25]
TBAA	8.50×10^{-5}	Plewa and Wagner [25]
IAA	3.20×10^{-6}	Plewa and Wagner [25]
I-THMs		
DCIM	4.13×10^{-3}	Richardson *et al.* [26]
BCIM	2.42×10^{-3}	Richardson *et al.* [26]
DBIM	1.91×10^{-3}	Richardson *et al.* [26]
CDIM	2.41×10^{-3}	Richardson *et al.*
BDIM	NA	Not available
TIM	6.60×10^{-5}	Richardson *et al.* [26]
HNMs		
TCNM	5.36×10^{-4}	Plewa *et al.* [27]
HKs		
1,1-DCP	NA	NA
1,1,1-TCP	NA	NA
HALs		
TCAL	1.16×10^{-3}	Jeong *et al.* [28]
BDCAL	2.04×10^{-5}	Jeong *et al.* [28]
DBCAL	5.15×10^{-6}	Jeong *et al.* [28]
TBAL	3.56×10^{-6}	Jeong *et al.* [28]
HANs		
DCAN	5.73×10^{-5}	Muellner *et al.* [29]
BCAN	8.46×10^{-6}	Muellner *et al.* [29]

Table A.5. continued

Chinese hamster ovary cell comparative cytotoxicity of target halogenated DBPs		
	LC_{50} (M)	Reference
BCAM	1.71×10^{-5}	Plewa *et al.* [30]
DBAM	1.22×10^{-5}	Plewa *et al.* [30]
TCAM	2.05×10^{-3}	Plewa *et al.* [30]
DBAN	2.85×10−6	Muellner et al. [29]
TCAN	1.60×10−4	Muellner et al. [29]

NA: not available

Table A.6. Lifetime excess cancer risk of target N-nitrosamines [31]

	$LECR_{50}$ (M)	10^{-6} lifetime excess cancer risk (ng/L)		
		USEPA's	California 27 CCR	Federal Register 2014-24582
***N*-Nitrosamines**				
NDMA	4.04×10^{-6} [a]	0.7	3	0.6
NMEA	1.70×10^{-5} [a]	2	1.5	3
NDEA	1.96×10^{-6} [a]	0.2	1	0.4
NDPA	2.69×10^{-5} [a]	5	5	7
NPYR	9.99×10^{-6} [a]	20	15	2
NPIP	1.53×10^{-5} [b]	NA	3.5	NA
NDBA	9.49×10^{-5} [a]	6	3	30
NMOR	2.15×10^{-5} [b]	NA	**5**	NA
NDPhA	1.76×10^{-2} [c]	7000	NA	NA

[a] Calculated based on the age-adjusted 10^{-6} lifetime excess cancer risk values in Federal Register 2014-24582 [b] Calculated based on the 10^{-6} lifetime excess cancer risk values derived from California 27 CCR §25705; [c] Calculated based on the 10^{-6} lifetime excess cancer risk value in the USEPA's IRIS database.

Table A.7. Bromide and bromate concentration

	Bromide [μg/L]	Bromate [μg/L]*
0.5 mg O_3/mg DOC		
Sys. Inf	67	BQL
O_3 eff.	68	BQL
BAF eff (15 min EBCT)	66	BQL
BAF eff (30 min EBCT)	66	BQL
BAF eff (45 min EBCT)	68±1.68	BQL
0.7 mg O_3/mg DOC		
Sys. Inf	63	BQL
O_3 eff.	68±0.75	BQL
BAF eff (15 min EBCT)	66	BQL
BAF eff (30 min EBCT)	65	BQL
BAF eff (45 min EBCT)	70	BQL
1.0 mg O_3/mg DOC		
Sys. Inf	61	BQL
O_3 eff.	71±0.75	BQL
BAF eff (15 min EBCT)	67	BQL
BAF eff (30 min EBCT)	69	BQL
BAF eff (45 min EBCT)	73	BQL
1.0 mg O_3/mg DOC (Enhanced Ozonation)		
Sys. Inf	64±0.29	BQL
GAC eff (adsorption effect)	64	BQL
O_3 eff. + GAC eff.	63	12.5±0.28
BAF eff (15 min EBCT)	63	4.2±0.14
BAF eff (30 min EBCT)	61	5.5±0.17
BAF eff (45 min EBCT)	64	6.5±0.30

*BQL: 1 μg/L, n=3

Chloramination condition and DBP analysis

For UFC chloramination, the pH of the sample was first adjusted to ~8 using 4 mM borate buffer, and preformed monochloramine was added to the sample (5 mg/L monochloramine). The samples were then stored in the dark for 3 days at room temperature (~21C) The total chlorine residual (>1 mg/L Cl2) was quenched after the 3 days with 33 mg/L ascorbic acid, DBP samples were extracted immediately afterward.

Eight *N*-nitrosamines (*N*-nitrosodimethylamine (NDMA), *N*-nitrosomorpholine (NMOR), *N*-nitrosomethylethylamine (NMEA), *N*-nitrosodiethylamine (NDEA), *N*-nitrosodi-*n*-propylamine (NDPA), *N*-nitrosodi-*n*-butylamine (NDBA), *N*-nitrosopyrrolidine (NPYR), *N*-nitrosopiperidine (NPIP)) were extracted using a modified USEPA 521 method (500mL per sample)[32]. Seven classes of DBPs were analyzed using a modified USEPA method 551.3[33] including four regulated (THM4: trichloromethane (TCM), tribromomethane (TBM), dibromochloromethane (DBCM), and bromodichloromethane (BDCM)), four haloacetonitriles (HANs: trichloroacetonitrile (TCAN), dichloroacetonitrile (DCAN), bromochloroacetonitrile (BCAN), and dibromoacetonitrile (DBAN)), six iodinated THMs (I-THMs: bromochloroiodomethane (BCIM), bromodiiodomethane (BDIM), chlorodiiodomethane (CDIM), triiodomethane (TIM), dichloroiodomethane (DCIM), and dibromoiomethane (DBIM)), four haloacetamides (HAMs : trichloroacetamide (TCAM), bromochloroacetamide (BCAM), dichloroacetamide (DCAM), and dibromoacetamide (DBAM)), four haloacetaldehydes (HALs): trichloroacetaldehyde (TCAL), bromodichloroacetaldehyde (BDCAL), dibromochloroacetaldehyde (DBCAL), and tribromoacetaldehyde (TBAL)), two haloketones (HKs: (1,1,1-trichloropropanone (1,1,1-TCP), and 1,1-dichloropropanone (1,1-DCP)), and one halonitromethane (HNM): (chloropicrin (TCNM)). Ten haloacetic acids (HAAs: chloroacetic acid (CAA), bromoacetic acid (BAA), iodoacetic acid (IAA), dichloroacetic acid (DCAA), bromochloroacetic acid (BCAA), dibromoacetic acid (DBAA), trichloroacetic acid (TCAA), bromodichloroacetic acid (BDCAA), dibromochloroacetic acid (DBCAA), and tribromoacetic acid (TBAA)) were measured using a modified USEPA. Method 552.3 (50 mL per sample). Analytical methods details were described previously [34, 35]. Extracts were analyzed by GC-MS, with method reporting limits between 0.05-0.20 μg/L for halogenated DBPs, and 2 ng/L for *N*-nitrosamines. Details on GC-MS analysis are available in Zeng et al.[34].

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APPENDIX B

SUPPLEMENTARY INFORMATION FOR: SIMULTANEOUS OZONE AND GRANULAR ACTIVATED CARBON TREATMENT OF MICROPOLLUTANTS DURING POTABLE RESUE OF MUNICIPAL WASTEWATER EFFLUENT

Modified from a paper submitted for possible publication in *Science of the Total Environment*[1]

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Sulfamethoxazole, atenolol, trimethoprim, fluoxetine, carbamazepine, primidone, DEET, gemfibrozil, naproxen, triclosan, ibuprofen, caffeine, acetaminophen, triclocarban, TCEP and sucralose were purchased as a custom stock in methanol from Environmental Resources Associates (Golden, CO). Meprobamate stock in methanol was purchased from Cerilliant (Round Rock, TX). Sulfamethoxazole-d4, trimethoprim-d9, meprobamate-d3, gemfibrozil-d6, and sucralose-d6 stocks in methanol were purchased from Toronto Research Chemicals (Ontario, Canada). Atenolol-d7, fluoxetine-d8, carbamazepine-d10, primidone-d5, DEET-d7, naproxen-d3, triclosan-d3, ibuprofen-d3, caffeine-d9, acteminophen-d4, and triclocarban-d4 stocks in methanol were purchased from C/D/N Isotopes (Quebec, Canada). TCEP-d12 stock in methanol was purchased from Isotec (St. Louis, MO). Methanol and MTBE were purchased from Honeywell (Muskegon, MI), sodium azide from Alfa Caesar (Ward Hill, MA), and ascorbic acid from Mallinckrodt Baker (Phillipsburg, NJ). Stock standards solutions for target analytes and their isotopically-labelled versions used as internal standards (IS) were prepared in methanol and stored at -20^{o}C.

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A total of nine *N*-nitrosamines (listed in Table S1) were extracted as reported in Holady et al. [1] from which only NMOR could be detected and is included in the manuscript. Extracts were analyzed using an Agilent 7890 gas chromatograph coupled to a 7010 triple quadrupole mass spectrometer equipped with a PAL3 autosampler (Agilent Technologies, Santa Clara, CA, USA). A 2 µL injection volume was used for all sample analyses set at 200 °C in splitless mode. Separation was performed using an Agilent DB-624 column (30 m x 250 µm x 1.4 µm) with a constant helium flow rate set at 1.2 mL/min. Initial oven temp was set at 35 °C and held for 2 min, then ramped to 150 °C at 10 °C/min and held for 5 min, and then ramped to 250 °C at 25 °C/min and held for 4.5 min for a total run time of 27 min. The MS was configured for electron ionization (EI) and multiple reaction monitoring (MRM). All nitrosamines were quantified using isotope dilution. Mass spectrometer instrument parameters are listed in Table S2. A method detection limit (MDL) study was performed by spiking 1 L of deionized water (n=12 replicates) close to the expected reporting limit (5.0 ng/L). Using a Student T-test, method report limits (MRL) were set at 3 to 5 times the MDL.

Table B.1. Nitrosamine MRM transition, collision energy, and quantitative isotope

Nitrosamine	**Abbreviation**	**Precursor Ion (m/z)**	**Product Ion (m/z)**	**CE**	**Isotope**
N-Nitrosodimethylamine	NDMA	74	44	5	d_6-NDMA
		74	42	20	
N-Nitrosomethylethylamine	NMEA	88	71	4	d_3-NMEA
		88	73	5	
N-Nitrosodiethylamine	NDEA	102	85	4	d_{10}-NDEA
		102	56	20	
N-Nitrosodipropylamine	NDPA	130	113	4	d_{14}-NDPA
		130	58	10	
N-Nitrosomorpholine	NMOR	116	86	4	d_8-NMOR
		116	56	12	
N-Nitrosopyrollidine	NPYR	100	70	8	d_8-NPYR
		100	55	8	
N-Nitrosopiperidine	NPIP	114	84	8	d_{10}-NPIP
		114	55	22	
N-Nitrosodibutylamine	NDBA	158	141	4	d_{18}-NDBA
		158	99	10	
N-Nitrosodiphenylamine	NDPhA	169	141	33	d_6-NDPhA
		169	92	35	

Table B.2. LC-MS/MS analytical parameters for determination of selected micropollutants

Micropollutant	Q1 Mass	Q3 Mass	Retention time (min)	DP (V)	EP (V)	CE (V)	CXP (V)
ESI positive scheduled MRM							
sulfamethoxazole	254	156	1.89	86	10	23	10
sulfamethoxazole confirmation	254	92	1.89	81	10	41	6
sulfamethoxazole-d^4	258	160	1.89	56	10	25	12
atenolol	267	145	2.00	90	10	35	10
atenolol confirmation	267	116	2.00	65	10	28	10
atenolol- d^7	274	145	2.00	61	10	37	10
caffeine	195	110	2.05	56	10	32	10
caffeine confirmation	195	42	2.05	56	10	63	6
caffeine-d^9	204	144	2.05	56	10	37	8
primidone	219	162	2.35	66	10	19	10
primidone confirmation	219	91	2.35	66	10	41	8
primidone-d^5	224	167	2.35	66	10	25	10
trimethoprim	291	261	2.38	106	10	35	8
trimethoprim confirmation	291	123	2.38	106	10	32	12
trimethoprim- d^9	300	234	2.38	71	10	35	16
meprobamate	219	158	2.60	71	10	10	10
meprobamate confirmation	219	97	2.60	71	10	20	8
meprobamate- d^3	222	161	2.60	56	10	13	10
TCEP	285	99	3.12	61	10	18	4
TCEP Confirmation	285	161	3.12	66	10	13	14
TCEP-d^{12}	297	102	3.12	66	10	45	4
carbamazepine	237	165	3.32	90	10	57	10
carbamazepine confirmation	237	194	3.32	105	10	17	10
carbamazepine- d^{10}	247	204	3.32	61	10	31	20
DEET	192	119	3.92	76	10	13	10
DEET confirmation	192	91	3.92	101	10	35	6
DEET- d^7	199	126	3.92	76	10	25	10
fluoxetine	310	44	6.12	77	10	20	7
fluoxetine confirmation	310	148	6.12	72	10	13	7
fluoxetine-d^8	315	44	6.12	62	10	40	7

Table B.2. continued

ESI negative scheduled MRM							
Micropollutant	**Q1 Mass**	**Q3 Mass**	**Retention time (min)**	**DP (V)**	**EP (V)**	**CE (V)**	**CXP (V)**
acetaminophen	150	107	1.82	-60	-10	-24	-5
acetaminophen confirmation	150	108	1.82	-60	-10	-22	-5
acetaminophen-d^4	154	111	1.82	-65	-10	-26	-5
sucralose	395	35	2.12	-60	-10	-40	-5
sucralose confirmation	397	35	2.12	-60	-10	-44	-5
sucralose-d^6	403	35	2.12	-60	-10	-44	-5
Naproxen	229	169	2.58	-30	-10	-40	-10
naproxen confirmation	229	185	2.58	-30	-10	-9	-10
naproxen-d^3	232	173	2.58	-35	-10	-20	-13
Ibuprofen	205	161	3.82	-53	-10	-10	-7
ibuprofen confirmation	205	159	3.82	-53	-10	-9	-7
ibuprofen-d^3	208	164	3.82	-53	-10	-10	-7
Gemfibrozil	249	121	4.96	-45	-10	-9	-5
gemfibrozil confirmation	249	127	4.96	-45	-10	-18	-13
gemfibrozil-d^6	255	121	4.96	-40	-10	-20	-7
Triclocarban	313	160	5.20	-55	-10	-5	-11
triclocarban confirmation	315	162	5.20	-55	-10	-6	-11
triclocarban-d^4	321	164	5.20	-65	-10	-18	-11
Triclosan	287	35	5.22	-35	-10	-18	-4
triclosan confirmation	289	37	5.22	-45	-10	-30	-4
triclosan-d^3	294	37	5.22	-45	-10	-30	-4

Table B.3. Method reporting limits for select micropollutants included in this study

Micropollutant	**MRL [ng/L]**
Triclosan	1.0
Sulfamethoxazole	0.25
Carbamazepine	0.50
Trimethoprim	0.25
Naproxen	0.50
Gemfibrozil	0.25
Atenolol	1.0

Table B.3. continued

Micropollutant	MRL [ng/L]
Fluoxetine	0.50
Ibuprofen	1.0
DEET	1.0
Primidone	0.50
Sucralose	25
Meprobamate	0.25
TCEP	10
Caffeine	5.0
Triclocarbon	2.0
N-Nitroso-n-propylamine	5.9
N-Nitrosodi-n-butylamine	5.9
N-Nitrosodiethylamine	5.9
N-Nitrosodimethylamine	2.9
N-Nitrosodiphenylamine	5.9
N-Nitrosomethylethylamine	2.9
N-Nitrosomorpholine	5.0
N-Nitrosopiperidine	5.9
N-Nitrosopyrrolidine	5.9

Table B.4. Methods for water quality parameters

Water quality parameter	Method
Alkalinity	Standard Method 2320 B
pH	Standard Method 4500 HB
Total organic carbon (TOC)	Standard Method 5310 B
Turbidity	Standard Method 2130 B
Anions	EPA 300.0
Cations	EPA 200.7
UV absorbance	Standard Method 5910 B

Table B.4. continued

Water quality parameter	Method
Bromide	EPA 300.0
Bromate	EPA 302

Table B.5. Water quality characteristics of tertiary effluent

Parameter	Dimension	CCWRD Tertiary effluent (system influent)
pH	-	6.9±0.1
Alkalinity, Total	mg/L	128±1.5
Br^-	µg/L	248±13.3
DOC	mg-C/L	7.7±0.4
UVA_{254}	cm^{-1}	0.118±0.007
UVA_{280}	cm^{-1}	0.0904±0.005
NO_3^-	mg-N/L	13.6±0.77
NO_2^-	mg-N/L	0.02±0.0
PO_4^{3-}	mg-P/L	0.0345±0.010
F^-	mg/L	0.83±0.11

Table B.6. MPs concentration in CCWRD tertiary effluent

Micropollutant	Units	Concentration
Triclosan	ng/L	27.0±4.35
Triclocarban	ng/L	<2.0
Sulfamethoxazole	ng/L	742.50±56.19
Carbamazepine	ng/L	142.50±23.62
Trimethoprim	ng/L	15.25±3.59
Naproxen	ng/L	19.25±1.89
Gemfibrozil	ng/L	1.37±0.20
Atenolol	ng/L	37.50±8.81
Fluoxetine	ng/L	26.50±1.73
Ibuprofen	ng/L	<1.0
DEET	ng/L	135.25±58.63
Primidone	ng/L	145.0±26.45
Sucralose	ng/L	48500±5196.152

Table B.6. continued

Micropollutant	Units	Concentration
Meprobamate	ng/L	242.50±25.0
TCEP	ng/L	240.0±15.0
N-Nitroso-n-propylamine	ng/L	<5.9
N-Nitrosodi-n-butylamine	ng/L	<5.9
N-Nitrosodiethylamine	ng/L	<5.9
N-Nitrosodimethylamine	ng/L	15.5±6.35
N-Nitrosodiphenylamine	ng/L	<5.9
N-Nitrosomethylethylamine	ng/L	<2.9
N-Nitrosomorpholine	ng/L	<5.0
N-Nitrosopiperidine	ng/L	<5.9
N-Nitrosopyrrolidine	ng/L	<5.9

Table B.7. Structure of selected micropollutants and grouping according to their second-order rate constants with O3 and OH, respectively

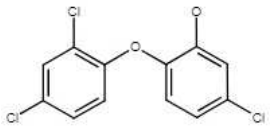
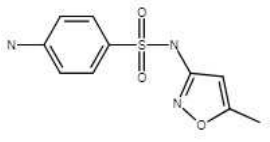
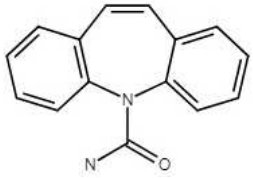
Micropollutants (application)	Structure	$K_{O3,\ pH\ 7}$ [$M^{-1}s^{-1}$]	$K_{\cdot OH}$ [$M^{-1}s^{-1}$]	Log K_{OW} [a]
Group I: High reactivity with O_3 and $\cdot OH$				
Triclosan (antimicrobial)		2.7×10^{6} [2]	9.6×10^{9} [3]	4.76
Sulfamethoxazole (antibiotic)		5.7×10^{5} [4]	5.5×10^{9} [4]	0.89
Carbamazepine (anticonvulsant)		3.0×10^{5} [4]	8.8×10^{9} [4]	2.45

Table B.7. continued

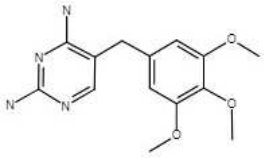
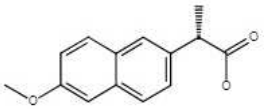
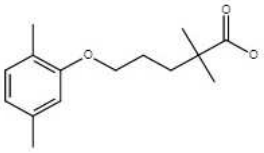
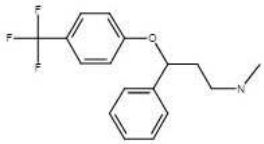
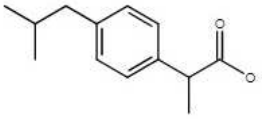
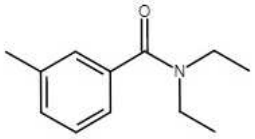
Micropollutants (application)	Structure	$K_{O3,\ pH\ 7}$ [$M^{-1}s^{-1}$]	$K_{\cdot OH}$ [$M^{-1}s^{-1}$]	Log K_{OW} [a]
Trimethoprim (antibiotic)		2.7×10^5 [5]	6.9×10^9 [5]	0.91
Naproxen (anti-inflammatory)		2.0×10^5 [6]	9.6×10^9 [7]	3.18
Group II: Moderate reactivity with O_3 and high reactivity with ·OH				
Gemfibrozil (lipid regulator)		~ 2.0×10^4 [8]	10×10^9 [9]	4.77
Fluoxetine (psychotropic drug)		n.a.	8.4×10^9 [10]	4.05
Group III: Low reactivity with O_3 and moderate reactivity with ·OH				
Ibuprofen (anti-inflammatory)		9.6 [4]	7.4×10^9 [4]	3.97
DEET (insect repellent)		<10 [3]	5.0×10^9 [11]	2.18

Table B.7. continued

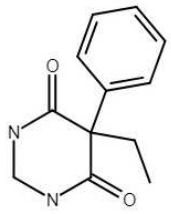
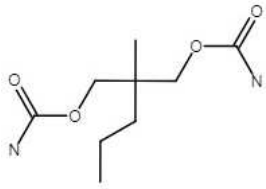
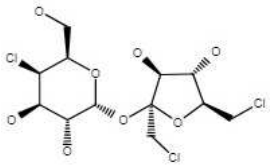
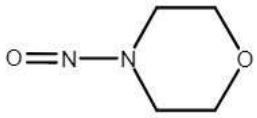
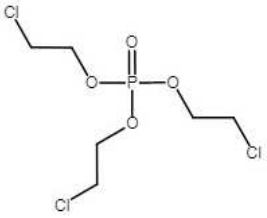
Micropollutants (application)	Structure	$K_{O3, pH\ 7}$ [$M^{-1}s^{-1}$]	$K_{\cdot OH}$ [$M^{-1}s^{-1}$]	Log K_{OW} [a]
Primidone (anticonvulsant)		<10 [3]	6.7×10^9 [12]	0.91
Meprobamate (antianxiety drug)		<1 [3]	3.7×10^9 [3]	0.70
Sucralose (artificial sweetener)		<0.1 [2]	1.5×10^9 [13]	-1.0
NMOR (nitrosamines)		n.a.	1.75×10^9 [14]	-0.18 [15]
Group IV: Low reactivity with O_3 and ·OH				
TCEP (flame retardant)		<1 [3]	7.4×10^8 [8]	1.7 [16]

Table B 8. Elimination of Group III (except NMOR) and Group IV of micropollutants during single ozonation, single adsorption, O_3/GAC treatment process at four different conditions: 0.3 mg O_3/mg DOC, 0.5 g GAC/L, 0.3 mg O_3/mg DOC, 2.0 g GAC/L, 0.5 mg O_3/mg DOC, 0.5 g GAC/L, and 0.5 mg O_3/mg DOC, 2.0 g GAC/L

Compound	Single adsorption	Single ozonation	Sum single O3 and adsorption	O3/GAC	% Enhanced
0.3 mg O3/mg DOC, 0.5 g/L GAC					
DEET	4%	54%	58%	58%	X

Table B.8. continued

Compound	Single adsorption	Single ozonation	Sum single O3 and adsorption	O3/GAC	% Enhanced
Primidone	11%	59%	70%	61%	X
Sucralose	5%	21%	26%	38%	12%
Meprobamate	6%	23%	29%	35%	6%
TCEP	11%	2%	13%	15%	2%
0.3 mg O3/mg DOC, 2.0 g/L GAC					
DEET	20%	54%	74%	69%	X
Primidone	22%	59%	81%	69%	X
Sucralose	13%	21%	34%	42%	8%
Meprobamate	23%	23%	46%	60%	14%
TCEP	19%	2%	21%	44%	23%
0.5 mg O3/mg DOC, 0.5 g/L GAC					
DEET	5%	71%	76%	76%	X
Primidone	11%	77%	88%	83%	X
Sucralose	5%	25%	30%	49%	19%
Meprobamate	6%	54%	60%	60%	X
TCEP	11%	10%	21%	24%	3%
0.5 mg O3/mg DOC,2.0 g/L GAC					
DEET	20%	71%	91%	82%	X
Primidone	22%	77%	99%	87%	X
Sucralose	13%	25%	38%	65%	27%
Meprobamate	23%	54%	77%	75%	X
TCEP	19%	10%	29%	47%	18%

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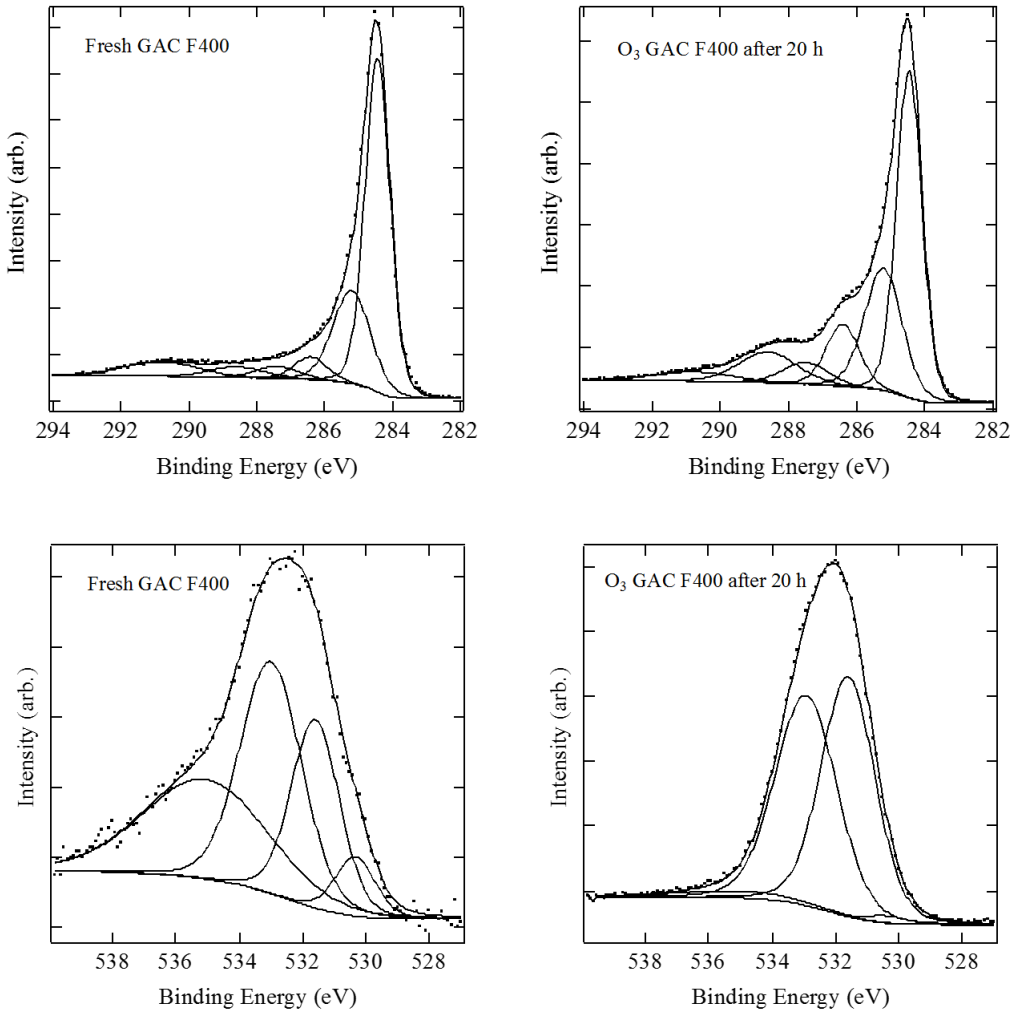

Figure B.1. High-resolution XPS spectra of O1s and C1s of fresh GAC and GAC after 20 hours of O_3/GAC

APPENDIX C

SUPPLEMENTARY INFORMATION FOR: EFFECT OF PRE-OZONATION ON NANOFILTRATION MEMEBRANE FOULING DURING WATER REUSE APPLICATIONS

Modified from a paper published in the Journal *Separation and Purification Technology*[1]

Hooman Vatankhah[2†], Conner C. Murray[2], Jacob W. Brannum[2], Johan Vanneste[2], Christopher Bellona[2*]

The results of modelling of SBMBR effluent at different recoveries (Figure S1) predicted four different scaling candidates (hydroxyapatite ($Ca_5(PO_4)_3(OH)$), silicon dioxide (SiO_2), calcium sulfate-dihydrate ($CaSO_4.2H_2O$), and dicalcium phosphate ($CaHPO_4$)). The scaling tendency of dicalcium phosphate, and calcium sulfate-dihydrate showed a slow increase with increasing recovery while silicon dioxide displayed a sharper increase with increasing recovery. In case of hydroxyapatite, the OLI software predicted a potential of scaling for all the system recoveries tested. Overall, besides hydroxyapatite (scaling tendency of 1), the scaling tendency of the other three candidates was predicted to be below one. However, the result of ESEM-EDS analysis (results presented in SI) did not show any indication of inorganic fouling for all experiments. The results of OLI software and ESEM-EDS indicates that inorganic scaling during fouling experiments was minimal and that organic matter fouling dominated. In addition, because fouling experiments were conducted at low recovery conditions (<2 percent), inorganic scaling was likely minimal

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[1]Reprinted from Separation and Purification Technology, 2018, 203-211

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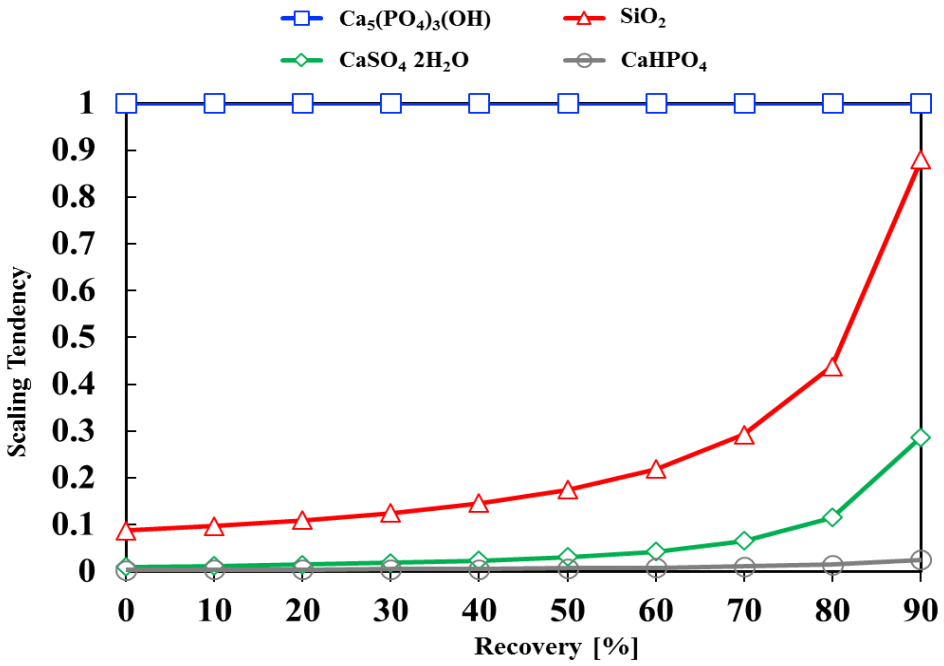

Figure C.1. OLI prediction of dominant scaling tendencies as a function of water recovery (0-90%)

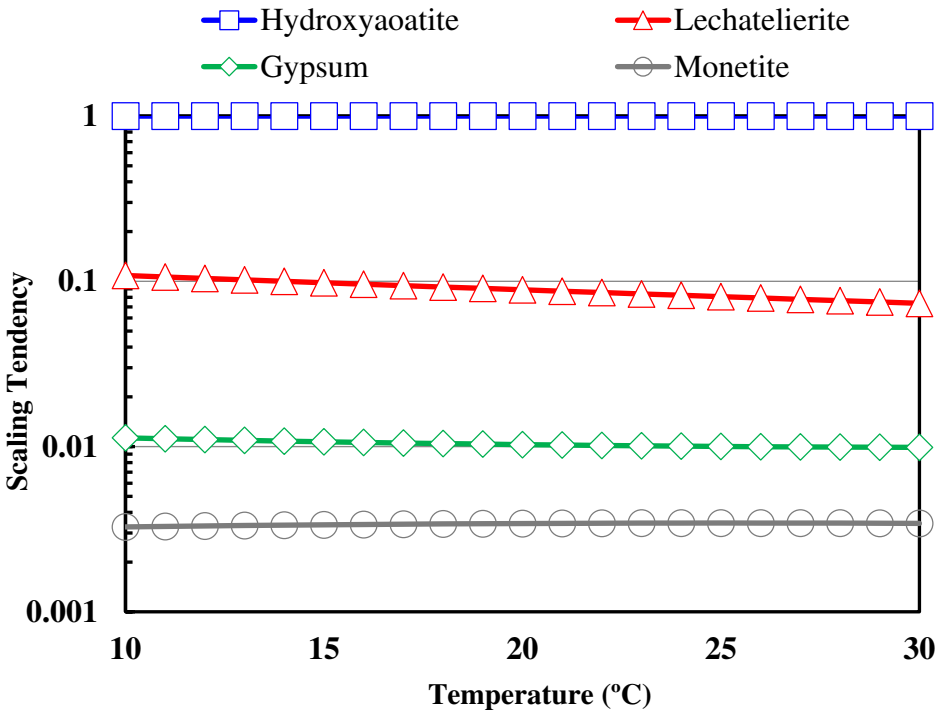

Figure C.2. OLI fouling tendency prediction as a of temperature

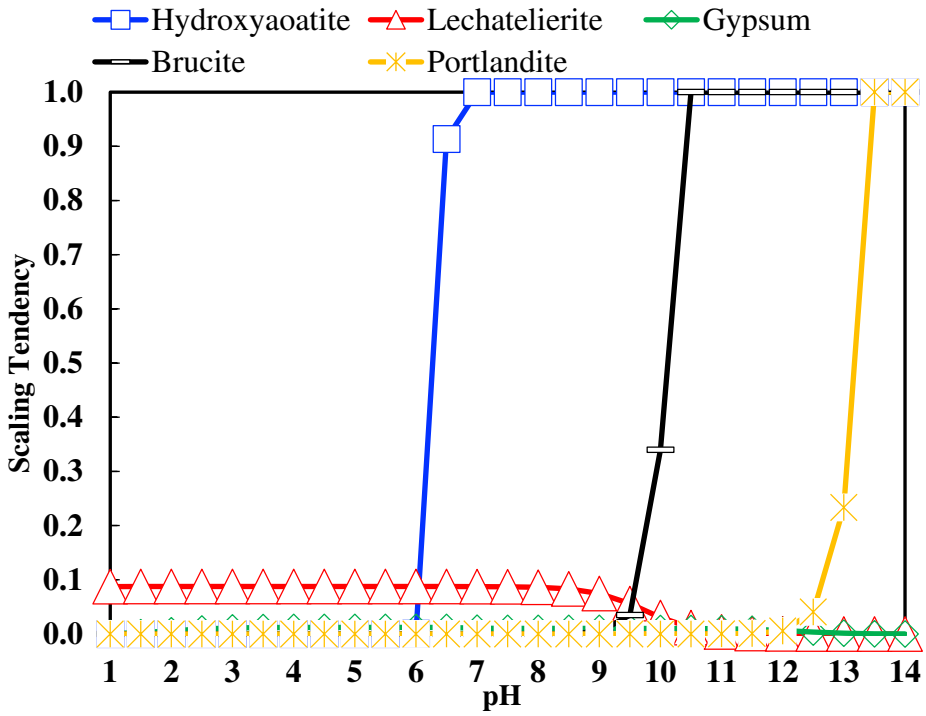

Figure C.3. OLI fouling tendency prediction as a function of pH

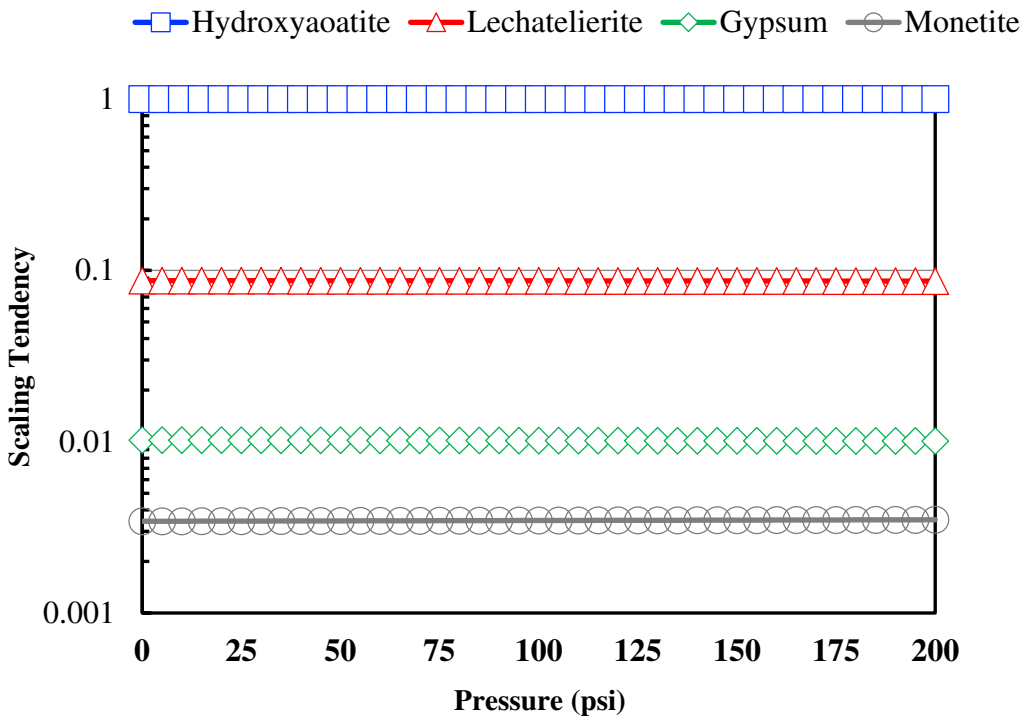

Figure C.4. OLI fouling tendency as a function of pressure