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Removal of Disinfection Byproducts in Drinking Water Using Biological Filtration

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REMOVAL OF DISINFECTION BYPRODUCTS IN DRINKING WATER USING BIOLOGICAL FILTRATION

BY

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This dissertation is approved as a creditable and independent investigation by a candidate for the Doctor of Philosophy degree and is acceptable for meeting the dissertation requirements for this degree. Acceptance of this does not imply that the conclusions reached by the candidate are necessarily the conclusions of the major department.

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ABSTRACT

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Drinking water disinfection is essential to protecting public health from waterborne diseases. However, the reaction of disinfectants with natural organic matter (NOM) can form carcinogenic disinfection byproducts (DBPs). Drinking water treatment facilities employ precursor control and alternative disinfectants to minimize regulated DBPs formation to comply with Environmental Protection Agency (EPA) guidelines. Despite their efficacy, some limitations have been observed during the application, such as increased cost of enhanced coagulation, high demand for sludge disposal, inconsistency in precursor removal, and formation of more toxic unregulated and unknown DBPs. Therefore, it is important to develop more efficient and safe strategies for DBPs control.

This study proposed a new strategy “pre-chlorine/biofiltration/post-chlorine treatment” to control DBPs formation in drinking water. The main objective of this study is to systematically analyze this strategy on overall DBPs control. The following tasks were performed to achieve the project objective: 1) investigating the potential of biofiltration technology for different groups of DBPs control and evaluating the impact of disinfect switch from chlorine to chloramine on biofilters performance on different DBPs removal; 2) studying the key factors that impact the performance of the biofilter on total organic halogen (TOX), unknown DBPs (UTOX), haloacetic acids (HAAs),

dihaloacetonitriles (DHANs) removal, developing kinetic models and temperature activity coefficients to predict different DBPs species removal rates under various conditions; and 3) evaluating the pre-chlorination - DBP biofiltration - post-treatment water treatment strategy in DBPs removal and overall DBPs formation potential control, and investigating the impact of backwash on biofilters performance on DBP removal.

The results of long-term biofiltration experiments using the City of Brookings drinking water indicate that biofiltration is an effective technology for DBPs control. Biofilters can consistently remove approximately 52% of the total organic halogens (TOX), 97% of haloacetic acids (HAAs), 14% of trihalomethanes (THMs), and 63% of unknown DBPs (UTOX) in chlorinated drinking water. Biofilters also effectively remove 46% of TOX, 14% of THMs, 96 % of HAAs, and 48% of UTOX from chloraminated drinking water. The two activated carbon biofilters (GAC 300 and 200) exhibited better DBP biofiltration efficiencies than sand and anthracite biofilters. The switch from chlorine to chloramine had little impact on HAAs biodegradation in GAC biofilters. However, it decreased UTOX biodegradation by 15%, indicating that the UTOX formed in the chloraminated water is less biodegradable than those formed in chlorinated water. Moreover, TOX spikes was observed in GAC biofilter effluents after switching to chloraminated water, which was mainly attributed to the leaching of THMs. Therefore, attention should be paid to potential DBPs leaching from GAC biofilters when switching disinfectant from chlorine to chloramine.

The DBP biofiltration kinetic study results indicate that a first-order model can adequately describe the degradation of different groups of DBP in GAC biofilters, including HAAs, unknown DBPs, and Dihaloacetonitriles (DHANs), across varied empty

bed contact times (EBCTs) ($R^2 > 0.95$). The biodegradation rate constants (k values) for these DBPs increased with increasing temperatures. Extending the EBCT is an effective method to improve DBPs removal, particularly at lower temperatures. In addition, the biodegradation rate constants for the studied DBPs at 5 - 20 °C were 0.106 - 0.273 min^{-1} for DCAA, 0.081 - 0.235 min^{-1} for TCAA, 0.020 - 0.046 min^{-1} for chlorinated UTOX and 0.018 - 0.040 min^{-1} for chloraminated UTOX. DHANs, including dichloroacetonitrile (DCAN), bromochloroacetonitrile (BCAN), and dibromoacetonitrile (DBAN), show effective biodegradability with k values between 0.098 and 0.427 min^{-1}. In conclusion, the observed biodegradability order of the studied DBPs is: DCAN > BCAN > DBAN > DCAA > TCAA > Cl_2-UTOX > NH_2Cl-UTOX > Chloroform. The developed first-order model and temperature activity coefficients offer a tool for predicting DBPs biodegradation rates under varying temperatures and EBCTs.

Furthermore, the results indicate that the DBP-preformation - biofiltration - post-treatment strategy effectively controls the formation potential of various DBP groups. Biofiltration could remove up to 57% of preformed TOX, mainly attributed to the degradation of unknown DBPs and HAAs. Although post-treatment with chlorine and chloramine would lead to some DBP re-formation, this strategy was able to reduce the overall formation potentials of different groups of DBPs. Compared to pre-chlorine and post-chlorine treatment, the pre-chlorine/biofiltration/post-chlorine treatment reduced 71% of HAAs, 37% of DHANs, 44% of UTOX and 17% of THMs. When post-chloramine was used, the corresponding formation potential reductions were 90% of HAAs, 83% of DHANs, 43% of UTOX and 10% of THMs at an EBCT of 15 min.

Therefore, the DBP-preformation - biofiltration - post-treatment strategy can significantly decrease the overall exposure of DBPs within the distribution system.

CHAPTER 1

INTRODUCTION

1.1 Background

Natural water sources often contain harmful microorganisms such as bacteria, viruses, and parasites that can lead to severe waterborne diseases like cholera, typhoid fever, and amoebic dysentery, which can pose a significant threat to human health. Therefore, strict microbiological controls are essential to ensure the safety of drinking water. Drinking water disinfection has proven to be an effective way to reduce the prevalence of waterborne diseases in drinking water, representing a significant public health achievement. Chlorine and chloramines are two widely used chemical disinfectants that have been employed in water treatment facilities for the past decades. Both are powerful oxidants that can inactivate various types of microorganisms, including bacteria, viruses, and parasites. However, they can react with natural organic matter (NOM), bromide, and iodide in the water, leading to the formation of unintended disinfection byproducts (DBPs). DBPs have emerged as a significant concern in drinking water treatment due to their potential negative impact on human health. Epidemiological studies have reported that there are associations between exposure to DBPs contaminated water and the increased risk of adverse health effects, such as bladder cancer, miscarriage, and congenital disabilities (Nieuwenhuijsen et al., 2009, 2000b; Richardson et al., 2007). As a result, drinking water facilities are mandated to control not only the presence of microorganisms but also DBPs in water to protect public health. To regulate the presence of disinfection byproducts (DBPs) in drinking water, the United States Environmental Protection Agency (EPA) has published EPA Stage 1 and Stage 2

Disinfectants and Disinfection Byproducts Rules (DBPRs) to control DBPs in drinking water (USEPA, 2019). To date, 11 DBPs have been regulated, including TTHM, HAA5, bromate, and chlorite. However, it is well established that chemical disinfection can produce a large number of unregulated and unknown DBPs that are potentially harmful to human health.

Drinking water treatment facilities employ various strategies to minimize regulated DBPs formation to comply with EPA regulations, including precursor control (reducing the NOM in the water), and using alternative disinfectants such as chloramine, or chlorine dioxide, which have lower reactivity with organic matter and bromide compared to free chlorine. Although conventional DBPs control strategies have proven effective in reducing the formation of regulated DBPs, some limitations have been observed during their application. Pre-treatment processes like coagulation and filtration can be expensive, require additional operations, and may not always effectively remove all organic matter. Switching to alternative disinfectants requires changes in water treatment infrastructure and can lead to the formation of more unregulated and unknown DBPs (Allen et al., 2022; Hua and Reckhow, 2008; Richardson et al., 2007). Consequently, it is as important to control those DBPs as well as THMs and HAAs to ensure water safety.

Biological filtration, also known as biofiltration, is an eco-friendly technology that has gained significant attention for its potential in controlling organic and inorganic contaminants during water treatment. Filtration media can be naturally converted to biological filters over time, allowing microorganisms to grow and form a biofilm on the media surface. These microorganisms metabolize biodegradable organic matter or

nutrients as energy sources, facilitating the removal of organic pollutants. To date, limited studies have been working on DBPs control using biofiltration. Considering the limitation of the conventional DBPs control strategies, exploring the possibility of biofiltration for DBPs control from drinking water is meaningful in drinking water treatment.

1.2 Formation of Disinfection Byproducts in Drinking Water

Chlorine is the most widely used disinfectant worldwide due to its cost-effectiveness, ease of operation, and broad-spectrum microorganism control efficacy. Chlorine is typically added to water in the form of chlorine gas, liquid sodium hypochlorite, or solid calcium hypochlorite. Upon its addition to water, chlorine initiates a chemical reaction known as chlorination, during which hypochlorous acid (HOCl) and hypochlorite ions (OCl^-) are formed. These compounds are highly reactive and can destroy pathogens by damaging their cellular structures and disrupting essential biological functions. However, chlorine can react with NOM in the water, leading to DBPs formation. The most common DBPs formed during the chlorination process are THMs (including chloroform, bromodichloromethane, dibromochloromethane, and bromoform) and HAAs (including monochloro-, dichloro-, trichloro-, monobromo-, dibromo-, tribromo-, bromochloro-, bromodichloro-, and chlorobromo- acetic acids), constituting approximately 23% and 22% of the Total Organic Halogen (TOX) in chlorinated water, respectively (Hua and Reckhow, 2008). Other DBPs such as Dihaloacetonitriles (DHANs), Haloketones (HKs), and Chloropicrin (CP) account for another 2 - 4% of TOX. Furthermore, approximately 50% of the TOX in chlorinated

water have not been identified and characterized due to the complexity of the mixture and the analytical challenges associated with their identification and quantification.

In recent years, chloramine has emerged as a crucial disinfectant in public water systems. Many drinking water treatment facilities have switched to chloramine as a secondary disinfectant for maintaining residual disinfection throughout the distribution system. The formation of chloramine occurs when ammonia is added to chlorinated drinking water. Compared to free chlorine, chloramines display a lower reactivity, thereby creating a substantially smaller disinfectant demand and lowering chlorine consumption to maintain a desired chlorine residual in the water. This subsequently reduces treatment costs. Also, because of the reduced oxidizing power, chloramine's interaction with NOM in the water leads to fewer DBPs formation, suppressing over 90% of THMs and HAAs formation compared to chlorine (Hua and Reckhow, 2008). This is one of the most important factors contributing to the demand of replacing chlorination with chloramination for drinking water treatment facilities.

Chloraminated water contains a higher percentage of unregulated and unknown (>80%) DBPs. Many of these unknown DBPs possess much higher toxicity levels than those currently regulated (Allen et al., 2022; Li and Mitch, 2018; Wu et al., 2022; Yeom et al., 2021). Therefore, additional analytical and toxicological studies are required to evaluate the advantages and disadvantages of using chloramine.

In summary, chloramination can produce less THMs, HAAs, and TOX compared to chlorination. However, considering the toxicity of emerging and unknown DBPs. The prevalence of using chloramine as disinfectant needs further study and consideration.

1.3 Impact Factors of DBPs Formation

The formation of disinfection byproducts (DBPs) in drinking water is influenced by several critical factors, including the contact time between disinfectants and water, the characteristics of natural organic matter (NOM), water pH, and temperature. Each of these factors plays a significant role in the formation and concentration of DBPs. Therefore, it is crucial to control these variables during water treatment processes to effectively manage and minimize DBP formation, ensuring the safety of drinking water.

1.3.1 Contact Time

Sufficient contact time between water and disinfectants is important for effectively inactivating or killing the microorganisms in water. This parameter also significantly impacts the formation of DBPs. During the chlorination process, as the concentration of free chlorine decreases, the reaction rate of chlorination diminishes. The decline of chlorine concentrations subsequently hinders the continued formation of disinfection byproducts (DBPs). Previous studies reported a rapid DBPs formation within the first few hours to 24 hours, and the UTOX-to-TOX ratio decreased with contact time in both chlorinated and chloraminated water (Hong et al., 2013; Hua and Reckhow, 2008; Xie, 2003).

1.3.2 NOM

NOM is a complex mixture of organic compounds in water and originated from decayed plants, leaves, algae, and animal matter decomposition. NOM's structural characteristics, including aromaticity, functional group composition, and specific DBP precursors, can considerably impact the DBPs during water treatment. NOM with a

higher proportion of aromatic constituents, primarily found in humic and fulvic acids, exhibits higher reactivity with disinfectants, thereby leading to elevated DBPs formation (Reckhow et al., 1990). This heightened reactivity is attributed to their π-electron systems, which can readily involve in reactions with disinfectants (Westerhoff et al., 1999). Another study reported that NOM precursors with high molecular weight produce 67-75% more THMs compared to low molecular weight NOM (Chowdhury, 2013). Additionally, the presence and distribution of functional groups, such as phenolic, carboxylic, and carbonyl moieties, also impact DBP formation due to their inherent reactivity with disinfectants (Shao et al., 2023; Young et al., 2018). Furthermore, specific compounds including amino acids and peptides can directly serve as precursors and form Nitrogen-DBPs which generally exhibit higher toxicity compared to their carbonaceous counterparts (Bond et al., 2012a; Dotson and Westerhoff, 2009).

1.3.3 Water pH

Water pH is a critical factor that affects DBPs formation. In the process of chlorination, the alkaline condition typically favors the formation of THMs and DHAA. Conversely, the acidic condition favors the formation of THAA and UTOX. A study conducted by Hua and Reckhow (2008) reported notable variations in DBPs concentrations at different pH levels. For example, THM concentration at pH 10 was three times higher compared to pH 5 and the DHAA concentration at pH 10 was 1.3 times higher than at pH 5. Conversely, THAA and UTOX show the opposite trend. Reducing chlorination pH level to 10 suppressed 90% of THAA and 47% of UTOX formation.

The pH levels also influence the stability of DBPs, as the hydrolysis and degradation rates of various DBPs are often pH-dependent, which can impact their overall stability in water. For instance, the hydrolysis rate of bromoform ($CHBr_3$) increases significantly under alkaline conditions, making it less stable at high pH values (Lin and Manley, 2012; Zhang et al., 2015). The stability of HAAs, such as dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA), is also influenced by pH. The deprotonation of DCAA and TCAA occurs at alkaline conditions, resulting in the formation of their corresponding anions, which are more susceptible to hydrolysis and subsequent degradation (Uyak et al., 2007; Wang et al., 2021). The pH levels also play an essential role in haloacetonitriles (HANs) stability. Yu and Reckhow (2015) found that the decomposition rates of HANs increased with increasing pH, with the most substantial impact observed for TCAN, which was in agreement with previous observations regarding HAN hydrolytic stability (Glezer et al., 1999; Oliver, 1983; Reckhow et al., 2001). However, it should be pointed out that the hydrolysis of THMs, particularly chloroform ($CHCl_3$), is relatively slow and not significantly affected by pH changes (Shams El Din et al., 1998; Torrentó et al., 2014). In addition, pH can impact the ionization state of functional groups in NOM, such as carboxylic and phenolic groups (Adusei-Gyamfi et al., 2019). Depending on their ionization state, these functional groups can react with disinfectants. For example, deprotonated phenolic groups are more reactive with chlorine compared to their protonated counterparts, implying that the reactivity of phenolic moieties with chlorine is increased at higher pH values (Criquet et al., 2015). However, the hydrolysis rate of bromoform ($CHBr_3$) increases significantly

under alkaline conditions, making it less stable at high pH values (Lin and Manley, 2012; Zhang et al., 2015).

1.3.4 Temperature

Temperature is another important factor that impacts DBP formation by affecting the reaction kinetics of disinfectants with NOM, as well as the stability and decay of disinfectants. Generally, higher temperatures accelerate the reaction between NOM and disinfectants, resulting in elevated DBPs formation. Liu and Reckhow (2013) conducted a study to understand the formation of DBPs in hot and cold water (8 - 55 °C) in a simulated distribution system. The study found that temperature significantly influences DBP formation, with elevated temperatures correlating with higher DBP concentrations. Specifically, hot water (55 °C) showed an increased formation of total trihalomethanes (TTHMs), HAAs, and other DBPs compared to cold water (20 °C). Many studies have also reported the highest formation of THM in summer primarily due to the elevated water temperature (Rodriguez et al., 2004; Toroz and Uyak, 2005).

1.4 Conventional Disinfection Byproducts Control Strategies

Considering the impact factors of DBPs formation, conventional control methods have focused on optimizing the disinfection processes and DBPs precursor control. It is challenging to achieve a balance between effective disinfection and minimizing DBP formation. Insufficient disinfection can lead to pathogenic outbreaks, posing risks to public health. Conversely, excessive disinfection can result in DBPs formation, which also raises concerns about public health (Richardson et al., 2007).

1.4.1 Optimization of Disinfection Process

Optimization of disinfection methods mainly focuses on using alternative disinfection methods to chlorine, such as chloramines, ozone, and ultraviolet (UV) disinfection. The selection and combination of different disinfectants can significantly impact the types and quantities of DBPs formed during the disinfection process.

A widely employed approach is to pre-treat water with ozone or chlorine dioxide prior to chlorination. Ozone and chlorine dioxide are powerful oxidants that are highly effective in inactivating a wide range of pathogens and can oxidize the precursors (NOM) of DBPs. They do not generate a significant amount of DBPs. They can destroy the aromatic and conjugated structures of NOM and transfer large aromatic and long aliphatic chain structures to small and hydrophilic organics. This transformative process increases the biodegradability of the NOM (Zhai et al., 2014). Following this pre-oxidation step, chlorination is applied as a secondary disinfection process. Studies have shown that the use of ozone or chlorine dioxide before chlorination can reduce 50% - 98% of THMs and 25% - 94% of HAAs formation depending on the choice of disinfectant for the secondary disinfection process (Hua and Reckhow, 2007; Zhai et al., 2014). However, the implementation of ozone or chlorine dioxide as pre-treatment agents also presents certain issues through the reaction with natural organic matter (NOM). Chlorine dioxide can react with NOM to form chlorite, which is one of the EPA-regulated DBP (Yang et al., 2021). Similarly, ozone can lead to bromate formation in water with high bromide levels, which is another EPA-regulated DBP (Wu et al., 2021). In addition, as previously mentioned, chloramines reduce the formation of halogenated DBPs compared to chlorine but can lead to the production of nitrogenous DBPs and

unknown DBPs, which are less studied and may cause more serious health effects (Muellner et al., 2007; Yu and Reckhow, 2017). Chloramination could also bring issues with biological stability in the distribution system, potentially prompting the growth of nitrifying bacteria, which causes nitrite and nitrate formation, posing substantial risks to human health (Regan et al., 2003).

UV is another disinfection option and does not lead to halogenated DBP formation. However, it is important to note that the disinfection efficiency is adversely impacted by water turbidity and suspended matter, therefore water needs to be pre-filtered before UV treatment. Another consideration is that UV disinfection does not provide a disinfectant residual in the water. Additional chlorine or chloramine disinfectant is required to provide the required residual to control microbial regrowth in the distribution system. Despite UV does not lead to the formation of halogenated DBPs, previous studies reported that UV radiation can transfer certain NOM fractions into more biodegradable compounds, potentially leading to microbial growth in distribution systems (Bazri et al., 2012; Sharpless and Linden, 2003).

1.4.2 DBPs Precursor Control

DBPs precursor control is a conventional treatment method widely applied in drinking water treatment facilities for DBPs control. As NOM is one of the most important factors for DBPs formation, precursor control strategies primarily aim to remove or alter NOM prior to disinfection, thereby reducing DBPs formation. Various techniques are employed in precursor control, including coagulation-filtration, membrane filtration, activated carbon adsorption, and biological filtration.

Coagulation-filtration is a well-established method used in water treatment facilities for NOM removal. The coagulation-filtration method includes a series of processes: coagulation, flocculation, sedimentation, and filtration. The treatment begins with coagulation by adding a certain dosage of coagulants, usually aluminum sulfate (alum) and ferric chloride, to the raw water. The coagulant can neutralize the particles' charges and cause suspended particles to bind together to form flocs. Following the coagulation, the water is slowly mixed to increase the aggregated particles to form larger flocs, which subsequently settle out of the water under gravity in sedimentation basins. The treated water is then filtered by media or membrane filters to remove the remaining particulate flocs. Although this method can be effective in NOM control, it has several limitations. For example, it cannot guarantee the complete elimination of NOM, especially for low-molecular-weight or hydrophilic NOM (Ghernaout, 2014; Jacangelo et al., 1995; Matilainen et al., 2010; Sharp et al., 2006). Additionally, determining the appropriate coagulant dosage can be difficult. An overestimated dosage can result in sludge production and disposal issues, while inadequate coagulation can lead to poor efficiency in NOM control. Another factor needs to be considered is water pH, as it can significantly affect coagulation efficiency. Additional pH adjustment steps may be necessary in cases of extreme pH levels (Chow et al., 2009; Hu et al., 2006; Qin et al., 2006; Yu et al., 2007).

Membrane filtration has been noticed as a promising technology for NOM control in drinking water treatment facilities in recent years. Reverse osmosis (RO) and nanofiltration can provide excellent NOM removal, significantly reducing DBP formation during disinfection. Studies have shown that membrane filtration can remove 70 - 99% of

NOM from water, therefore greatly reducing DBPs formation (Bond et al., 2012b; Ersan et al., 2016; Kitis et al., 2001; Koprivnjak et al., 2006). Although membrane filtration technology offers significant advantages in NOM control, several challenges restrict its wide application. During the process of membrane filtration, microorganisms, and NOM especially the hydrophobic fraction can accumulate on the membrane surface or block the pores of the membrane, reducing the filtration efficiency over time (Bond et al., 2012b; Howe et al., 2006; Jung et al., 2006; Zularisam et al., 2006). Therefore, membrane filtration requires regular cleaning and replacement. In addition, membrane filtration requires high operating pressures and thus increases the operation cost. Moreover, membrane systems are complex to operate and require careful monitoring and control to ensure effective operation.

Activated carbon filtration is an effective method for NOM control. Activated carbon is a porous media with a high surface area that provides numerous sites for NOM adsorption. It can attract a wide range of organic molecules due to hydrophobic and π-π interactions, making it highly effective for NOM removal (Matilainen et al., 2005; Menya et al., 2018). Activated carbon is particularly effective at removing the aromatic and high-molecular-weight fractions of NOM, which are the most reactive with disinfectants and, thus, the most important contributors to DBPs formation (Marais et al., 2018; Velten et al., 2011b). The efficacy of sorption processes for NOM removal varies largely from 50% to 95%, depending on temperature, contact time, water qualities and physicochemical properties of GAC media (Dias et al., 2007; Iriarte-Velasco et al., 2008; Matilainen et al., 2006; Menya et al., 2018). However, the adsorption capacity of activated carbon can be

exhausted over time. Therefore, the carbon needs to be regenerated or replaced periodically to maintain the effectiveness of NOM control.

Biological filtration, also known as biofiltration, is an eco-friendly technology that has gained significant attention for its potential in controlling organic and inorganic contaminants during water treatment. Filtration media can be naturally converted to biological filters over time, allowing microorganisms to grow and form a biofilm on the media surface. These microorganisms metabolize biodegradable NOM or nutrients as energy sources, facilitating the removal of organic pollutants. Recent studies have reported 15 - 65% of DOC removal in biological filters (Cuthbertson et al., 2020; Kirisits et al., 2019; Korotta-Gamage and Sathasivan, 2017; Liu et al., 2022). Sand, anthracite, and GAC are the most common biofilter media. Among the various biofilter media, GAC has gained increased interest as the unique porous structure provides a large surface area for microorganisms to attach and grow. This porous structure can help host a phylogenetically more diverse community, therefore, a GAC biofilter can remove different types of pollutants (Vignola et al., 2018). Additionally, the porous structure creates microenvironments that shield the microorganisms from rapid changes in the external environment, thereby enhancing the stability and effectiveness of the biofiltration process and leading to higher pollutant removal efficiency (Basu et al., 2016; Fox et al., 1990; Urfer et al., 1997a).

Despite applying various strategies, challenges persist in regions with high NOM concentrations as not all NOM can be completely removed from the water. The residual NOM can still react with disinfectants to form DBPs. Moreover, it is worth noting that

DBPs tend to accumulate with water age (Hua and Reckhow, 2008). Consequently, areas with high water age often face more pronounced challenges related to DBP control.

1.5 Biodegradation of Disinfection Byproducts

Biofiltration has been traditionally and widely used for DBPs precursor control. Recent studies have reported that biofiltration can also directly remove some DBPs. However, only limited DBPs have been studied for removal efficiency in biofilters to date. Further study is necessary to explore the full extent of DBP removal efficiency in biofilters and optimize their performance in DBP control.

1.5.1 Haloacetic Acids

HAAs are one of the largest DBPs groups in chlorinated water. In the 1990s, HAAs biodegradation was suspected to occur in drinking water distribution systems. Singer *et al.*, (1993) reported the rapid elimination of HAAs in chlorinated water during aquifer storage and proposed aerobic biofiltration as the removal mechanism. In 1994, Williams et al., (1994) reported that the lowest HAAs concentrations were observed at the longest residence time location in the distribution systems due to biodegradation and the concentration declination. Since then, systematic studies have been carried out to investigate the biodegradation of HAAs in BAC filters. These studies have explored the effects of different parameters including concentrations, contact time, temperature, and biomass concentration and confirmed that HAAs are highly biodegradable. The biodegradation pathway of HAAs involves several key steps: 1) dehalogenation, where halogen atoms are removed by dehalogenase enzymes via reductive or hydrolytic mechanisms, resulting in the formation of intermediate compounds including glycolic

acid, glyoxylic acid, and oxalic acid; 2) oxidation or reduction reaction, catalyzed by various enzymes, such as oxidases, dehydrogenases, or reductases, therefore producing simple organic compounds; 3) cleavage of carbon-carbon bonds by enzymes like decarboxylases or dioxygenases, resulting in the removal of a carboxyl group or the incorporation of molecular oxygen into the substrate; and 4) mineralization, converting smaller molecules into inorganic compounds, such as CO_2, H_2O, and inorganic salts (Ellis et al., 2001; Kim and Kang, 2008; Tang et al., 2013; Xie and Zhou, 2002a). Most previous studies have reported 90 - 100% of HAAs removal in biofiltration systems with chlorine residuals < 0.3 mg/L environment (Bayless and Andrews, 2008; Cuthbertson et al., 2020, 2019; Tang and Xie, 2016a; Tung and Xie, 2009; Xie and Zhou, 2002a).

1.5.2 Trihalomethanes

THMs are the most prominent class of DBPs in chlorinated water. They are composed of a methane molecule and the three hydrogen atoms that have been substituted by halogen atoms. Studies have shown that THMs are generally resistant to biodegradation under typical environmental conditions due to their stable chemical structures (Cuthbertson et al., 2020, 2019; Kim and Kang, 2008; Liu et al., 2017; Sinha et al., 2021; Wobma et al., 2000). THMs have limited capacity to serve as direct carbon and energy sources for microbial growth, and they do not readily break down in the environment by microorganisms (Cuthbertson et al., 2020; Wobma et al., 2000). Although no bacteria string has been found can use THMs as a direct growth substrate, it has been reported that the aerobic cometabolism process can be applied for limited THMs degradation (7 - 24% removal) in nitrifying biofilters with 4 mg N/liter of total ammonia nitrogen addition (Wahman et al., 2011a, 2011b). However, drinking water treatment

plants often lack the prerequisites for the cometabolism (e.g., high concentration of target bacteria - Nitrosomonas Europaea, primary substrates >4 mg/L ammonia for bacteria growth). Moreover, several studies reported that the TCM degradation products (phosgene or other intermediates such as aldehydes) are toxic, which can inhibit the ammonia-oxidizing activity of Nitrosomonas Europaea (Cappelletti et al., 2012; Wahman et al., 2006). Therefore, it is hard to biodegrade THMs in drinking water treatment biofilters. Most studies have reported less than 25% removal in both lab-scale and pilot-scale biofiltration systems (Cuthbertson et al., 2020; Kim and Kang, 2008; Tang and Xie, 2016b; Wahman et al., 2011a; Wobma et al., 2000).

1.5.3 Emerging DBPs

1.5.3.1 N-Nitrosodimethylamine

N-Nitrosodimethylamine (NDMA) is a nitrosamine DBP from the reaction of chloramines, specifically dichloramine, with organic nitrogen-containing compounds. Formation precursors include secondary, tertiary, and quaternary amine-containing compounds (Mitch and Sedlak, 2002). They have garnered considerable scientific attention due to the potential environmental persistence and high carcinogenicity (Krasner et al., 2013). The World Health Organization (WHO) has established drinking water guidelines for NDMA (maximum allowable concentration ≤0.1 µg/L). Recent studies have highlighted that the biodegradation of NDMA appears to be primarily facilitated by specific strains of bacteria, including Ralstonia pickettii PKO1, Pseudomonas mendocina KR1, Rhodococcus ruber ENV425, Methylosinus tri-chosporiumOB3b and Mycobacterium vaccae JOB-5 (Sharp et al., 2005). These bacteria engage in reductive denitrosation processes, whereby the nitroso group of NDMA is

reduced by specific enzymes, such as soluble methane monooxygenase (sMMO), propane monooxygenase (PMO), and toluene 4-monooxygenases, leading to the breakdown of the NDMA molecules (Fournier et al., 2009; Sharp et al., 2005). To date, few studies have systematically analyzed NDMA removal in biofiltration systems. Considering their toxicity and the potential of biofiltration technology, further studies should aim to quantify NDMA removal efficiency and explore the impact factors of the biofilter performance in NDMAs control.

1.5.3.2 Dihaloacetonitriles

Dihaloacetonitriles (DHANs) are a class of disinfection by-products (DBPs) formed during water treatment with disinfectants such as chlorine, chloramine, chlorine dioxide, or ozone, with the highest concentrations detected in chloraminated finished drinking water (Bond et al., 2012a; Richardson et al., 2007). Dichloroacetonitrile (DCAN), bromochloroacetonitrile (BCAN), and dibromoacetonitrile (DBAN) are the three DHAN species that have gained increasing attention due to their potential adverse health effects and widespread occurrence in drinking water supplies. Despite their lower concentrations than regulated DBPs such as trihalomethanes and haloacetic acids, DHANs are considered significant drivers of cytotoxicity in drinking water (Allen et al., 2022; Richardson et al., 2007). The WHO has established drinking water guidelines for two haloacetonitriles: 20 μg/L for DCAN and 70 μg/L for DBAN. Conventional water treatment methods, such as coagulation and filtration are generally ineffective in removing DHAN precursors. Therefore, it is crucial to develop more effective methods for DHAN removal from drinking water. So far, the study of DHANs' biodegradability remains a relatively unexplored domain compared to THMs and HAAs. As previous

research has shown that biological filtration can effectively remove certain DBPs such as HAAs (Tang and Xie, 2016b; Wobma et al., 2000; Xie and Zhou, 2002b). It is worthwhile to investigate the potential of this technology for DHANs removal.

1.5.3.3 Unknown Disinfection Byproducts

While more than 700 DBPs have been identified, a significant proportion remains undiscovered. Measurement of total organic halogen (TOX) showed that over 50% and 80% of TOX formed during the chlorination and chloramination, respectively, remain unknown (Hua and Reckhow, 2007). The UTOX compounds have shown a wide range of molecular weight distribution. The molecular weight (MW) distribution of UTOX exhibited approximately 40% for the size range below 0.5 kDa, 44% for the range of 0.5 - 3 kDa, 14% for the range of 3 - 10 kDa, and 2% for the range above 10 kDa (Hua and Reckhow, 2006a). Experiments with XAD-4/8 resin fractionation revealed that the hydrophobicity of UTOX in chlorinated water was 26%, 33%, and 41% for hydrophobic, transphilic, and hydrophilic fractions, respectively (Hua and Reckhow, 2006a). Many aromatic halo-DBPs have been identified in drinking water recently. These include compounds such as halophenols, halohydroxybenzaldehydes, halohydroxybenzoic acids, halosalicylic acids, halohydroquinones, halonitrophenols, halopyrroles, and halophenylacetonitriles (Jiang et al., 2020; Liu and Zhang, 2014; Pan and Zhang, 2013; Yang and Zhang, 2013; Zhai and Zhang, 2011).

Given the existing technological limitations and capabilities, identifying all types of DBPs is an extremely difficult task. Therefore, the idea of considering UTOX as a collective entity and developing effective methods for UTOX control is valuable and essential to minimize the adverse impacts of DBPs on public health. To date, research on

the control of unknown DBPs is limited, and even less attention has been given to their biofiltration. A comprehensive understanding of their biodegradability is important, as it has the potential to significantly enhance public health protection and inform future applications of biofiltration in water treatment processes.

1.6 Potential Factors Affecting Biofilters Performance in DBPs Removal

1.6.1 Materials

While conventional filtration systems typically use granular materials such as sand, anthracite and GAC as filtration media, when it comes to biofiltration systems, it is advantageous to utilize GAC as part or all of the filtration. Thanks to the large surface area, irregular surface, and surface charge, GAC can support a higher density of microorganisms (4 - 8 times more biomass per gram of media) and phylogenetically more diverse microbial community compared to sand and anthracite (Basu et al., 2016; Fox et al., 1990; Vignola et al., 2018; Wang et al., 2006). Conventionally, it is important to replace the GAC once the adsorption capacity is saturated. But when the filter is operated in biofiltration mode, and the GAC can be naturally transformed into biological activated carbon (BAC) after adsorption is exhausted. GAC is used as a growth media for beneficial microorganisms to attach. Consequently, the enhanced microbial density could potentially enhance the removal of contaminants within a biofilter. In a pilot-scale study for DOC removal by GAC and anthracite biofilters, at an EBCT of 8 min, GAC achieved approximately 11 - 14% of DOC removals while anthracite showed only about 1 - 3% (Thiel et al., 2006). Doubling the EBCT to 16 min increased the DOC removal in GAC to about 15 - 20%. Another full-scale study found that GAC and anthracite showed similar removal efficiency at warmer temperatures (21 - 24 °C). However, at colder temperatures

(1-3 °C), average TOC removal of 23% was observed in GAC filters, while 14% was observed for the anthracite filters (Emelko et al., 2006). Liu, Huck and Slawson, (2001) investigated the effects of media type and chlorinated backwash on biological NOM removal in a bench-scale study. The study found that NOM removal in GAC/sand filters similar at both 5 °C and 20 °C, whereas anthracite/sand filters exhibited inconsistent results.

In summary, while various media types can support biofiltration, GAC filters generally provide more robust media surface for microbial growth that can maintain high DOC removal efficiency under different operation conditions. As DBPs removal in biofilters remains an underexplored area, it is valuable to compare the impact of different materials on biofilters performance in DBPs removal.

1.6.2 Temperature

Temperature plays an important role in dictating the efficiency of biofilters performance in contaminant removal efficiency, as it directly impacts microbial growth and degradation rates. According to a study by Selbes *et al.* (2016), both dissolved organic carbon and dissolved organic nitrogen removals were significantly decreased at water temperatures between 10-15 °C compared to those between 15-24 °C. Similar data were reported by Moona *et al.* (2021), who found that DOC removal efficiency decreased by 27% when the temperature decreased from 17 to 9 °C. Moreover, Liu, Huck and Slawson, (2001) reported that temperature was an important factor in achieving steady-state removal of NOM. GAC filters started in warmer temperatures achieved about 70 % removal of glyoxal after 20-40 days, while colder temperature start-ups took >60 days to achieve a similar removal rate. While low temperatures may negatively impact

biofiltration performance, some studies suggest that these effects can be mitigated with appropriate operating conditions. Hozalski, Bouwer and Goel, (1999) reported that extending the EBCT can help counteract the adverse impact of lower water temperatures, thereby attaining the same steady-state removal efficiencies.

Therefore, it is important to explore the impacts of temperature on biofilter performance on DBPs removal of biofilters. And it is crucial to develop and employ effective strategies to counteract the potential adverse effects of colder temperatures on biofiltration to ensure consistent performance of biofiltration throughout the year.

1.6.3 Empty Bed Contact Time (EBCT)

EBCT is widely recognized as another important impact factor of biofilter performance in contaminant control. EBCT represents water residence time within a filter, which is typically measured in minutes and calculated by dividing the volume of the filter bed by the flow rate of the water.

$$\boldsymbol{EBCT} = \frac{\boldsymbol{Empty\ Bed\ Volume}\ (\boldsymbol{cm^3})}{\boldsymbol{Flow\ Rate}\ (\frac{\boldsymbol{cm^3}}{\mathbf{min}})}$$

Studies have shown that longer EBCTs enhance substrate utilization and result in more contaminant removal efficiency. Several studies have reported an apparent correlation between EBCT and NOM removal. Wang and Summers (1994), for example, found that hydraulic loading rate (HLR) within a range of 1.5-15 m/h did not affect NOM removal when measured at the same EBCT. However, increasing the EBCT from 3 to 33 minutes leads to an increase in DOC removal from 16% to 24%. Similarly, Carlson and Amy (1998) observed comparable DOC removal rates in two anthracite biofilters

operating at different HLRs (5.0 and 9.7 m/h) but with the same EBCT (10 and 11 min). Another study revealed a correlation between operational temperatures and EBCT, which indicated that lower temperatures required longer EBCT to reach stable conditions (Hozalski et al., 1999). Thus, EBCT should be carefully selected to achieve the desired removal at specific influent conditions.

1.6.4 Backwash

Proper backwashing is important to optimizing the performance of biofilters. This process works through various mechanisms including the detachment and elimination of biomass such as bacteria, protozoa, and other microorganisms. Additionally, backwashing facilitates the redistribution of media along with its attached biomass, neutralizes any potential oxidants present in the backwash water, and effectively removes accumulated particles. Supplemental methods such as air scour, and chlorine can further enhance routine backwashing procedures.

In a comprehensive study by Emelko *et al.*, (2006), the effects of air scour and subfluidized backwash on TOC and oxalate removal were investigated across a temperature range of 1-24 °C. No significant TOC removal variation was observed in GAC/sand filters and anthracite/sand filters, regardless of the presence or absence of air scour. This indicates that both TOC and oxalate removal were unaffected by collapse pulsing.

Liu, Huck and Slawson, (2001) explored the impact of backwashing with chlorinated water (0.5 mg Cl_2/L) at 20 °C on BOM removal in both GAC and anthracite/sand biofilters. Results showed no significant impact on BOM removal in both

biofilters. However, a decrease in glyoxal removal in the anthracite/sand filter was observed when exposed to chlorine. At 5 °C, chlorine appeared to have a detrimental effect on BOM removal in the anthracite/sand biofilter, but not in the GAC filter, implying that GAC biofilters may possess a greater resilience to changes in temperature and backwash conditions. Wert *et al.*, (2008) found that BOM removal was not impacted by backwash procedures and filtration rates. After 165 days of operation, the biofilter achieved 60% BOM removal. Similar results were also reported by Hozalski, Bouwer and Goel, (1999b), which indicated that backwashing had negligible effects on BOM removal unless biomass loss during backwashing exceeds 60%. This finding implies that backwashing does not adversely affect biofilter performance up to a certain threshold.

In conclusion, regular and effective backwashing is essential to maintaining biological filter performance. Although backwash did not significantly impact the NOM removal, the impact on DBPs removal is still unclear. Understanding the effects of backwash on DBPs removal in biofilters is essential to enhance biofilter performance.

1.7 Research Objectives

Given the high toxicity of emerging and unknown DBPs, and the limitations of traditional technologies for DBPs control, this research project proposes a new DBP control strategy, “pre-chlorination - DBP biofiltration - post-treatment water treatment” to minimize the DBPs formation potentials in the drinking water. In this strategy, per-chlorination of drinking water will produce a large amount of regulate, unregulated, and unknown DBPs. These DBPs may include many intermediate halogenated compounds that could form regulated THMs and HAAs upon further chlorination. Then, biofiltration will be used to remove these pre-formed DBPs. Certain amounts of DOC will also be

removed by this biofiltration stage. After the pre-formed DBPs and DOC levels are reduced by biofiltration, post-chlorination or chloramination will be used to achieve required disinfection and maintain residual disinfectant in the distribution system. The main objective of this study is to systematically analyze this strategy on overall DBPs control. This project involves in the following research tasks:

(1) Investigating the potential of biofiltration technology for different DBP species control and studying the impact of disinfect switch from chlorine to chloramine on biofilters performance.

(2) Investigating the key factors impacting the performance of the biofilter on total organic halogen (TOX), unknown DBPs (UTOX), Haloacetic Acids (HAAs) removal, and developing kinetics model and temperature activity coefficients to predict different DBPs species removal rates under various conditions.

(3) Evaluating GAC biofilters for DHANs removal and studying the impact of initial concentration, EBCT, and temperature on BAC filter performance for DHANs removal and developing kinetic models and temperature activity coefficients to predict DHANs biodegradation rates under various conditions.

(4) Evaluating the “pre-chlorination - DBP biofiltration - post-treatment water treatment strategy” for the reduction of overall DBPs formation potential.

1.8 Dissertation Overview

In chapter 2, “Biofiltration of Disinfection Byproducts in Chlorine and Chloramine Treated Drinking Water”, four different lab-scale biofilters with different media (sand, anthracite, and two different GAC) were built to evaluate long-term

biofiltration of TOX, THMs, HAAs and unknown DBPs in drinking water. After 360 days of operation pf chlorinated water, the influent water was switched to chloraminated water to investigate the impacts of disinfectant switch on the performance of biofilters in DBPs removal.

In Chapter 3, “Determination of Disinfection Byproducts Removal Kinetics in Granular Activated Carbon Biofilters”, duplicate lab-scale GAC biofilters were constructed and operated for six months to evaluate the biodegradation of DBPs. Humic acids were used as precursors to produce DBPs during chlorination and chloramination and were used as the feed to the biofilters. The biofilters were operated under different temperatures (5, 10, and 30 °C) and empty bed contact times (5, 10, 15, 20, and 30 min) to evaluate the removal efficiency of THMs, HAAs, and UTOX. Kinetic models were developed to describe the biodegradation of different groups of DBPs in biofilters. Furthermore, the temperature activity coefficient of each DBPs was calculated to reflect the impact of temperature on their biodegradation.

In Chapter 4, “Evaluation of the Impacts of Initial Concentration, Empty Bed Contact Time, and Temperature on Dihaloacetonitriles Removal in Biological Activated Carbon Filters”, duplicate lab-scale biofilters with GAC 300 were constructed and operated for 120 days to evaluate the removal efficiency of DHANs in BAC filters. Subsequently, biofilters were operated under varying DHANs initial concentrations (1-4 mM), EBCTs (5-30 min), and temperatures (5-20 °C) to analyze the impacts of these factors on DHANs removal. Kinetic models were developed to describe the biodegradation of DCAN, BCAN, and DBAN in biofilters. Additionally, the temperature

activity coefficient of each DHAN was calculated to assess the impact of temperature on their biodegradation.

In Chapter 5, “Removal of Disinfection Byproducts by Pre-Chlorination - Biofiltration: A New Strategy to Controlling DBPs in Drinking Water”, duplicate lab-scale biofilters with GAC 300 were constructed and operated with chlorinated water for four months to establish biological stability. Subsequently, the biofiltrated water was post-treated with chlorine and chloramine. The formation of DBPs during the 24-hour post-treatment was monitored. The DBP formation potentials of raw water with and without biofiltration, were compared to comprehensively evaluate the DBP pre-formation- biofiltration-post chlorination and chloramination technology for the control of DBP formation potential.

CHAPTER 2

BIOFILTRATION OF DISINFECTION BYPRODUCTS IN CHLORINE AND CHLORAMINE TREATED DRINKING WATER

2.1 Introduction

Disinfection of drinking water is critical to protect public health from waterborne diseases. However, chemical disinfectants can also react with natural organic matter (NOM), bromide, and iodide in the water to form unintended disinfection byproducts (DBPs) (Hua et al., 2006; Krasner et al., 1989; Richardson et al., 2007; Singer, 1994). Epidemiological studies have reported low but significant associations between the ingestion of some DBPs with adverse health risks, including adverse reproductive outcomes, colorectal and bladder cancer (Li and Mitch, 2018; Nieuwenhuijsen et al., 2000a; Richardson et al., 2007; Villanueva et al., 2007). To minimize the health concerns of DBPs exposure on human health, U.S.EPA has published EPA Stage 1 and Stage 2 Disinfectants and Disinfection Byproducts Rules (DBPRs) to control DBPs in drinking water. Currently, only 11 out of over 700 identified DBPs are regulated, including THM_4, HAA_5, bromate, and chlorate. The measurement of total organic halogen (TOX) indicated that >50% of the total organic halogen (TOX) formed during the chlorination is still unknown (Hua and Reckhow, 2007). To comply with EPA regulations, many drinking water treatment plants are switching from chlorine to chloramine for secondary disinfection to reduce the formation of THMs and HAAs. Evidence shows that chloraminated water contains a higher percentage of unknown (>80%) DBPs (Hua and Reckhow, 2007). Many newly identified DBPs (such as aromatic species) were reported to be much more toxic than the regulated DPBs (Ersan et al., 2019; Han et al., 2021;

Muellner et al., 2007; Richardson et al., 2007; Simmons et al., 2002; Stalter et al., 2016). Therefore, the current DBP regulations and monitoring of individual DBP may underestimate the adverse health effects of DBPs exposure. TOX is a surrogate parameter that has been widely used for total organic halogens detection in drinking water (Chen et al., 2021; Hua and Reckhow, 2006b; Simmons et al., 2002; Yang et al., 2014). It is also a good indicator of the overall toxicity of DBPs of a water sample (Li et al., 2017; Richardson et al., 2007). Therefore, studies of TOX removal from drinking water are necessary to minimize the human health risk concerns associated with DBPs.

As one of the sustainable technologies that can effectively remove organic and inorganic matter from water, biological filtration has been increasingly used for drinking water treatment in the last two decades (Cohen, 2001; Simpson, 2008). Compared with traditional filtration systems, biofiltration system can effectively remove various contaminants, such as NOM, nitrogen compounds (Aslan and Cakici, 2007; Cai et al., 2014), heavy metals (Katsoyiannis and Zouboulis, 2004; Pacini et al., 2005; Pokhrel and Viraraghavan, 2009), and biological contaminants (Schijven et al., 2013); and produce biologically stable water with low turbidity (Bruce E. Rittmann, 1984). The biodegradation process is carried out by the microbial communities that grow in the form of biofilms attached to the filter media (Xu et al., 2020). The biofiltration system is commonly applied in water treatment plants prior to disinfection application to remove biodegradable NOM and many other contaminants, thereby helping minimize the formation of DBPs and reduce the occurrence of bacteria regrowth in the distribution system (Basu et al., 2016; Chen et al., 2016; Terry and Summers, 2018). Sand, anthracite,

and granular activated carbon (GAC) are the most common biofilter media (Xu et al., 2020).

Although biofiltration has been widely used for DBPs precursor control, limited information is available on the application of biofiltration for the removal of preformed DBPs in during drinking water. Recent studies found that HAAs can be directly removed via biofiltration. For example, nearly complete removal (80% -100%) of HAAs could be achieved in biofilters, indicating that biofiltration could be a viable solution for HAA control (Bayless and Andrews, 2008; Kim and Kang, 2008; Singer et al., 1993; Tung and Xie, 2009; Xie and Zhou, 2002b; Zhang et al., 2009). The biodegradation of HAAs is a hydrolysis-oxidation process in which a hydroxyl group replaces the halogen atom, and the removal efficiency is positively correlated to temperature (Bayless and Andrews, 2008; Cuthbertson et al., 2019; Grigorescu et al., 2010; Kim and Kang, 2008; Tung and Xie, 2009). Apart from HAAs, the biofiltration of THMs has also been previously investigated. However, the results indicated that biofiltration was ineffective in THMs control (<15% removal efficiency) whether in lab-scale or pilot-scale studies (Cuthbertson et al., 2019; Kim and Kang, 2008; Tang and Xie, 2016b). The reason was that the biodegradation of THMs under aerobic conditions was thermodynamically unfavorable. The three-halogen components are more oxidized than oxygen, preventing the aerobic biodegradation reaction from inserting oxygen into THMs (Wobma et al., 2000). Therefore, THMs have no/limited potential to serve as direct carbon and energy source for microbial growth.

To date, majority of DBPs biofiltration studies aimed at regulated DBPs removal. Information about TOX and unknown DBPs biofiltration is still lacking in the literature. The evaluation of TOX and unknown DBPs removal via biofiltration could provide a new tool for the control of unknown DBPs in drinking water. Moreover, as more drinking water treatment facilities switch disinfectant from chlorine to chloramine, a study of the impacts of disinfectants switch on biofilters performance is necessary.

The primary objective of this study was to assess the effectiveness of different biofilters for DBPs, especially TOX and unknown DBPs removal from chlorinated and chloraminated water. The secondary objective of this study was to evaluate the impacts of the disinfectant switch on biofilters' performance on different DBPs control. To achieve this, four different biofilters (sand, anthracite, and two different GAC) were built to evaluate the TOX and unknown DBPs long-term biofiltration in chlorinated water. After 360 days of operation, the influent water was switched to chloraminated water to investigate the impacts of the disinfectant switch on biofilters performance on TOX and unknown DBPs control.

2.2. Materials and Methods

2.2.1 Filter Media and Biofilter Design

Sand, anthracite, and two types of granular activated carbon (GAC 200 and GAC 300) were used as filter media. Sand and anthracite were provided by Red Flint Sand and Gravel, and GAC 200 (Calgon Filtrasorb® 200) and GAC 300 (Calgon Filtrasorb® 300) were provided by Calgon Carbon. All media were rinsed in ultrapure water (18 mΩ-cm) produced by a Barnstead GenPure System (Thermo Fisher, Waltham, MA) and air-dried

for 3 days before use. Each media was then packed into a glass chromatography column (Omnifit, 10 cm length, 1.5 cm diameter, with two fixed endpieces) to achieve a 6 cm column height. The packing density, and specification of each media were summarized in Table 2.1.

2.2.2 Biofilter Influent Water

The biofilter influent water used in the experiment was the tap water produced by Brookings Drinking Water Treatment Facility, which is located in the south of Brookings County, SD. This water treatment facility uses groundwater as the drinking water supply. The treatment processes consist of raw water aeration, rapid mixing, flocculation, sedimentation, rapid sand filtration, disinfection, and a chemical feed system for lime, sulfuric acid, sodium polyphosphate, fluoride, and disinfectant. Chlorine was applied as a disinfectant for secondary disinfection prior to October 2020. To decrease the formation of THMs and HAAs, Brookings Water Treatment Facility switched the disinfectant from chlorine to chloramine in October 2020.

The tap water was collected and stored at room temperature (20 °C) for five days and then dechlorinated with sodium sulfite before use. The characteristics of influent water are summarized in Table 2.2.

2.2.3 Biofiltration Experiments

The filter media were inoculated through seeding 432 bed volumes (BV) of natural surface water (with 10-min empty bed contact time [EBCT]) in the packed columns. The nature surface water was collected from the Big Sioux River (Brookings County, SD) and stored at room temperature (20 °C) for 24 hours before use. The

concentrations of fecal and total coliforms of the collected surface water were 21 MPN/ mL and 140 MPN/mL.

The experiments were separated into two phases: Phase 1 (day 1 to day 360) used tap water that had been disinfected by chlorine (referred to as chlorinated water), and Phase 2 (day 361 to day 540) used tap water that had been disinfected by chloramine (referred to as chloraminated water). In Phase 1, the columns were fed with dechlorinated water with 15-min EBCT to investigate the TOX and individual DBPs removal in biofilters with different media. After 310 days of operation, the columns were operated at EBCT 10, 15, and 20 minutes using a variable-speed peristaltic pump (Masterflex L/S, Cole-Parmer, Vernon Hills, IL) to investigate the impacts of hydraulic retention time on the DBPs biodegradation. The columns were operated at each flow rate for 14 days. The first 7 days were used as the stabilization period to ensure that steady-state removal was reached for each flow rate (the removal efficiency stabilized within ± 1% in 4 days in a row), and the last 7 days were used as the sampling period. In Phase 2, the influent water was switched to chloraminated water, and the columns were operated with 15-min EBCT for another 180 days. The variations of DBPs removal in each column were monitored to investigate the impacts of the disinfectant switch on the performance of biofilters in DBPs removal, as well as the TOX and UTOX long-term biofiltration in chloraminated water.

Samples for TOX measurement were acidified to pH 2 with nitric acid. Samples for THM measurement were adjusted to pH 4.5-5.5 with phosphate buffer. All samples were then stored at 4 °C and analyzed within two weeks.

Throughout the experiment, the room temperature was kept constant at 20 °C. The filters were stirred weekly to remove biomass formed on the filter to avoid filter clogging, and no backwash was performed.

2.2.4 Analytical Methods

All solutions used in this study were prepared with ultrapure water (18 mΩ-cm) produced by a Barnstead GenPure System (Thermo Fisher, Waltham, MA). The fecal and total coliform were quantified by Colilert 18 method (IDEXX; Westbrook Maine). The DOC concentrations were measured by a TOC-V CSH Analyzer (Shimadzu Corp., Kyoto, Japan) according to Standard Method 5310 B (Baird et al., 2017). Chlorine, chloramine residuals were determined by the DPD ferrous titrimetric method. The TOX was determined using the adsorption-combustion-titration method with a Mitsubishi TOX-100 Analyzer (Cosa Xentaur Inc., Norwood, NJ) based on standard method 5230B (Baird et al., 2017). HAA_9 (including monochloro-, dichloro-, trichloro-, monobromo-, dibromo-, tribromo-, bromochloro-, bromodichloro-, and chlorobromo- acetic acids) were measured using liquid/liquid extraction with methyl-tertiary-butyl-ether (MTBE) followed by derivatization with acidic methanol and analyzed by gas chromatography with an electron capture detection (GC/ECD, Thermo Fisher, TRACE 1310) according to U.S.EPA 552.3. THM_4 (chloroform, bromodichloromethane, dibromochloromethane, and bromoform), three dihaloacetonitriles (dichloro-, bromochloro-, and dibromoacetonitrile), three haloketones (dichloro-, trichloro-, 1,2-dibromo-3chloropropanone), as well as several other chlorine and bromine containing compounds (trichloroethylene, 1,2-dibromoethane, 1,2-dibromo-3-chloropropane, tetrachloroethylene, and chloropicrin) were analyzed by liquid/liquid extraction with pentane and by GC/ECD according to U.S.

EPA 551.1. The UTOX concentration was calculated by the difference between TOX and the sum of the measured DBPs concentration (as Cl).

2.3. Results and Discussion

2.3.1 TOX and DOC Removal in Chlorinated Water

Figure 2.1a shows the influent and effluent TOX concentrations of the four biofilters during the 310 days of operation. The TOX concentration of influent water was stable between 142.6 to 167.7 μg/L, with 155.1 μg/L on average. The TOX distribution was 30.3% THMs, 13.9% HAAs, 2.9% minor products, and 52.9% UTOX.

No significant TOX removal was observed for the first 14 days in the anthracite column. While the TOX removal efficiency progressively increased and stabilized at 36.0% on average, with ± 3-7% variability after 150 days of operation. A similar trend was also observed in the sand biofilter. The difference in the TOX removal between anthracite and sand biofilters was not statistically significant after reaching the steady state (day 210-310, $P > 0.05$ of Student's T-Test). Unlike the anthracite and sand biofilters, the TOX removal in GAC biofilters consists of adsorption and biodegradation processes. GAC 200 filter exhibit removal percentage of 87.1 - 88.5% during the first three weeks, indicating that TOX could be effectively removed via physical adsorption. Then, the effluent TOX concentrations gradually increased. After day 130, GAC 200 filter entered the steady state and can consistently remove 51.1% of TOX on average. The steady TOX removal can be attributed to biological activity (Simpson, 2008; Yuan et al., 2022). The removal of TOX in the GAC 300 biofilter followed similar trend but with higher removal efficiency in both the early adsorption stage (92.5% - 95.0%) and steady

state (52.5% on average). The TOX removal between GAC 200 and GAC 300 in the steady state is statistically significant according to the student's T-Test (day 130-310, $P < 0.05$).

The result shows that GAC biofilters have overall better performance than sand and anthracite biofilters in TOX removal in chlorinated water. At the early stages of filtration, TOX can be effectively removed through GAC adsorption. When all biofilters reached the bioactive steady state, GAC biofilters showed approximately 15% higher TOX removal than sand and anthracite biofilters. It is likely that GAC particles could support higher microorganism densities than sand an anthracite due to the microporous structure, large surface area, irregular surface, and surface charge (Basu et al., 2016; Fox et al., 1990; Urfer et al., 1997a). Media that can support more biomasses would be expected to exhibit higher biodegradability, resulting in greater TOX removal. One study showed that with the same packing height, 0.7 mm GAC media retained 4.4-4.9 times more biomass in weight than that attached on the 0.35 mm sand and 0.7 mm anthracite after 300 days of operation (Fox et al., 1990). Apart from the biomass quantity, the phylogenetically more diverse microbial community in GAC media might also be an important factor led to the better TOX biodegradation in GAC biofilters (Vignola et al., 2018). In addition, the biodegradable components that are adsorbed on GAC media can be subsequently consumed by bacteria that grow on the GAC surface, leading to the partially bio-regeneration of GAC (Chang and Rittmann, 1987; Li and Digiano, 1980; Yuan et al., 2022).

Compared to the TOX biofiltration, similar tendencies were observed in DOC results (Figure 2.1b). In the steady state, the average DOC removal efficiencies in

anthracite, sand, GAC 200, and GAC 300 biofilters were 16.3%, 19.2%, 31.3%, and 33.6%, respectively. In addition, it took less time (90-110 days) to reach a stable state. A comparable accumulation period for DOC removal was previously reported by Velten *et al.* (2011). In their study, the pilot-scale GAC biofilters reached a steady state after 91 days of operation under the condition of 15.76-minute EBCT, 1.1 mg/L influent DOC, and 7 °C. The average DOC removal was 22% under the steady state, which is lower than what we observed. The reason might be that the lower temperature used in their study limited the microbial activity (Emelko et al., 2006; Moll et al., 1999), resulting in a lower DOC consumption by bacteria.

TOX quantifies the total amount of halogenated DBPs in the water. Toxicity studies found TOX concentration was positively correlated with biological activities, demonstrating that TOX is a good indicator for the overall toxicity of DBPs of a water sample (Han and Zhang, 2018; Kristiana et al., 2009; Li and Mitch, 2018; Lyon et al., 2014; Richardson et al., 2007). Figure 2.1a shows that up to 50% of the TOX can be dehalogenated via biofiltration. The removal of TOX by biofilters is higher than DOC, but the time needed to reach a steady biofiltration was 30-40 days longer than that for DOC. This may suggest that bacteria community for TOX removal in drinking water requires a longer time to fully establish biodegradation potentials compared to organic carbon biodegradation. Certainly, the influent concentrations and media adsorption capacity could also affect the time required to reach stable biodegradation conditions. Further studies about the identification of target microbial species related to TOX removal and the composition of target microbial species at different time points are required to better understand TOX biofiltration processes.

2.3.2 THMs, HAAs, DHANs, HKs, CP, and UTOX Removal in Chlorine Disinfected Water

The removal of THMs, HAAs, HKs, CP, DHANs, and UTOX were also measured during the steady state. The average concentration and removal efficiency of each group of DBPs in the four biofilters are given in Table 2.3. The concentrations of DBPs in influent and treated effluent are given in Table 2.4.

2.3.2.1 THMs Removal

THMs are the most prominent class of halogenated DBPs in drinking water. The average influent THMs concentration from day 270 to 310 was 45.5 μg/L (with 54.7% TCM, 24.5% BDCM, 16.5% of DBCM, and 4.2% of TBM; THM_4 -BSF = 0.234). Only 13.8%-14.6% of THMs were removed in GAC biofilters, and 7.0% - 7.5% of THMs were removed in sand and anthracite biofilters (Table 2.3, Table 2.4). The results indicated that the biofiltration was not effective in THMs removal. Similar results were also reported in previous studies (Kim and Kang, 2008; Tang and Xie, 2016b; Wobma et al., 2000). For example, Kim and Kang (2008) found less than 10% THMs removal in BAC biofilters (9.8 min EBCT) after four months of operation in a drinking water treatment plant. Tang and Xie (2016) reported only 9% of THMs removal in lab-scale column BAC filters with 5.8 min EBCT. The low biodegradation of THMs is mainly attributed to the chemical characteristics, lack of biodegradation prerequisites, and toxicity of degradation products. THMs biodegradation under aerobic conditions is thermodynamically unfavorable. Most aerobic biodegradation processes involve the insertion of oxygen into a bond on the target compound, while the three-halogen constituents of THMs are already more oxidized than oxygen (Vogel, 2017; Wobma et al., 2000). Therefore they have no

potential to be used as a primary substrate. Although the bacteria string that can use THMs as a direct growth substrate has not been found, it has been previously reported that the cometabolism process can be applied for limited THMs removal (7-24% elimination) in nitrifying biofilters with the addition of 4 mg N/liter $TOTNH_3$ (Wahman et al., 2011a, 2011b). However, the drinking water treatment plants often lack the prerequisites for the cometabolism process (e.g., high concentrations of target bacteria - Nitrosomonas Europaea, primary substrates >4 mg/L ammonia for bacteria growth). Moreover, several studies reported that some THMs (such as chloroform) degradation products (phosgene or other intermediates such as aldehydes) are toxic which can inhibit the biological activities of the target bacteria (Cappelletti et al., 2012; Wahman et al., 2006). Therefore, it is hard to biodegrade THMs in drinking water treatment biofilters.

2.3.2.2 HAAs Removal

Table 2.3 shows that the average influent HAAs concentration from day 270 to day 310 was 20.8 μg/L (with 75.2% DHAAs and 24.8% THAAs; HAA-BSF = 0.432). Compared to THMs biodegradation, nearly complete HAA removal (>95%) were observed in all biofilters, suggesting that aerobic biofiltration is effective for HAAs control. This is consistent with previous lab-scale and pilot-scale studies (Kim and Kang, 2008; Ratasuk et al., 2008; Tang and Xie, 2016b; Wobma et al., 2000). The biodegradation of HAAs under aerobic conditions was a hydrolytic-oxidation dehalogenation reaction in which enzymes such as dehalogenase can transform HAAs into intermediate compounds (such as glycolic acid, glyoxylic acid, and oxalic acid). Intermediate compounds are then further decomposed into simple organic compounds by oxidases, dehydrogenases, or reductases enzymes, and eventually mineralized to CO_2,

H_2O, and inorganic salts (Ellis et al., 2001; Grigorescu et al., 2010; Janssen et al., 1985; Kim et al., 2004; Tang and Xie, 2016b; Wobma et al., 2000; Xie and Zhou, 2002a).

2.3.2.3 DHANs, HK and CP Removal

Compared with THMs and HAAs, information about the biodegradation of DHANs, HKs, and CP is limited. As shown in Table 2.4, the average concentration of DHANs was 2.76 μg/L (DHANs-BSF =0.234) in chlorinated water. The average DHANs removal efficiency was 49.3%, 50.9%, 70.0%, and 72.1% in anthracite, sand, GAC 200, and GAC 300, respectively. The higher removal efficiency of the GAC biofilters could be related to the enhanced biological activities in the GAC biofilters as previously mentioned in section 2.3.1. The results suggest that biofiltration could be used as a viable method for DHANs control via biodegradation. In contrast to DHANs, both HKs and CP have a relatively low (< 4%) removal efficiency. It should be noted that the low concentration (< 3 μg/L) of these DBPs in this study might greatly impact the accuracy of the analysis, more studies are needed to evaluate the biodegradability and possible factors that are related to the biodegradation of DHANs, HKs and CP.

2.3.2.4 UTOX Removal

As shown in Table 2.3, the average UTOX concentration in the chlorinated water was 79.4 μg/L, accounting for 52.9% of TOX. Up to 63% of UTOX were removed in GAC biofilters, which were about 20% higher than anthracite and sand biofilters.

Hua and Reckhow, (2006a) shows that the molecular weight (MW) distribution of UTOX was 40%, 44%, 14%, and 2% for the size range <0.5 kDa, 0.5 - 3 kDa, 3 - 10 kDa, >10 kDa, respectively. XAD - 4/8 resin fractionation tests further indicated the

hydrophobicity of UTOX in chlorinated water was 26%, 33%, and 41% for hydrophobic, transphilic, and hydrophilic fractions, respectively.

Approximately 100 novel halo-DBPs have been identified over recent years, the majority of them were aromatic halo-DBPs and studies have shown that those DBPs are much more genotoxic and carcinogenic than corresponding aliphatic halo-DBPs (Jiang et al., 2020; Liu and Zhang, 2014; Pan and Zhang, 2013; Yang and Zhang, 2013; Zhai and Zhang, 2011). Han *et al.* (2021) reported that aromatic fractions constituted 26-36% of TOX in chlorinated water. The results of this study suggest that most of the UTOX compounds in the tested chlorinated water can be biodegraded by biofiltration.

2.3.3 The Impacts of EBCT on TOX Removal

EBCT is one of the critical design parameters affecting biofilter performance. Many studies found that longer EBCTs can increase the substrate's utilization, leading to more NOM and other contaminant removals (Lechevallier et al., 1992; Liu et al., 2022; Zhang et al., 2017). Table 2.5 presents the biofilters performance on TOX removal at EBCT 10-20 min. The results show that the TOX removal increased with longer EBCT, and GAC biofilters can maintain high TOX removal on the wide range of EBCT. However, the increment is not proportionated with the increased EBCT. A two-fold increase of EBCT only enhanced 8-12% of TOX removal. Similar results were reported in a DOC biofiltration study that compared to the impacts of EBCT at low temperatures, EBCT changes would have less impact on DOC removal at 20 °C (Liu et al., 2022). Future studies about the impacts of temperature on TOX biofiltration are recommended to fully understand the TOX biofiltration. This result suggests that compared to the minor

improvement of TOX removal, maintaining a lower EBCT is more practicable during water treatment at high temperatures.

2.3.4 Impacts of Chlorine-Chloramines Switch on TOX Removal

Figure 2.2 and Table 2.6 present the TOX removal in different biofilters after switching to chloraminated water. Switching to chloramine decreased the average influent TOX concentration from 150.1 μg/L to 65.1 μg/L, with 21.7% THMs, 13.1% HAAs, 1.9% minor DBPs, and 63.3% UTOX of the TOX distribution. The TOX concentrations in anthracite and sand biofilters effluents were slightly high in the first week, and then rapidly decreased and stabilized between 39.9-45.9 μg/L. The average TOX removal efficiencies in the anthracite and sand biofilters were 32.9% and 34.6%, respectively, about 5% lower than that in chlorinated water.

Unlike anthracite or sand biofilters, the TOX concentration in GAC biofilters effluents reached about 72 μg/L one day after switching to chloraminated water. This concentration is higher than the influent TOX concentration. Then the TOX concentration in GAC 200 and GAC 300 progressively decreased and stabilized between 34.9-39.1 μg/L after 60 days of operation, with 44.4% and 45.4% of TOX removal, respectively. It is clear that TOX leaching occurred in GAC biofilters between day 1 to day 60. The use of chloramine decreased about 56% of TOX formation, leading to a lower concentration gradient for the adsorption process in the water. Therefore, part of the adsorbed non-biodegradable DBPs released from the GAC media, leading to a high TOX concentration in effluent water. After 80 days of operation, GAC biofilters went back to the equilibrium condition. Compared with the performance in chlorine disinfected water at the steady state, the TOX removal efficiency of GAC biofilters in chloraminated water at the steady

state decreased about 6% (Table 2.3, Table 2.6), implying that the TOX formed in chloraminated water is relatively more challenging to biodegrade than those in chlorinated water.

2.3.5 Impacts of Chlorine-Chloramine Switch on THMs, HAAs, UTOX Removal

To reveal what DBPs were leaching out from the GAC biofilters after switching to chloramine. HAAs, THMs and unknown DBPs concentrations were also measured during the experiment. The results are given in Figure 2.3.

2.3.5.1 Impacts on THMs

The average influent THMs concentration in the chloraminated water was 14.1 μg/L (Figure 2.3a). Both GAC biofilters detected a high concentration of THMs after switching to chloraminated water. The THMs concentration gradually decreased and stabilized at 12-14 μg/L, with 13.2 and 14.6% removal in GAC 200 and 300 biofilters (Table 2.6). Like TOX leaching, the reduced THM concentrations might be the reason for the THMs leaching. It is well documented that THMs are hard to be biodegraded and the removal in the GAC biofilters is mainly attributed to physical adsorption (Kim and Kang, 2008; Wobma et al., 2000). Switching the disinfection method from chlorine to chloramine decreased about 70% of THMs formation (Table 2.3, 2.6, 2.7). Therefore, part of the adsorbed THMs was desorbed from the GAC media, leading to the high THM concentration in GAC effluent.

2.3.5.2 Impacts on HAAs

According to Figure 2.3b, the average influent concentration of HAAs in chloraminated water was 8.5 μg/L. The effluent HAAs concentrations were stabilized

between 0.3-0.6 ug/L throughout the 180 days of operation, with >93% removal on average (Table 2.6, 2.7). Compared with the HAAs removal in chlorinated water, switching to chloramine did not impact the HAAs removal in GAC biofilters.

2.3.5.3 Impacts on UTOX

Figure 2.3c shows the variation of UTOX concentration after switching to chloraminated water. The influent UTOX concentration was 41.4 μg/L, accounting for 63% of the TOX formation. Switching from chlorine to chloramine increased about 10% UTOX/TOX ratio. This is consistent with previous study that chloramine could produce a higher percentage of UTOX than chlorine (54.9% UTOX in chlorinated water, 80.2% UTOX in chloraminated water) (Hua and Reckhow, 2007). However, the UTOX/TOX ratio in our chloraminated water was lower than that observed in Hua's results. The possible reason could be attributed to the chloramine generation method in the Brookings Drinking water treatment facility. Instead of adding chloramine, this water treatment plant uses a two-step method to generate chloramine. In the first step, the chlorine gas is first fed into water, and in the second step, ammonia sulfate is mixed into the water to generate chloramine. Although short in the reaction time, chlorine can still react with NOM to form plentiful of THMs, leading to a lower UTOX/TOX ratio.

Figure 2.3c shows that the effluent UTOX concentration required 60 days to reach stable conditions after switching to chloramine. Up to 32.2 μg/L of UTOX were observed in GAC biofilters in the first few days. The UTOX concentration gradually decreased and stabilized at 21-23 μg/L, with 45-47% removal efficiency. Compared with chlorinated water, switching to chloramine decreased about 15 percentage points in UTOX removal in both GAC biofilters and decreased about 10 percentage points UTOX removal in

anthracite and sand biofilters (Table 2.6). These results suggest that the UTOX in chloraminated water are more challenging to be biodegraded than those formed by chlorination. The changes in molecular size distribution and hydrophobicity of UTOX might be the reasons. Smaller compounds are hydrolyzed easily by microorganisms, while larger compounds need to be hydrolyzed prior to utilization (Dimock and Morgenroth, 2006; Karahan et al., 2008). A study showed that the TOX formed by chloramination (NH_2Cl-UTOX) typically has higher molecular weight than those formed by chlorination; this could be one reason leading to lower NH_2Cl-UTOX removal (Hua and Reckhow, 2006a). Apart from the particle size, the hydrophobicity of the organic matter is another factor that impacts its biodegradation. Previous studies have shown that the hydrophilic acids of organic matter are easier to be biodegraded by microorganisms than hydrophobic acids (Chen et al., 2011; Jandl and Sletten, 1999; Qualls and Haines, 1992). Hua and Reckhow, (2007) found that UTOX in chloraminated water is more hydrophobic than in chlorinated water. Therefore, the UTOX formed in chloraminated water is more resistant to be removed via biofiltration.

2.3.6 Comparison of Adsorption and Biodegradation for TOX Removal in Biofilters

The adsorbed and biodegraded TOX during the 540 days of operation in each media were calculated and given in Table 2.8. GAC 300 has the best TOX control capacity and removed over 56% of the fed TOX in this study. A quarter of the removed TOX in GAC 300 was attributed to physical adsorption, and three quarters were removed through biodegradation. Anthracite and sand removed about 30% of fed TOX during the 540 days operation, and >98% of the removed TOX was via biodegradation.

2.4. Conclusions

This study was conducted to investigate the DBPs removal in chlorinated water and chloraminated water using four biofilters. The results suggest that biological filtration is an effective technology for TOX, HAAs, and UTOX removal from chlorinated and chloraminated water. It takes 130 -150 days to establish a stable biodegradation environment in different filters. After that, more than 50% of the TOX was consistently biodegraded in GAC biofilters, with 96% HAAs removal, 14% THMs removal, and 60% UTOX removal. GAC 300 has the best adsorption capacity and biodegradation ability, followed by GAC 200, sand, and anthracite. Switching to chloramine had little impact on HAAs biodegradation in GAC biofilters. However, it decreased UTOX biodegradation by 15 percentage points, which indicates that the UTOX formed in the chloraminated water is more resistant to biodegradation than those formed in chlorinated water. Moreover, 60 days of TOX leaching was observed after switching to chloraminated water, mainly attributed to THMs (58%) and UTOX (41%). Therefore, attention should be paid to potential DBPs leaching from GAC biofilters when switching disinfectant from chlorine to chloramine. This study provided valuable information about the biodegradability of TOX and UTOX in drinking water using biological filtration.

Table 2.1 Characteristics of Filter Materials

Media	Effective Size (mm)	minimum Iodine Number (mg/g)	Apparent Density (g/cm^3)	Dry Weight of Media in Column (g)	Packing Density[a] (g/cm^3)	Drainable Porosity [b]
Anthracite	0.90-1.00	--	1.41	9.51	0.9	0.513
Sand	0.45-0.55	--	1.96	18.28	1.72	0.559
GAC 200	0.55-0.75	850	0.69	6.74	0.64	0.585
GAC 300	0.80-1.00	900	0.64	5.72	0.54	0.561

[a] Packing densities were determined by dividing the weight of dry packing material with the bed volume.
[b] Drainable porosities were determined by dividing the volume of drained water with the bed volume.

Table 2.2 Biofilter Influent Water Quality

Parameters	Experimental Phase I Chlorinated Water (Days of operation: 360)	Experimental Phase II Chloraminated Water (Days of operation: 180)
pH	8.1 ± 0.1	8.2 ± 0.1
DOC (mg/L)	1.86 ± 0.13	2.01 ± 0.15
UV 254 (cm^{-1})	0.035 ± 0.005	0.050 ± 0.006
SUVA L/(mg·m)	1.88 ± 0.3	2.45 ± 0.2
TP (mg/L as P)	0.22 ± 0.1	0.24 ± 0.1
TN (mg/L as N)	0.14 ± 0.03	1.1 ± 0.05
THMs (µg/L)	45.5 ± 1.6	14.1 ± 0.1
HAAs (µg/L)	20.8 ± 0.25	8.5 ± 0.06
TOX (µg/L)	155.1 ± 10.2	65.7 ± 4.9

Table 2.3 TOX, HAA, THM and UTOX Removal in Chlorinated Water by Biofilters Under Stable Conditions. (Experiment conditions: EBCT=15 min, temperature=20 °C. Sampling days: 270-310 days of Phase I Experiment.)

Sample	TOX		THMs	
	Conc. (µg/L)	Removal (%)	Conc. (µg/L)	Removal (%)
Influent	150.0 ± 1.8	--	45.5 ± 1.6	--
Anthracite Effluent	94.5 ± 1.1	37.1 ± 0.2	42.4 ± 0.8	6.8 ± 0.2
Sand Effluent	93.8 ± 1.1	37.4 ± 0.1	42.0 ± 0.9	7.6 ± 0.2
GAC 200 Effluent	75.3 ± 1.1	50.1 ± 0.2	39.0 ± 1.3	14.0 ± 0.3
GAC 300 Effluent	72.7 ± 1.2	51.5 ± 0.2	38.8 ± 1.2	14.6 ± 0.2
Sample	HAAs		UTOX	
	Conc. (µg/L)	Removal (%)	Conc. (µg/L)	Removal (%)
Influent	20.8 ± 0.25	--	79.4 ± 1.1	--
Anthracite Effluent	1.0 ± 0.02	95.1 ± 0.2	47.3 ± 0.6	40.4 ± 0.3
Sand Effluent	1.0 ± 0.01	95.2 ± 0.1	47.0 ± 0.6	40.8 ± 0.3
GAC 200 Effluent	0.8 ± 0.01	96.4 ± 0.1	32.0 ± 0.4	59.7 ± 0.3
GAC 300 Effluent	0.7 ± 0.01	96.6 ± 0.1	29.9 ± 0.4	62.5 ± 0.2

Table 2.4 Average Individual DBP Concentrations during the Biofiltration Experiments under Stable Conditions

(a) DBP concentrations in biofilter influent and treated effluents for Phase I chlorinated water experiment

DBPs (mg/L)	Biofilter Influent	Treated Effluents			
		Anthracite	Sand	GAC 200	GAC 300
Trichloromethane	24.89	23.68	22.82	21.49	21.5
Bromodichloromethane	11.15	9.95	9.98	9.57	9.53
Dibromochloromethane	7.50	6.89	7.34	6.71	6.57
Tribromomethane	1.91	1.84	1.86	1.33	1.21
Dichloroacetonitrile	1.71	0.69	0.66	0.26	0.22
Bromochloroacetonitrile	0.81	0.19	0.46	0.21	0.19
Dibromoacetonitrile	0.24	0.16	0.014	0.08	0.06
1,1-Dichloropropanone	0.14	0.13	0.13	0.13	0.13
1,1,1-Trichloropropanone	0.83	0.83	0.83	0.81	0.81
Chloropicrin	0.62	0.60	0.62	0.59	0.60
Monochloroacetic acid	0	0	0	0	0
Monobromoacetic acid	0	0	0	0	0
Dichloroacetic acid	9.58	0.34	0.31	0.22	0.20
Bromochloroacetic acid	3.99	0.25	0.26	0.24	0.22
Dibromoacetic acid	2.03	0.10	0.09	0.07	0.06
Trichloroacetic acid	2.84	0.06	0.06	0.05	0.06
Bromodichloroacetic acid	1.51	0.14	0.14	0.08	0.08
Dibromochloroacetic acid	0.76	0.11	0.13	0.09	0.09
Tribromoacetic acid	0.05	0.01	0.01	0.01	0.01

Table 2.5 Effects of HRT on TOX Removal in Chlorinated Water by Biofilters. (Experiment conditions: EBCT=10, 15, 20 min; temperature=20°C; Each EBCT was operated for 14 days. Samples were analyzed for last 7 days.)

Biofilter	TOX Removal (%)		
	EBCT 10 min	EBCT 15 min	EBCT 20 min
Anthracite	30.3 ± 0.2	36.8 ± 0.2	41.1 ± 0.1
Sand	31.4 ± 0.3	37.6 ± 0.2	42.9 ± 0.2
GAC 200	45.4 ± 0.3	49.9 ± 0.2	55.7 ± 0.2
GAC 300	48.7 ± 0.3	52.9 ± 0.3	57.2 ± 0.2

Table 2.6 TOX, HAA, THM and UTOX Removal in Chloraminated Water by Biofilters Under Stable Conditions. (Experiment conditions: EBCT=15 min, temperature=20 °C; Sampling days: 140-180 days of Phase II Experiment.)

Sample	TOX		THMs	
	Conc. (µg/L)	Removal (%)	Conc. (µg/L)	Removal (%)
Influent	65.1 ± 0.5	--	14.1 ± 0.1	--
Anthracite effluent	43.8 ± 0.3	32.8 ± 0.5	13.2 ± 0.1	6.6 ± 0.2
Sand effluent	43.2 ± 0.4	33.6 ± 0.4	13.0 ± 0.1	7.3 ± 0.3
GAC 200 effluent	36.0 ± 0.2	44.7 ± 0.2	12.2 ± 0.1	13.2 ± 0.4
GAC 300 Effluent	35.1 ± 0.3	46.2 ± 0.3	12.0 ± 0.1	14.6 ± 0.3
Sample	HAAs		UTOX	
	Conc. (µg/L)	Removal (%)	Conc. (µg/L)	Removal (%)
Influent	8.5 ± 0.06	--	41.2 ± 0.3	--
Anthracite Effluent	0.5 ± 0.01	93.8 ± 0.2	28.9 ± 0.2	29.9 ± 0.3
Sand Effluent	0.5 ± 0.01	93.9 ± 0.2	28.5 ± 0.2	30.9 ± 0.2
GAC 200 Effluent	0.4 ± 0.01	94.8 ± 0.1	22.2 ± 0.1	46.1 ± 0.3
GAC 300 Effluent	0.4 ± 0.01	95.3 ± 0.2	21.5 ± 0.2	47.9 ± 0.3

Table 2.7 Average Individual DBP Concentrations during the Biofiltration Experiments under Stable Conditions.

(b) DBP concentrations in biofilter influent and treated effluents for Phase II chloraminated water experiment

DBPs (mg/L)	Biofilter Influent	Treated Effluents			
		Anthracite	Sand	GAC 200	GAC 300
Trichloromethane	5.55	5.13	5.10	4.90	4.83
Bromodichloromethane	4.15	3.90	3.86	3.71	3.68
Dibromochloromethane	2.94	2.75	2.70	2.63	2.58
Tribromomethane	1.44	1.37	1.38	0.98	0.93
Dichloroacetonitrile	0.47	0.09	0.08	0.27	0.23
Bromochloroacetonitrile	0.08	0.02	0.01	0.02	0.02
Dibromoacetonitrile	0.02	0.01	0.01	0.01	0.01
1,1-Dichloropropanone	0.41	0.38	0.39	0.35	0.34
1,1,1-Trichloropropanone	0.12	0.12	0.12	0.12	0.11
Chloropicrin	0.33	0.33	0.32	0.32	0.32
Monochloroacetic acid	0	0	0	0	0
Monobromoacetic acid	0	0	0	0	0
Dichloroacetic acid	3.97	0.23	0.21	0.16	0.16
Bromochloroacetic acid	1.59	0.10	0.10	0.08	0.07
Dibromoacetic acid	1.06	0.07	0.07	0.06	0.05
Trichloroacetic acid	0.67	0.03	0.03	0.03	0.03
Bromodichloroacetic acid	0.59	0.05	0.06	0.07	0.06
Dibromochloroacetic acid	0.52	0.03	0.03	0.02	0.02
Tribromoacetic acid	0.05	0.01	0.01	0.01	0.01

Table 2.8 Comparison of Adsorption and Biodegradation for TOX Removal in Biofilters. (Total TOX fed into each filter during the 540 days operation was 72118 µg.)

Sample	Cumulative Removed TOX (µg)	Adsorption		Biodegradation	
		TOX (µg)	%	TOX (µg)	%
Anthracite	21609	303	1.4	21306	98.6
Sand	22391	291	1.3	22100	98.7
GAC 200	39439	10321	26.2	29118	73.8
GAC 300	40682	10333	25.4	30349	74.6

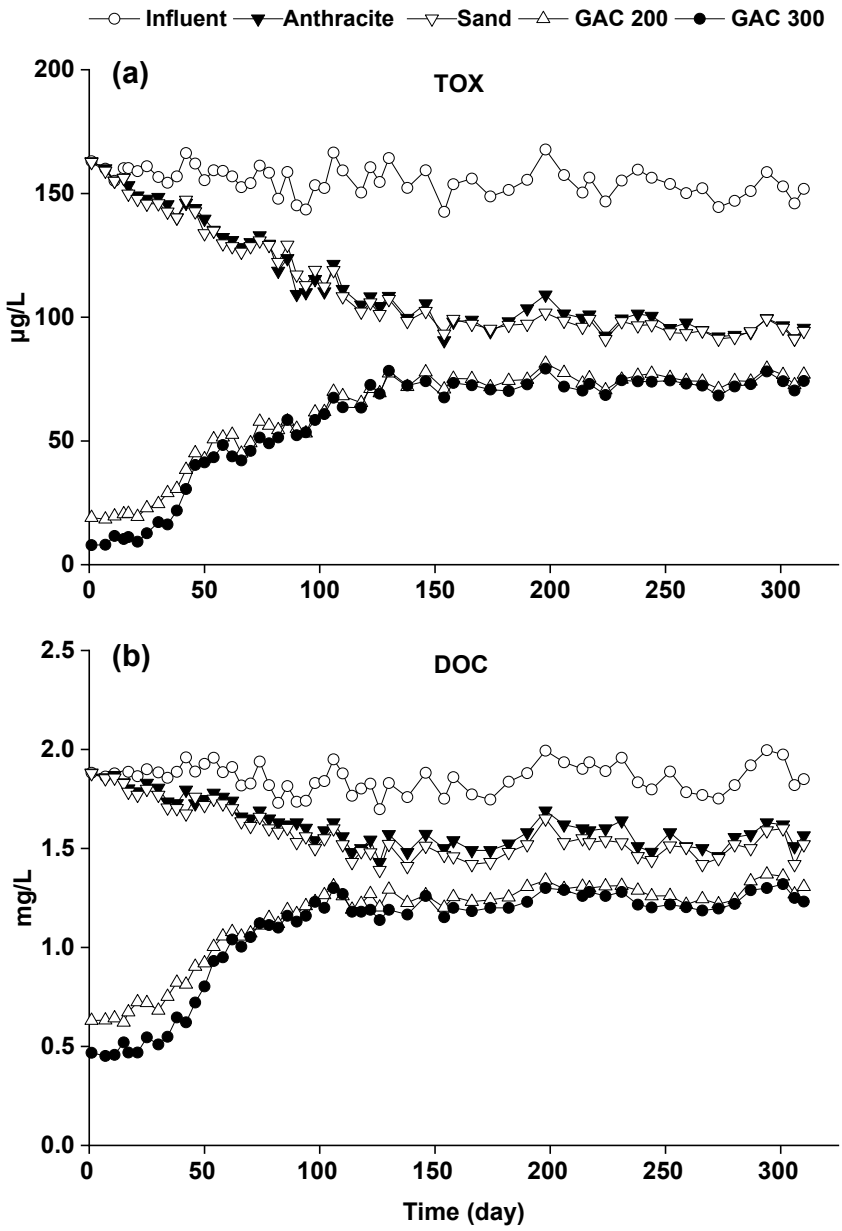

Figure 2.1 TOX and DOC Removal in Chlorinated Water by Filters. (Biofilter influent: chlorinated tap water, quenched residuals; Experiment conditions: EBCT=15 min, temperature=20 °C.)

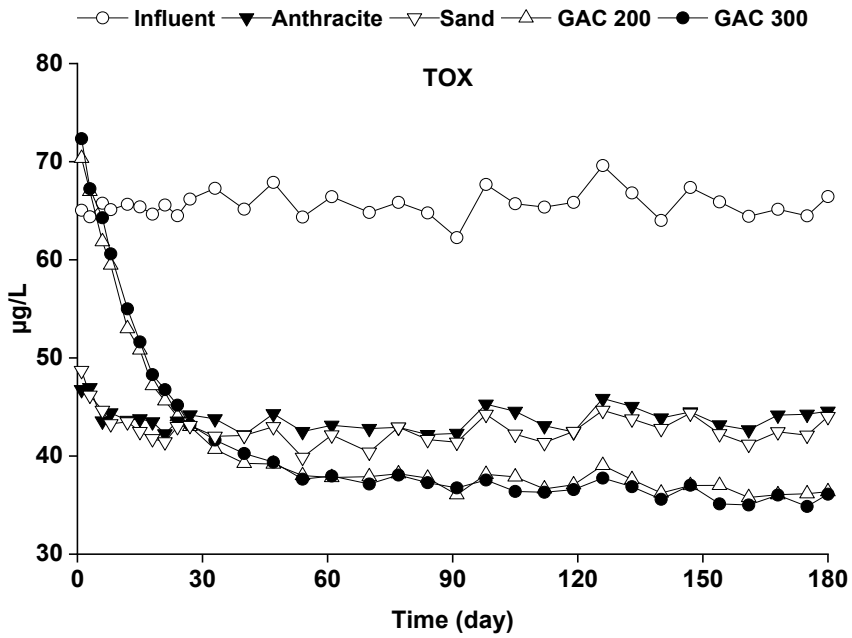

Figure 2.2 Effect of Chlorine-Chloramine Switch on TOX Removal in Biofilters. (Biofilter influent: chloraminated tap water, quenched residuals; Biofilter media: used media after 360 days operation with chlorinated tap water; Experiment conditions: EBCT=15 min; temperature=20 °C.)

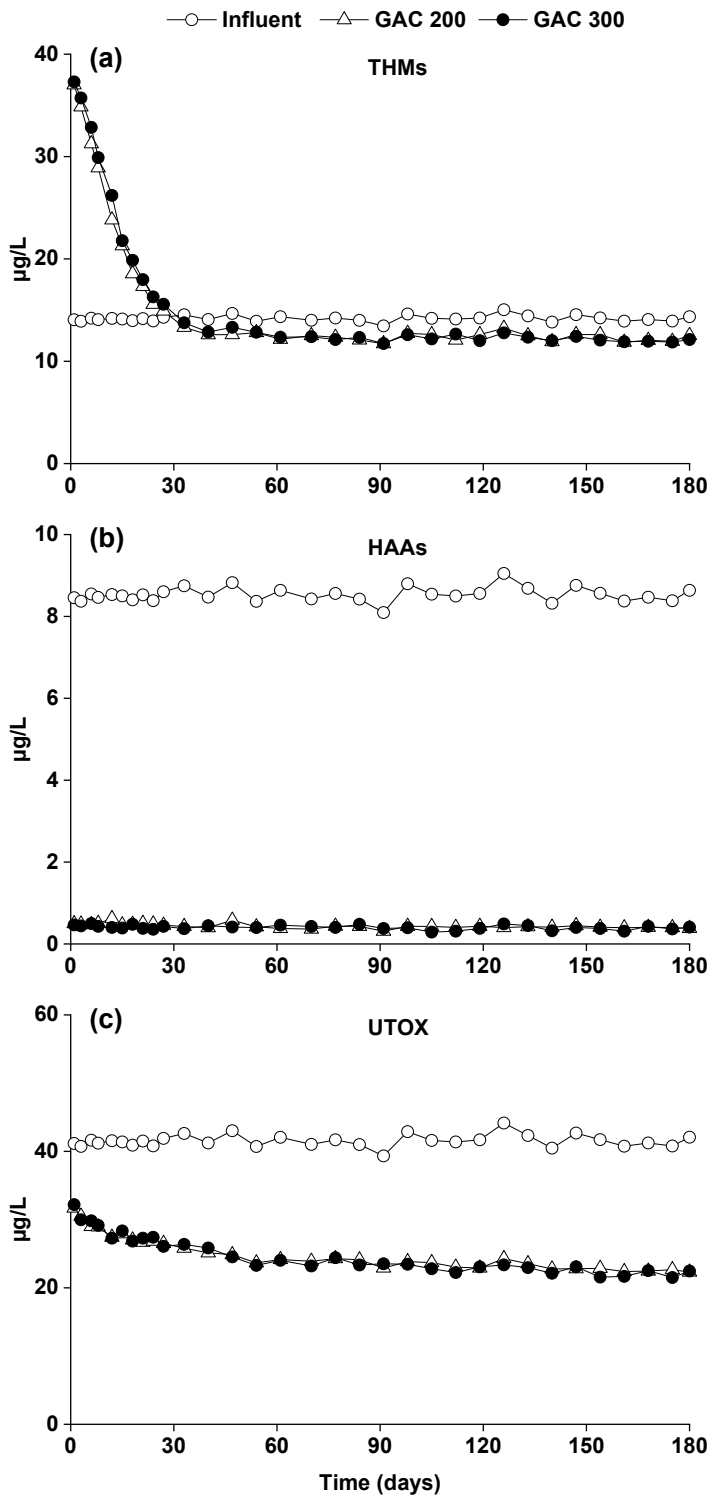

Figure 2.3 Effect of Chlorine-Chloramine Switch on THM, HAA and UTOX Removal in Biofilters. (Biofilter influent: chloraminated tap water, quenched residuals; Biofilter media: used media after 360 days operation with chlorinated tap water; Experiment conditions: EBCT=15 min; temperature=20 °C.)

CHAPTER 3

DETERMINATION OF DISINFECTION BYPRODUCTS REMOVAL KINETICS IN GRANULAR ACTIVATED CARBON BIOFILTERS

3.1 Introduction

Drinking water disinfection is essential in protecting public health from waterborne diseases. However, chemical disinfectants can react with natural organic matter (NOM), bromide, and iodide present in the water, resulting in the formation of DBPs. DBPs have emerged as a significant concern in drinking water due to their potential adverse effects on humans. Epidemiological studies have shown associations between exposure to water containing DBPs and an increased risk of adverse human health effects, including bladder cancer, miscarriage, and birth defects. Though trihalomethanes (THMs) and haloacetic acids (HAAs) have been regulated by Environmental Protection Agency (EPA), analysis of total organic halogen (TOX) has indicated that more than 50% of the chlorinated DBPs and more than 80% of the chloraminated DBPs remain unknown. Recent research suggests that the toxicity of drinking water is primarily driven by unregulated and unknown DBPs rather than by regulated compounds. Consequently, it is important to control those DBPs to ensure water safety.

Drinking water treatment facilities employ various strategies to minimize DBP formation, including precursor control (reducing the NOM in the water), and using alternative disinfectants such as chloramine, or chlorine dioxide, which have lower reactivity with organic matter and bromide compared to chloramine. Although

conventional DBPs control strategies have proven effective in reducing the formation of regulated DBPs, some limitations have been observed during the application. Precursor control like enhanced coagulation and filtration can be expensive, require additional operations, and may not always effectively remove all organic matter. Membrane filtration requires regular cleaning to prevent membrane clogging and maintain high performance. The membrane replacement is expensive, and the membrane systems are complex to operate and require careful monitoring and control to ensure effective operation (Bond et al., 2012b; Howe et al., 2006; Jung et al., 2006; Zularisam et al., 2006). Activated carbon can be exhausted during the operation. Therefore, the carbon needs to be regenerated or replaced to maintain the effectiveness of NOM control. Alternative disinfectants can lead to other DBPs formation issues. For example, chlorine dioxide can react with NOM to form chlorite (Yang et al., 2021); ozone can lead to bromate formation in water with high bromide levels (Wu et al., 2021); and chloramines can lead to the production of nitrogenous DBPs and unknown DBPs (Muellner et al., 2007; Yu and Reckhow, 2017)**.**

Biological filtration, also known as biofiltration, is an eco-friendly technology that has gained significant attention for its potential in controlling organic and inorganic contaminants during water treatment. Filtration media can naturally transition to biological filters over time, allowing microorganisms to grow and form a biofilm on the media surface. These microorganisms metabolize biodegradable organic matter or nutrients as energy sources, facilitating the removal of organic pollutants. Recent studies have shown biofiltration can effectively remove haloacetic acids (HAAs). For example, Kim and Kang (2008) reported >90% HAAs removal in biologically active carbon (BAC)

filters with 9.8 min EBCT; Xie and Zhou (2002) reported HAAs removal efficiencies ranging from 80% to 100% using BAC filtration with 20 min EBCT, while Tang and Xie (2016) observed >70% HAA removal efficiencies in BAC filters using swimming pool water with 6.4 min EBCT. The biofiltration of trihalomethanes (THMs) has also been investigated. However, results indicated that THMs are generally resistant to biodegradation under typical environmental conditions due to their stable chemical structure. THMs have limited potential to serve as direct carbon and energy sources for microbial growth, and they do not readily break down in the environment by microorganisms. Most studies reported less than 25% removal in typical biofiltration systems (Cuthbertson et al., 2020; Kim and Kang, 2008; Tang and Xie, 2016b; Wahman et al., 2011a; Wobma et al., 2000). Despite these findings, no comprehensive study has been conducted on the unknown DBPs removal in biofilters. Considering the potential toxicity and the knowledge gaps about the health effects of unknown DBPs, understanding their removal kinetics in biofilters is essential for protecting public health and guiding the application of biofiltration in water treatment processes.

Biofilters performance can be influenced by various factors, with empty bed contact time (EBCT) and temperature playing critical roles. EBCT represents water residence time within a filter, which is typically measured in minutes and calculated by dividing the volume of the filter bed by the flow rate of the water. Research has shown that extended EBCTs are able to increase exposure, enhance substrate utilization and result in more contaminant removal efficiency. Wang and Summers (1994), for instance, found that hydraulic loading rate (HLR) within a range of 1.5-15 m/h did not affect NOM removal when measured at the same EBCT. However, increasing the EBCT from 3 to 33

minutes lead to an increase in DOC removal from 16% to 24%. Similarly, Carlson and Amy (1998) observed comparable DOC removal rates in two anthracite biofilters operating at different HLRs (5.0 and 9.7 m/h) but with the same EBCT (10 and 11 min). Temperature is another crucial parameter that impacts biofilters performance regarding contaminant removal efficiency. Hozalski et al., (1999) reported that lower water temperature required longer EBCT to achieve the same steady-state removal. Selbes *et al.* (2016) revealed that both dissolved organic carbon and dissolved organic nitrogen removals were significantly decreased at water temperatures between 10-15 °C compared to those between 15-24 °C. Similar data were reported by Moona *et al.* (2021), who found that DOC removal efficiency decreased by 27% when the temperature decreased from 17 to 9 °C. Higher temperatures and longer EBCTs increase contaminant removal. Thus, EBCT should be carefully selected to achieve the desired removal at specific influent temperatures.

Therefore, the objectives of this study were to: 1) evaluate biofiltration performance for DBPs control in chlorinated and chloraminated water and 2) investigate the impacts of temperature and EBCT on DBPs biofiltration in BAC biofilters. To achieve these objectives, four lab-scale biofilters with granular activated carbon (GAC 300, 0.8-1.0 mm) were constructed and operated for four months to achieve biostable conditions. EBCTs of 5-30 min and temperatures of 5-20 °C were then applied to determine DBPs removal kinetics at different conditions. Comparisons were made based on the extent and rate of DBP removal, while temperature effects were quantified using temperature activity coefficients.

3.2 Materials and Method

3.2.1 Materials

All solutions used in the experiments were prepared using ultrapure water (18 mΩ-cm) generated by a Barnstead GenPure water purification system (Thermo Fisher, Waltham, MA). All chemicals other than humic acid used in the experiments were analytical grade from Fisher Chemical. The humic acid used in the experiments was obtained from Sigma-Aldrich. After dissolving in ultrapure water, the humic acid was filtered through 0.45 μm membranes to make a 0.688 g/L stock solution.

3.2.2 Preparation of Simulated Drinking Water

The simulated drinking water was prepared according to a specific recipe and contained 80 mg/L of alkalinity, 50 mg/L of Ca, 20 mg/L of Mg, 2 mg/L of nitrate, 0.5 mg/L of phosphate, as well as 3 mg/L of DOC (humic acid) to simulate typical drinking water. Addition of selected trace metals including Fe^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+}, Mo^{2+}, Ni^{2+}, B^{3+}, Se^{6+} ensured that microbial growth was not limited (Table 3.1) (Hua et al., 2016; Young and Tabak, 1993). The water composition is summarized in Table 3.1. The pH of the water was adjusted to 8.0 ± 0.1 to simulate the typical drinking water condition. Following a 24-hour reaction period with disinfectant (3.0 ± 0.1 mg/L of chlorine or chloramine), chlorine and chloramine residuals were quenched with 110 % of the required stoichiometric amount of sodium sulfite.

3.2.3 Biologically Activated Carbon Filter

Bituminous coal-based GAC 300 (Calgon Filtrasorb® 300, 0.8 - 1.0 mm) was selected as the filter media. After collection from Calgon Carbon, the GAC media was

rinsed with ultrapure water (18 mΩ-cm) and air-dried for three days prior to use. BAC filters were constructed in glass chromatography columns with 10 cm in length and 1.5 cm in diameter (Omnifit, two fixed endpieces). Each of the four columns was packed with 5.64 g of GAC 300 to achieve a 6 cm column height. Detailed information of the media specifications and packing density can be found in Table 3.2. A peristaltic pump (Masterflex L/S, Cole-Parmer, Vernon Hills, IL) was used to maintain the designed flow rate through the filter, with the rotation rate adjusted between 48.6 and 8 rpm to achieve an empty bed contact time (EBCT) ranging from 5 and 30 minutes.

3.2.4 Biofiltration Experiments

The GAC column reactors were inoculated by a river sample collected from Big Sioux River (Brookings County, SD) to supply natural microbial communities for the experiments. A total of 430 bed-volumes of the river sample was pumped through each of the reactor at an EBCT of 10 min.

Following inoculation, BAC filters 1 and 2 were fed with chlorinated water, and BAC filters 3 and 4 were fed with chloraminated water. The filters were operated at 1.06 mL/min with a 10-minute EBCT for 120 days to achieve bio-stable conditions. After 120 days of operation, EBCT 30, 20, 15, 10, and 5 minutes at a room temperature 20°C were applied to BAC filters to investigate the impacts of hydraulic retention time on DBPs biodegradation. The filters were operated for two weeks at each flow rate, with the first week used for column stabilization, and the last seven days used for sample collection and analysis.

Upon completion of the initial experiments, the BAC filters and simulated water were transferred to a temperature-controlled water bath (bath circulator, Model 2050, Caron Products) set at 10 °C. The filters were allowed to stabilize at this temperature for two weeks with a 10-min EBCT before conducting DBP biodegradation kinetics experiments. These experiments were conducted following the same procedures as those performed at 20 °C. Finally, the same procedures were repeated at 5 °C.

3.2.5 Analytical Methods

The residuals of chlorine and chloramine were quantified using the DPD ferrous titrimetric method. The TOX was determined using the adsorption-combustion-titration method with a Mitsubishi TOX-100 Analyzer (Cosa Xentaur Inc., Norwood, NJ) following standard method 5230B (Baird, Eaton and Rice, 2017). HAA_9 including monochloro-, dichloro-, trichloro-, monobromo-, dibromo-, tribromo-, bromochloro-, bromodichloro-, and chlorobromo- acetic acids, were extracted using liquid/liquid extraction with methyl-tertiary-butyl-ether (MTBE), derivatized with acidic methanol, and analyzed by gas chromatography with electron capture detection (GC/ECD, Thermo Fisher, TRACE 1310) according to U.S.EPA 552.3. THM_4, including chloroform, bromodichloromethane, dibromochloromethane, and bromoform, three dihaloacetonitriles (dichloro-, bromochloro-, and dibromoacetonitrile), three haloketones (dichloro-, trichloro-, 1,2-dibromo-3chloropropanone), and several other chlorine and bromine containing compounds (trichloroethylene, 1,2-dibromoethane, 1,2-dibromo-3-chloropropane, tetrachloroethylene, and chloropicrin) were extracted by liquid/liquid method with pentane and analyzed by GC/ECD according to U.S. EPA 551.1. The

UTOX concentration was calculated by subtracting the total measured disinfection byproduct (DBP) concentrations (as Cl) from the TOX concentration.

3.2.6 Data Analysis

Several models have been developed in the literature to describe the biodegradation kinetics of organic pollutants (Barbara A. Bekins, Ean Warren, 1998; Bishop, 1997; Chang and Alvarez-Cohen, 1995; Knightes and Peters, 2000). The first-order kinetics model is commonly used as a convenient method to describe the organic compounds biodegradation progress in biofilters. This model assumes that the biodegradation rate is directly proportional to the pollutant's concentration (Black and Bérubé, 2014; Liu et al., 2022; Terry and Summers, 2018; Urfer et al., 1997b). In this study, the biodegradation of halogenated organic compounds is assumed to fit the first-order kinetic equation, and biodegradation can be expressed in the following form:

$$C_t = C_0 e^{-kt} \qquad (3.1)$$

where C_t represents the DBP concentration after an EBCT of t (min); k represents the DBP removal rate constant (min^{-1}).

The temperature activity coefficients (θ) were subsequently calculated by fitting the DBP removal rate constants to the linearized form of the commonly employed power law relationship, based on the linear regression of the Arrhenius equation, which is commonly used in the sanitary engineering field to reflect the impact of temperature (Metcalf and Eddy, 2014; Peleg et al., 2012; Rittmann and McCarty, 2001).

$$K_T = k_{20}\theta^{(T-20)} \qquad (3.2)$$

where K_T is the DBP degradation rate constant at temperature T in ◦C, θ is the temperature activity coefficient.

Statistical analyses including first-order kinetic model and nonlinear curve - power law fitting were done in OriginPro (2021).

3.3 Results and discussion

3.3.1 Removal of Chlorinated and Chloraminated Water DBPs in GAC Filters

Figure 3.1 presents influent and effluent DBPs concentrations from GAC filters over a 100-day operation using chlorinated water at 20°C, with a 10-min EBCT. Throughout the experiment, the influent TOX concentration remained constant at 300 ± 8 µg/L, and the effluent displayed an initial 82% TOX removal. As operation time increased, a breakthrough of TOX occurred due to the GAC filter saturation, resulting in a gradual increase in the effluent TOX levels. After about 80 days of operation, effluent TOX levels plateaued, biofiltration became the primary removal mechanism of DBP, and the GAC filter achieved a biologically stable state with a 40% TOX removal efficiency.

The removal pattern of THMs was similar to TOX but with varying removal efficiencies. THMs exhibited stable removal efficiencies after 80 days of operation. The initial removal efficiency of THMs was 92%, which can be attribute to the adsorption process. And the average removal efficiency at biologically stable conditions was 14%.

The removal of haloacetic acids (HAAs) exhibited a different pattern. An initial effluent concentration 9 µg/L was observed, which is corresponding to a 87% removal efficiency. This initial HAA removal is presumably caused by the adsorption process. The HAA removal slowly declined and reached a plateau stage between the third and

fourth weeks of operation. During this period, the average HAA removal was 79%. This HAA removal plateau may be attributed to the decline in the adsorption process and the increase in the biodegradation. After that, the effluent HAAs gradually deceased, suggesting that biodegradation became the predominate pathway for HAA removal. The HAA degrading bacteria communities fully developed and the HAA removal reached stable stage after approximately five weeks of operation. Near-complete removal was observed during the remaining period of the experiment. It is important to note that the initial adsorption of HAAs by GAC is slightly lower than that by biofiltration.

The removal curve of UTOX is similar to TOX removal. A nearly linear increase trend was observed during the 120 days of operation, with 73% of initial removal efficiency. After 80 days of operation, UTOX removal achieved a stable condition with 45 ± 3% removal efficiency for the remaining experiment. The linear increment likely results from the competition between GAC adsorption and biofiltration.

The variations of DBPs removal efficiencies during the 100 days operation can be attributed to differences in the physicochemical properties and biodegradability among different categories of DBPs. Initially, the high removal efficiencies of DBPs were mainly due to the adsorptive capacity of the GAC filters. As the GAC filters approached saturation, biological mechanisms became increasingly important for DBP removal. The impact of GAC saturation on removal rates varied across different DBPs due to their varying degradability. The removal rate of the hardest-to-degrade THMs was most affected by GAC saturation, followed by UTOX. On the other hand, for the more easily degradable HAAs, biodegradation eventually took over their removal in GAC filters, allowing high removal efficiencies to be maintained throughout the experiment.

This observation is consistent with previous studies that reported that HAAs are more biodegradable compared to THMs. THMs are generally resistant to biodegradation under typical environmental conditions due to their stable chemical structure. THMs have limited potential to serve as direct carbon and energy sources for microbial growth, and they do not readily break down in the environment by microorganisms (Kim and Kang, 2008; Tang and Xie, 2016b; Wobma et al., 2000). HAAs are easily biodegradable compounds, and the biodegradation pathway of HAAs involves several key steps: 1) dehalogenation, where halogen atoms are removed by dehalogenase enzymes via reductive or hydrolytic mechanisms, resulting in the formation of intermediate compounds including glycolic acid, glyoxylic acid, and oxalic acid; 2) oxidation or reduction reaction, catalyzed by various enzymes, such as oxidases, dehydrogenases, or reductases, therefore producing simple organic compounds; 3) cleavage of carbon-carbon bonds by enzymes like decarboxylases or dioxygenases, resulting in the removal of a carboxyl group or the incorporation of molecular oxygen into the substrate; and 4) mineralization, converting smaller molecules into inorganic compounds, such as CO_2, H_2O, and inorganic salts (Ellis et al., 2001; Tang and Xie, 2016b; Tang et al., 2013; Xie and Zhou, 2002a).

DBPs removal from chloraminated water in GAC filters exhibited similar trends to that in chlorinated water, as shown in Figure 3.2. Although lower in concentrations, the time for GAC filters to achieve biological statable condition was close to the time it took in chlorinated water (70-80 days). This result indicated that DOC is likely to be the predominant factors of GAC saturation instead of DBPs concentration. THMs and HAAs demonstrated the same removal efficiency upon reaching a biologically stable state as in

chlorinated water. However, TOX and UTOX exhibited 6-15% lower removal efficiency, which was 34% and 30% compared to 40% and 45% in chlorinated water.

The lower removal efficiency of UTOX in chloraminated water suggests that the UTOX in chloraminated water is more resistant to biodegradation. Potential reasons for this include changes in molecular size distribution and hydrophobicity of UTOX. As demonstrated by Hua and Reckhow (2006), TOX formed by chloramination exhibits higher molecular weight than that formed by chlorination. Studies on organic matter biodegradation have shown that smaller compounds are more easily hydrolyzed by microorganisms, while larger compounds require hydrolyzed prior to utilization (Dimock and Morgenroth, 2006; Karahan et al., 2008). Hydrophobicity of organic matter may influence its biodegradability. Previous studies have indicated that hydrophilic acids within organic matter are more readily biodegraded by microorganisms compared to hydrophobic acids (Chen et al., 2011; Jandl and Sletten, 1999; Qualls and Haines, 1992). Hua and Reckhow (2007) found that UTOX in chloraminated water is more hydrophobic than in chlorinated water. As a result, the UTOX formed in chloraminated water is more resistant to removal via biofiltration.

3.3.2 Impact of Temperature and EBCT on DBPs Removal

Figure 3.3 represents the average removal of DCAA, TCAA, chlorinated water UTOX, and chloraminated water UTOX. By comparing the degradation rate of two HAAs and two types of UTOX under the same EBCT, DCAA exhibits a generally higher removal rate (51% - 98%) compared to TCAA (39% - 98%). And UTOX removal in chloraminated water (9% - 66%) is higher than that from chlorinated water (7% - 57%). The ANOVA analysis indicates that raising the temperature enhances the removal of

HAAs and UTOX at an EBCT 5-15 min ($P < 0.05$). Higher EBCT can significantly increase HAAs and UTOX removal at temperatures below 10 °C, while the improvement is less substantial at 20 °C. The results indicated that increased temperature could improve biofilter performance for DCAA, and TCAA removal, especially at low EBCT. Similarly, increasing the EBCT enhances DBPs removal, with the effect being more pronounced at lower temperatures. These findings align with previous research that temperature significantly impacts biofilter performance at shorter EBCT (Liu et al., 2022; Moll et al., 1999). Therefore, the impact of temperature and EBCT on biofilters should be studied together, as the DBPs removal efficiency in biofilters relies on both factors.

3.3.3 Impact of Temperature on DBPs Removal Kinetics

Based on previous discussions, the kinetics of DCAA, TCAA, Cl_2-UTOX, and NH_2Cl-UTOX removal in biofilters were quantified by integrating a first-order model (equation 3.1). Figure 3.4 shows the calculated first order degradation rate constants of DCAA, TCAA, and UTOX compounds under 5-20 °C conditions. The results show that the R^2 values were 0.97-0.99, indicating that the first-order model can well describe the HAA and UTOX removal in biofilters at different EBCT.

Table 3.3 summarizes the rate constants, half-lives and temperature coefficients for each group of DBPs. For DCAA, the removal rate constant increased from 0.1055 to 0.2725 min^{-1} as the temperature increased from 5 to 20 °C. The removal rate of TCAA, Cl_2-UTOX and NH_2-Cl followed a similar tendency. Overall, the DBPs removal rate constants in the biofilters increased as the temperature increased. The biofiltration rates of the DBPs ranked as DCAA > TCAA > Cl_2-UTOX > NH_2Cl-UTOX.

The temperature activity coefficients (θ) can be used to connect the estimated rate constants that occur across diverse temperatures and to present the multiple rate constants across different temperatures by using a single rate constant at a reference temperature, such as 20 °C. An activity coefficient >1 indicates a positive effect of temperature on rate constants, and a larger number represents a more significant impact of temperature. The temperature activity coefficient of biofilters was calculated by aligning Equation (3.2) with the removal rate constants estimated at different temperatures. Figure 3.4 represents the application of Equation (3.2) to the DCAA, TCAA Cl_2-UTOX and NH_2-Cl-TOX removal rate constants in relation to temperature. All R^2 values were >95%, indicating that Equation (3.2) could adequately model the impact of temperature on different DBPs removal rate constant. The temperature activity coefficient of TCAA was 1.068, followed by DCAA (1.063), Cl_2-TOX (1.054), and NH_2Cl-TOX (1.048), indicating that temperature positively impacted their removal. Therefore, the impact of temperature on different DBPs and DOC removal in GAC biofilters was found to be TCAA > DCAA > Cl_2-TOX > NH_2Cl-TOX.

3.3.4. Implication on the Operation of Biofilters for DBPs Removal

The results of this research indicated that the performance of biofilters in DBPs removal is temperature-depended. Therefore, the DBPs removal in biofilters can vary throughout the year, especially for regions located in the north, where winter temperatures are significantly lower than in the summer months; the DBPs removal in biofilters may be challenging in cold conditions. This study suggests that extending EBCT is an approach to counteract the effects of low temperatures on biofilters. The required EBCT to achieve a certain level of DBPs removal in biofilters at a specific

temperature can be calculated by integrating equations (3.1) and (3.2), resulting in Equation (3.3).

$$\text{EBCT} = \frac{Ln(\frac{C_t}{C_0})}{-K_R\theta^{(T-T_R)}} \qquad (3.3)$$

where C_t represents the DBP concentration in biofilter effluent at an operated temperature T (°C); C_0 represents the DBPs concentration in influent; K_R represents the DBPs removal rate constant at the reference temperature of T_R (e.g., 20 ◦C). For example, to achieve an 80% removal of DCAA at 15 °C, the EBCT required for GAC filters was estimated to be 8.0 min.

3.4 Conclusion

This study systematically studied the impact of temperature and EBCT on GAC biofilters performance on DCAA, TCAA, chlorinated water UTOX, and chloraminated water UTOX removal. The key findings are summarized as follows.

(1) The biodegradability of UTOX in chloraminated water was lower than in chlorinated water, likely due to changes in molecular size distribution and hydrophobicity.

(2) The impact of EBCT on DBPs removal in biofilters was more pronounced at low temperatures. For regions experiencing considerable seasonal temperature fluctuation, extending the EBCT could counteract the effects of low temperatures on biofilter performance on DBPs removal.

(3) The developed first-order model and temperature activity coefficients offer tools for predicting DBP removal rates under various temperatures and EBCT, providing valuable information for biofilter operations in water treatment processes.

Further research should aim to refine these predictive models and explore additional measures to enhance GAC biofilter performance under a broader range of conditions. Moreover, a standard method of detecting the fraction of non-degradable UTOX should be developed and considered in the model to better predict the unknown DBPs removal.

Table 3.1 Water Quality of Simulated Drinking Water.

pH	8.0
DOC (mg/L)	3.0
Alkalinity (as $CaCO_3$, mg/L)	80.0
Ca (as $CaCO_3$, mg/L)	50.0
Mg (as $CaCO_3$, mg/L)	20.0
Nitrate (as N, mg/L)	2.0
Phosphate (PO_4^{3-} as P, mg/L)	0.5
Fe^{2+} (mg/L)	0.100
Cu^{2+} (mg/L)	0.050
Zn^{2+} (mg/L)	0.050
Mn^{2+} (mg/L)	0.020
Co^{2+} (mg/L)	0.002
Mo^{2+} (mg/L)	0.005
Ni^{2+} (mg/L)	0.005
B^{3+} (mg/L)	0.050
Se^{6+} (mg/L)	0.020

Table 3.2 Filter Material

Media	Effective Size (mm)	Minimum Iodine Number (mg/g)	Apparent Density (g/cm^3)	Dry Weight of Media in Column (g)	Packing Density [a] (g/cm^3)	Drainable Porosity [b]
GAC 300	0.80-1.00	900	0.64	5.64	0.53	0.557

[a] Packing density was determined by dividing the weight of dry packing material with the bed volume.

[b] Drainable porosity was determined by dividing the volume of drained water with the bed volume.

Table 3.3 First-order Rate Constants and Temperature Activity Coefficients for Biodegradation of DCAA, TCAA, UTOX.

DBP	Temperature (°C)	K_{EBCT} (min^{-1})	$t_{1/2}$ [a] (min)	R^2	Temperature activity coefficient (θ)
DCAA	5	0.106	6.57	0.987	1.063 ± 0.007
	10	0.162	4.28	0.991	
	20	0.273	2.54	0.983	
TCAA	5	0.081	8.59	0.985	1.068 ± 0.007
	10	0.130	5.35	0.993	
	20	0.235	2.95	0.984	
Cl_2-UTOX	5	0.020	34.11	0.974	1.054 ± 0.013
	10	0.034	20.54	0.984	
	20	0.046	13.63	0.995	
NH_2Cl-UTOX	5	0.018	38.94	0.974	1.048 ± 0.012
	10	0.028	24.79	0.976	
	20	0.040	17.36	0.985	

[a] The half-life represents the EBCT takes for the corresponding DBP to fall to half of the influent concentration.

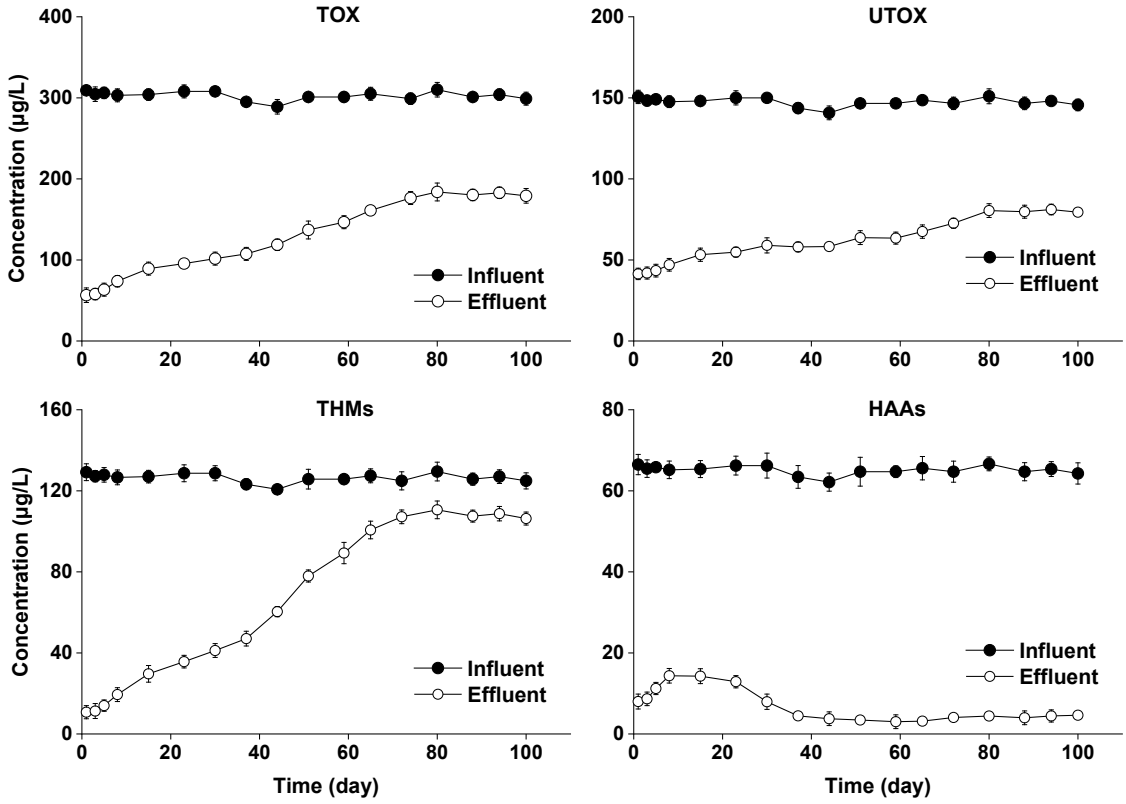

Figure 3.1 DBPs Removal in Chlorinated Water by GAC Filters. (Biofilter influent: chlorinated simulated water; quenched residuals; Experiment conditions: EBCT = 10 min, temperature = 20 °C. Error bars represent the standard errors of duplicate experiments.)

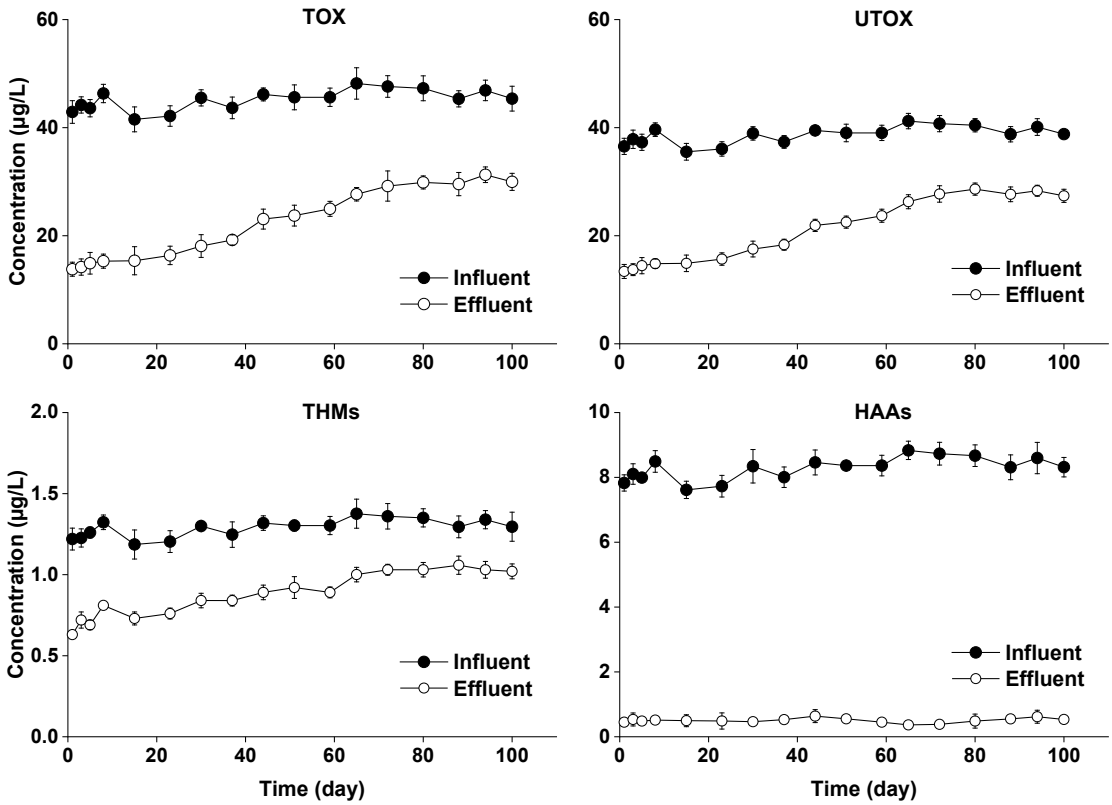

Figure 3.2 DBPs Removal in Chloraminated Water by GAC Filters. (Biofilter influent: chloraminated simulated water; quenched residuals; Experiment conditions: EBCT = 10 min, temperature = 20 °C. Error bars represent the standard errors of duplicate experiments.)

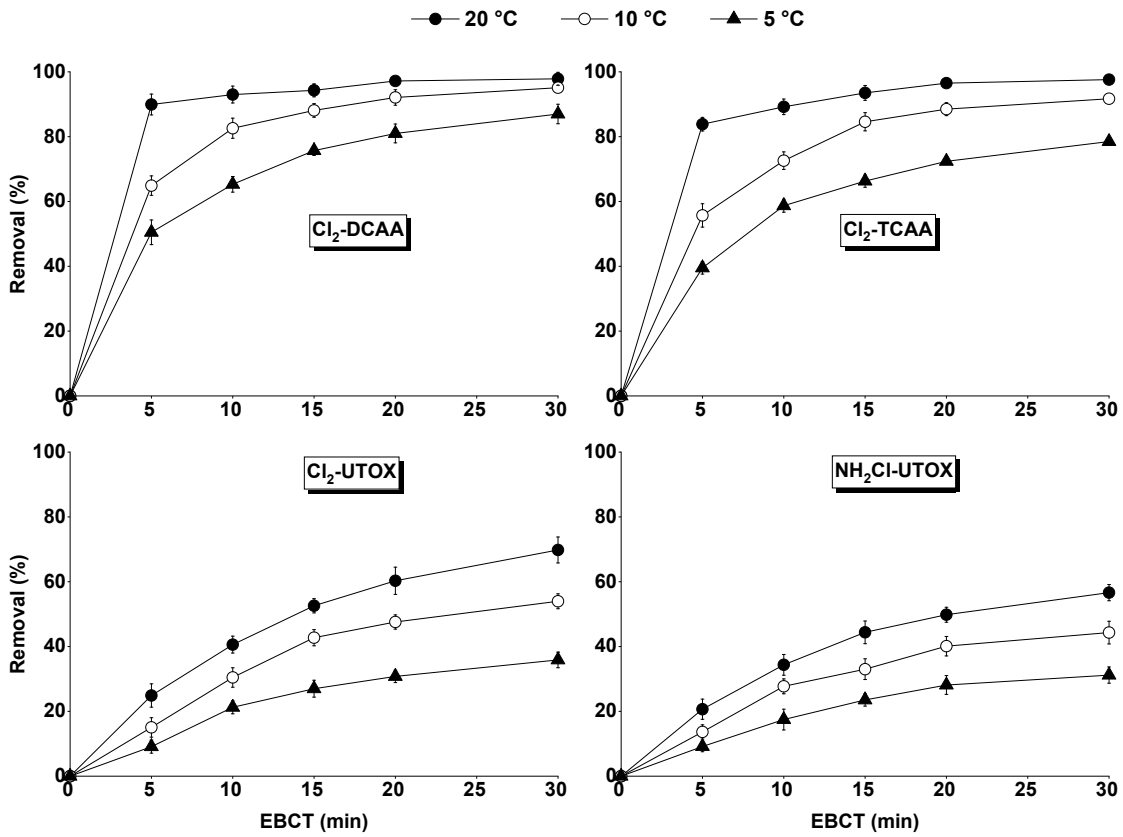

Figure 3.3 DBPs Removal in Biofilters During Stable Stage. (Biofilter influent: chlorinated and chloraminated simulated water; quenched residuals; Experiment conditions: EBCT 5-30 min, temperature 5-20 °C. Error bars represent the standard errors of eight samples collected from duplicate experiments.)

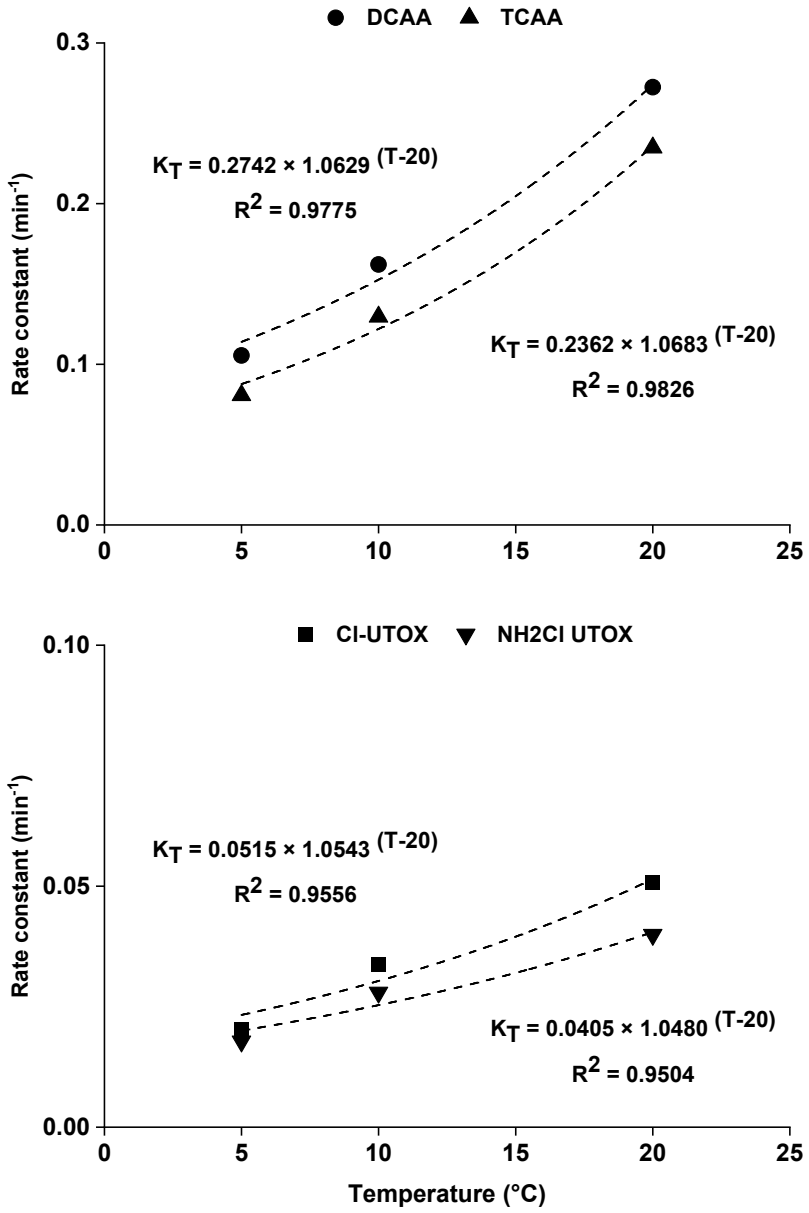

Figure 3.4 Rate Constant vs Temperature.

CHAPTER 4

EVALUATION OF THE IMPACTS OF INITIAL CONCENTRATION, EMPTY BED CONTACT TIME AND TEMPERATURE ON DIHALOACETONITRILES REMOVAL IN BIOLOGICAL ACTIVATED CARBON FILTERS

4.1 Introduction

Dihaloacetonitriles (DHANs) are a class of nitrogenous disinfection by-products (DBPs) formed during water treatment with disinfectants such as chlorine, chloramine, chlorine dioxide, or ozone. Dichloroacetonitrile (DCAN), bromochloroacetonitrile (BCAN), and dibromoacetonitrile (DBAN) are the three DHAN species that have gained increasing attention due to their ubiquitous in disinfected water and potential adverse health effects (Richardson et al., 2007). Despite their lower concentrations compared to regulated DBPs such as trihalomethanes (THMs) and haloacetic acids (HAAs), DHANs are considered important toxicity drivers in drinking water (Allen et al., 2022; Lau et al., 2020). Several DHAN toxicity studies have shown that these compounds have cytotoxic (cell-damaging), genotoxic (DNA-damaging), and possibly carcinogenic (cancer-causing) effects, which have been observed in both human cell line studies and animal models (Muellner et al., 2007; Richardson et al., 2007; Wagner and Plewa, 2017). Toxicity analysis using mammalian cells showed that DHANs (especially DBAN, the 5th most cytotoxic DBP) exhibit 10 −1000 times higher cytotoxicity and genotoxicity than the regulated THMs. Recognizing the potential health risks of these compounds, the WHO has established drinking water guidelines of 20 µg/L for DCAN and 70 µg/L for DBAN.

In recent years, many utilities have been transitioning from chlorine disinfection to chloramine disinfection to comply EPA Stage 2 Disinfectants/Disinfection Byproducts Rule. While this shift may help utilities comply with regulatory standards for certain DBPs, it may also inadvertently result in an increase in N-DBPs, including DHANs. In addition, some utilities are treating water sources contaminated by algae and municipal wastewater, and both are major contributors to dissolved organic nitrogen (DON) and, consequently, precursors to N-DBPs. N-DBP precursors were found to be in low molecular weight and low electrostatic charge relative to bulk natural organic matter (NOM), which makes them recalcitrant to removal by conventional water treatment methods, such as coagulation and filtration (Bond et al., 2012a; Zhang et al., 2020). U.S. EPA Information Collection Rule (ICR) reported up to 41.0 μg/L of haloacetonitriles in water treatment facilities (McGuire et al., 2002), highlighting the need to develop more effective methods to control DHANs in drinking water.

Biofiltration is an environmentally friendly technology that has been extensively investigated for organic and inorganic contaminant control. Filtration media can naturally transition to biological filters over time, allowing microorganisms to grow and form a biofilm on the media surface. These microorganisms metabolize biodegradable NOM or nutrients as energy sources, facilitating the removal of organic pollutants. Sand, anthracite, and GAC are the most common biofilter media. GAC has gained increased attention in recent years. Studies have shown that using GAC as biofilter media has many advantages. Their unique porous structure can host more bacteria in quantity and a more diverse community therefore leading to higher contaminant removal. Additionally, this porous structure creates microenvironments that shield the microorganisms from rapid

changes in the external environment, thereby enhancing the stability and effectiveness of the biofiltration process and leading to higher pollutant removal efficiency (Basu et al., 2016; Fox et al., 1990; Urfer et al., 1997a). Previous studies indicated that biological filtration can effectively remove certain DBPs, such as HAAs (up to 99%) and unknown DBPs (up to 70%). However, the potential of this technology for DHANs removal has not been systematically evaluated.

The performance of biofilters can be considerably impacted by empty bed contact time (EBCT) and temperature. EBCT represents water residence time within the filter, and it is calculated by dividing the filter bed volume by the flow rate. Research has shown that longer EBCTs can enhance substrate utilization and result in more contaminant removal efficiency. For example, Wang and Summers (1994) reported that increasing the EBCT from 3 to 33 minutes leads to an increase in DOC removal from 16% to 24%. However, when the operation EBCT was kept the same, variation of hydraulic loading rate (HLR) between 1.5-15 m/h had little impact on NOM removal. Similarly, Carlson and Amy (1998) observed comparable DOC removal rates in two anthracite biofilters operating at different HLRs (5.0 and 9.7 m/h) but with the same EBCT (10 and 11 min). Temperature is another crucial parameter that can directly impact biofilters performance regarding contaminant removal efficiency, as microbial growth and degradation rates are linked to temperature. Selbes *et al.* (2016) reported that both dissolved organic carbon and dissolved organic nitrogen removals were significantly decreased at water temperatures between 10-15 °C compared to those between 15-24 °C. Similar data were reported by Moona *et al.* (2021), who found that DOC removal efficiency decreased by 27% when the temperature decreased from 17 to 9 °C. In

addition, Hozalski, Bouwer and Goel, (1999) found that lower water temperature required prolonged EBCT to achieve equivalent steady-state removal. These findings emphasize that EBCT and temperature are important parameters for biofilter performance.

This study aims to 1) evaluate the performance of GAC biofilters for DHANs removal and 2) evaluate the impact of initial concentration, EBCT, and temperature on BAC filter performance for DHANs removal. To achieve this, lab-scale biofilters with granular activated carbon were constructed and operated for 120 days to eachieve stable biofiltration of DHANs. After that, biofilters were operated at varying DHANs initial concentration (1-4 mM), temperature (5-20 °C), and empty bed contact times (EBCTs) (5-30 min) to analyze DHANs removal kinetics.

4.2 Materials and Method

4.2.1 Materials

Unless otherwise specified, all chemicals used in the experiments were analytical grade and purchased from Fisher Scientific Co. All solutions were prepared using ultrapure water (18 mΩ-cm) generated by a Barnstead GenPure water purification system (Thermo Fisher, Waltham, MA). The humic acid used in the experiments was obtained from Sigma-Aldrich. After dissolving in ultrapure water, the humic acid solution was filtered through 0.45 μm membranes to make a 0.688 g/L stock solution. DCAN and DBAN were purchased from Sigma-Aldrich. BCAN was purchased from Toronto Research Chemical.

4.2.2 Preparation of Simulated Drinking Water

Simulated water was prepared to mimic the characteristics of typical drinking water. The simulated drinking water quality is given in Table 4.1. To avoid inhibitions in microbial growth, addition of selected trace metals including Fe^{2+} (0.1 mg/L), Cu^{2+} (0.05 mg/L), Zn^{2+} (0.05 mg/L), Mn^{2+} (0.02 mg/L), Co^{2+} (0.02 mg/L), Mo^{2+} (0.05 mg/L), Ni^{2+} (0.05 mg/L), B^{3+} (0.05 mg/L), Se^{6+} (0.02 mg/L) were added in the simulated water (Hua et al., 2016; Young and Tabak, 1993). Water pH was adjusted to 7.0 ± 0.1. Following a 24-hours reaction period with 3 mg/L of chlorine, chlorine residuals were quenched with 110 % of the required stoichiometric amount of sodium sulfite. Quantitative DCAN, BCAN and DBAN stocking solution were then added to the treated water to achieve 2 mM of each of the DCANs (equivalent to 22, 30, and 40 μg/L, respectively). Influent water was changed every 3 days to minimize the impact of DHANs self-decomposition on biofilter loading.

4.2.3 Biologically Activated Carbon Filter

Bituminous coal-based GAC 300 (Calgon Filtrasorb® 300, 0.8 - 1.0 mm) was selected as the filter media. The GAC media was rinsed with ultrapure water (18 mΩ-cm) and air dried for three days prior to use. Duplicate GAC filters were constructed in glass chromatography columns with 10 cm in length and 1.5 cm in diameter (Omnifit, two fixed endpieces). Each column was packed with 5.64 g of GAC 300 to achieve a 6 cm column height. Detailed media specifications and packing density information can be found in Table 4.2. A peristaltic pump (Masterflex L/S, Cole-Parmer, Vernon Hills, IL) was used to maintain the designed flow rate through the filter, with the rotation rate

adjusted between 48.6 and 8 rpm to achieve an empty bed contact time (EBCT) ranging from 5 and 30 minutes.

4.2.4 Biofiltration Experiments

The experiment commenced with inoculating 432-bed volumes (BV) of natural surface water in each column with 10-min empty bed contact time (EBCT). The natural surface water was obtained from Big Sioux River (Brookings County, SD).

Following inoculation, BAC filters were loaded with simulated water for 120 days to establish bio-stable conditions. The filters were operated at 1.06 mL/min with a 10-min EBCT and DCAN, BCAN and DBAN concentration of 2 mM, respectively, at 20 °C. After 120 days of operation, the influent DHAN concentration was switched to 1 and 4 mM to investigate the impact of initial concentration on DHAN removal in biofilters. After that, the DHAN concentration was switched back to 2 mM of DHAN and operated at 10 min EBCT for two weeks for column stabilization. EBCT 30, 15, 10, 5, 2.5 min were then applied to BAC filters to investigate the impacts of EBCT on DHANs biodegradation. The filters were operated for two weeks at each condition. The first week was used for column stabilization, and the last seven days was used for sample collection and analysis.

After completion of the previous experiments, the BAC filters and simulated water were transferred to a temperature-controlled water bath (bath circulator, Model 2050, Caron Products) set at 10 °C. The filters were allowed to stabilize at this temperature for two weeks with a 10-min EBCT before conducting DBP biodegradation

kinetics experiments. These experiments were conducted following the same procedures as those performed at 20 °C. Finally, the same procedures were repeated at 5 °C.

Each filter was manually stirred to disrupt the biofilm each week to mitigate biofilter clogging.

4.2.5 Analytical Methods

The chlorine residual was analyzed using the DPD ferrous titrimetric method. The TOX was determined using the adsorption-combustion-titration method with a Mitsubishi TOX-100 Analyzer (Cosa Xentaur Inc., Norwood, NJ) following standard method 5230B (Baird, Eaton and Rice, 2017). DCAN, BCAN, and DBAN were extracted by liquid/liquid method with pentane and analyzed by GC/ECD according to U.S. EPA 551.1 method.

4.2.6 Data Analysis

The first-order kinetics model is commonly used as a convenient method to describe the organic compounds biodegradation progress in biofilters. This model assumes that the biodegradation rate is directly proportional to the pollutant's concentration (Black and Bérubé, 2014; Liu et al., 2022; Terry and Summers, 2018; Urfer et al., 1997b). In this study, the DHAN biodegradation data was fitted to the first-order kinetic equation model, as expressed in the following form:

$$C_t = C_0 e^{-kt} \qquad (4.1)$$

where C_t represents the target DBP concentration after an EBCT of t (min); k represents the target DBP removal rate constant (min^{-1}).

The temperature activity coefficients (θ) were subsequently calculated by fitting the DBP removal rate constants to the linearized form of the commonly employed power law relationship, based on the linear regression of the Arrhenius equation, which is commonly used in the sanitary engineering field to reflect the impact of temperature (Metcalf and Eddy, 2014; Peleg et al., 2012; Rittmann and McCarty, 2001).

$$K_T = k_{20}\theta^{(T-20)} \qquad (4.2)$$

where K_T is the DBP degradation rate constant at temperature T in ◦C, θ is the temperature activity coefficient.

Statistical analyses including first-order kinetic model and nonlinear curve-power law fitting were done in OriginPro (2021).

4.3 Results and Discussion

4.3.1 Removal of DHANs in GAC Filters

Figure 4.1 presents the TOX, UTOX, THMs, HAAs removal in GAC biofilters during the 120 days operation at 20 °C and EBCT of 10 min. Prior to the DHANs spiking, the average TOX concentration in the chlorinated influent was measured at 298 µg/L, composed by 22% THMs, 19% HAAs, and 58% UTOX. DCAN, BCAN, and DBAN were spiked into the influent to achieve 2 mM, and the concentration remained constant at 22 ± 2.1 µg/L, 30 ± 2.2 µg/L, and 40 ± 2.6 µg/L, respectively.

DBPs were effectively removed through adsorption at the initial stages of the experiment. Specifically, the GAC filters achieved TOX, UTOX, THMs, HAAs removal efficiency at 78%, 90%, 92%, and 88%, respectively. Breakthroughs of TOX, UTOX, THMs were observed after 10 days, and the effluent concentration gradually increased

between day 10-50 and plateaued after 70-80 days of operation. After 80 days, GAC filters achieved a biologically stable state and can consistently remove 38% TOX, 44% UTOX, and 14% THMs (Table 4.3).

The removal of HAAs in GAC biofilters presented distinct patterns. GAC biofilters could initially eliminate up to 88% of HAAs. After approximately 10 days of operation, the HAA concentration in the effluent gradually increased and peaking on day 20, and remained stable for three weeks. A gradual decline was observed after day 40, and eventually stabilized after a 60-day operational period, maintaining an 88-92% removal efficiency throughout the remaining experiment.

Figure 4.2 shows the DCAN, BCAN, and DBAN removal in GAC biofilters during the 120 days operation at 20 °C and EBCT of 10 min. GAC filters removed >98% of DCAN at the early stage of the experiment. The concentration of DCAN in the effluent experienced a minor increase after the first 10 days, reached a peak around day 30 with 93% removal efficiency, then declined and ultimately stabilized after 50 days of operation. Near-complete removal was observed during the remaining period of the experiment. Similar trends were also observed in BCAN and DBAN removal. The results suggest that DHANs are readily biodegradable compounds. The initial high removal can be attributed to the adsorption capacity of the activated carbon. As the operation continued, activated carbon reached saturation, leading to an increase in the effluent DHANs concentrations. Simultaneously, the biodegradation capability gradually built up and become the predominant pathway for DHAN after adsorption sites are exhausted. It should be noted that the addition of DHANs did not impact HAAs and THMs removal. The biodegradation pathways of HANs may include the followings: 1) the nitriles in

HANs were hydrolyzed to amide groups via nitrile hydratase, resulting in HAMs formation, and 2) the nitriles were hydrolyzed to carboxylic acids via nitrilase enzyme, leading to the HAMs formation (Peterson et al., 2023a).

The results indicated that, under the condition of the study, it takes 70-80 days of operation time for GAC biofilters to achieve a biologically stable state condition for TOX and UTOX removal. In contrast, for HAAs and DHANs, the stabilization time was 20-30 days shorter due to their easy biodegradability.

4.3.2 Impact of Initial Concentration on DHANs Removal

The DHAN concentration in the drinking water can fluctuate due to the variation of water quality and the disinfection methods employed are different in different regions. The U.S. EPA Information Collection Rule (ICR) has reported levels up to 41.0 μg/L of DHANs at water treatment facilities. Therefore, this study investigates DHANs removal within biofilters at concentrations ranging from 1 mM to 4 mM to cover a wide range of DHAN concentration. The results are given in Figure 4.3.

Under operating conditions of 20 °C and an EBCT of 10 min, GAC biofilters can almost completely remove all DHANs (>98%) even at the highest concentration of 4 mM (corresponding to 44 μg/L DCAN, 60 μg/L DBAN, and 80 μg/L DBAN) tested in this study. This observation suggests that initial concentration does not significantly affect the removal efficiency of DHANs in biofilters. Moreover, the high removal efficiency also suggests that DHANs are highly susceptible to biodegradation.

4.3.3 Impact of Temperature and EBCT on DBPs Removal

Figure 4.4 depicts the average DCAN, BCAN, and DBAN removal achieved in GAC filters under various EBCT and temperature conditions. Comparing the average degradation rates at three temperatures at the same EBCT, DCAN shows the highest average removal rate ranging from 34% to 85%, followed by BCAN (32% - 82%) and DBAN (31% - 79%). According to the ANOVA analysis, increasing the temperature significantly enhanced the removal of DCAN, BCAN, and DBAN in BAC filters within an EBCT of 2.5-30 minutes ($P < 0.05$). Moreover, higher EBCT notably increased the removal of DCAN, BCAN, and DBAN at temperatures below 5-10°C, while the improvement is less substantial at 20 °C, particularly within an EBCT of 10-30 minutes ($P > 0.05$).

The results and analysis suggest that temperature enhancements have a more significant impact under lower EBCT conditions. Similarly, an increase in EBCT also improves the removal of DHANs, with the benefits of EBCT being more significant at lower temperatures. These findings align with previous research addressing the impacts of temperature and EBCT on NOM biofiltration in BAC filters (Liu et al., 2022; Moll et al., 1999). Thus, simultaneously studying the impacts of temperature and EBCT on biofilters is essential as both these factors determine DBP removal efficiency.

4.3.4 Impact of Temperature on DBPs Removal Kinetics

The kinetics of DCAN, BCAN, and DBAN removal in biofilters were quantified by integrating the experimental data to the first-order model (equation 4.1). Figure 4.5 presents the first-order rate constants at different temperatures. The coefficient of

determination (R^2) value was > 0.97 for all conditions, indicating that the first-order model adequately describes the DCAN, BCAN, and DBAN removal in biofilters.

The DHANs removal rate constants and the temperature coefficients are given in Table 4.4. In general, the increasing temperatures increased the DHAN removal rate constants in GAC biofilters. For DCAN, the rate constants increased from 0.1136 to 0.4268 min^{-1} as the temperature increased from 5 to 20 °C. The removal rate constants of BCAN and DBAN followed a similar tendency but with a relatively lower number. In Chapter 3, the removal rate constants of DCAA (0.1055-0.2725 min^{-1}), TCAA (0.0807 - 0.2349 min^{-1}), Cl-UTOX (0.0203 - 0.0455 min^{-1}), and NH2-UTOX (0.0178 - 0.0399 min^{-1}) under the same temperature conditions were analyzed. Therefore, the biodegradability of different DBP species can be expected in the following order: DCAN > BCAN > DBAN > DCAA > TCAA > Cl_2-UTOX > NH_2Cl-UTOX > chloroform.

The temperature activity coefficients (θ) can connect the estimated rate constants across diverse temperatures and present the multiple rate constants across different temperatures using a single rate constant at a reference temperature, such as 20 °C. An activity coefficient >1 indicated a positive effect of temperature on rate constants, the larger number, the more significant the impact of temperature. The temperature activity coefficient of DHANs in biofilters was calculated by aligning Equation (4.2) with the removal rate constants estimated at different temperatures. Figure 4.4 represents the application of Equation (4.2) to the DCAN, BCAN, and DBAN removal rate constants concerning temperature. All R^2 values were > 0.98, indicating that Equation (4.2) could adequately model the impact of temperature on different DHAN removal rate constants. The temperature activity coefficient of DCAA, BCAN and DBAN was 1.0843, 1.0847

and 1.0831, respectively, indicating that temperature positively impacted their removal. In Chapter 3, the calculated temperature activity coefficient of TCAA, DCAA, Cl_2-TOX, and NH_2Cl-TOX were 1.0683, 1.0629, 1.0620, and 1.0527. The impact of temperature on different DBPs and DOC removal in GAC biofilters was found to be BCAN ≈ DCAN ≈ DBAN > TCAA ≈ DCAA > Cl_2-TOX > NH_2Cl-TOX.

4.3.5 Implication on the operation of biofilters for DBPs removal

The results of this research indicated that the performance of biofilters in DHANs removal is temperature-depended. Therefore, the DHANs removal in biofilters can vary throughout the year. This study suggests that extending the EBCT is an approach to counteract the effects of low temperatures on biofilters. The required EBCT to achieve a certain level of DHANs removal in biofilters at a specific temperature can be calculated by integrating equations (4.1) and (4.2), resulting in equation (4.3).

$$\text{EBCT} = \frac{Ln(\frac{C_t}{C_0})}{-K_R\theta^{(T-T^R)}} \qquad (4.3)$$

where C_t represents the DBP concentration of biofilter effluent at an operated temperature T (°C); C_0 represents the DBPs concentration of influent; K_R represents the DBPs removal rate constant at the reference temperature of T_R (e.g., 20 ◦C). For example, to achieve an 80% removal of DCAN at 15 °C, the EBCT required for GAC biofilters was estimated to be 5.74 min.

4.4 Conclusion

This study systematically studied the DHANs removal at various conditions. The key findings are summarized as follows.

(1) GAC biofilters can effectively remove more than 98% of the influent DHANs even at the extreme concentration (44 μg/L DCAN, 60 μg/L DBAN, and 80 μg/L DBAN) and the removal does not significantly impact by the initial DHAN concentration.

(2) Longer EBCT generally increased the removal rate of DHANs, and the impact of EBCT was more pronounced at low temperatures.

(3) The developed first-order model and temperature activity coefficients offer tools for predicting DBP removal rates under various temperatures and EBCT, providing valuable information for biofilter operations in water treatment processes.

Table 4.1 Water Quality of Simulated Drinking Water.

pH	7.0 ± 0.1
DOC	3.0 ± 0.2 mg/L
Alkalinity (as $CaCO_3$)	80.0 ± 2 mg/L
Ca (as $CaCO_3$)	50.0 ± 1 mg/L
Mg (as $CaCO_3$)	20.0 ± 0.5 mg/L
Nitrate (as N)	2.0 ± 0.1 mg/L
Phosphate (PO_4^{3-} as P)	0.5 ± 0.03 mg/L
TOX	298.2 ± 12.1 µg/L
THMs	74.5 ± 5.0 µg/L
HAAs	93.1 ± 7.1 µg/L
DCAN	11-44 µg/L (1-4 mM)
DBAN	15-60 µg/L (1-4 mM)
BCAN	20-80 µg/L (1-4 mM)
UTOX	179.8 ± 8.7 µg/L

Table 4.2 Filter Material

Media	Effective Size (mm)	Minimum Iodine Number (mg/g)	Apparent Density (g/cm^3)	Dry Weight of Media in Column (g)	Packing Density [a] (g/cm^3)	Drainable Porosity [b]
GAC 300	0.80-1.00	900	0.64	5.64	0.53	0.557

[a] Packing density was determined by dividing the weight of dry packing material with the bed volume.

[b] Drainable porosity was determined by dividing the volume of drained water with the bed volume.

Table 4.3 DBPs Removal in GAC Biofilters at Biostable State.

	THMs	HAAs	DHANs	UTOX
Influent (μg/L)	74.5	93.3	96.0	173.2
Effluent (μg/L)	64.1	12.1	0.6	97.0
Removal (%)	14	87	99	44

Table 4.4 First-order Rate Constants and Temperature Activity Coefficients for Biodegradation of DCAN, BCAN, and DBAN.

DBP	Temperature (°C)	K (min^{-1})	$t_{1/2}$ [a] (min)	R^2	Temperature activity coefficient (θ)
DCAN	5	0.114	6.10	0.987	1.084 ± 0.009
	10	0.205	3.39	0.978	
	20	0.427	1.62	0.994	
BCAN	5	0.102	6.83	0.984	1.085 ± 0.013
	10	0.196	3.53	0.978	
	20	0.401	1.73	0.995	
DBAN	5	0.098	7.08	0.981	1.083 ± 0.013
	10	0.189	3.67	0.983	
	20	0.379	1.83	0.995	

[a] The half-life represents the EBCT takes for the corresponding DBP to fall to half of the influent concentration.

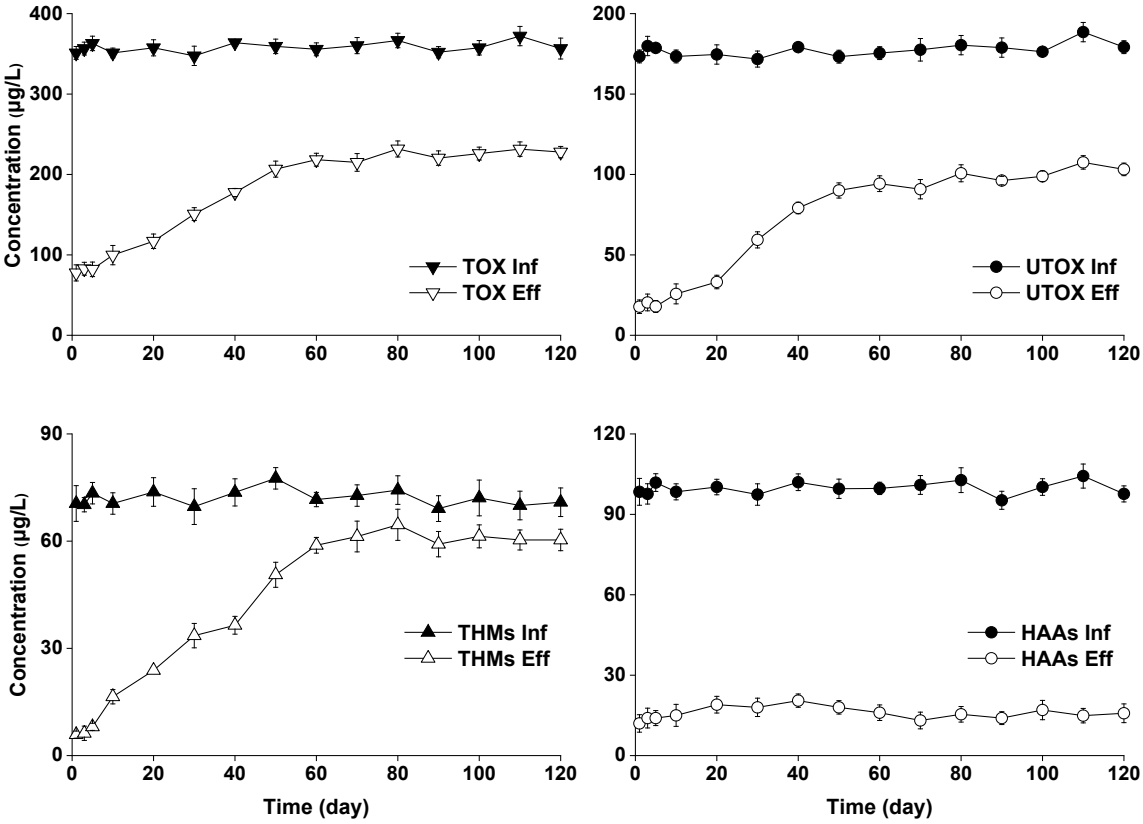

Figure 4.1 TOX, UTOX, THMs, HAAs Removal in GAC Filters. (Biofilter influent: simulated chlorinated water, quenched residuals. Experiment conditions: EBCT = 10 min, temperature = 20 °C. Error bars represent the standard errors of duplicate experiments.)

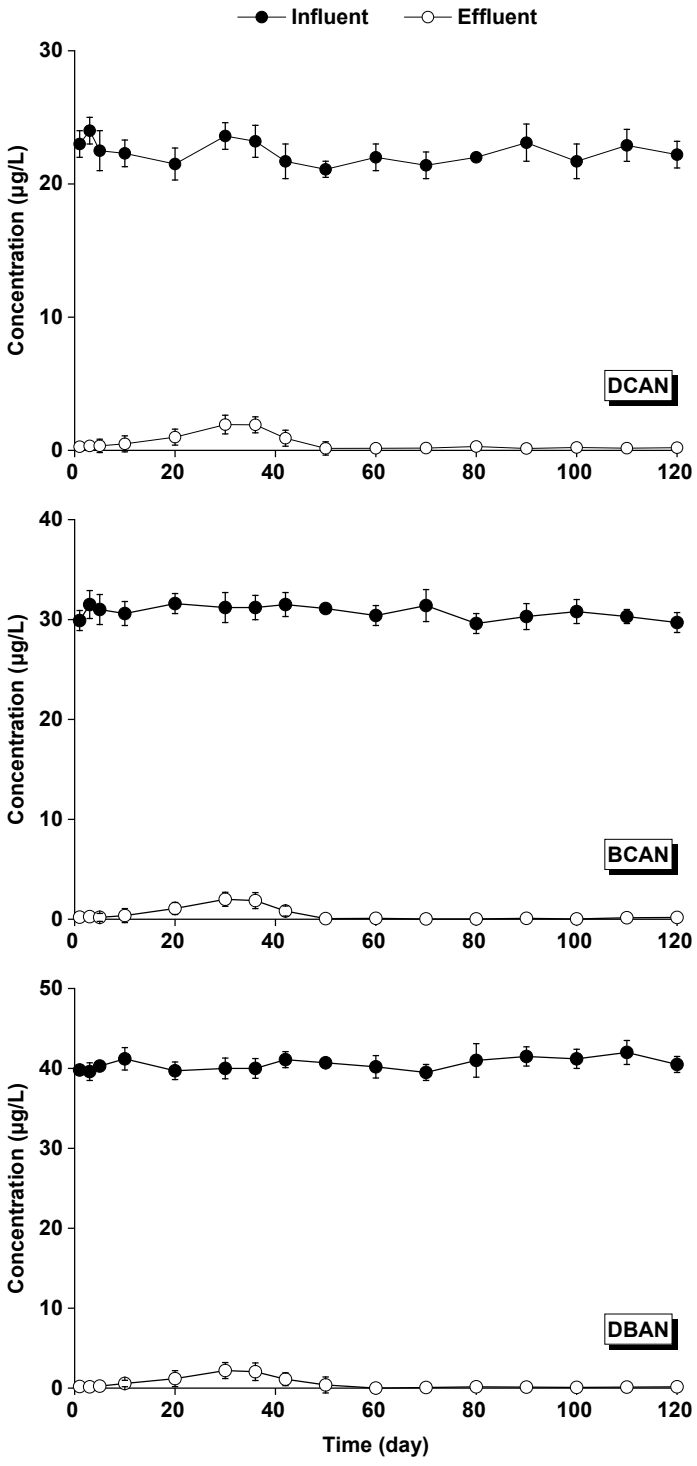

Figure 4.2 DCAN, BCAN and DBAN Removal in GAC Filters. (Biofilter influent: simulated chlorinated water, quenched residuals. Experiment conditions: EBCT = 10 min, temperature = 20 °C. Error bars represent the standard errors of duplicate experiments.)

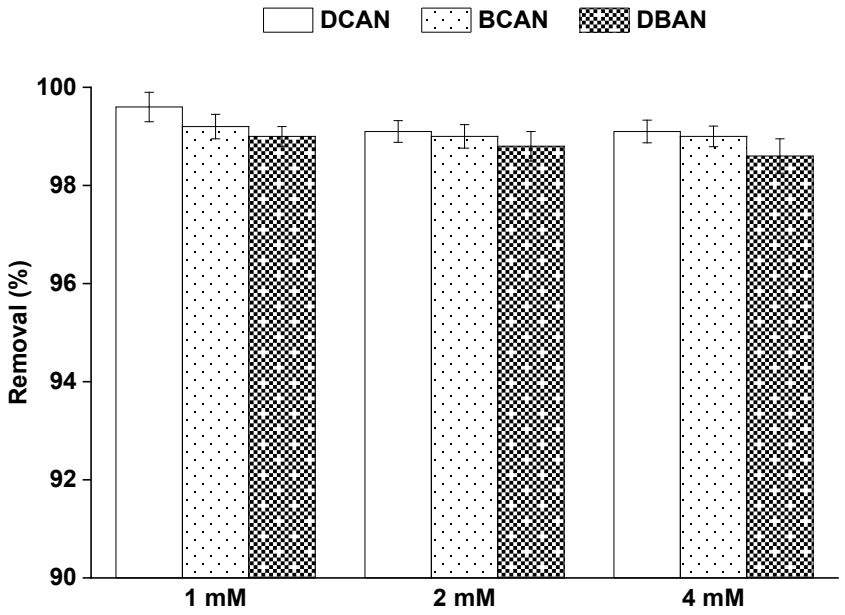

Figure 4.3 Impact of Influent Concentration on DHANs Biodegradation. (Biofilter influent: chloraminated simulated water, quenched residuals, spiked DHANs; Experiment conditions: EBCT = 10 min, temperature = 20 °C, DHANs concentration = 1-4 mM. Error bars represent the standard errors of duplicate experiments.)

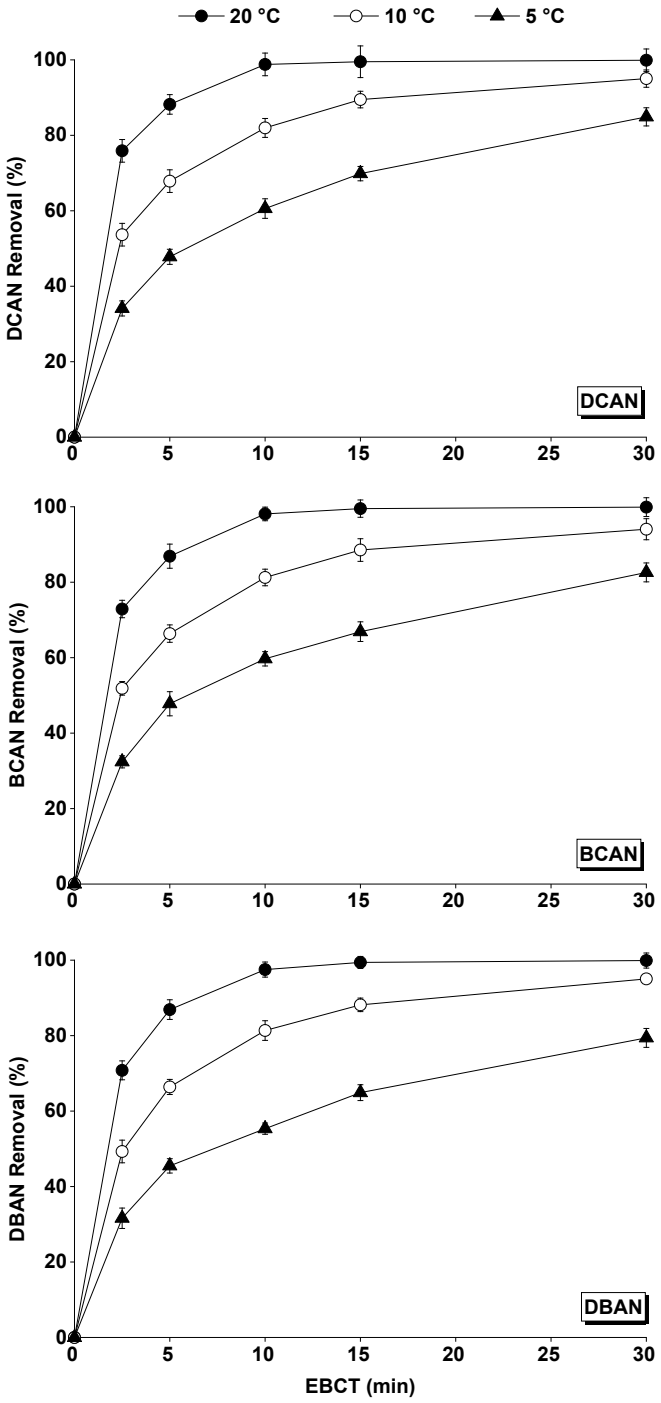

Figure 4.4 Impact of Temperature and EBCT on DHANs Removal in GAC Biofilters. (Biofilter influent: chlorinated simulated water, quenched residuals, spiked DHANs; Experiment conditions: EBCT 5-30 min, temperature 5-20 °C, DCAN = 2 mM, DBAN = 2 mM, BCAN = 2 mM. Error bars represent the standard errors of six samples collected from duplicate experiments.)

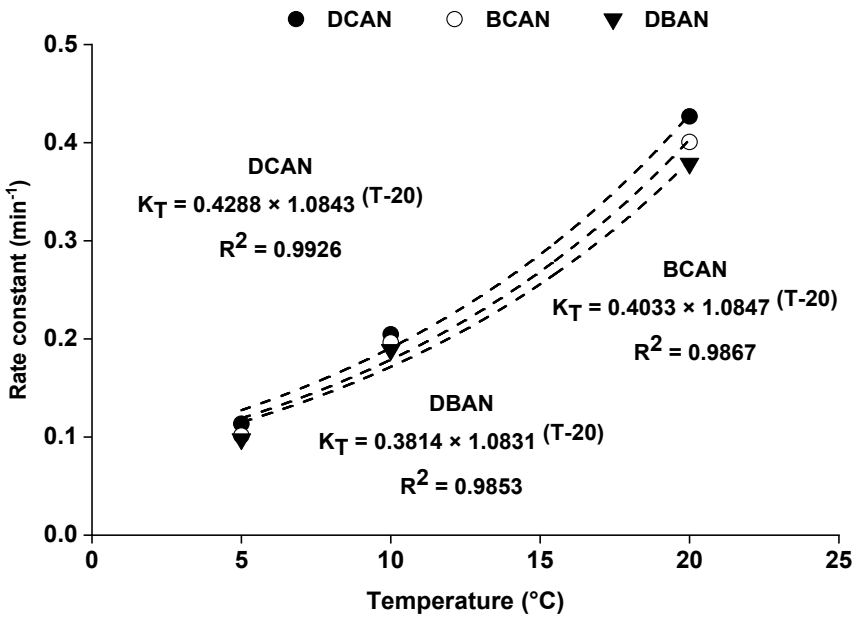

Figure 4.5 Rate Constant vs. Temperature.

CHAPTER 5

REMOVAL OF DISINFECTION BYPRODUCTS BY PRE-CHLORAINATION - BIOFILTRATION: A NEW STRATEGY TO CONTROL DBPS IN DRINKING WATER

5.1 Introduction

Drinking water disinfection for waterborne disease control is one of the most significant public health accomplishments of the previous century. However, the reaction of chlorine with natural organic matter (NOM) can inevitably form toxic disinfection byproducts (DBPs) and raise public health concerns. In drinking water, the EPA has regulated 11 DBPs, including four Trihalomethanes (THM4), five Haloacetic acids (HAA5), chloride, and bromate. Water treatment facilities have implemented various treatment strategies to comply with EPA regulations. These include precursor control and the utilization of alternative disinfectants to reduce DBP formation.

Pretreatment technologies such as coagulation, membrane filtration, and granular activated carbon (GAC) adsorption are common precursor control strategies. Coagulation can reduce natural organic matter (NOM) but has limitations like increased costs, increased sludge production, incomplete NOM removal, and required additional pH adjustment steps to maintain the coagulation efficiency (Chow et al., 2009; Ghernaout, 2014; Hu et al., 2006; Jacangelo et al., 1995; Matilainen et al., 2010; Qin et al., 2006; Sharp et al., 2006; Yu et al., 2007). Membrane filtration is a promising NOM control technology that can effectively remove NOM. However, the high-pressure operation and complexity of membrane systems increase the operation costs and maintenance

requirements. GAC adsorption offers effective NOM removal due to its large adsorption area. However, its capacity can deplete over time therefore regular carbon regeneration or replacement is required to maintain efficiency.

Many water treatment facilities employ alternative disinfection methods such as chloramine, ozone, chlorine dioxide, and UV to control regulated DBPs formation. While chloramine effectively mitigates THMs and HAAs, it can produce potentially hazardous nitrogenous-DBPs (N-DBPs). Chloramines in the distribution system can lead to nitrifying bacteria growth and nitrite and nitrate formation issues (Regan et al., 2003). Ozone, though effective, can lead to bromate formation in waters with high bromide levels. Chlorine dioxide's reaction with NOM can lead to chlorite formation. UV avoids the formation of halogenated DBPs, but the disinfection efficiency is adversely impacted by water turbidity and suspended matter. In addition it doesn't provide a disinfectant residual, necessitating secondary disinfection. Some studies reported that UV radiation can transform some NOM into more biodegradable compounds, potentially promoting microbial growth in the distribution system (Bazri et al., 2012; Sharpless and Linden, 2003). Given these limitations and potential health risks associated with these alternative disinfection methods, there is a clear need for more efficient and safe strategies for DBPs control.

During the advanced treatment of highly impacted source water, pretreatment with chlorine before the final disinfection is often essential. This strategy provides multiple benefits, managing membrane fouling, controlling biofilm formation in pumping and piping systems of the treatment unit, preventing bromate formation, mitigating N-nitrosamine precursor emergence, and enhancing the odor and taste of the treated water

(Acero et al., 2005; Karanfil et al., 2008; Shah et al., 2012; Verdugo et al., 2020; Zheng et al., 2023). However, prechlorination can also lead to DBPs formation. Therefore, pre-chlorination should be carefully controlled to avoid excessive DBP formation.

Biological filtration (biofiltration) is an eco-friendly and robust technology that has gained significant attention for organic and inorganic contaminants during water treatment. Filtration media can naturally transition to biological filters over time, allowing microorganisms to grow and form a biofilm on the media surface. These microorganisms metabolize biodegradable NOM or nutrients as energy sources, facilitating the removal of organic pollutants. Recent studies have shown that biofiltration can effectively remove haloacetic acids (HAAs). For example, Kim and Kang (2008) reported >90% HAAs removal in biologically active carbon (BAC) filters with 9.8 min EBCT; Xie and Zhou (2002) reported HAAs removal efficiencies ranging from 80% to 100% using BAC filtration with 20 min EBCT; and Tang and Xie (2016) observed >70% HAA removal efficiencies in BAC filters using swimming pool water with 6.4 min EBCT. The biofiltration of trihalomethanes (THMs) has also been investigated. Results indicated that THMs are generally resistant to biodegradation under typical environmental conditions due to their stable chemical structure. THMs have limited potential to serve as direct carbon and energy sources for microbial growth, and they do not readily break down in the environment by microorganisms. In addition to these findings, the results in previous chapters (chapter 2, 3, and 4) suggest that biofiltration can also effectively control unknown DBPs and dihaloacetonitriles (DHANs). Therefore, DBP preformation - biofiltration is a viable alternative method for DBPs control. After biofiltration, chemical disinfectants such as chlorine and chloramine are required to

maintain residual disinfectants in the distribution system. So far, DBP preformation - biofiltration technology for DBP formation potential control has yet to be carefully explored. This study will provide valuable information for this technology application in DBPs control.

The research objectives of this study were to: 1) evaluate biofiltration for different groups of DBPs formation potential control; 2) investigate the DBP formation kinetics during the chlorine or chloramine post-treatment; 3) investigate the impacts of EBCT on biofilters performance in DBP formation potential control, and 4) investigate the impacts of routine backwash on DBP removal and formation potential. To achieve these objectives, two lab-scale biofilters with granular activated carbon (GAC 300, 0.8-1.0 mm) were constructed and operated for four months to achieve biologically stable conditions. Chlorine and chloramine post-treatment were performed for the biofilter-treated water. During the 24 hours post-treatment, DBP formation kinetics were monitored, and the final DBP formation potential was compared to evaluate the DBP pre-formation- biofiltration technology for DBP formation potential control.

5.2 Materials and Method

5.2.1 Materials

Unless otherwise specified, all chemicals used in the experiments were analytical grade and purchased from Fisher Scientific Co. All solutions were prepared using ultrapure water (18 mΩ-cm) generated by a Barnstead GenPure water purification system (Thermo Fisher, Waltham, MA). The humic acid used in the experiments was obtained from Sigma-Aldrich. After dissolving in ultrapure water, the humic acid solution was

filtered through 0.45 μm membranes to make a 0.688 g/L stock solution. The dichloroacetonitrile was obtained from Sigma-Aldrich, and the bromochloroacetonitrile was obtained from Toronto Research Chemical.

5.2.2 Preparation of Simulated Drinking Water

Table 5.1 shows the simulated drinking water quality. Addition of selected trace metals including Fe^{2+} (0.1 mg/L), Cu^{2+} (0.05 mg/L), Zn^{2+} (0.05 mg/L), Mn^{2+} (0.02 mg/L), Co^{2+} (0.02 mg/L), Mo^{2+} (0.05 mg/L), Ni^{2+} (0.05 mg/L), B^{3+} (0.05 mg/L), Se^{6+} (0.02 mg/L) were added in the simulated water to avoid inhibitions in microbial growth (Hua et al., 2016; Young and Tabak, 1993). After a 24-hours reaction period with 2.5 mg/L of chlorine, no chlorine residuals left in the water.

5.2.3 Biologically Activated Carbon Filter

Bituminous coal-based GAC 300 (Calgon Filtrasorb® 300, 0.8 - 1.0 mm) was selected as the filter media. After collection from Calgon Carbon, the GAC media was rinsed with ultrapure water (18 mΩ-cm) and air-dried for three days before use. Duplicate BAC filters were constructed in glass chromatography columns with 10 cm in length and 1.5 cm in diameter (Omnifit, two fixed endpieces). Each column was packed with 5.64 g of GAC 300 to achieve a 6 cm column height. Detailed information of the media specifications and packing density can be found in Table 5.2. A peristaltic pump (Masterflex L/S, Cole-Parmer, Vernon Hills, IL) was used to maintain the designed flow rate through the filter, with the rotation rate adjusted between 48.6 and 8 rpm to achieve an empty bed contact time (EBCT) ranging from 5 and 30 minutes.

5.2.4 Biofiltration Experiments

At the beginning of the experiment, 432-bed volume (BV) of natural surface water with 10-min of empty bed contact time (EBCT) was inoculated in each column. The natural surface water was collected from Big Sioux River (Brookings County, SD) and stored at room temperature 20 °C for 24 hours before being introduced into GAC filters.

Following inoculation, BAC filters were loaded with pre-chlorinated water for 120 days to achieve bio-stable conditions. The filters were operated at 15-min EBCT and 20 °C for 120 days to achieve stable biodegradation conditions. Effluent samples were collected from each biofilter and post-treated by Cl_2 or NH_2Cl (with 2.5 mg/L disinfection dosage) to simulate secondary disinfection treatment. The post-treated samples were collected at 0.5, 2, 4, 8, and 24 h and analyzed the TOX, THMs, HAAs, and UTOX concentration.

EBCT was then adjusted to 30 and 5 minutes to investigate the impacts of retention time on DBP formation potential reduction. After sample collection, Cl_2 or NH_2Cl were added to the effluent to achieve 2.5 mg/L concentration and react for 24 hours. Samples were analyzed for TOX, THMs, HAAs, and UTOX. The filters were operated for two weeks at each flow rate, with the first week used for column stabilization and the last seven days used for sample collection and analysis.

After completing the previous experiments, EBCT was adjusted to 15 min and stabilized for two weeks. The backwash procedure was then performed for both filters. Each filter was manually stirred to disrupt the biofilm and flushed with chlorine-free raw

drinking water for 15 min with an EBCT of 2.5 min. The EBCT was adjusted back to 15 min after backwash. And biofilter effluents were then collected at 6-, 12-, 24-, and 48-hours following backwash to study the impacts of backwash on DBPs removal and DBPs formation potential in biofilters.

In addition to backwash studies, a weekly backwash was performed following the same procedure throughout the experiment to mitigate filter clogging.

5.2.5 Analytical Methods

The chlorine and chloramine residuals were analyzed using the DPD ferrous titrimetric method. The DOC concentrations were measured by a TOC-V CSH Analyzer (Shimadzu Corp., Kyoto, Japan) according to Standard Method 5310 B (Baird et al., 2017). The TOX was determined using the adsorption-combustion-titration method with a Mitsubishi TOX-100 Analyzer (Cosa Xentaur Inc., Norwood, NJ) following standard method 5230B (Baird, Eaton and Rice, 2017). HAA_9, including monochloro-, dichloro-, trichloro-, monobromo-, dibromo-, tribromo-, bromochloro-, bromodichloro-, and chlorobromo- acetic acids, were extracted using liquid/liquid extraction with methyl-tertiary-butyl-ether (MTBE), derivatized with acidic methanol, and analyzed by gas chromatography with electron capture detection (GC/ECD, Thermo Fisher, TRACE 1310) according to U.S.EPA 552.3. THM_4, including chloroform, bromodichloromethane, dibromochloromethane, and bromoform, three dihaloacetonitriles (dichloro-, bromochloro-, and dibromoacetonitrile), three haloketones (dichloro-, trichloro-, 1,2-dibromo-3chloropropanone), and several other chlorine and bromine-containing compounds (trichloroethylene, 1,2-dibromoethane, 1,2-dibromo-3-chloropropane, tetrachloroethylene, and chloropicrin) were extracted by liquid/liquid

method with pentane and analyzed by GC/ECD according to U.S. EPA 551.1. The UTOX concentration was calculated by subtracting the total measured disinfection byproduct (DBP) concentrations (as Cl) from the TOX concentration.

5.3 Results and Discussion

5.3.1 Removal of DBPs in GAC Filters

Figure 5.1 shows the influent and effluent DBP concentration from GAC filters over a 120-day operation period. The influent TOX concentration averaged 255.3 µg/L, was composed of 21.8% THMs, 17.3% HAAs, 58.6% UTOX, and 2.3% other DBPs. In the preliminary phase of the experiment, GAC filters exhibited 83% TOX removal. However, as the GAC media became saturated over time, the effluent TOX concentration increased, leading to a decrease in TOX removal efficiency. After 100 days, GAC achieved a biologically stable state and could consistently remove 46% TOX from the influent water (Figure 5.2).

The UTOX and THMs removal displayed similar patterns but with different removal efficiencies. GAC filters removed 74% of UTOX and 94% of THMs at the initial stage of the experiment. Breakthroughs of UTOX and THMs were observed between day 3 to day 90. After 100 days of operation, the removal efficiency for both UTOX and THMs plateaued, sustaining an average removal rate of 42% for UTOX and 11% for THMs (Figure 5.2).

HAAs removal in GAC biofilters displayed a distinct pattern. The initial effluent concentration of HAAs was 3.43 µg/L with 88 % removal efficiency. Effluent HAA peaked at day 20, then gradually declined from day 20 to day 40, and stabilized after 60

days of operation. Near-complete removal was observed for the remaining period of the experiment.

In the early stages of the experiment, DBP removal was mainly due to GAC adsorption. However, as the GAC media gradually saturated, biological processes (biodegradation) increasingly dominated DBP removal. Upon achieving a biologically stable state, the removal efficiency of different DBP is primarily determined by their biodegradability. THMs, for example, have been proven resistant to biodegradation because their stable chemical structure limits their potential to serve as direct carbon and energy sources for microbial growth. Their resistance to microbial degradation results in a notable decrease in removal efficiency after GAC becomes saturated. In contrast, HAAs are easily biodegradable compounds, and many studies have reported over 90% removal in biofilters. Enzymes like dehalogenase can transform HAAs into intermediate compounds such as glycolic acid, glyoxylic acid, and oxalic acid, which are then further broken down into simple organic compounds by oxidases, dehydrogenases, or reductases enzymes, and ultimately mineralized to CO_2, H_2O, and inorganic salts (Ellis et al., 2001; Tang and Xie, 2016b; Tang et al., 2013; Xie and Zhou, 2002a). Therefore, the saturation of GAC did not impact HAAs removal in the GAC filters. Biodegradation eventually became the dominant removal mechanism in GAC filters, sustaining high removal efficiencies throughout the experiment.

5.3.2 DBP Formation Characteristic of Biofilter Effluent

Figure 5.3 shows the DBPs formation in biofiltrated water during chlorine and chloramine post-treatment. The TOX, UTOX, THMs, and HAAs concentration was observed to increase with the increase in reaction time.

In the post-chlorinated effluent samples, the concentrations of TOX and UTOX increased rapidly within the first 30 minutes, followed by a gradual rise, ultimately reached 249.0 µg/L and 129.3 µg/L after 24 hours of reaction. The formation of THMs and HAAs followed a similar trend, -a rapid initial formation followed by a more gradual growth rate.

Same as in chlorinated water, the DBPs concentration in chloraminated water also increased with the contact time. A rapid increase of TOX and UTOX was observed during the initial four hours. This increase accounted for approximately 69% of the TOX and 83% of the UTOX formed over the 24-hour reaction. Subsequently, the concentrations of TOX and UTOX steadily increased and reached 159.0 µg/L and 100.8 µg/L respectively. HAAs exhibited a similar formation pattern to TOX and UTOX but with much lower concentration. Only small quantities of THMs were observed during the chloramine post-treatment.

Hua and Reckhow, (2008) previously explored the impact of reaction time on DBP formation during chlorination and chloramination in the raw water of drinking water treatment facilities and reported that the majority of UTOX, HAAs, and THMs were quickly formed at the first few houses. Similar results were observed in this study, suggesting that the DBP formation trends in biofiltered water resemble those observed in raw water. Under the condition of the study, post-treatment of biofilter effluent with 2.5 mg/L of chlorine generated 1.78-, 1.67-, 6.81-, and 1.65- times higher concentrations of TOX, THMs, HAAs, and UTOX, respectively, compared to corresponding DBP concentrations in the biofilter effluent, after 24h reaction time. Similarly, post-treatment of biofilter effluent with 2.5 mg/L of chloramine also increases the DBP concentrations

compared to the biofilter effluent. The increase is 1.14-, 1.06-, 1.64-, and 1.16- times for TOX, THMs, HAAs, and UTOX after 24h reaction time.

5.3.3 Comparison of DBP Formation Potential of Different Treatment Strategies

Figure 5.4 compares the reduction of DBP formation potential using different treatment strategies for an EBCT of 15 min. In the first treatment strategy - Pre-chlorination - Biofiltration - Post-chlorination, GAC biofilters effectively reduced TOX formation from 434 µg/L to 249 µg/L, corresponding to a 42.6% reduction in TOX formation. The reduction is mainly attributed to the suppression of UTOX (44%) and HAAs (71%) formation, contributing to 57% and 29% of reduced TOX.

In the second treatment strategy - Pre-chlorination - Biofiltration - Post-chloramination, GAC biofilters reduced TOX formation from 290 µg/L to 159 µg/L, corresponding to a 45.1% reduction in TOX formation. The reduction is mainly attributed to the suppression of UTOX (43%) and HAAs (90%) formation, contributing to 56% and 35% of reduced TOX.

The results indicate that both treatment strategies (1) pre-chlorinating - biofiltration - post-chlorination and (2) pre-chlorinating - biofiltration - post-chloramination, are effective in the overall DBPs formation control, and the control efficiency of each group of DBP follows this order: HAAs (71-90%) > UTOX (43-44%) > THMs (10-17%).

5.3.4 Impact of EBCT on GAC Biofilters Performance on DBP Formation Potential Control

Figure 5.5 shows the impact of EBCT on biofilter performance on DBP formation potential control. A positive relation between EBCT and different DBP formation potential reduction was observed during the experiment.

5.3.4.1 Impact of EBCT on HAAs Formation Potential Reduction

In effluent samples post-treated with chloramine, the average HAAs formation potential reduced by 77%, 90%, and 96% at EBCT 5, 15, and 30 min, respectively (Figure 5.5). Nearly complete suppression of HAAs formation was observed when EBCT is higher than 15 min. This is mainly due to the high HAAs removal (>95%) and low HAAs formation (< 4 μg/L) during chloramine treatment.

Compared to the reduced HAAs formation potential in post -chloramine treatment, post-chlorinated water exhibited a lower reduction in HAAs formation potential. The average reduction ranged between 50% and 78% for EBCT 5 to 30 minutes.

In conclusion, the results suggest that biofiltration can effectively control HAAs formation potentials, even at short EBCT conditions.

5.3.4.2 Impact of EBCT on THMs Formation Potential Reduction

Compared to the decreasing of HAAs formation potential, a substantially lower reduction of THMs was observed in post-chlorinated effluent samples (Figure 5.5). The average THMs formation potential was reduced by 5- 26% at EBCT 5 - 30 min.

Moreover, even lower reductions of THMs formation potential were observed in post-chloraminated effluent samples. The average THMs formation potential decreased by 7 - 13% at EBCT 5 - 30 min. This phenomenon is more likely attributed to their low biodegradability.

5.3.4.3 Impact of EBCT on UTOX Formation Potential Reduction

Figure 5.5 shows a positive correlation between the reduction of UTOX formation potential and operation EBCT. In post-chlorinated water, increased EBCT from 5 to 30 min improves the UTOX reduction from 26% to 56%. Similar reduction rates were observed in post-chloraminated water, with 28%, 43%, and 61% reductions at EBCT 5, 15, and 30 min. NOM removal through biofilters also contributes to the decrease of UTOX formation. Moreover, longer EBCT aids in the degradation of unknown DBPs and NOM. Consequently, an EBCT of 30 min resulted in the highest UTOX formation potential reduction.

In conclusion, the results indicate that per-chlorination - biofiltration is a viable method to effectively control the potential formation of unknown DBPs, and this reduction exhibits a positive correlation with operation EBCT.

5.3.4.4 Impact of EBCT on Nitrogenous DBPs Formation Potential Reduction

In this study, only DCAN (2.84 μg/L) was identified due to the absence of bromine or iodine ions in the water (Figure 5.2). Results show that GAC biofilters can effectively eliminate 100% DCAN from the influent water. The high removal efficiency is consistent with results in Chapter 4 and recently reported by Peterson, Summers and

Cook, (2023). The removal of DCAN in the biofilters could be attributed to biodegradation and self-decomposition.

Biodegradation of DCAN occurs through a hydrolysis process catalyzed by the enzyme nitrile hydratase. This process involves the hydrolysis of the nitrile group into amide groups, which subsequently transform into haloacetic acids (HAA) and haloacetamides (HAMs) (Peterson et al., 2023b). In addition to biodegradation, DCAN can self-decompose in the water without free chlorine, with the degradation rate increasing with higher water pH (Reckhow et al., 2001). According to DCAN degradation kinetics reported in the literature, the calculated DCAN degradation in this study was less than 0.142 μg/L, which accounts for approximately 5% of the total degraded DCAN, indicating that biofiltration dominant the DCAN removal in the biofilters (> 95%).

Subsequent treatments with chlorine and chloramine following biofiltration lead to the reformation of DCAN, with concentrations ranging from 0.34 to 3.61 μg/L (Figure 5.6). And the formation was positively associated with EBCT. The reformation of DCAN is likely attributed to the biofilm detaching from the biofilters as the primary precursors of DHANs are nitrogenous compounds (including amino acids, proteins, peptides, and nucleic acids), which are abundantly present in bacteria and biofilm (Bond et al., 2012b; Oliver, 1983; Reckhow et al., 1990; Ueno et al., 1996).

Despite the reformation, biofiltration was still effective in suppressing the overall formation of DCAN. Specifically, chlorine used in post-treatment shows a DCAN suppression range of 39 - 60%, while chloramine displays a higher range of 77 - 89%. Thus, biofiltration offers a promising strategy to control DCAN formation potential.

5.3.5 Impact of Backwashing on DBP Control from Biofilters

Biofilter backwashing is essential to control excessive biomass accumulation and headless buildup to maintain biofilter performance. In a typical drinking water treatment plant, the frequency of backwashing can range from once every few days to once every few weeks (Kim et al., 2014; Liu et al., 2016; Smith et al., 1998). It is important to understand the impact of backwash on DBPs removal in biofilters.

Figure 5.7 shows the impact of backwashing on the biofilter performance in TOX formation control. TOX removal decreased by 7-8% points for the samples collected at 6h after backwashing. However, this negative effect rapidly rebounded after 12 hours of operation.

In addition to DBP degradation, Figure 5.7 presents the impact of backwashing on DOC removal. Similarly, backwashing led to a reduction of up to 5% points in the DOC removal. These reductions quickly recovered after 12 hours of operation.

Therefore, the biofilters performance on DBP removal and DBPs formation control would not be significantly impacted by backwashing. Any adverse effects could quickly recover after 12 hours of operation. It should be noted that the backwash was performed at 20 °C, and the backwash water does not contain disinfectant. Given the fact that ambient temperature and backwashing procedures (such as the inclusion of chlorine or chloramine in the backwash) could potentially exacerbate the impact on biofilters performance (Basu et al., 2016; Moll et al., 1999; Wert et al., 2008). Further research is required to examine the effects of various backwash conditions on biofilter performance in DBPs control.

5.4 Conclusion

This study comprehensively investigated DBP-preformation - biofiltration technology for removal and formation potential control of different DBP species. The significant potential for biodegradation of HAAs, DHANs, and unknown DBPs was observed. Biofiltration could remove up to 58% of TOX, primarily attributed to the degradation of unknown DBPs and HAAs. Although post-treatment with chlorine and chloramine would lead to DBPs re-formation, biofiltration technology can still effectively suppress the DBP formation potential. The DBPs formation potential reduction is a positive correlated with EBCT. Overall, the control efficiency followed this order: HAAs (53 - 96%) > DCAN (25- 85%) > UTOX (27 - 61%) > THMs (5 - 26%). Biofiltration also reduced DCAN formation potential under various EBCT conditions.

Overall, the “DBP-preformation - biofiltration - post-treatment” water treatment strategy is effective for HAAs, DCAN, and UTOX removal and formation control. The application of this strategy can significantly mitigate the associated health risks of DBPs in treated water.

Table 5.1 Water Quality of Simulated Drinking Water.

pH	7.0 ± 0.1
DOC	3 ± 0.2 mg/L
Alkalinity (as $CaCO_3$)	80.0 ± 2 mg/L
Ca (as $CaCO_3$)	50.0 ± 1 mg/L
Mg (as $CaCO_3$)	20.0 ± 0.5 mg/L
Nitrate (as N)	2.0 ± 0.1 mg/L
Phosphate (PO_4^{3-} as P)	0.5 ± 0.03 mg/L
TOX	258.2 ± 8.1 µg/L
THMs	63.1 ± 4.0 µg/L
HAAs	74.4 ± 6.2 µg/L
DCAN	2.8 ± 0.3 µg/L
UTOX	151.1 ± 7 µg/L

Table 5.2 Filter Material

Media	Effective Size (mm)	Minimum Iodine Number (mg/g)	Apparent Density (g/cm^3)	Dry Weight of Media in Column (g)	Packing Density [a] (g/cm^3)	Drainable Porosity [b]
GAC 300	0.80-1.00	900	0.64	5.64	0.53	0.557

[a] Packing density was determined by dividing the weight of dry packing material with the bed volume.

[b] Drainable porosity was determined by dividing the volume of drained water with the bed volume.

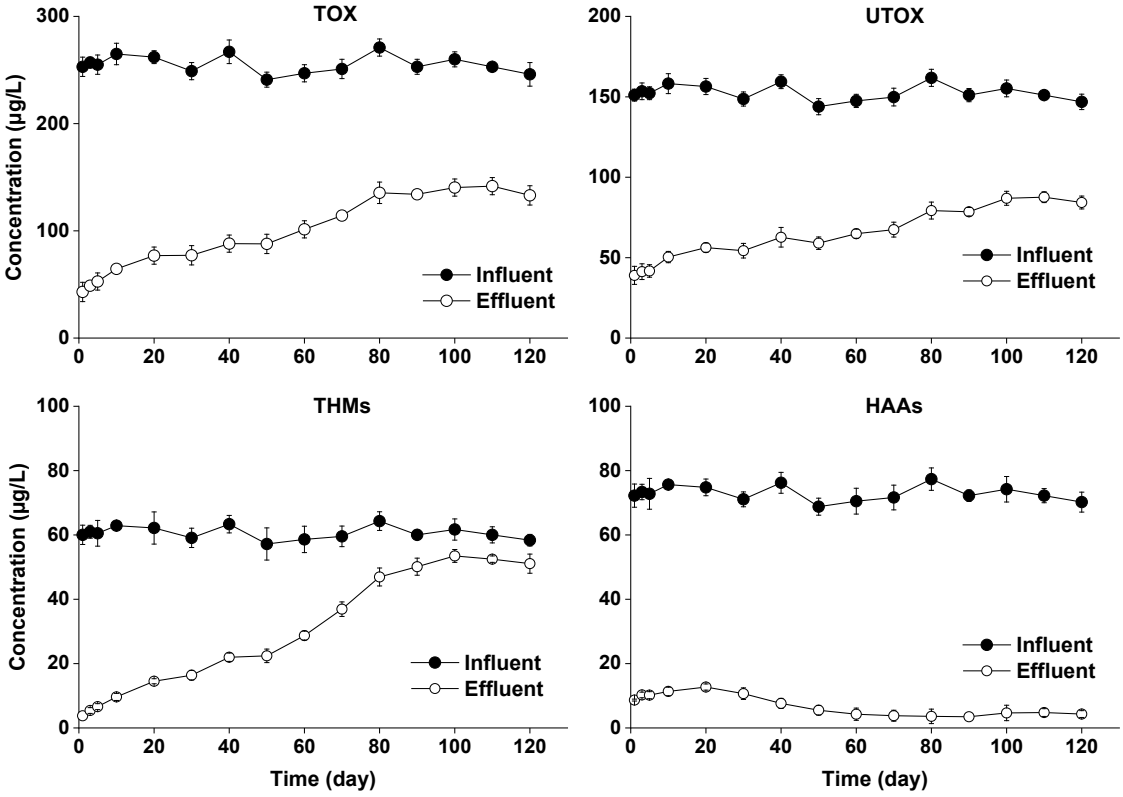

Figure 5.1 DBPs Removal in Chlorinated Water by GAC Filters. (Biofilter influent: chlorinated simulated water. Experiment conditions: 20 °C, EBCT = 10 min. Error bars represent the standard errors of duplicate experiments.)

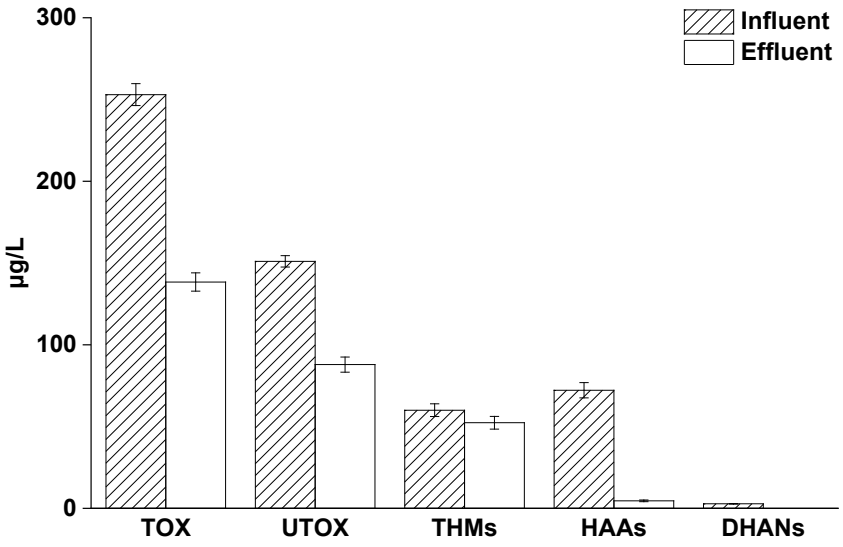

Figure 5.2 Biofiltration of DBPs Under Stable Conditions. (Experiment conditions: 20 °C, EBCT=10 min. Sampling days: 100-120 days.)

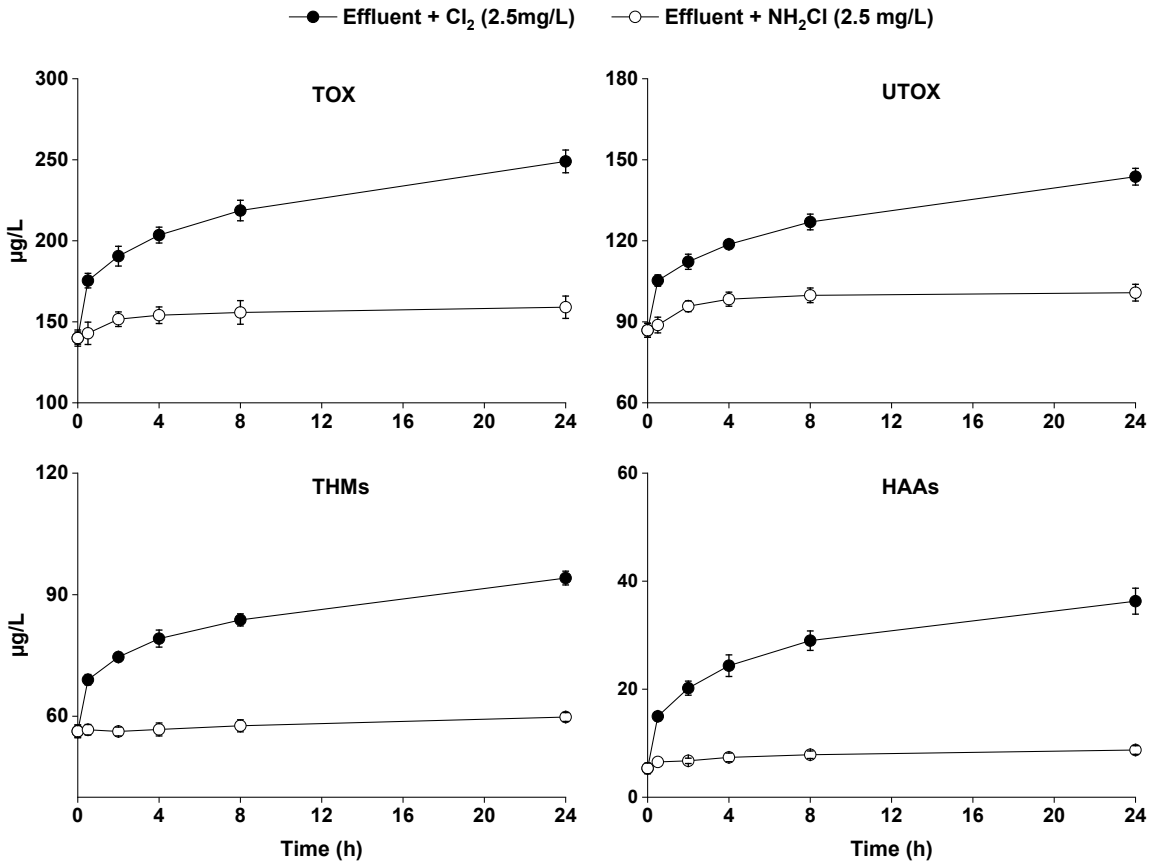

Figure 5.3 Post-treatment of Biofilter Effluent - 24h DBPs Formation. (Experiment conditions: 20 °C, EBCT = 15 min; post-treatment condition: 20 °C, disinfectant concentration = 2.5 mg/L. Error bars represent the standard errors of duplicate experiments.)

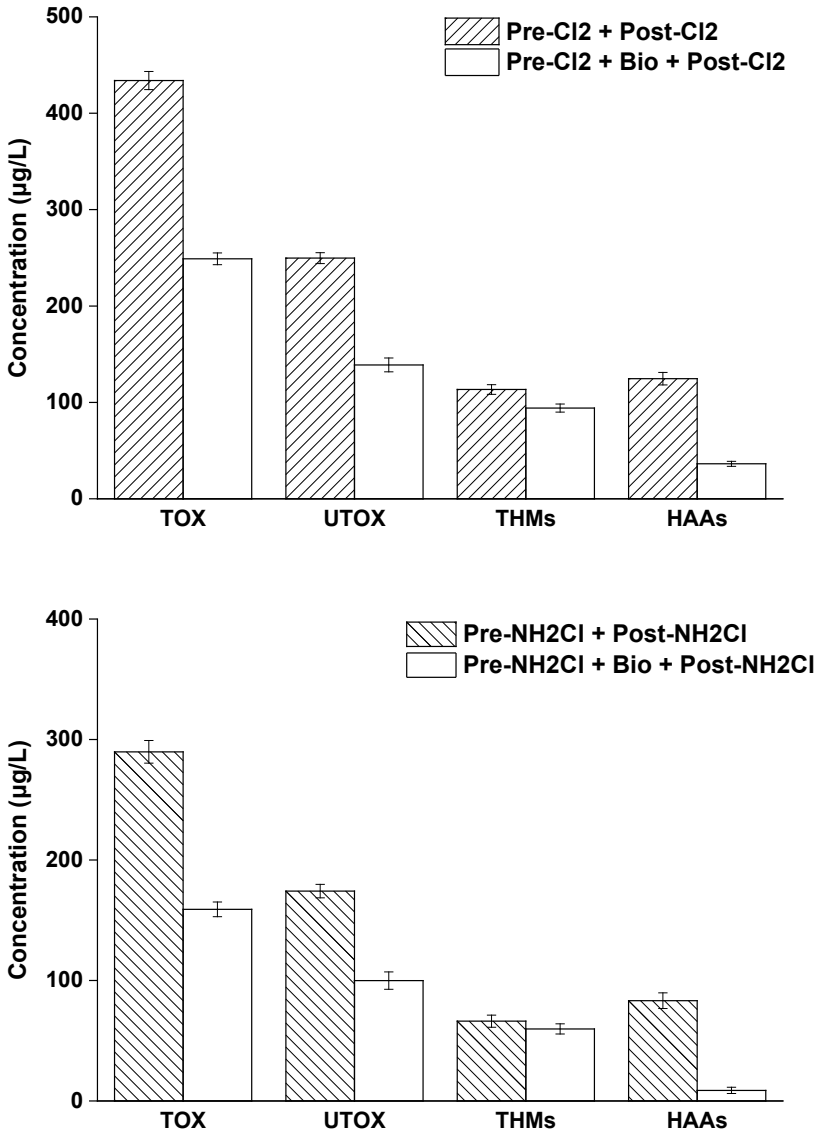

Figure 5.4 Reduction of DBP Formation Potential after Biofiltration. (Biofilter influent: chlorinated simulated water; experiment conditions: 20 °C, EBCT = 15 min. Error bars represent the standard errors of duplicate experiments.)

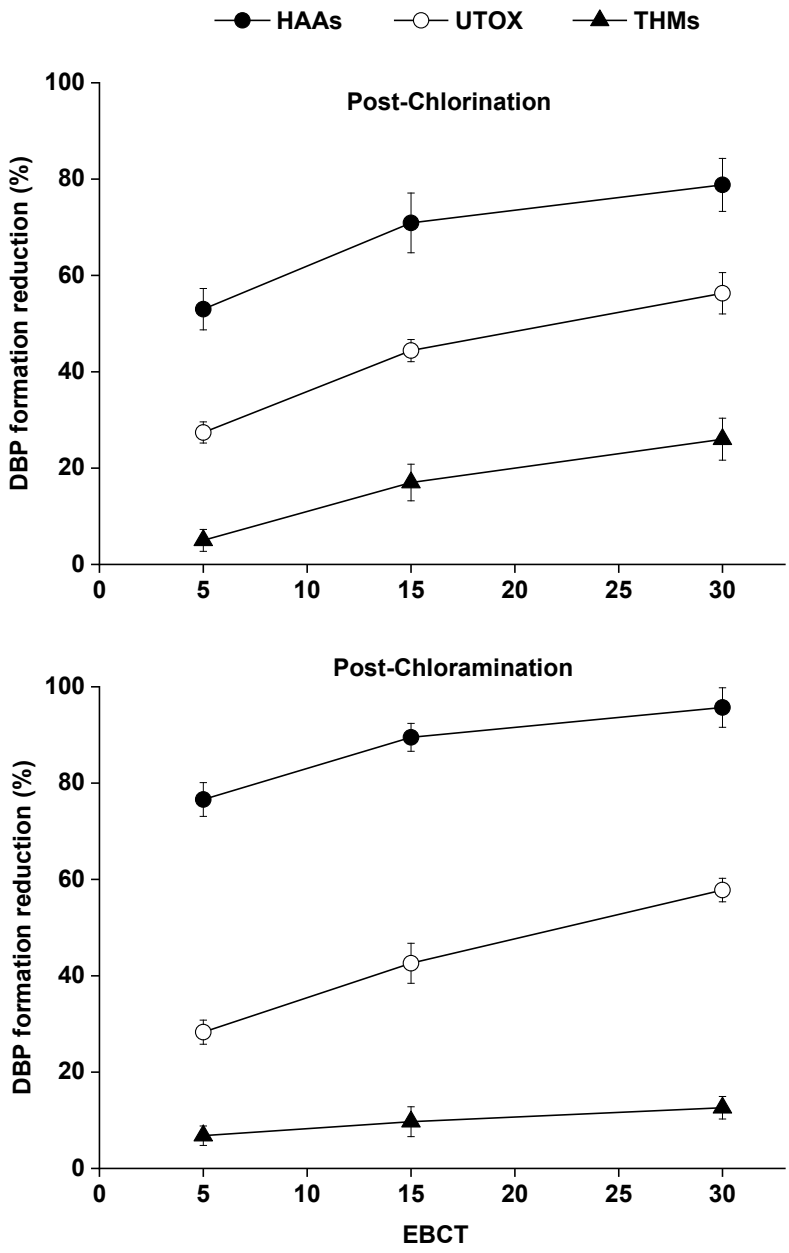

Figure 5.5 Impact of EBCT on GAC Biofilters Performance on THMs, HAAs and UTOX Formation Potential Control. (Experiment conditions: 20 °C, EBCT 5-30 min. Error bars represent the standard errors of duplicate experiments.)

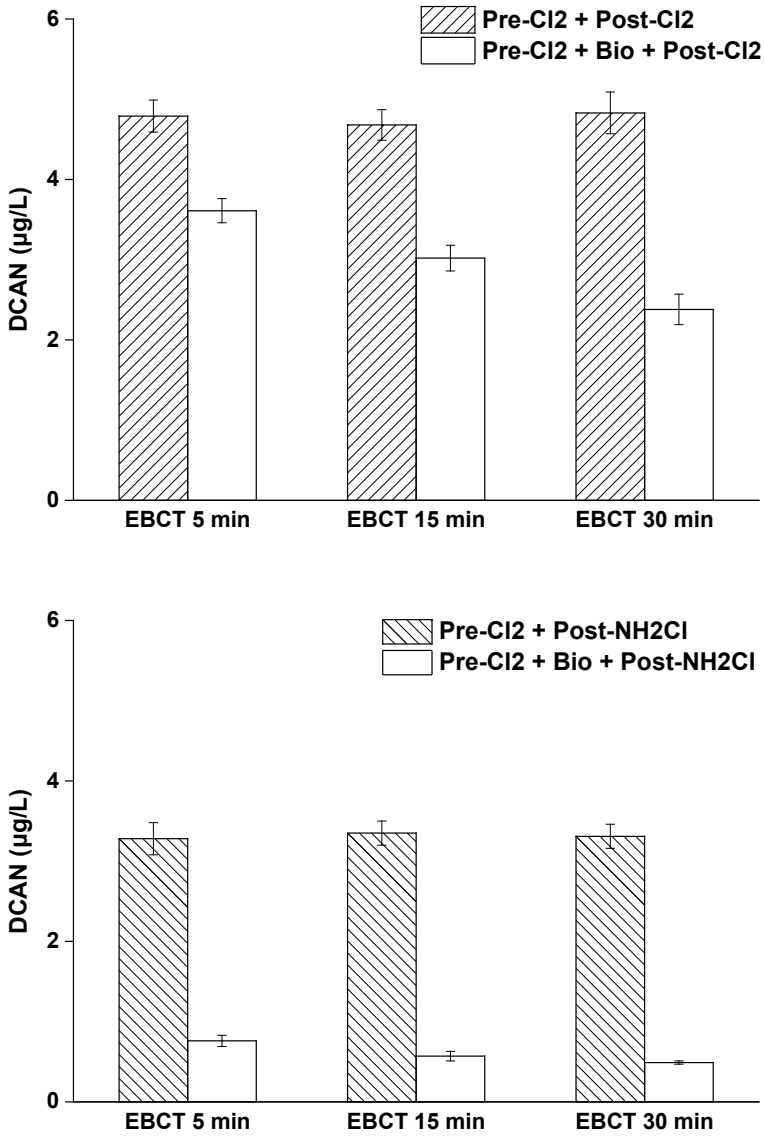

Figure 5.6 Impact of EBCT on GAC Biofilters Performance on DCAN Formation Potential Control. (Experiment conditions: 20 °C, EBCT 5-30 min. Error bars represent the standard errors from duplicate experiments.)

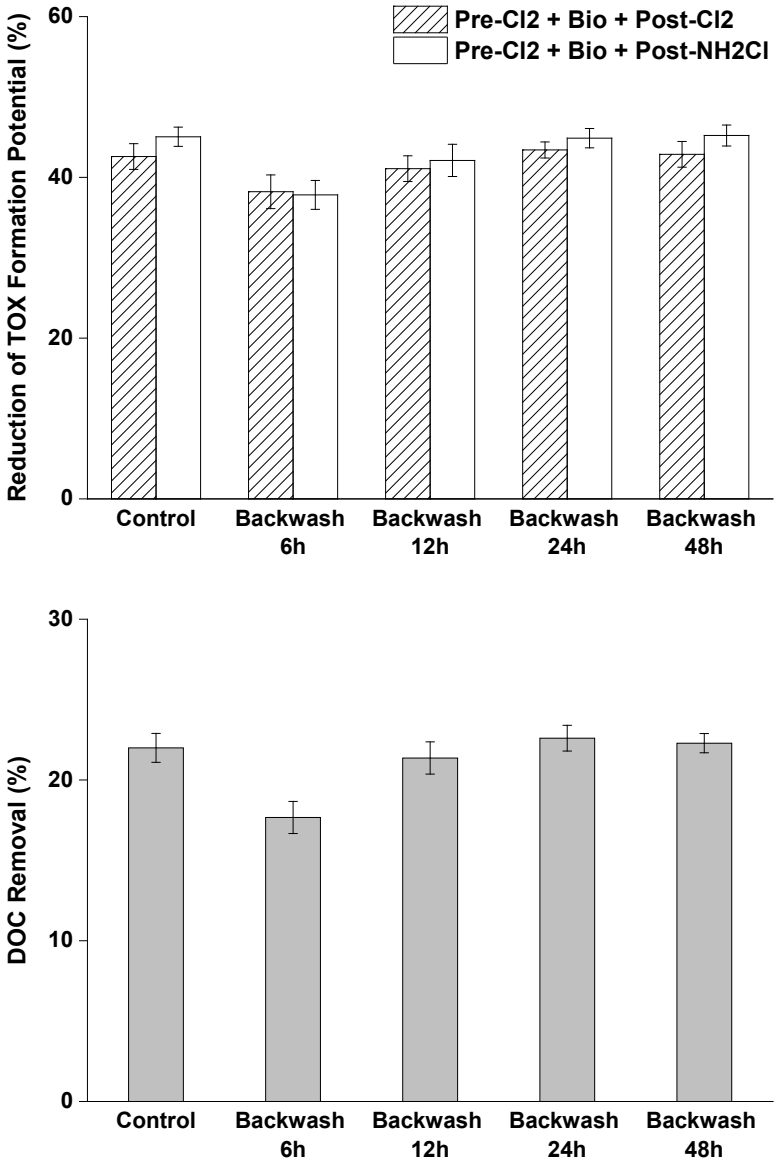

Figure 5.7 Impact of Backwash on Biofilters Performance on TOX and DOC Removal. (Backwash conditions: 20 °C, EBCT=2.5 min, backwash duration=15 min. Control represents DBPs formation potential reduction (or DOC removal) in GAC biofilters at biostable condition. Error bars represent the standard errors of three backwash cycles.)

CHAPTER 6

SUMMARY

6.1 Conclusion

6.1.1 Establishment of DBPs Biofiltration System

Laboratory experiments indicated that establishing a stable DBPs biofiltration system takes three to five months, depending on the influent condition.

Once stable biofiltration is achieved, GAC biofilters can consistently remove 50% of the TOX, with 96% HAAs, 98% DHANs, 14% THMs, and 60% UTOX removal. In contrast, sand and anthracite biofilters display about 15% lower TOX removal when compared to GAC biofilters. This reduced performance is likely due to their lower density of microorganisms and a less diverse microbial community. Given these observations, employing GAC is recommended for optimizing the effectiveness of DBPs biofiltration.

6.1.2 Impact Factors of DBP Biodegradation

EBCT and temperature are the most important impact factors for DBPs removal in the biofilters. Higher temperatures and longer EBCT can increase the biodegradation of UTOX, HAAs, and DHANs. The impact of EBCT is more pronounced at low temperatures. For regions experiencing considerable seasonal temperature fluctuation, extending the EBCT could counteract the effects of low temperatures on biofilter performance in DBPs removal.

In addition to temperature and EBCT, the switch disinfectants can also impact DBPs removal in biofilter systems. Switching from chlorinated to chloraminated water resulted in 60 days of TOX leaching, mainly attributed to THMs (58%) and UTOX (41%). Therefore, attention should be paid to potential DBPs leaching from GAC biofilters when switching disinfectant methods.

6.1.3 Biodegradability of TOX, UTOX, THMs, HAAs, DHANs

Under the biostable state at 20 °C and 15-min EBCT, biofilters with sand, anthracite, and GACs were found to remove 37 - 53% of TOX in chlorinated water and 33 - 47% in chloraminated water. The UTOX in chloraminated water showed more resistance to biodegradation than that in chlorinated water, with removal rates of 30 - 48% versus 40 - 63%. THMs exhibited significant resistance to biodegradation (7 - 15% removal). However, biofilters eliminated nearly all HAAs and DHANs, with removal rates of 94 - 96% and 98 - 99%, respectively.

The first-order model can adequately describe the UTOX, HAAs, and DHANs removal kinetics in biofilters. The DBP biodegradation rate constants (k values) for the studied DBPs at 20 °C were calculated as follows: Cl_2-UTOX = 0.046 min^{-1}, NH_2Cl-UTOX = 0.040 min^{-1}, TCAA = 0.235 min^{-1}, DCAA = 0.273 min^{-1}, DCAN = 0.427 min^{-1}, BCAN = 0.401 min^{-1}, and DBAN = 0.379 min^{-1}.

In summary, the biodegradability order of the studied DBPs was determined as: DCAN > BCAN > DBAN > DCAA > TCAA > Cl_2-UTOX > NH_2Cl-UTOX > Chloroform.

6.1.4 DBPs Formation Potential Control by Pre-chlorination - Biofiltration - Post-treatment Process

The “DBP-preformation - biofiltration - post-treatment” water treatment strategy is effective for HAAs, DCAN, and UTOX removal and formation control. Biofiltration could remove up to 57% of preformed DBPs, primarily attributed to the degradation of unknown DBPs and HAAs. Although post-treatment with chlorine and chloramine would lead to some DBP re-formation, biofiltration technology can still effectively suppress 53 - 96% HAAs, 25 - 89% DHANs, 27 - 61% UTOX, and 5 - 26% THMs formation potentials, and the reduction is in positive correlation with extended EBCT.

Biofiltration also reduced the DCAN formation potential under various EBCT conditions.

6.2 Applications of Biofiltration for DBPs Control During the Drinking Water Treatment

This study proposed a new strategy for DBPs control by introducing an biofiltration system for removal of per-formed DBPs in a drinking water treatment plant.

The proposed strategy involves pre-chlorination of the raw water at the intake structure or within rapid mixing tanks. This initial treatment is specifically designed to maximize DBP formation. Following pre-chlorination, the standard procedures of coagulation, flocculation, sedimentation, and filtration are implemented. The treated water is subsequently directed through the biofiltration system to remove preformed DBPs, and finally, chlorine or chloramine may be added for disinfection.

The result of this study demonstrated significant reductions in various DBPs, including HAAs, DHANs, UTOX, and THMs. Specifically, this method can potentially suppress the formation potential of HAAs, DHANs, UTOX, and THMs by 53 - 96%, 25 - 85%, 27 - 61%, and 5 - 26% at different EBCTs, respectively.

Overall, this water treatment strategy presents an effective and promising solution for reducing DBP exposure and improving the treated water quality.

6.3 Recommendations for Future Research

This research suggests that the pre-chlorination - biofiltration - post-treatment strategy is a viable and effective technology for DBPs control. The followings are recommended for future research:

1. The first-order model and temperature activity coefficients that have been developed in this study allow for the prediction of DCAA, TCAA, DCAN, BCAN, DBAN, Cl_2-UTOX, NH_2-Cl UTOX removal rates under varying temperatures and EBCTs. It is recommended that future research focuses on improving the predictive models and explore additional methods to optimize GAC biofilter performance under a broader range of conditions. Moreover, a standard method of detecting the fraction of non-degradable UTOX should be developed and considered in the models to better predict the unknown DBPs removal.

2. Future work should investigate the effects of various backwash strategies on DBPs biofiltration within the biofilters. These strategies may include varying the backwash duration, intensity, water composition (with chlorine or chloramine, disinfect dosage), and temperature.

3. Future studies are recommended to evaluate the capability of biofiltration for removing and controlling the formation of other priority unregulated DBPs, including but not limited to haloacetamides (HAMs), halonitromethanes (HNMs), and bromine- and iodine-containing DBPs (Br- and I-DBPs). After this evaluation, a cytotoxicity statistical analysis could be implemented. This analysis would comprehensively evaluate the efficiency of the pre-chlorination - biofiltration - post-treatment strategy in overall DBPs toxicity control.

4. The combinations of biofiltration with other treatment strategies (e.g., chlorine dioxide, UV, ozone) on DBPs control can be studied to extend this technology application during the drinking water treatment.

5. Lastly, pilot-scale and full-scale studies are strongly recommended. These studies will provide insights into the performance of biofilters in controlling DBPs under real-world conditions, further validating the applicability and potential of the technology in practical situations.

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