ASSESSMENT OF AN ADVANCED OXIDATION SYSTEM FOR THE GENERATION OF OXIDATIVE SPECIES AND EFFECTIVENESS OF TREATING SYNTHETIC AND REAL STORMWATER

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ABSTRACT

Stormwater (SW) is a type of wastewater that is of current concern for municipalities, especially in urban settings with large amounts of impervious areas. Stormwater contains high concentrations of contaminants that can cause large pollutant loading into receiving water bodies if left untreated. Many Best Management Practices (BMPs) in North America focus on minimizing the flood risk and pollution caused by SW, however, SW capture and beneficial reuse have become of increasing importance in areas and times of water scarcity. Stormwater treatment is usually needed to meet water quality targets required for beneficial reuse and for safe release of SW into receiving environments. Of recent interest are electrochemical Advanced Oxidation Processes (eAOPs) for SW treatment as they are cost effective, easy to operate and maintain, and have shown promise for SW treatment. An industry partner has developed an eAOP for treatment of wastewaters known as the Advanced Oxidation System (AOS) which was the technology used for research conducted in this thesis.

In Chapter 2, the AOS was shown to create iodide and chloride oxidative species that were used for operating parameter assessment and improved understanding of the system effectiveness and efficiency. Determining the optimum type and concentration of added salt, in addition to the optimal applied voltage is imperative to achieve the most effective treatment. The oxidative species were collected from the AOS anodes and cathodes and determined using a simple UV-vis spectrophotometric method. Iodate and periodate were determined for experiments using iodide addition and the optimal treatment parameters were 12 V and 10 ppm KI (potassium iodide). Chlorite and chlorate were measured for chloride with 6 V and 5 ppm NaCl (sodium chloride) were the optimal parameters. Iodate and chlorite were the dominant species created within the AOS, with oxidative species generally being created at reactor anodes and destroyed at cathodes.

The AOS treatment effectiveness for disinfection and decontamination was assessed for both synthetic (Chapter 2) and real (Chapter 3) stormwaters. Treatments included iodide addition, chloride addition, and no salt addition which were compared to determine the most effective SW treatment condition. Overall, the AOS performed well for the disinfection of *Escherichia coli* when iodide was used, showing 6 log removal for synthetic SW and 3.5 log removal for real SW. Organics removal was not as effective using the current AOS operation and design parameters. For example, the AOS was able to remove 50% of the chemical oxygen demand using iodide and

70% of the total organic carbon using chloride. For real SW, the pre-treatment of the SW via a coagulation/flocculation process using either alum or ferric chloride achieved reasonable solids removal.

Future work using the AOS could include investigating the creation of other oxidative species in the reactor beyond iodide and chloride species; further improvement of the organics removal through assessment of operating parameters; determination of the removal of other contaminants in SW such as heavy metals and polyaromatic hydrocarbons; testing different coagulants and pre-treatment technologies; assessing the creation of oxidative by-products in the treated SW effluent; and comparing the toxicity of the raw and treated SW.

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LIST OF ABBREVIATIONS

ACS: American Chemical Society
AO: Advanced Oxidation
AOS: Advanced Oxidation System
BOD: Biological Oxygen Demand
BMPs: Best Management Practices
C/F: Coagulation/Flocculation
COD: Chemical Oxygen Demand
CoS: City of Saskatoon
CLS: Canadian Light Source
DC: Direct Current
DI: Deionized
DW: Dry Weather
eAOP: Electrochemical Advanced Oxidation Process
EC: Electrical Conductivity
ECO: Electrocoagulation
E. coli: *Escherichia-Coli*
EF: Electroflotation
EFe: Electro-Fenton method
EGH: East Gordie Howe
KI: Potassium Iodide
LID: Low Impact Development
LB: Lysogeny Broth
LBA: LB Agar
MF: Microfiltration
NaCl: Sodium Chloride
NTU: Nephelometric Turbidity Units
PAHs: Polyaromatic Hydrocarbons
RO: Reverse Osmosis
RPM: Rotations Per Minute

SCMs: Stormwater Control Measures

SFCW: Surface Flow Constructed Wetland

SSR: South Saskatchewan River

SSW: Synthetic Stormwater

SW: Stormwater

TOC: Total Organic Carbon

TDS: Total Dissolved Solids

TSS: Total Suspended Solids

UF: Ultrafiltration

UofS: University of Saskatchewan

WW: Wet Weather

Chapter 1 : Background and Literature review

1.1 Introduction

Pollution caused by municipal sanitary and stormwater wastewater effluents has been of increasing concern for governments and environment management agencies as it can negatively impact human and ecosystem health (Veissman et al., 2009). Stormwater (SW) is a type of municipal wastewater that is of current interest for municipalities throughout Canada (and worldwide) including the current study focus on the City of Saskatoon (CoS). Based on the concern of SW outfall impacts on the local South Saskatchewan River (SSR), the CoS has partnered with the University of Saskatchewan (UofS) to collect and determine SW quality from city SW outfalls selected based on the urban catchment land use type (variable) and size of the contributing area (focus on large catchments). Urban SW is generally collected via storm drainage systems and contains pollutants from industrial, residential, and agricultural sources. These pollutants include inorganics, organics, dissolved and suspended solids, and pathogens that can contribute significant pollutant loading to receiving water bodies if not managed properly (Arora & Reddy, 2015; Aryal et al., 2010; Chong et al., 2013; Clark & Pitt, 2012; Göbel et al., 2007; Okochi & McMartin, 2012; Roy et al., 2008; Water Security Agency, 2015).

Common water quality indicators and contaminants that can be readily analyzed include electrical conductivity (EC), total dissolved solids (TDS), turbidity, total suspended solids (TSS), biological oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), pathogens (such as *Escherichia coli*), heavy metals (such as lead), and polyaromatic hydrocarbons (PAHs) (Aryal et al., 2010; Christensen & Li, 2014). These indicators can be categorized into representative groups including physical, chemical, and pathogenic categories as shown schematically in Figure 1-1 (Christensen & Li, 2014; Omer, 2019). Turbidity (typical units NTU) and TSS (mg/L) can be used to assess the concentration of suspended particulates found in SW, while TDS (mg/L) and EC (µs/cm) are used to measure the SW dissolved particulates and presence of ions, respectively. These particulates contain and transport organic and inorganic pollutants in SW. For example, vehicles, construction debris, and erosion transported via runoff are sources of particulates in SW (Aryal et al., 2010).

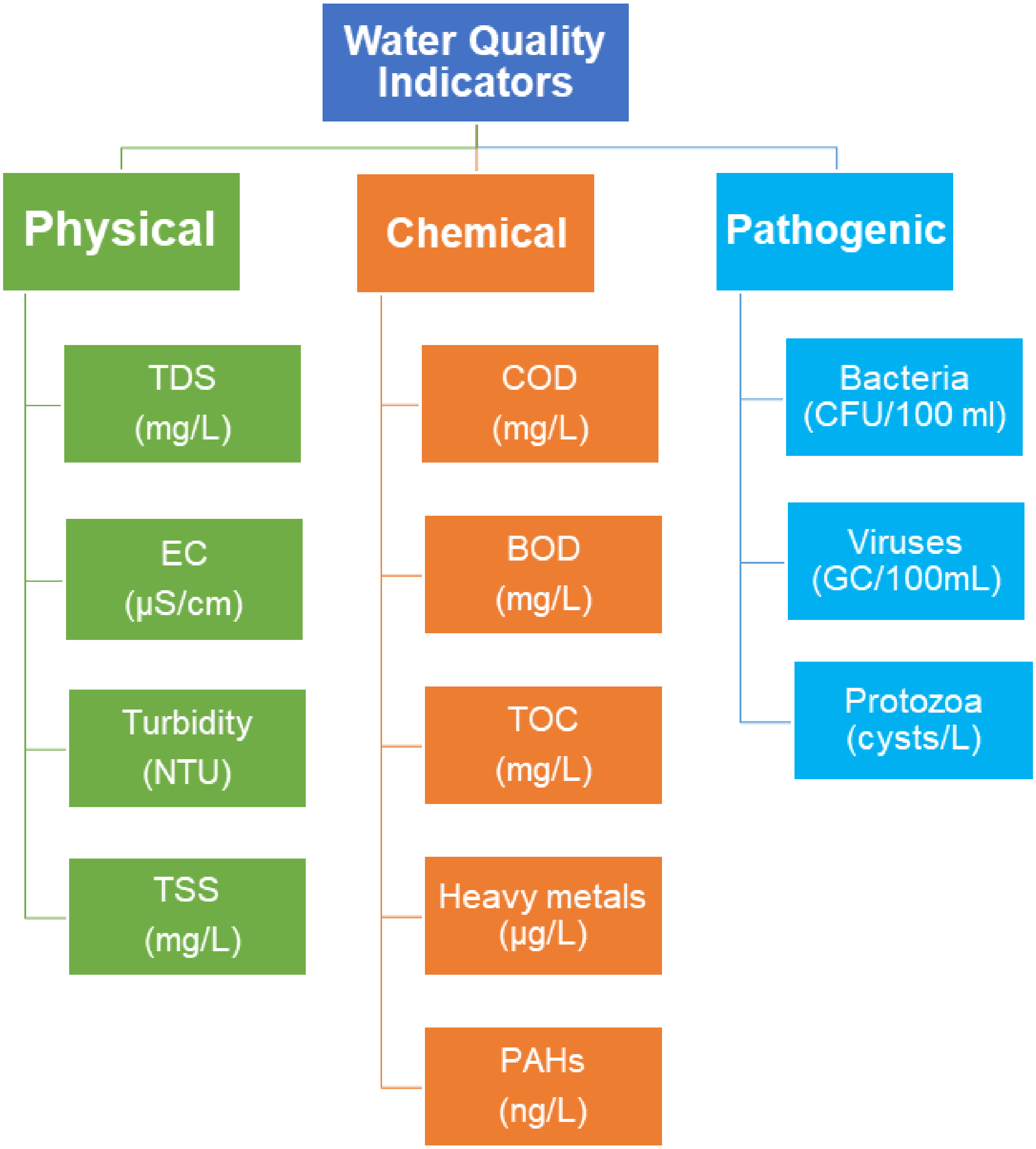


Figure 1-1: Categories of water quality indicators including physical, chemical, and pathogenic categories. Typical units are shown in parentheses below each individual indicator.

The BOD (mg/L) and COD (mg/L) are indicators of the amount of degradable organic matter in water (Figure 1-1). The BOD is used to determine the amount of oxygen that bacteria consume while degrading organic material, while the COD is used to assess the amount of oxygen that is consumed to oxidize all the organic matter into water and carbon dioxide. The TOC (mg/L) is an indicator of the concentration of the organic carbon in SW with sources including natural origins such as animal waste and vegetation, while also including anthropogenic sources such as oil and grease (Erickson et al., 2013). Heavy metals (µg/L) are commonly considered to be toxic metals found in SW given high concentrations and typically originate primarily from human activities. For example, vehicles and industrial processes are sources of heavy metals that may include lead, chromium, zinc, nickel, copper, and cadmium (Aryal et al., 2010). Hydrocarbons (ng/L) are also found in SW with PAHs being the most prevalent originating from sources such as vehicle exhausts, road surface materials, and degradation of vehicle tires (Aryal et al., 2010).

Pathogens can be classified into bacteria (CFU/mL), viruses (GC/100 mL), and protozoa (cysts/L) (Christensen & Li, 2014) (Figure 1-1). Pathogens from human origins found in SW are usually an indicator of municipal wastewater infiltration into SW. The most commonly found and measured human-sourced pathogens include the fecal coliforms including *Escherichia coli* and *Enterococcus* spp. In addition to bacteria, viruses that can be found in SW may include human adenoviruses and noroviruses. Lastly, *Cryptosporidium* spp. and *Giardia* spp. are protozoa that have been found in SW (Ahmed et al., 2019).

Given the high contamination of SW with a variety of pollutants, its treatment is needed to reduce potential negative impacts of SW effluents on receiving water bodies. There have been many technologies developed for treating various wastewaters including SW, municipal sewage, and industrial effluents. Major categories of wastewater treatment processes include physical, chemical, biological, and advanced treatment (Moussa et al., 2017; Veissman et al., 2009). Physical processes separate pollutants based on physical properties (e.g., particulate settling) from wastewater, typically without significantly changing the chemical and biological characteristics of the wastewater. Chemical treatment requires the addition of chemicals for wastewater treatment and may include coagulation/flocculation (C/F), chlorination, and ion exchange processes. Biological processes, such as trickling filters, aerated lagoons, and activated sludge, use a variety of different microorganisms to degrade and remove pollutants from wastewater streams.

One wastewater treatment technology of interest for this thesis is a specific type of advanced treatment technology known as electrochemical Advanced Oxidation Processes (eAOPs). An industry partner has developed a novel eAOP called the Advanced Oxidation System (AOS) for treatment of various wastewater matrices that was used for SW treatment in this thesis. This AOS has traditionally relied upon the addition of iodide to create iodide oxidative species for the wastewater treatment process; however, the use of chloride oxidants for treatment also has potential given chloride is often naturally found in wastewaters (Sirés et al., 2014). Thus, consideration of chloride for SW treatment may reduce the need for addition of salts, such as iodide, for optimal SW treatment.

Using this AOS technology, the goal of the research conducted for Chapter 2 of this thesis was to investigate the iodide oxidative species produced within the AOS and determine the preliminary AOS treatment capacity using synthetic SW. The determination of the oxidative species formed within the AOS reactor and treating synthetic SW was done to help to better understand the AOS process, while also assessing the impacts of AOS treatment parameters including the applied voltage and influent iodide or chloride concentrations for assessment of the reactor treatment performance.

The goal of the research conducted for Chapter 3 of this thesis was to test the effectiveness of the AOS for treating real SW collected within the CoS using different salt additions. A C/F pre-treatment step using alum or ferric chloride as the coagulant was included in the treatment process to help to minimize solids from entering the AOS which may negatively impact its performance. The effectiveness of the AOS was assessed by comparing various organic, physical, and biological water quality parameters before and after each treatment step including COD, BOD, TOC, TSS, TDS, EC, pH, and *E. coli*.

1.2 Stormwater Best Management Practices (BMPs), Guidelines and Regulations, and Treatment Technologies

1.2.1 Overview of Best Management Practices (BMPs) and Low Impact Developments (LIDs)

Stormwater Best Management Practices (BMPs) are commonly used by municipalities and water management agencies to minimize the potential negative impacts of SW pollution and flooding both within urban areas and for nearby water bodies. However, managing the flood risk is typically the primary focus of water management, with water quality a secondary interest that is more recently becoming of greater importance for municipalities. For example, Low Impact Developments (LIDs) are a type of BMP that many communities have implemented that are designed to improve SW effluent water quality for discharge, however there is also a potential for LIDs to be used for SW capture and reuse if designed properly (Mitchell et al., 2007; Shimabuku et al., 2018). The most common LID technologies currently used for SW pollution reduction are natural treatment methods that include grassed swales, constructed wetlands, detention ponds, and biofilters (Ortega Sandoval et al., 2019).

Stormwater management guidelines and regulations are important for the design and implementation of SW treatment technologies as they provide for both water quantity and quality parameters that must be met for SW effluents. For example, Stormwater Control Measures (SCMs) are an example of a quantitative SW regulation that has been widely adapted in North America (Fletcher et al., 2015). However, SW quality regulations have not been as widely adopted in North America. For example, as of 2020, there are no clear SW quality regulations in Canada. Recently, Engineer's Canada have made suggestions of water quality targets for nutrients, heavy metals, and pathogens, among others that may be used to inform future development of SW quality regulations in Canada (Valley Credit Conservation & Zizzo Strategy, 2018). Canadian municipal sewage wastewater effluent quality regulations can also provide an idea of potential future SW quality regulations (Government of Canada, 2016). Stormwater storage and reuse has also become of interest in the process of SW management; thus, SW beneficial reuse guidelines have also been developed by various municipalities in North America. Therefore, any BMPs considered must meet SW quantity and quality guidelines and regulations to help to minimize negative environmental impacts, while perhaps may also be needed for potential SW beneficial reuse opportunities.

1.2.2 Stormwater reuse guidelines and regulations

Stormwater is increasingly being considered as an asset, rather than a liability, for water management agencies (W. Feng et al., 2019; McArdle et al., 2011; Zodrow et al., 2017). Thus, SW capture and beneficial reuse is becoming of increasing importance especially in times and areas of water scarcity in regions worldwide. Captured SW can be beneficially reused for many purposes including irrigation, non-potable uses and potable uses, with each reuse potentially having different treatment technologies based on the required jurisdictional water quality guidelines and/or regulations. Therefore, it has been suggested that ‘fit for purpose’ treatment criteria and systems should be developed depending on the suggested end use of the captured SW (Mitchell et al., 2007; Shimabuku et al., 2018; Zodrow et al., 2017, Aryal, 2010). An example of developed ‘fit for purpose’ criteria are the Los Angeles County Department of Public Health’s (LACDPH) Guidelines for Alternate Water Use (LACDPH, 2016; Shimabuku et al., 2018). The guidelines include acceptable beneficial uses, water quality guidelines, recommended treatment processes, and monitoring and reporting requirements for SW. The specific LACDPH guidelines dictate that the reclaimed SW can only be re-used for non-potable uses in industrial, commercial, and municipal facilities. Additionally, the achievement of NSF 350 water quality standards, characterization of the chemical components of the SW influent, and annual reporting of the final treated water quality is required for SW reuse (LACDPH, 2016). The NSF 350 standard provides requirements for water quality parameters including BOD, TSS, turbidity, *E. coli*, and pH (Bruursema, 2011).

A wide variety of SW beneficial reuse guidelines and/or regulations have been developed by municipalities and states in the United States, each with their own specific water quality criteria (Shimabuku et al., 2018). Despite the SW beneficial reuse and quality guidelines and/or regulations in Canada that are under review, typically municipalities and provinces do not currently allow for SW reuses beyond uses including irrigation and toilet flushing (Government of Alberta, 2019; Health Canada, 2010; Ontario Ministry of the Environment, 2019). The presence of pathogens (such as fecal microbes) and recalcitrant contaminants in SW, in conjunction with a negative public perception for reuse of any ‘wastewater’ are major barriers to implementation of SW beneficial reuse in Canadian municipalities (McArdle et al., 2011; Ontario Ministry of the Environment, 2019; Shen et al., 2019; Zodrow et al., 2017, Aryal 2010). Thus, SW treatment technologies may be used to adequately remove SW contaminants such as *E. coli*, TSS, BOD, and recalcitrant pollutants to achieve the required water quality for beneficial reuse. However, successful SW reuse treatment technologies must be effective, inexpensive, have low maintenance requirements, and meet the water quality criteria that are required for beneficial reuse (Arora & Reddy, 2015; Clark & Pitt, 2012; Okochi & McMartin, 2012). Over time, the negative public perception for beneficial reuse may be overcome by successful implementation of these SW treatment technologies in combination with public information campaigns to inform the community of the benefits and safety of treated SW for reuse purposes.

1.2.3 Stormwater treatment technologies

There have been many technologies developed for SW treatment with most originating from adaptation of either municipal sewage wastewater or industrial wastewater treatment technologies. These treatment technologies can be categorized into four groups including: (1) Natural; (2) Natural and filtration; (3) Membrane separation; and (4) Advanced oxidation. These categories of SW treatment are presented in Table 1-1 including advantages and disadvantages for each process as presented in the literature. Stormwater ponds and wetlands are typical types of natural treatment methods as explained in Section 1.2.3.1 and examples are shown in Figure 1-2. Stormwater biofilters are a natural filtration treatment processes as discussed in Section 1.2.3.2 and examples are shown in Figure 1-3. Microfiltration and ultrafiltration are membrane treatment processes that can be used for SW treatment as presented in Section 1.2.3.3 and Figure 1-4. Lastly, the currently considered treatment technology for this thesis is included in the overview of eAOPs in Section 1.2.3.4 and Figure 1-5.

1.2.3.1 Stormwater ponds and wetlands

Stormwater ponds and wetlands are commonly used natural SW treatment methods with stormwater ponds (both wet and dry ponds) being widely adapted in the current study municipality of the CoS (Aryal et al., 2010; CH2M Hill, 2014; Erickson et al, 2014 Headley & Tanner, 2008). An example of these treatment technologies is surface flow constructed wetlands (SFCW) which are a type of wetland used for both stormwater retention and treatment purposes. Figure 1-2 shows a cross section schematic (Panel A) and top view (Panel B) of a typical SCFW. A SFCW generally consists of series of shallow basins that are flooded having low permeable soils (Figure 1-2A). The basins are densely vegetated with plant species such as cattails and bulrushes (Figure 1-2B) that provide nutrient uptake and a create a suitable substrate for microbial, algae, and invertebrate species that aid in the treatment of SW pollutants (CH2M Hill, 2014).

Table 1-1 provides an overview of the advantages and disadvantages of the natural treatment method as represented currently by SW ponds and wetlands. Stormwater ponds and wetlands offer a low maintenance, passive treatment system that is simple to operate (Erickson et al., 2014; Headley & Tanner, 2008). SW ponds and wetlands have shown reduction of TSS, total phosphorous, total nitrogen, nitrogen oxide, metals, and bacteria (CH2M, 2014; Erickson et al., 2014). In addition to beneficial SW pollutant treatment, SW ponds and wetlands can also add

Table 1-1. Advantages and disadvantages of selected SW treatment technologies.

Treatment	Technology	Advantages	Disadvantages	References
Natural	Stormwater ponds and wetlands	• Passive treatment • Low maintenance and simple to operate • Enhance aesthetic and habitat • SW flow retention • Suspended solids and nutrient removal	• Less effective in removing fine and dissolved contaminants • Relatively large area needed • Unable to provide pathogen removal required for reuse • Less effective in cold climates	Aryal et al., 2010; CH2M Hill, 2014; Erickson et al., 2013; Headley & Tanner, 2008
Natural and filtration	Biofilters	• Effective control of nutrients, microbes, and heavy metals. • Environmentally friendly • Low energy requirement • No chemical addition required • Simple to maintain and operate	• Variable treatment performance • Lack of adaptability to operating conditions • Unable to provide pathogen removal required for reuse	Aryal et al., 2010; W. Feng et al., 2018; Hatt et al., 2007; Mitchell et al., 2007; Payne et al., 2018; Shen et al., 2019
Membrane separation	Micro/ultra filtration	• High removal efficiency for TSS, Coliforms and BOD • Efficient treatment • Ease of operation • Small footprint	• Maintenance needed to prevent membrane fouling • Damage to filter media caused by cleaning • Lack of selectivity to treat target pollutants • High energy costs	Aryal et al., 2010; McArdle et al., 2011; Ortega Sandoval et al., 2019; Zodrow et al., 2017
Advanced Oxidation	eAOPs	• High treatment efficiency • Low resource consumption • Can treat a wide range of wastewaters • Disinfection of pathogens • Removal of recalcitrant pollutants, organics and micropollutants	• High electrode costs • Low conductance of wastewaters can decrease treatment effectiveness • Concerns of toxic by-products in treated water	Y. Feng et al., 2016; Mickova, 2015; Radjenovic & Sedlak, 2015; Sirés et al., 2014

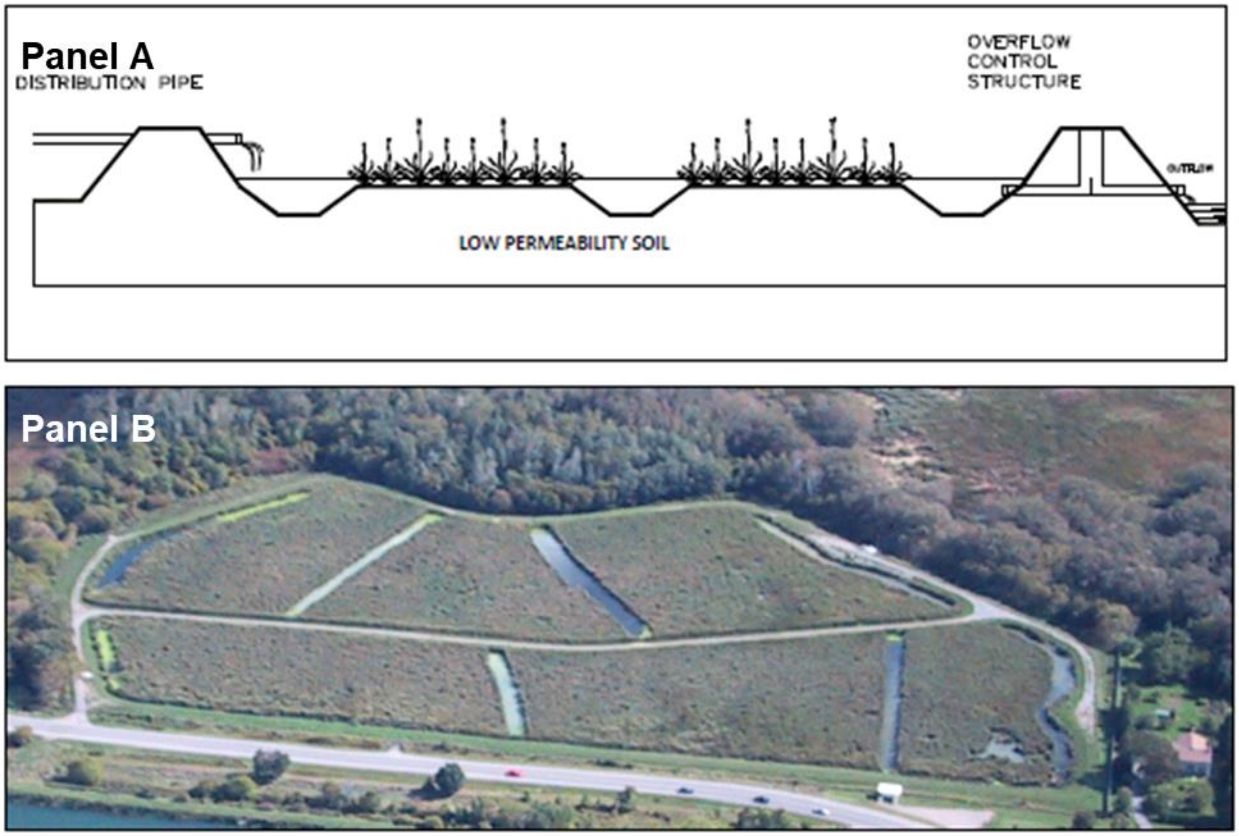


Figure 1-2: Cross section schematic (Panel A) and top view photo (Panel B) of a typical surface flow constructed wetland (SFCW). Adapted from CH2M Hill (2014).

aesthetic (for humans) and habitat (for the environment) values, while SW retention helps to manage volumetric flows into receiving water bodies (CH2M, 2014; Headley & Tanner, 2008). Drawbacks of SW ponds and wetlands can include their being less effective at removing fine and dissolved contaminants as compared to larger particles, while the treated effluents typically cannot meet the pathogen water quality criteria required for direct beneficial reuse (Aryal et al., 2010; Headley & Tanner, 2008). Additionally, SW ponds and wetlands also require a relatively large areas for adequate SW retention and treatment purposes. For example, SW ponds and wetlands require land areas of 2-3% and 3-5% of their respective impervious watershed catchment areas. Further, SW ponds and wetlands are not as effective in colder climates, due to potential freezing of wetlands and subsequent lower rates of pollutant uptake (Aryal et al, 2010).

Overall, SW ponds and wetlands are a good option for SW quantity and quality management particularly for areas of new development where the availability of adequate land area is not a major issue. However, a colder climate in areas such as the Canadian prairies and limited land availability in mature neighbourhoods of urban areas make the consideration of SW ponds and wetlands either very challenging or even impossible. In addition, SW ponds and wetlands can not be used as a beneficial reuse treatment method given their treated SW effluents have not shown promise in meeting relevant water quality guidelines and/or regulations.

1.2.3.2 Stormwater biofilters

Stormwater biofilters are considered to be natural filtration systems that have been shown to be effective for SW treatment (Hatt et al., 2007; Macnamara & Derry, 2017; Mitchell et al., 2007; Shen et al., 2019; Zinger et al., 2007). Figure 1-3 shows a cross section schematic of an example biofilter design (Macnamara & Derry, 2017) (Panel A) and top view of an example biofilter installed in a parking lot in Australia (Zinger et al., 2007) (Panel B). The SW biofilters typically consist of basins or trenches that contain vegetation that grows in a layer of soil, gravel, and/or sand. The SW infiltrates through the various filter layers and is eventually collected in the bottom drainage layer (Figure 1-3A) (Zinger et al., 2007). Processes such as filtration, sorption, and plant and biofilm uptake of pollutants are used to treat SW pollutants within the biofilter. Thus, the design features of biofilters such as plant and media selection are important in enhancing pollutant removal rates (Payne et al., 2018).

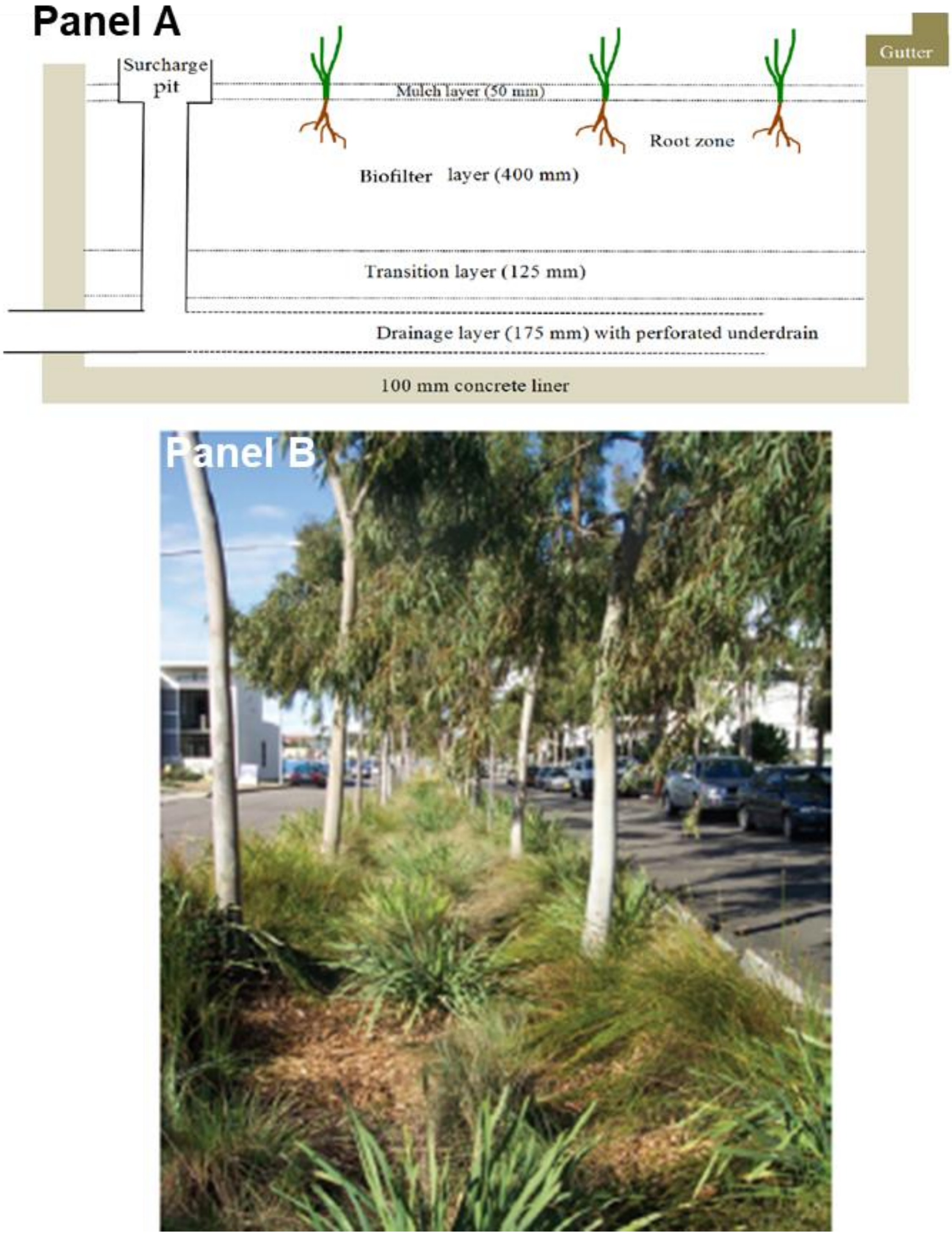


Figure 1-3: Cross section schematic (Panel A) and top view photo (Panel B) of a typical stormwater biofilter. Adapted from Macnamara & Derry (2017) (A) and Zinger et al. (2007) (B).

Table 1-1 lists the advantages and disadvantages of SW biofilters. Biofilters have been shown to be effective in treatment of SW nutrients, microbes, and heavy metals (W. Feng et al., 2019; Hatt et al., 2007; Mitchell et al., 2007; Shen et al., 2019). Advantages of using biofilters include being environmentally friendly, low energy requirements, requiring no chemical addition, and being simple to operate and maintain (Aryal et al., 2010). The disadvantages of using biofilters for SW reuse include their variability in treatment performance over time and the lack of *in situ* adaptability to varied operating conditions (Hatt et al., 2007; Shen et al., 2019). For example, Shen et al. (2019) found that a too short (< 12 h) or too long (> 14 days) period between storm events and large runoff volumes contributed to poor pathogen removal for a study biofilter. Thus, SW biofilters are unable to provide consistent and adequate pathogen removal required for beneficial reuse potential (W. Feng et al., 2018, 2019).

Overall, biofilters are a potentially valuable option for treatment of SW. However, similar to SW pond and wetlands presented in the previous Section, cold climates can negatively impact the performance of biofilters (Shen et al., 2019). Biofilters are also typically used in smaller areas as shown in Figure 1-3A where only locally collected SW is being treated; thus, use of biofilters for larger SW catchment areas may not be advisable. In addition, the SW treated with biofilters has not shown the ability to meet required water quality parameters for potential beneficial reuse.

1.2.3.3 Membrane separation processes

Membrane separation processes (MSPs) such as micro- and ultra-filtration (MF/UF) have been limited in application overall but have shown promise for SW treatment (McArdle, 2011; Ortega Sandoval et al., 2019). Microfiltration filters have an average pore size of 0.1 µm, while ultrafiltration filters average 0.01 µm. Figure 1-4 shows a cross section of a typical microfiltration system (Ortega Sandoval et al., 2019) (Panel A) and an example of a membrane separation filtration system (Contech Engineering Solutions, 2019) (Panel B). Stormwater is typically pre-treated for the removal of suspended solids prior to being processed via MF/UF to help to prevent clogging. The SW is typically pumped through the bottom of the filters in an upflow treatment direction with the permeate (treated SW) being collected at the top (Figure 1-4). Backflushing and cleaning of the filters must be done periodically to ensure filter longevity and treatment efficiency (Zodrow et. al., 2017).

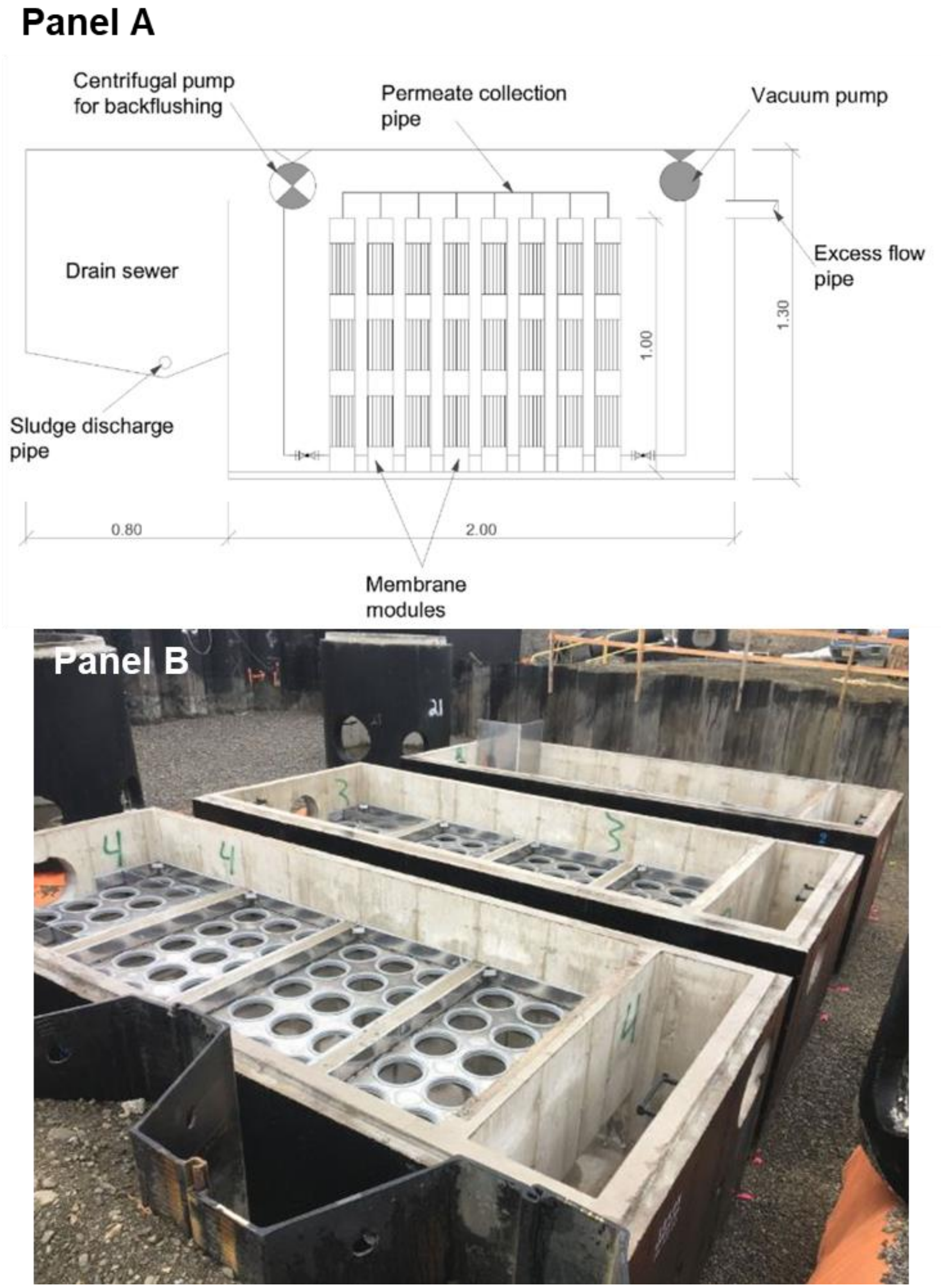


Figure 1-4: Cross section schematic (Panel A) and top view photo (Panel B) of a typical microfiltration system. Adapted from Sandoval et al. (2019) (A) and Contech Engineering Solutions (2019) (B).

Table 1-1 presents the advantages and disadvantages of MSPs. Advantages of MSPs include ease of operation, small footprints, and highly efficient treatment (Aryal et al., 2010). The MSPs have shown large SW removal rates for TSS, coliforms, and BOD (Ortega Sandoval et al., 2019). Disadvantages of using MSPs include the maintenance needed to prevent membrane fouling, damage caused by cleaning, lack of selectivity to treat target pollutants, and potentially high energy costs (Zodrow et al., 2017; Ortega Sandoval et al., 2019). Ortega Sandoval et al. (2019) tested the use of MF and UF membrane separation processes and found that the UF was more efficient. However, there was low metal removal by UF, and the process was not able to achieve fecal coliform removals needed for beneficial reuse. Overall, MSPs, such as MF/UF, have shown to be effective for SW treatment, however both the excessive operating and maintenance costs and inability to meet reuse quality guidelines may limit the application of MF/UF systems for SW reuse.

1.2.3.4 Electrochemical Advanced Oxidation Processes

The use of electrochemical (EC) technologies for SW treatment are becoming more popular including eAOPs (Y. Feng et al., 2016). Figure 1-5 shows a schematic (Panel A) and example (Panel B) of an eAOP technology that was initially developed by an industry partner and tested in the current thesis. The eAOPs use electricity to generate oxidative species used for the treatment of wastewaters (Chen, 2004; Moreira et al., 2017; Sirés et al., 2014). Salts are generally used to create oxidative species at the reactor anodes that are reduced back to the safe-to-release salt species at the reactor cathodes. The design and operating parameters of eAOPs are important in optimizing the effectiveness of treatment including electrode material choice, applied voltage and/or current, and wastewater flow rates.

The advantages and disadvantages of eAOPs are shown in Table 1-1. The eAOPs have shown to be effective in pathogen disinfection and removal of organics, metals, recalcitrant pollutants, and micropollutants (Moreira et al., 2017; Sirés et al., 2014). The eAOPs are versatile in treating many wastewater matrices of varying water qualities with efficient pollutant removal rates. The eAOPs are also cost effective as compared to other EC technologies due to lower chemical and power consumption (Mickova, 2015; Radjenovic & Sedlak, 2015; Sirés et al., 2014). However, high electrode costs, low conductance of wastewaters, and concerns of toxic by-products have limited the application of eAOP technologies (Radjenovic & Sedlak, 2015; Sirés et al., 2014). The SW can have low conductance, so salts such as iodide and chloride can be added to increase

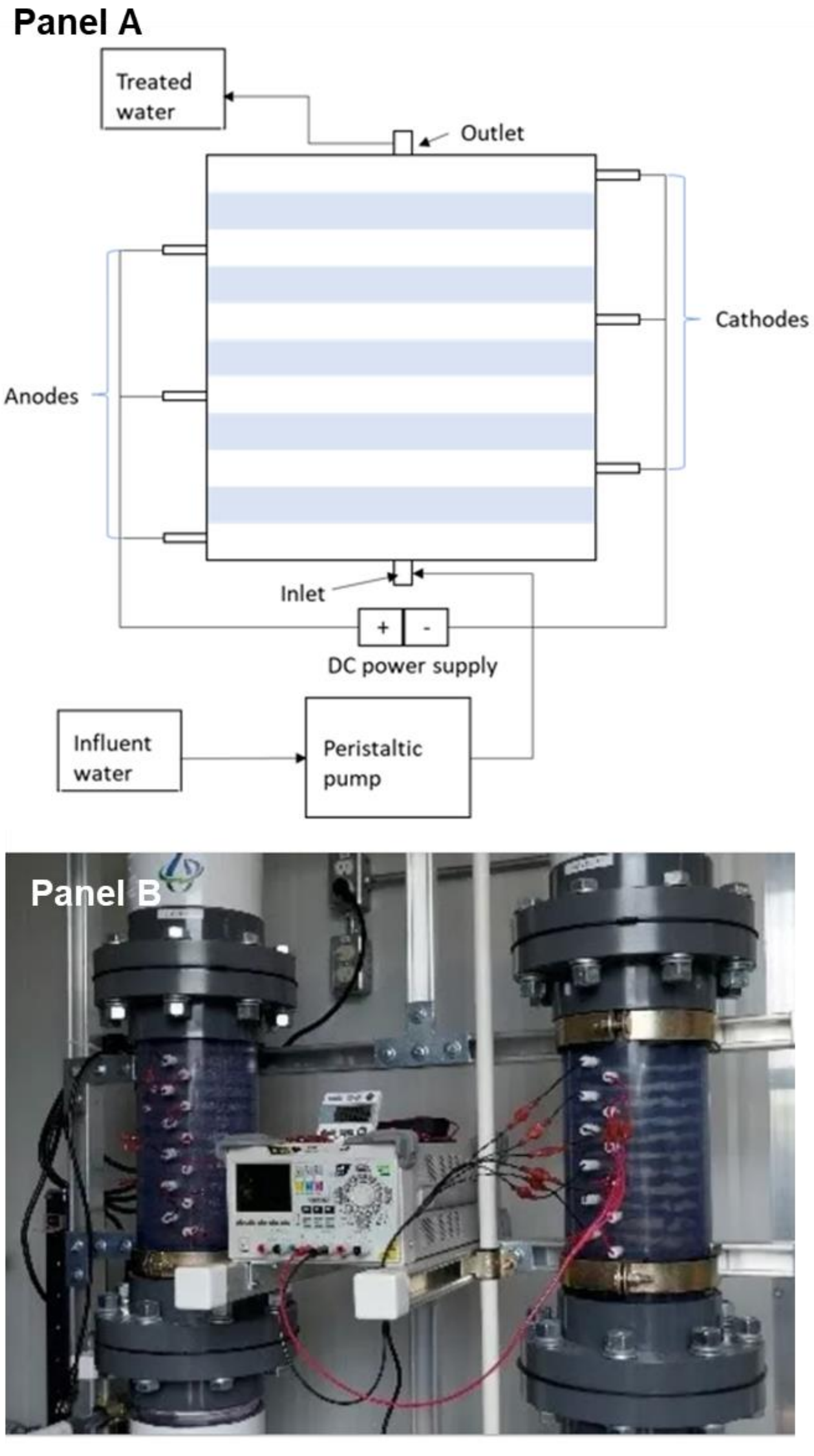


Figure 1-5: Cross section schematic (Panel A) and AOS photo (Panel B) of the current thesis eAOP system. Adapted from BioLargo Water.

conductance and resultant treatment efficiency. The removal of solids from SW is a recommended pre-treatment step for eAOPs as solids can reduce their efficiencies (Aryal, 2010). Solids have the potential to clog treatment systems and interfere with the reactions needed for effective treatment. Pre-treatment using C/F is commonly used in SW treatment (Clark & Pitt, 2012; Veissman et al., 2009), while common coagulants used for SW treatment include aluminum sulfate or alum, ferric salts, and various polymers (Veissman et al., 2009).

Overall, eAOPs have the ability to treat large volumes of highly contaminated SW using a small footprint. Technologies such as eAOPs may be valuable for use in urban areas, such as the currently studied CoS, where SW treatments technologies needing large areas, such as SW ponds and wetlands, cannot be readily deployed. Given the current thesis focus is on an eAOP technology, further discussion focused on EC technologies is provided in the following section.

1.3 Electrochemical Treatment Technologies

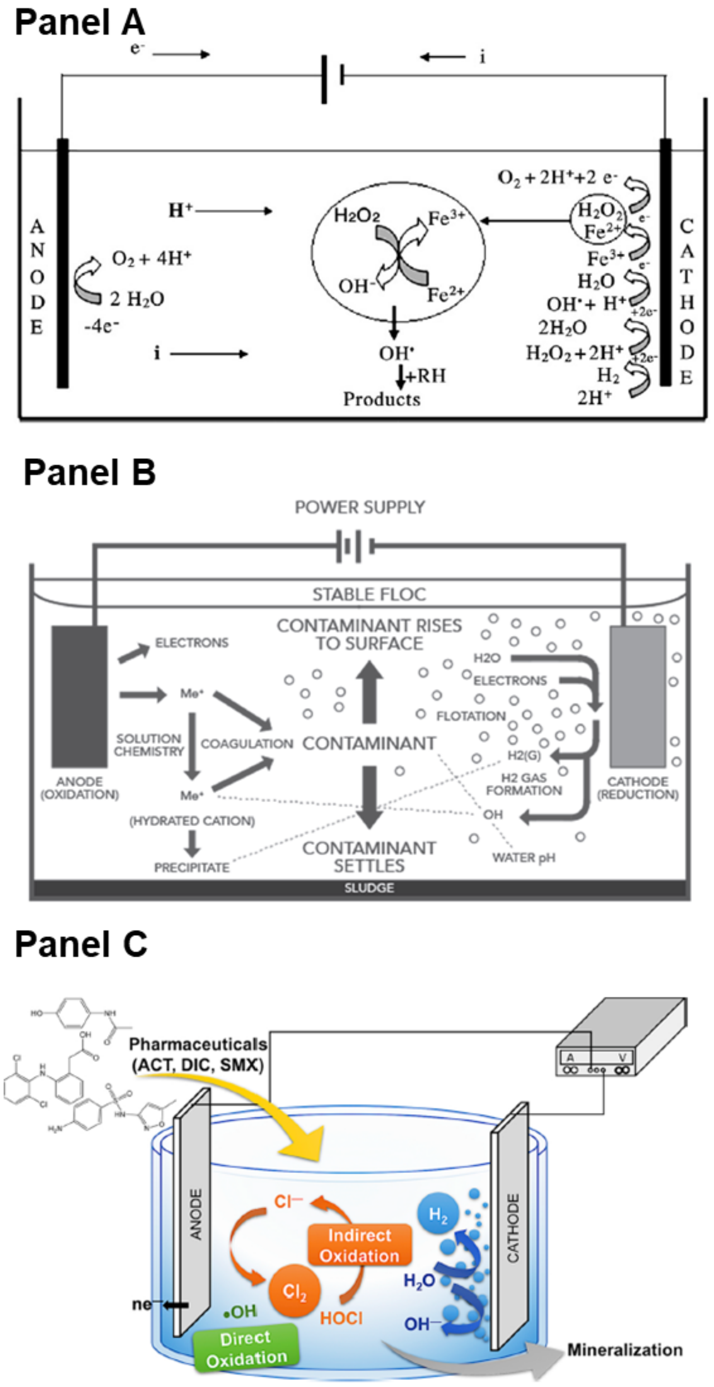
Many EC technologies have been investigated and used for the treatment of various wastewaters including: (1) electro-Fenton method; (2) electrocoagulation and electroflotation; and (3) eAOPs. Figure 1-6 presents an overview of the treatment mechanisms used in each of these technologies while Table 1-2 provides the advantages and disadvantages of each process.

1.3.1 electro-Fenton method

The reaction mechanisms of the electro-Fenton (EFe) method are presented in Figure 1-6: Panel A with an overview of advantages and disadvantages provided in Table 1-2. The EFe method uses hydrogen peroxide in acidic effluents and the Fenton's reagent (Fe^{2+}) as catalysts to form OH^- which is a strong oxidant for the treatment of organic pollutants (Moreira et al., 2017; Nidheesh & Gandhimathi, 2012; Oturan & Brillas, 2007; Sirés et al., 2014). The OH^- is created at a faster rate during the EFe method than in other EC technologies (Oturan et al., 2015) which allows EFe to efficiently treat a large range of contaminants such as persistent organic pollutants (Nidheesh & Gandhimathi, 2012; Oturan et al., 2015). In addition, the EFe method is easy to operate and maintain and the Fenton's reagent is relatively inexpensive (Nidheesh & Gandhimathi, 2012). One major limitation of the EFe method is that low wastewater pH conditions (pH ~3) are required for effective treatment making the treatment of SW challenging given the SW is usually pH 7 to 9. Thus, the pH of the SW would have to lowered prior to treatment to optimize the EFe method and

Table 1-2: Advantages and disadvantages of selected electrochemical treatment technologies

Technology	Advantages	Disadvantages	References
Electro-Fenton	• Creates powerful oxidants for treatment • Can treat wide range of pollutants • Inexpensive and easy to operate and maintain	• Low pH wastewater needed for effective treatment • Cost of chemical addition • Produce large amount of iron sludge	Moreira et al., 2017; Nidheesh & Gandhimathi, 2012; Oturan & Brillas, 2007; Sirés et al., 2014
Electrocoagulation/ Electroflotation	• No chemical addition required • EC produces less waste sludge than conventional coagulation • High performance in treating suspended solids and oil and grease • Higher treatment performance compared to other coagulation and flotation technologies	• Not well designed for stormwater treatment • High capital and operating costs • Requires electricity • Can negatively impact pH of stormwater	Chen, 2004; Moussa et al., 2017; Tadesse et al., 2019
eAOPs	• Can effectively remove a large range of pollutants including toxic and recalcitrant compounds • High degradation rates • Low energy consumption	• Production of OPBs and DPBs • Require high wastewater conductivity for efficient treatment • Requires electricity	Chen, 2004; Y. Feng et al., 2016; Moreira et al., 2017; Oturan & Brillas, 2007; Sirés et al., 2014



Panel A

Panel B

Panel C

Figure 1-6: Overview examples of electrochemical treatment technologies including: (A) electro-Fenton from Nidheesh & Gandhimathi (2012); (B) electrocoagulation/electroflotation from Posavčić et al., (2019); and (C) eAOPs from Liu et al., (2019).

then increased again after treatment to allow for discharge into receiving environments at neutral pH. The need for these pH adjustments would add extra cost and time to the SW treatment process. Additional limitations include the potential large costs associated with chemical addition required for SW treatment and for disposal of the typically large amount of iron sludge being produced from the EFe treatment process.

Overall, the EFe method is not likely to be a viable SW treatment method, mainly due to the low pH needed for treatment and the large amount of sludge produced. The large volumes of SW needing treatment would be difficult to adjust pH while the added process step would make the treatment process excessively long in duration.

1.3.2 Electrocoagulation (ECO) and Electroflotation (EF)

An overview of the electrocoagulation and electroflotation process is shown in Figure 1-6: Panel B with the advantages and disadvantages of this process outlined in Table 1-2. Electrocoagulation (ECO) generates in-situ coagulants from dissolving aluminum or iron ions from their respective anodes using electricity input. Aluminium and iron are commonly used in water and wastewater treatment, respectively, as they are both inexpensive and readily available metals (Posavčić et al., 2019). These metals are oxidized at the anode and form hydroxides which destabilize colloidal particles leading to the formation of flocs. These flocs can then be readily removed by sedimentation or flotation (Posavčić et al., 2019).

Electroflotation (EF) uses hydrogen or oxygen bubbles produced during water electrolysis at the cathodes which capture and float pollutants out of SW (Chen, 2004; Moussa et al., 2017; Posavčić et al., 2019). The small and uniform bubbles created during the EF process allow for an increased treatment efficiency as compared to other flotation technologies such as dissolved air flotation and impeller flotation. The smaller bubbles increase separation efficiency because they provide a relatively larger surface area for pollutant attachment (Chen, 2004; Tadesse et al., 2019).

A combination of ECO and EF processes are typically used for treatment of wastewaters that contain suspended solids, and oil and grease (Chen, 2004; Moussa et al., 2017; Posavčić et al., 2019). In addition this combination has shown to be successful in removal of *E. coli*, iron, arsenic, and turbidity. Current density, the presence of NaCl, pH and temperature are major factors impacting the effectiveness of ECO for wastewater treatment (Chen, 2004; Moussa et al., 2017). Electrocoagulation is more effective than conventional coagulation because no chemicals need to be added and, due to this lack of chemical addition, it generally produces less waste sludge as compared to conventional coagulation. In addition, ECO/EF systems have high solids removal efficiency, are typically low cost, and use a compact footprint (Chen, 2004; Moussa et al., 2017). Drawbacks of ECO/EF systems include that the technology is not designed for SW treatment, has high operating costs, and can negatively impact the pH of the wastewater (Moussa et al., 2017, Tadesse et al., 2019).

Overall, ECO and EF are well suited for the removal of suspended solids, pathogens, and metals from SW. However, ECO and/or EF has not been widely used for SW treatment and has not shown to be effective in treating SW to meet beneficial reuse standards.

1.3.3 Electrochemical Advanced Oxidation Processes (eAOPs)

Figure 1-6: Panel C shows an overview of the reactions involved in eAOPs and Table 1-2 presents the potential advantages and drawbacks of eAOPs. Electrochemical Advanced Oxidation Processes are low cost and efficient treatment technologies that have been shown to be effective for disinfection and removal of chemical contaminants, recalcitrant organic pollutants, and micropollutants from SW effluents (Moreira et al., 2017; Sirés et al., 2014). The eAOPs can be used for both direct and indirect oxidation of pollutants during the SW treatment process. Direct oxidation uses hydroxide radicals formed at the cathode via water hydrolysis to oxidize pollutants, however, indirect oxidation is the most common oxidation process used in eAOPs for SW treatment (Anawar & Ahmed, 2019; W. Feng et al., 2018, 2019). Indirect electro-oxidation uses *in situ* or added salts, such as chloride, to create oxidative species at the anode of the eAOP which can oxidize pollutants (Chen, 2004; Moreira et al., 2017; Sirés et al., 2014). Reactants commonly used for wastewater treatment and which are produced in eAOPs include chloride and iodide oxidative species, ozone, persulphate, hydrogen peroxide, and hydroxide radicals. The anodic material and the current density are important because if the anodic potential of the eAOP is too high, species that are hazardous and have no treatment benefit (such as chlorate and perchlorate) could be formed (Chaplin, 2014; Chen, 2004; Moreira et al., 2017; Radjenovic & Sedlak, 2015; Sirés et al., 2014). Thus, it is important to assess the eAOP prior to use for wastewater treatment. Knowing the optimal salt and current density for the particular eAOP design will maximize the concentration of “useful” oxidants created for treatment and minimize the creation of hazardous species. Assessment is also important to maximize cost effectiveness of the eAOP. The formation of organic and disinfection by-products should also be monitored as they can increase wastewater effluent toxicities (Drennan et al., 2019; Miklos et al., 2018; Radjenovic & Sedlak, 2015).

Advantages of eAOPs include high degradation rates of pollutants and low energy consumption (Chen, 2004; Y. Feng et al., 2016; Moreira et al., 2017; Oturan & Brillas, 2007; Sirés et al., 2014). In addition, eAOPs can also effectively remove a large range of pollutants including toxic and recalcitrant compounds. Potential drawbacks of eAOPs include the formation of organic and disinfection by-products (OBPs and DBPs), the associated costs of electrical energy, and the requirement of high conductivity SW for efficient treatment. (Chen, 2004; Y. Feng et al., 2016; Moreira et al., 2017; Oturan & Brillas, 2007; Sirés et al., 2014). However, salts such as NaCl, can be added to SW to increase conductivity leading to more effective SW treatment. For example, Feng et al. (2018) tested an eAOP system's disinfection capability for chloride amended synthetic and real SW using a commercial dimensional stable anode (DSA) made of iridium and ruthenium oxides-titanium oxides and a cathode made of pure titanium mesh. Total disinfection was achieved for the synthetic SW within 20 s when a current density of 4.2 mA/cm^2 was applied to the eAOP and it was found that chloride oxidation was the main disinfection mechanism for this system. The real SW was tested at a current density of 1.75 mA/cm^2 and showed complete disinfection for the two sites containing 200 and 9 mg/L chloride but not the third site with 2 mg/L chloride. The creation of Disinfection by-products (DBPs) was also studied, however, the DBPs concentrations determined were below Australian drinking water guidelines.

Overall, eAOPs have not been widely used for SW treatment applications due to its typically large variability of water volumes and water quality, and the low SW conductivity as compared to industrial and municipal wastewaters (W. Feng et al., 2018). This poses a challenge to apply existing eAOP technologies to SW, thus new eAOP technologies optimized for SW treatment are required. In addition, the high energy consumption needed to treat low contaminant SW concentrations limit the applicability of EC techniques in industry. Future development of eAOPs for SW treatment includes the need for decreasing of costs to better compete with the more conventional (and cheaper) SW treatment technologies. This may include the development of novel anodic materials more specifically made for SW treatment purposes which could result in the reduction of the input energy requirements for SW treatment. Further assessment of eAOPs must be done to better determine the feasibility of the applicability of eAOPs for use in SW treatment applications.

1.4 Thesis Partner Descriptions

BioLargo Water Canada Inc.

BioLargo Water Canada Inc. is based in Edmonton, Alberta, Canada and is a Canadian subsidiary of BioLargo Inc. located in California, United States. BioLargo Water has developed a novel eAOP termed the Advanced Oxidation System (AOS). The AOS is an electrochemical water treatment system that uses graphite as its electrode material, iodide oxidative species as the primary treatment mechanism, and a proprietary spacer to separate electrodes within the reactor. The AOS has exhibited disinfection capabilities for bacteria, viruses, and protozoa. In addition, the AOS has shown promise for the removal of organic contaminants and micropollutants from various wastewater matrices. Based on laboratory scale results, BioLargo Water is currently (as of 2020) testing pilot plants with the AOS for the treatment of SW and poultry and brewery wastewaters.

BioLargo Water provided the AOS reactors used for the current thesis research project, staff gave valuable advice and technical support, and partnered in funding through NSERC Engage and Engage Plus research grants with Dr. Kerry McPhedran. In addition, part of this thesis research was accomplished during the author's internship at BioLargo Water Canada Inc. from October 2019 through January 2020.

The City of Saskatoon

The City of Saskatoon (CoS) is a municipality located in Saskatchewan, Canada having a population of 275,000. The South Saskatchewan River (SSR) is the major water body flowing through the city which acts as both a source water for drinking water treatment, as well as a receiving water body for municipal sewage wastewater and SW effluents. There are over 100 SW outfalls resulting from catchment areas within the CoS, however, the focus of the SW research with the CoS has been the water quality of selected "major" outfalls that have the greatest potential impact on the SSR. These major outfalls were chosen due to their relatively large catchment areas and their use in both current and historical water quality testing programs.

The CoS provided information on the locations and catchment areas of the SW outfalls within the CoS, staff gave valuable advice and technical support, as well as partnered in funding for SW quality testing as part of an NSERC Engage grant with Dr. Kerry McPhedran.

1.5 Knowledge Gaps

The assessment of the eAOPs, such as the AOS, for SW treatment is needed to provide for effective disinfection and decontamination of SW. However, prior to this thesis research, the types of iodide and chloride oxidative species produced in the AOS, and their relevant concentrations throughout the AOS reactor, were not well known. For iodide, the oxidative species that were expected to be produced in the AOS were determined in a separate project at the HXMA beamline of the Canadian Light Source (CLS, SK, CA). For chloride, the species expected to be produced were researched from studies available in the literature. An analytical method to measure the concentrations of iodate, periodate, chlorite, and chlorate had to be developed as there was no previous simple, cost effective existing method for this specific application. This method was then used to compare the concentrations of oxidative species created using varying concentrations of salt (potassium iodide (KI) and sodium chloride (NaCl)) and applied voltage to optimize the operating parameters of the AOS. These knowledge gaps were addressed in the research study presented in Chapter 2 of the thesis.

A proposed application of the AOS is the treatment of SW, however, this wastewater was not previously evaluated for treatment using the AOS. In addition, SW treatment using eAOPs such as the AOS has been limited overall in the literature. Determining the effectiveness of the AOS for SW treatment was important for the potential full-scale treatment of SW. The use of iodide is known to be effective for SW treatment, however the use of chloride (which may be in the real SW without the need for its addition) and no salt addition to the AOS was unknown. In addition, the AOS has been untested for its effectiveness for simultaneous disinfection and decontamination of SW. Commonly used water quality indicators mentioned previously in the Introduction such as *E. coli*, COD and TSS could be used to quantify the effectiveness of SW treatment. A pre-treatment step to reduce the solids in SW must be used to maintain the treatment effectiveness of the AOS. The Chapter 2 and 3 studies presented in this thesis address these presented SW treatment knowledge gaps with synthetic SW used in the AOS as presented in Chapter 2 and real SW treatment using the AOS presented in Chapter 3.

1.6 Thesis Overview

1.6.1 Thesis Objectives

The focus of Chapter 2 was to improve the understanding the AOS process parameters and to optimize the AOS for SW treatment using a synthetic SW matrix. The specific objectives for this chapter included:

- To determine the types of iodide and chloride oxidative species created within the AOS reactor during the treatment process.
- To assess the resultant concentrations of the iodide and chloride oxidative species at various sections of the AOS using a range of applied voltages and concentrations of influent salt (iodide or chloride).
- To evaluate the effectiveness of the AOS for treating synthetic SW created using a typical recipe available in the literature.

The focus of Chapter 3 was to determine the effectiveness of the AOS for treatment of real SW using the results from Chapter 2 AOS assessment. The specific objectives for this chapter included:

- To collect representative real SW samples from the CoS SW outfalls during both wet weather and dry weather conditions for treatment using the AOS.
- To assess alum and ferric chloride for their effectiveness in a C/F process.
- To determine the effectiveness of the AOS for treating SW using treatments including iodide addition, chloride addition, or no salt added to the AOS influent water.
- To assess the capabilities of the AOS to provide both disinfection and decontamination of real SW.

1.6.2 Chapter 2 Overview

This chapter presents a study on the improved understanding and assessment of a version of the AOS reactor developed by the industry partner. The types and concentrations of oxidative species produced within different AOS reactor sections were assessed to determine the optimized parameters for voltage applied to the AOS and the necessary influent water initial salt concentration. Iodide and chloride oxidative species produced in the AOS were both investigated. First, iodide was added to the influent water at various concentrations based on initial results for industrial wastewater treatment completed by the industry partner. Chloride was then considered as an alternative to iodide given it is naturally found in various wastewaters and is more commonly used in eAOPs reviewed in the literature. A primary consideration for the research was the development of a fast and inexpensive method to determine the oxidative species in the reactor. Thus, a considerable portion of the research effort for this chapter was in the development of a simple method to measure the concentration of iodide and chloride oxidative species using UV-vis spectrophotometer. This method was then used for the assessment of the iodide and chloride oxidative species in the AOS. A synthetic stormwater (SSW) was considered as a preliminary SW matrix to test the effectiveness of the AOS for disinfection and decontamination prior to using it for treatment of real SW samples in Chapter 3 research.

1.6.3 Chapter 3 Overview

The primary focus of Chapter 3 was on the application of the AOS for treating real SW collected in the CoS. The treatment effectiveness of the AOS was assessed using three treatment: (1) iodide addition; (2) chloride addition; and (3) no salt addition. There were three major aspects of this research including stormwater collection, AOS treatment, and water quality testing. The SW was collected from two different outfalls in the CoS during various storm events. The SW treatment was done in a two-step process including coagulation/flocculation (C/F) as a pre-treatment step prior to the AOS. Pre-treatment was done to limit the solids entering the AOS that could potentially negatively affect the effectiveness of treatment and/or lead to clogging of the reactor. The SW quality before treatment and after each treatment step was analyzed in the Environmental Engineering laboratories at the UofS. The results of Chapter 3 were used to determine if the current AOS design and treatment parameters are effective for SW treatment for both for disinfection and decontamination.

1.6.4 Chapter 4 Overview

This chapter is the conclusion chapter of the thesis. It includes a summary of research findings in the previous chapters, the engineering significance of this work, and recommendations and future work.

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Chapter 2 : Assessment of an Electrochemical Advanced Oxidation System for Synthetic Stormwater Treatment

Overview

A version of this Chapter is planned to be submitted to the *Journal of Environmental Management* with the following details:

Nathan Bettman[1], Raquibul Alam[1], Laura Patterson-Fortin[2], and Kerry McPhedran[1] 2020. Assessment of an Electrochemical Advanced Oxidation System for Synthetic Stormwater Treatment. To be submitted.

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Nathan's role in the research included determining the types of iodide and chloride oxidative species to analyze, development of the spectrophotometric measuring method, operation the AOS and measurement of the oxidative species. Nathan also operated the AOS for the synthetic stormwater experiments and measured the *E. coli* concentrations. Nathan analyzed the results for both experiments and wrote the initial manuscript draft of this paper

Raquibul's role in the research was designing and interpreting the iodide oxidative species experiments. Raquibul assisted in the revision of this paper. Laura's role in the research was choosing the operating parameters used for the oxidative species and synthetic stormwater experiments. She also developed the experimental method used for the first set of synthetic stormwater experiments. Laura's team at BioLargo Water designed and packed the AOS reactors used in the research. Laura and BioLargo staff provided feedback and review of the paper

Kerry's role in the research was to guide the research throughout the design, operation and analyzing process. Kerry is the corresponding author and was involved in the writing and revisions of this paper prior to submission to the journal.

Abstract

Pollution from wastewaters, such as municipal, industrial, agricultural, and stormwaters, is of increasing concern as it negatively impacts human and ecosystem health. Wastewaters contain contaminants including organic matter, suspended and dissolved solids, pathogens, polyaromatic hydrocarbons, and heavy metals, among others. Many wastewater treatment methods have been developed to treat wastewater with electrochemical treatment technologies being of current interest. Electrochemical Advanced Oxidation Processes (eAOPs) such as the current Advanced Oxidation System (AOS) are a type of electrochemical treatment that creates oxidative species, such as iodide and chloride species, that can treat even recalcitrant contaminants. It is important to determine the concentrations and locations of oxidative species in eAOPs such as the AOS for process assessment of wastewater treatment. In this study, a spectrophotometric methodology was used to determine concentrations of iodide and chloride oxidative species (10, 25, and 50 ppm) within an AOS under various input voltages (6, 12, and 24 V). Monitored species included iodate and periodate for iodide treatments, while chlorite and chlorate were assessed for chloride treatments. Overall, it was found that iodate and chlorite were the dominant species created in their respective treatments. The optimal conditions for the efficient creation of oxidative species in the AOS were 12 V and 10 ppm potassium iodide and 6 V and 10 ppm sodium chloride, respectively. The use of iodide is recommended for wastewater treatment to effectively create oxidative species and to limit the amount of potentially hazardous by-products created by the AOS process. Following assessment, the AOS performance was tested for a synthetic stormwater matrix. Results indicated that the AOS performed well for reduction of *E. coli*; however, reduction of other contaminants were inconsistent indicating the need for further assessment of the AOS treatment process.

2.1 Introduction

A wide variety of anthropogenically contaminated wastewaters enter receiving waterbodies which are of ongoing concern globally due to their negative impacts on human and environmental health. Wastewaters may contain contaminants including dissolved and suspended solids, organic and inorganic matter, pathogens (including *Escherichia coli*), metals, pharmaceuticals, and polyaromatic hydrocarbons (PAHs), among others (Feng et al., 2016;

Fraser et al., 2018; Moreira et al., 2017; Oturan et al., 2015; Sirés et al., 2014; Taylor et al., 2015; Teh et al., 2016). Typical anthropogenic wastewaters include municipal, industrial, and agricultural wastewaters (Moreira et al., 2017; Sirés et al., 2014; Teh et al., 2016); landfill leachates (Moreira et al. 2015; Oturan et al. 2015); and municipal stormwaters (Feng et al., 2018; Fraser et al., 2018; Harper & Herr, 1987; Mohanty et al., 2014; Taylor et al., 2015). Many technologies have been developed for treatment of these wastewaters, however, there remain challenges in increasing efficiency and cost effectiveness for treatment of these wastewaters having widely varying matrices.

Conventional wastewater treatment processes can be categorized into physical, chemical, and biological processes. Physical processes are used for removal of solids. Examples of physical treatment methods include bar racks/screens, sedimentation, and filtration (Clark & Pitt, 2012; Mickova, 2015). Chemical processes can decrease turbidity through particle flocculation followed by sedimentation and/or filtration. Common chemical treatment processes include coagulation/flocculation (C/F) (Clark & Pitt, 2012; Harper & Herr, 1987; Sansalone & Kim, 2008; Teh et al., 2016); air stripping towers, activated carbon adsorption, and ion exchange processes (Ding et al., 2017; Ganiyu et al., 2018; Moreira, Soler, et al., 2015). In addition, chemical treatments are often used for disinfection with chlorine, ozone, and UV typically used based on their ability to economically kill a variety of pathogens (Clark & Pitt, 2012; Hussain et al., 2014; Mickova, 2015). Biological treatment systems use microorganisms to break down and remove organic matter. Examples include fixed growth, suspended solids growth, trickling filters, activated sludge, rotating biological contactor, facultative ponds, and aerated lagoons (Clark & Pitt, 2012; Fraser et al., 2018; Mickova, 2015; Mohanty et al., 2014; Moreira, Boaventura, et al., 2015). In general, these conventional processes are reasonably effective when used individually, or in treatment process trains; however, these may not be as effective in treating more complex and recalcitrant wastewater contaminants.

Of more recent interest are advanced wastewater treatment processes, such as electrochemical advanced oxidation process (eAOP) technologies which rely upon oxidative electrochemical species for wastewater treatment (Bergmann et al., 2014; Feng et al., 2016; Ganiyu et al., 2018; Moreira et al., 2015). Advantages of eAOP treatment processes include high versatility, high efficiency, low resource consumption, and potential cost effectiveness (Ding et al., 2017; Mickova, 2015; Radjenovic & Sedlak, 2015; Sirés et al., 2014). However, high electrode costs, the low conductance of some wastewaters, and the release of toxic by-products created during treatment can be challenges for the application of eAOP technologies (Bergmann et al., 2014; Mickova, 2015; Radjenovic & Sedlak, 2015). Generally, eAOPs have been used as a pre-treatment to increase efficiencies of downstream treatment processes or as a post-treatment polishing step to help to meet effluent standards (Chan et al., 2012; Moreira et al., 2015; Oturan et al., 2015). However, the effectiveness of eAOP treatment technologies needs further improvements to improve treatment efficiencies, reduce energy consumption, and, in turn, be more cost effective. A potentially low-cost method to increase the effectiveness is the addition of salts, such as iodide and chloride, that could reduce a treatment reactor's potential thereby increasing the efficiency of the oxidation process (Cañizares et al., 2006). Overall, the addition of salts may be beneficial for improved electrochemical treatment, however, the reactor conditions need to be optimized for various salt concentrations and salt types to create the most effective oxidants at low voltages for cost efficiency.

Currently, our research group has been assessing an eAOP known as the AOS (Figure 2-1; BioLargo Water Inc., AB, Canada) for the treatment of municipal and synthetic stormwaters. The determination of oxidative species created while treating real wastewaters is not realistic given the complex matrices of these waters and the short-lived nature of the created oxidative species within electrochemical reactors. Thus, the first objective of the current study was to assess the AOS potential for the treatment of wastewaters through the determination of concentrations of produced oxidative iodide and chloride species within the reactor. Three concentrations (10, 25, and 50 ppm) each of potassium iodide (KI) or sodium chloride (NaCl) prepared in distilled water (DI) were added to the influent AOS water and three voltage levels (6, 12, and 24 V) were applied to the AOS. The KI was chosen as iodide is known to create strong oxidative species such as iodate (IO_3^-) and periodate (IO_4^-); while NaCl was chosen given chloride is found in many wastewater matrices negating the need for its addition and creates oxidative species including hypochlorite (ClO^-), chlorite (ClO_2^-), and chlorate (ClO_3^-). In addition to DI water, tap water was considered in some experiments given it contains chloride in a simpler matrix than wastewaters, thus, oxidative species formed could be readily determined. Given the short-lived nature of the oxidative species, sampling and processing via typical instrumentation would not be feasible. Thus, a novel methodology of determination of both iodide and chloride species was used such that the species could be determined quickly via UV-vis spectrometry as described in the Methods section below.

Following this initial assessment of the AOS performance, the second objective of this research was the assessment of a synthetic stormwater matrix that was created including *E. coli* and a variety of other known stormwater contaminants to determine the potential for AOS to be used for treatment of real stormwaters. Results determined from the overall AOS assessment and assessment, in addition to the synthetic stormwater, may be useful in informing the treatment of real stormwaters and other wastewater matrices using this eAOP technology.

2.2 Methods

2.2.1 The Advanced Oxidation System (AOS)

The laboratory scale AOS schematic is shown in Figure 2-1 (BioLargo Water Inc., AB, Canada). The reactor has a 1-inch diameter with a series of alternating proprietary materials used as anodes and cathodes. The reactor was operated in an upflow configuration using a peristaltic pump set at a constant 5 mL/min flow rate for all experiments. The voltage was applied via a DC power supply with positive voltage to the anodes and negative voltage to the cathodes. Sampling ports were located throughout the reactor with five anode ports (A1-A5) and three cathode ports (C1-C2, C3=Outlet). The expectation was that oxidative species would be generated at the anodes and depleted at the cathodes; thus, the sampling ports were staggered to sample from each of these reactor volumes. Before each experiment, the reactor was 'recharged' to remove residual contaminants that could be in the reactor and to ensure the ability of the reactor to create oxidative species before samples were collected. Firstly, the reactor was flushed with distilled (DI) water for 30 min. Then, the voltage was turned on and the AOS run with either the iodide or chloride influent water for 30 min (treatment dependent). The samples were then taken from each port prior to analysis via UV-vis as discussed in the following section. To facilitate the reaction(s) used to measure the oxidative species, 1 mL each of the sample and 0.64 M KI, 2 mL of the buffer and 6 mL of water was mixed in a 10 mL flask. The mixture was then transferred to a glass cell to be read by the spectrophotometer. Several different buffers were used to adjust the pH of the sample in order to determine the individual oxidative species as shown in Appendix A (Table A-1). All experimental conditions included for assessment of the AOS are summarized in Table 2-1.

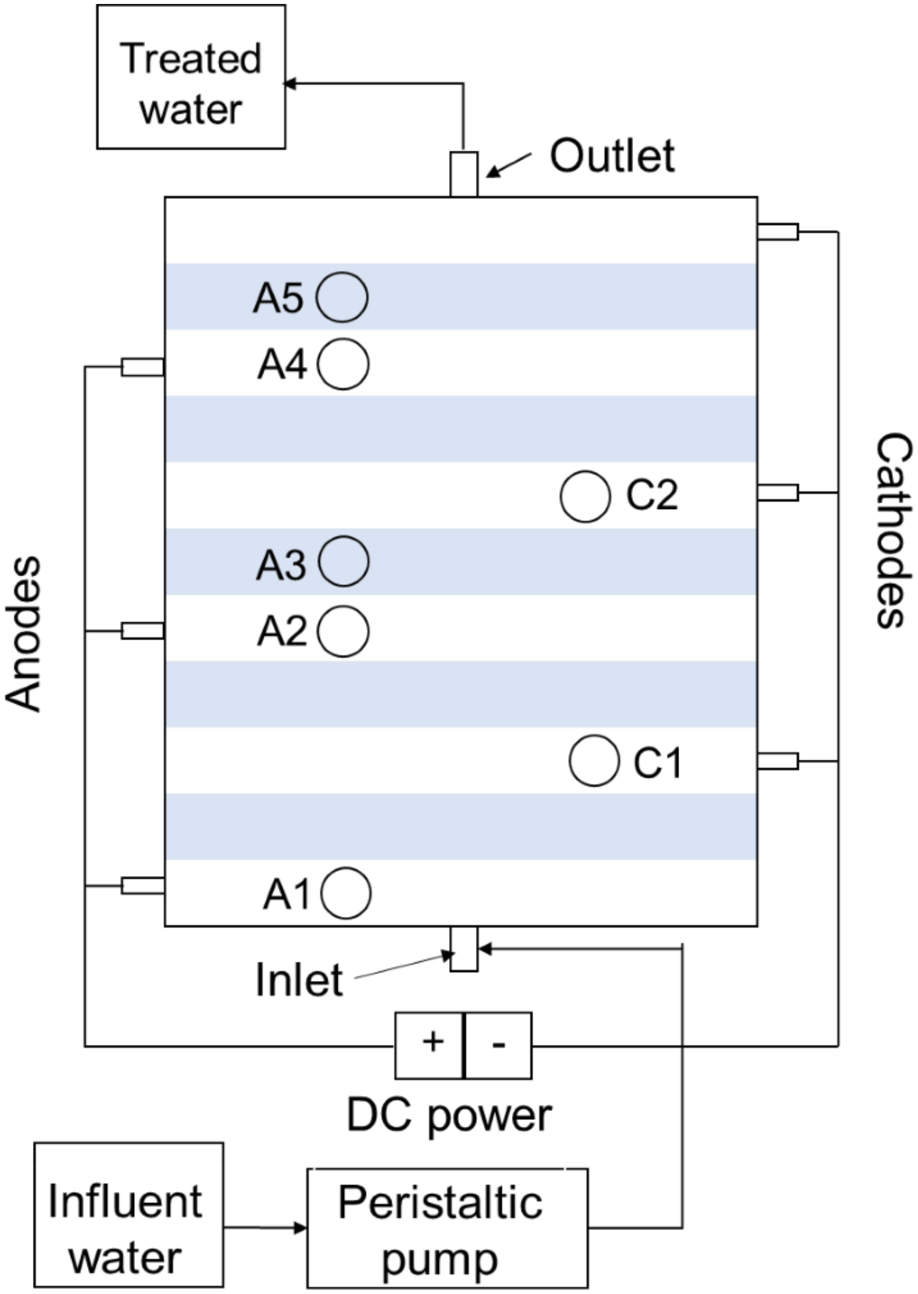

Figure 2-1: Schematic of the Advanced Oxidation System (AOS) reactor with alternating anodes and cathodes fed with DC power. Note that the numbers A1-5 represent 'anode' sampling ports on the reactor and C1-2 (and C3 outlet) represent 'cathode' sampling ports.

Table 2-1: Experimental conditions of various iodide (KI) and chloride (NaCl) concentrations and voltages. Note that the 'No salt' treatment includes only tap water at various voltages.

Treatment	Concentration (ppm)	Voltage (V)
KI	10	6
	10	12
	10	24
	25	6
	25	12
	25	24
	50	6
	50	12
	50 + Tap	6
	50 + Tap	12
	50 + Tap	24
NaCl	10	6
	10	12
	10	24
	25	6
	25	12
	25	24
	50	6
	50	12
	50	24
No salt	Tap	6
	Tap	12
	Tap	24

2.2.2 Determination of iodide and chloride oxidative species

The KI and NaCl were purchased from Fisher Scientific (Thermo Fisher Scientific, MA, USA) and were of ACS grade purity. The distilled water was produced via a Millipore Direct-Q 8 UV system with a conductivity of 18.2 MΩ/cm (Millipore Canada, ON, CA). The 10, 25, and 50 ppm solutions for each salt were produced fresh for each experimental run. A HACH DR 4000 UV-vis spectrophotometer (Hach Canada, ON, CA) with a 1-cm glass cell was used to determine the concentrations of the oxidative species. Calibration curves for each oxidative species at their corresponding absorbances were developed prior to experimental runs as discussed in the following sections. After recharging, the AOS was operated at the various concentrations and at 6, 12, and 24 V. The voltages were chosen based on the voltage levels that are commonly used in industry. A maximum voltage of 24 V was chosen to determine the voltage where there are no additional oxidative species formed compared to lower voltages applied to the AOS.

Samples were taken from each sampling port while the reactor was in operation, pH adjusted in a 10 mL flask, and ~1 mL was placed into the glass cell which was then immediately tested for absorbance. These experiments were conducted in Environmental Engineering laboratories at the University of Saskatchewan. The experiments for each voltage and current combination were not replicated due to time constraints.

2.2.3 Iodide species in AOS

The iodide species considered were iodate (IO_3^-) and periodate (IO_4^-) as they are predicted to be created by electrochemical oxidation. Prior to the current experiments, these have been shown to be the dominant species in the AOS based on parallel research done by our group at the HXMA beamline of the Canadian Light Source (CLS, SK, CA) as shown in Appendix A(Figure A-1). The iodide species were determined using a method described by Afkhami et al. (2001) based on their reaction with excess iodide to create triiodide (I_3^-) as follows (Eq. 1 and 2):

$$\mathrm{IO_4^-} + 11\,\mathrm{I^-} + 8\,\mathrm{H^+} \leftrightarrow 4\,\mathrm{I_3^-} + 4\,\mathrm{H_2O} \qquad (1)$$

$$\mathrm{IO_3^-} + 8\,\mathrm{I^-} + 6\,\mathrm{H^+} \leftrightarrow 3\,\mathrm{I_3^-} + 3\,\mathrm{H_2O} \qquad (2)$$

The concentration of the species was measured spectrophotometrically by measuring the absorbance of the triiodide at 352 nm (Afkhami et al., 2001; Feng et al. 2017; Wang et al. 2018). The reactions are pH dependent with periodate reacting at pH 6 and both species reacting at pH

3.3. These reactions will result in the creation of two equations for the absorbance values (Eq. 3 and 4); therefore, the concentration of each individual species can then be determined when both species are in a mixture by solving these equations simultaneously.

$$A_1 = a_1 + b_1C_{periodate} \quad (3)$$

$$A_2 = a_2 + b_2C_{periodate} + b'_2C_{iodate} \quad (4)$$

where A_1 and A_2 are the measured absorbances; a_1, b_1, a_2, b_2 and b'_2 are constants found when developing the calibration curves; and $C_{periodate}$ and C_{iodate} are the concentrations (mg/L) of each species. The absorbance of known concentrations of IO_3^- and IO_4^- were measured to develop the calibration curves (Eq. 3 and 4) with results presented in the Tables A-2 and A-3. An equation solver in Microsoft Excel was used to determine the constants in the equations.

2.2.4 Chloride species in AOS

Species tested for chloride speciation included hypochlorite (ClO^-), chlorite (ClO_2^-) and chlorate (ClO_3^-). As for the iodide species, these were chosen because they are predicted to be electrochemically generated in the reactor. Unfortunately, a similar experiment as the iodide species in the CLS was not completed for chloride species. The chloride species were determined using a similar method as for iodide using Equations 5 to 8 which indicate that the chloride species will react with excess iodide to form triiodide (Epstein and Kustin 1985; Mohammad et al. 2010; Narayana et al. 2005; Nowack and Von Gunten 1999).

$$\mathrm{ClO_3^-} + 6\,\mathrm{I^-} + 6\,\mathrm{H^+} \leftrightarrow 3\,\mathrm{I_2} + \mathrm{Cl^-} + 3\,\mathrm{H_2O} \quad (5)$$

$$\mathrm{ClO_2^-} + 4\,\mathrm{I^-} + 4\,\mathrm{H^+} \leftrightarrow 2\,\mathrm{I_2} + \mathrm{Cl^-} + 2\,\mathrm{H_2O} \quad (6)$$

$$\mathrm{ClO^-} + 2\,\mathrm{I^-} + 2\,\mathrm{H^+} \leftrightarrow \mathrm{I_2} + \mathrm{Cl^-} + \mathrm{H_2O} \quad (7)$$

$$\mathrm{I_{2+}}\,\mathrm{I^-} \leftrightarrow \mathrm{I_3^-} \quad (8)$$

The reactions are pH dependent and the absorbance of the triiodide was measured at different wavelengths to ensure that there is no interference between the oxidative chloride species. The concentration of hypochlorite was determined at a pH of 9.7 and a wavelength of 291 nm; hypochlorite and chlorite at pH 4 and 381 nm; and all three species at pH 4 and 300 nm (Tables A-4, A-5, and A-6). Note that the pH and wavelength for hypochlorite and chlorite were chosen by determining their maximum absorbances, while for all species it was chosen where contributing absorbances for all three species can be measured as a maximum. The three equations used to determine the concentrations of each species in a mixture included:

$$A_1 = a_1 + b_1C_{\text{hypochlorite}} \tag{9}$$

$$A_2 = a_2 + b_2C_{\text{hypochlorite}} + b'_2C_{\text{chlorite}} \tag{10}$$

$$A_3 = a_3 + b_3C_{\text{hypochlorite}} + b'_3C_{\text{chlorite}} + b''_3C_{\text{chlorate}} \tag{11}$$

where A_1, A_2, and A_3 are measured absorbances; a_1, b_1, a_2, b_2, b'_2, b_3, b'_3, b''_3 are constants found when developing the calibration curves; and $C_{\text{hypochlorite}}$ and C_{chlorite} and C_{chlorate} are the concentrations (mg/L) of the each species. The absorbance of known concentrations of ClO^-, ClO_2^- and ClO_3^- were measured to develop the calibration curves (Eq. 9-11) with results presented in the Tables A-4, A-5, and A-6. The constants in the calibration curves were determined by using the relationship between concentration and absorbance and an equation solver in Microsoft Excel.

2.2.5 Preparation of Synthetic Stormwater

Table 2-2 shows the general recipe for the synthetic stormwater (SSW) matrix that was used for AOS experimental testing. All the chemicals used in the SSW experiments were purchased from Fisher Scientific (Thermo Fisher Scientific, MA, USA) and were of ACS grade purity where applicable. Synthetic stormwater was used as a representative alternative to real stormwater given it can be easily and reliably replicated in any laboratory, thus allowing for the potential for direct comparisons between results of various studies. In comparison, real stormwater samples taken as part of a parallel study by our research group showed wide-ranging stormwater compositions which would be expected to have differing treatment assessment for each individual stormwater sample (Table A-15). Generally, there are many potential recipes for SSW in the literature that take this variability into consideration while also including differences due to location, time of year, and intensity of storm events. Ultimately, a SSW matrix was chosen based on literature that used a SSW to test urban stormwater treatment which has been used by a variety of researchers over the past 20 years (Davis et al., 1993; Hong et al., 2006; Okochi & McMartin, 2012). The SSW recipe can affect parameters, such as conductivity and concentration of solids, that can impact the effectiveness of treatment by the AOS.

There were two sets of SSW experiments used to test the AOS treatment process train.

Stormwater Experiment 1 focused on disinfection using the AOS given its potential usage for wastewaters, including stormwater, having bacterial contamination including *E. coli*. Stormwater Experiment 2 included the focus on *E. coli* while additionally investigated the decontamination capability of the AOS in a treatment train.

For Stormwater Experiment 1, sodium nitrate, glycine, dibasic sodium phosphate, bentonite, cupric sulfate, lead chloride, zinc chloride, and potassium iodide at the corresponding concentrations in Table 2-2 were mixed into a total volume of 120 L of reverse osmosis (RO) water (Millipore Canada, ON, CA). In addition, the *E. coli* standard strain was inoculated overnight in a 400 mL Luria-Bertani (LB) broth using a pre-streaked plate of the MC4100 strain. The inoculate was then spun in a centrifuge, resuspended in RO water, and added to the synthetic stormwater prior to running the experiments. The Stormwater Experiment 1 experiments were completed as part of an internship by N.B. at the laboratory facilities of BioLargo Water Inc. in Edmonton, AB.

For Stormwater Experiment 2, sodium nitrate, glycine, dibasic sodium phosphate, calcium chloride, and potassium iodide at the corresponding concentrations ranges shown in Table 2-2 (actual concentrations are included with experimental results in Table 2-5) were mixed into a total volume of 25 L of deionized (DI) water produced via a Millipore Direct-Q 8 UV system (Millipore Canada, ON, CA). The *E. coli* was prepared using the standard method given by the supplier (Microbiologics Inc., MN, USA) and added to the synthetic stormwater prior to running the experiments. These experiments were performed in the Environmental Engineering laboratories at the University of Saskatchewan in Saskatoon, SK.

Table 2-2: Synthetic stormwater (SSW) recipes (adapted from Davis et al. 2001; Hong, Seagren, and Davis 2006; Okochi and McMartin 2012) **Note**: SSW Experiment 2 concentrations indicate ranges with exact value used presented in Table 2-5

Component	**Material**	**Concentration**	**SSW Experiment**
NO_3^-	Sodium Nitrate	2 mg/L	1
		2 to 20 mg/L	2
Organic N	Glycine	4 mg/L	1
		6 to 40 mg/L	2
Phosphorus	Dibasic sodium phosphate	0.6 mg/L	1
		0.6 to 1.8 mg/L	2
Dissolved solids	Calcium chloride	120 mg/L	1
		120 to 600 mg/L	2
Suspended solids	Bentonite	25 mg/L	1
E. coli	*E. coli MC4100*	$6x10^6$ CFU/100ml	1
E. coli	E-power ATCC 51813	50 to 300 CFU/100mL	2
Copper	Cupric Sulfate	0.08 mg/L	1
Lead	Lead Chloride	0.08 mg/L	1
Zinc	Zinc Chloride	0.6 mg/L	1
Influent salt	Potassium Iodide	10 ppm	1
		5 ppm	2

2.2.6 Synthetic Stormwater treatment using the AOS

The Stormwater Experiment 1 focused on testing the disinfection of *E. coli* in a laboratory setup that included a modified version of the AOS reactor with a 2” diameter and 12 chamber configuration (BioLargo Water Inc., AB, Canada), a peristatic pump, and a direct current (DC) power supply. The prepared SSW was pumped through the AOS in an upflow direction at a constant 1 L/min flow rate and the AOS was connected to a DC power supply set at a constant 250 mA current. The current density applied to the AOS for the Stormwater Experiment 1 was approximately 3 mA/cm^2.

Samples to test the residual *E. coli* concentration were collected from the treated effluent every 30 min (including a time “0” sample). The samples were plated on LB agar (LBA) plates using a spiral plater, the plates were incubated at 35 °C for 24 h, and the colonies on the incubated plates were counted. In addition, a sample from the “stock” SSW prior to treatment was collected and plated to determine the initial *E. coli* concentration. Note that experiments did not include any pre-treatment prior to the AOS for these runs. The Stormwater Experiment 2 included a pre-treatment C/F step and the AOS treatment step. The C/F step would be expected to be used as an initial treatment process for the treatment of real stormwater to, at a minimum, decrease solids loading onto the AOS which could potentially lead to clogging of the reactor. Alum was chosen as the coagulant based on previous research (Harper & Herr, 1987) and its historic use for water and wastewater treatment C/F. A jar test was conducted using a jar test apparatus (Phipps and Bird, USA) to determine the optimum concentration of alum for the pre-treatment process of SSW. In addition, the jar test apparatus was also used for the C/F pre-treatment step for these experiments. The ASTM standard of rapid mixing at 120 RPM for 1 min, slow mixing at 30 RPM for 20 min, and settling for 30 min (ASTM International, 2013) was used all experiments. The AOS laboratory setup consisted of influent pre-treated SSW, a VWR variable speed medium-high flow peristaltic pump (VWR International, AB, Canada) set at a constant pump rate (100 mL/min), a DC power supply (Newark, ON, Canada) set at a constant 40 mA current, and the 1” 6 chamber laboratory scale AOS reactor (Figure 2-1) which was used in the assessment of iodide and chloride experiments. The current density applied to the AOS for Stormwater Experiment 2 was approximately 2 mA/cm^2.

Samples were taken prior to treatment, after C/F, and after the AOS (end of the process train). The total dissolved solids (TDS), electrical conductivity (EC), and pH meters were tested using typical laboratory meters. The chemical oxygen demand (COD) was measured using a HACH spectrophotometer and the corresponding HACH COD vials and digester (HACH USA, CO, USA). The total suspended solids (TSS) was measured using Standard Methods for quantifying solids in wastewaters ("2540 SOLIDS (2017)," 2018). A Lotix combustion total organic carbon (TOC) analyzer (Teledyne Tekmar, OH, USA) related standard method was used to measure the TOC concentrations. Lastly, *E. coli* was measured using m-ColiBlue24 Broth PourRite Ampules (Hach USA, CO, USA). Note that the current applied was different for each reactor from Stormwater Experiments 1 and 2 due the differing AOS sizes (12 vs. 6 chambers; 2" vs. 1") which impacted the current density within each AOS. The current density within the AOS was approximately 3 mA/cm^2 for Stormwater Experiment 1 as compared to 2 mA/cm^2 for Stormwater Experiment 2. However, the resultant applied voltages were in the ~7 to 8 V range for both experimental conditions.

2.3 Results and Discussion

2.3.1 Iodide Results

The concentrations of iodate and periodate formed using 10, 25, and 50 ppm KI concentrations at various voltages are shown in Figure 2-2 (Panels A, B, and C) as total oxidative iodide concentrations while the raw data for the concentrations of each individual species are presented in Table A-7 (10 ppm), A-8 (25 ppm), and A-9 (50 ppm). The resultant current that was applied to the reactor for each experimental condition is shown in Table 2-3.

Table 2-3: Measured current (A) applied to the AOS at constant voltage inputs for various experimental treatments of iodide (KI), chloride (NaCl), and no salt added. Note: Each voltage and salt combination experiment were not replicated due to time constraints.

	Current (A)		
Treatment	**6 V**	**12 V**	**24 V**
10 ppm KI	0.01	0.02	0.07
25 ppm KI	0.02	0.05	0.10
50 ppm KI	0.01	0.05	0.10
Tap + 50 ppm KI	0.08	0.22	0.65
10 ppm NaCl	0.01	0.04	0.15
25 ppm NaCl	0.01	0.05	0.20
50 ppm NaCl	0.02	0.07	0.25
No salt added	0.02	0.07	0.31

Overall, iodate was the dominant oxidative species at all KI concentrations and all applied voltages, typically having 5 to 10 times higher concentrations than periodate for all sampled anode and cathode ports. Periodate typically started to form at the higher applied voltage of 24 V, thus requiring more input energy to be created. This higher energy input resulted in much higher currents applied in the AOS (Table 2-3), which also increased with increasing salt concentrations, and generated excessive heat (~40-45 °C) that could potentially impact the integrity of the AOS. However, higher treatment temperatures may increase the effectiveness of treatment if the AOS is designed to handle larger temperatures. This could be due to faster reaction rates predicted with an increase of temperature. Creation of oxidative species increased with increasing voltages for all KI concentrations with 24 V showing the highest generation in all experiments (Figure 2-2). There was a large amount of bubbles generated noticed visually in the AOS and heat generated noticed physically from the samples collected from the sample ports by the AOS when 24V was applied. However, the excessive heat generation, coupled with the increased costs that would be expected for the higher voltage input, make the 24 V application unlikely for use in real wastewater treatment.

Iodate was found in both the anodes and cathodes, while periodate was only found in the cathodes. The concentration of the oxidative species increased after the anodes and decreased after the cathodes indicating that iodide was being oxidized at the anodes and reduced at the cathodes. This difference between samples between the anodes and cathodes was more prominent at higher voltages and KI concentrations given the higher reduction/oxidation potential at large voltages and concentrations of salt in the reactor. It should be noted that the sampling ports on the reactor are not perfectly aligned with anodes/cathodes and are closely spaced together, thus, complete reduction/oxidation between them would not be expected. This could be due to issues in the packing process, which could be solved by using a commercial reactor design.

In general, iodide oxidative species that can be formed include hypoiodous acid (HOI), iodite (IO_2^-) iodate (IO_3^-) and periodate (IO_4^-) with iodate being the most commonly formed and stable species (Wang et al., 2018; Ye et al., 2012). The use of iodide is more desirable than other salts, such as chloride and bromide, because the hazardous oxidative iodide species formed are readily transformed back to nonhazardous iodide (Feng et al., 2017). However, hazardous iodinated disinfection by-products such as iodoforms can also be formed (Wang et al., 2018; Ye et al., 2012).

The percentage of total oxidative species generated based on the input KI concentration total are shown in Figure 2-3 (Panels A, B, and C). As would be expected, as voltage increased there was also an increase in the oxidative iodate and periodate species, particularly at the anodes, with 10 ppm totals of 40-70%, 80-90%, and approximately 100% for 6, 12 and 24 V inputs, respectively. Following the same trend, 25 ppm totals were 20-60%, 50-100% and 85-100% and 50 ppm totals were 15-30%, 70-90% and 80-100%, respectively. Clearly, the lower the applied voltage, the lower the formation of oxidative species regardless of the initial concentrations. Interestingly, there was a possibility that other oxidative species such as HOI and IO_2^- were being formed at lower voltages (Wang et al., 2018; Ye et al., 2012) but these were not determined in the current study. However, it is unlikely that HOI is formed since acidic conditions are needed for formation and it is an unstable species (Wang et al. 2018). Based on this analysis, the optimal combination of maximum oxidative species and voltage selection for use in the AOS for treatment purposes would be 10 ppm and 12 V. The 10 ppm concentration had the highest percentage of iodate and periodate created; thus, an increased dosage may be unnecessary for treatment purposes. The 12 V treatments were markedly higher than the 6 V treatments, while the 24 V treatment was only marginally better than the 12 V treatment overall. In addition, the added cost of applying 24 V versus 12 V and the potential negative impacts of the heat generation at 24 V make the 12 V option recommended.

The next experimental treatment considered tap water with 50 ppm KI treated in the AOS at 6, 12 and 24 V. The concentrations of the oxidative periodate and iodate species for the tap water treatment are shown in Figure 2-4 in comparison to the 50 ppm KI DI water results shown previously, while the individual species raw data is included in Table A-10. Interestingly, the tap water showed higher oxidative species concentrations for the 6 V and 12 V experiments versus the DI water results. In addition, the difference in concentration between the anodes and cathodes when tap water was used was greater than DI water. The increase in oxidative species may be due to the increased current (about 4 to 8 times higher) that was applied through the reactor at the same KI concentration and voltage applied for the tap water versus DI water treatments(Table 2-3). The increased current can be attributed to the larger number of ions present in tap water versus DI water. Clearly, tap water results indicate that iodide species may be naturally found in the tap water which can be oxidized within the AOS. Alternatively, the tap water may have other oxidative species present, or created in the AOS, that could have contributed to the added absorbance given this is a non-specific methodology for determination of iodide species. For example, chloride is known to be present in tap water created in the City of Saskatoon (CoS) (City of Saskatoon, 2017) and is a common chemical added for protection of treated water before distribution. Given this result, chloride was assessed for its potential to create oxidative chloride species within the AOS in the next stage of experiments.

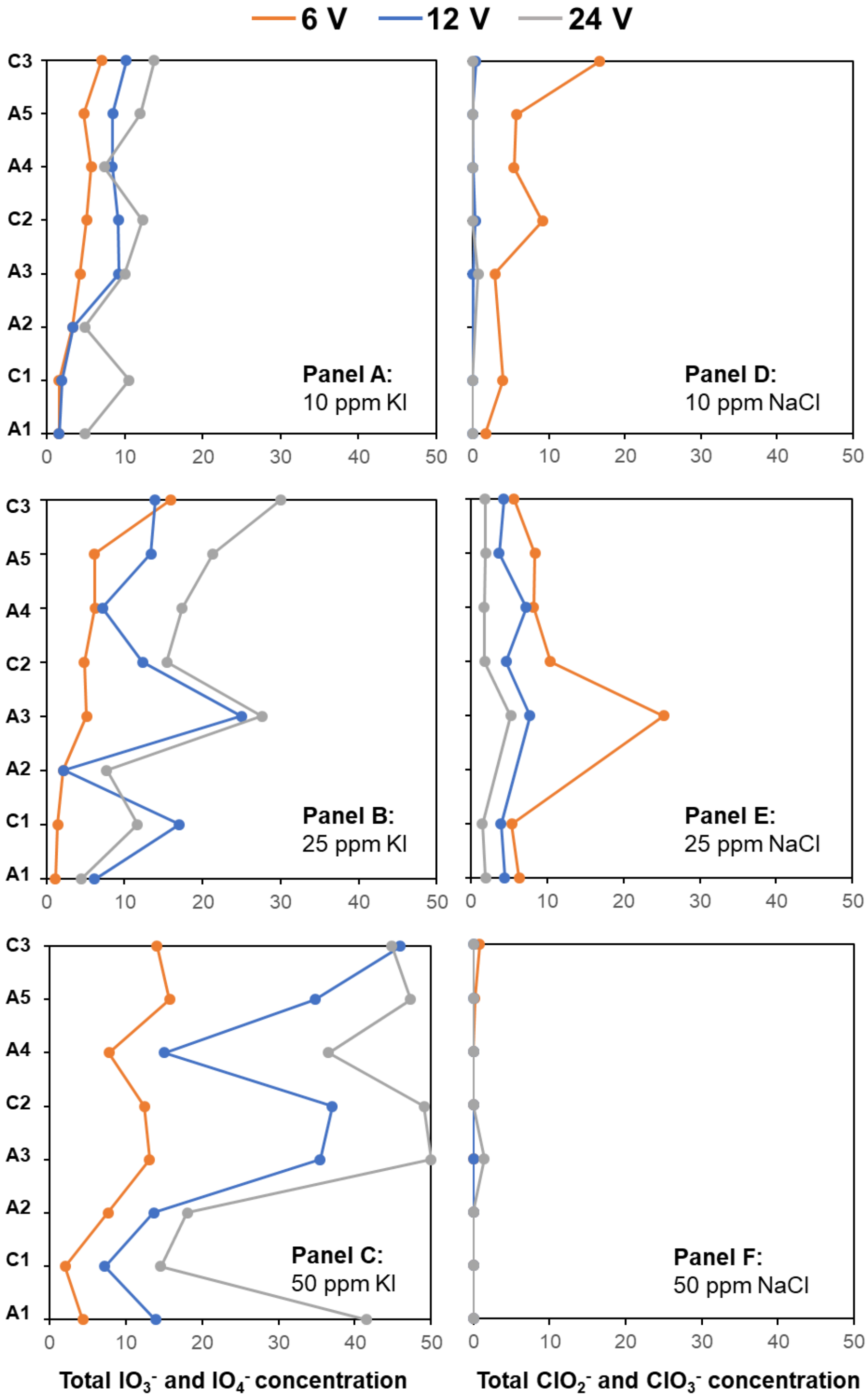

Figure 2-2 : Concentrations of oxidative iodide (Panels A, B, C) and chloride (Panels D, E, F) species present in the AOS at various KI and NaCl doses.

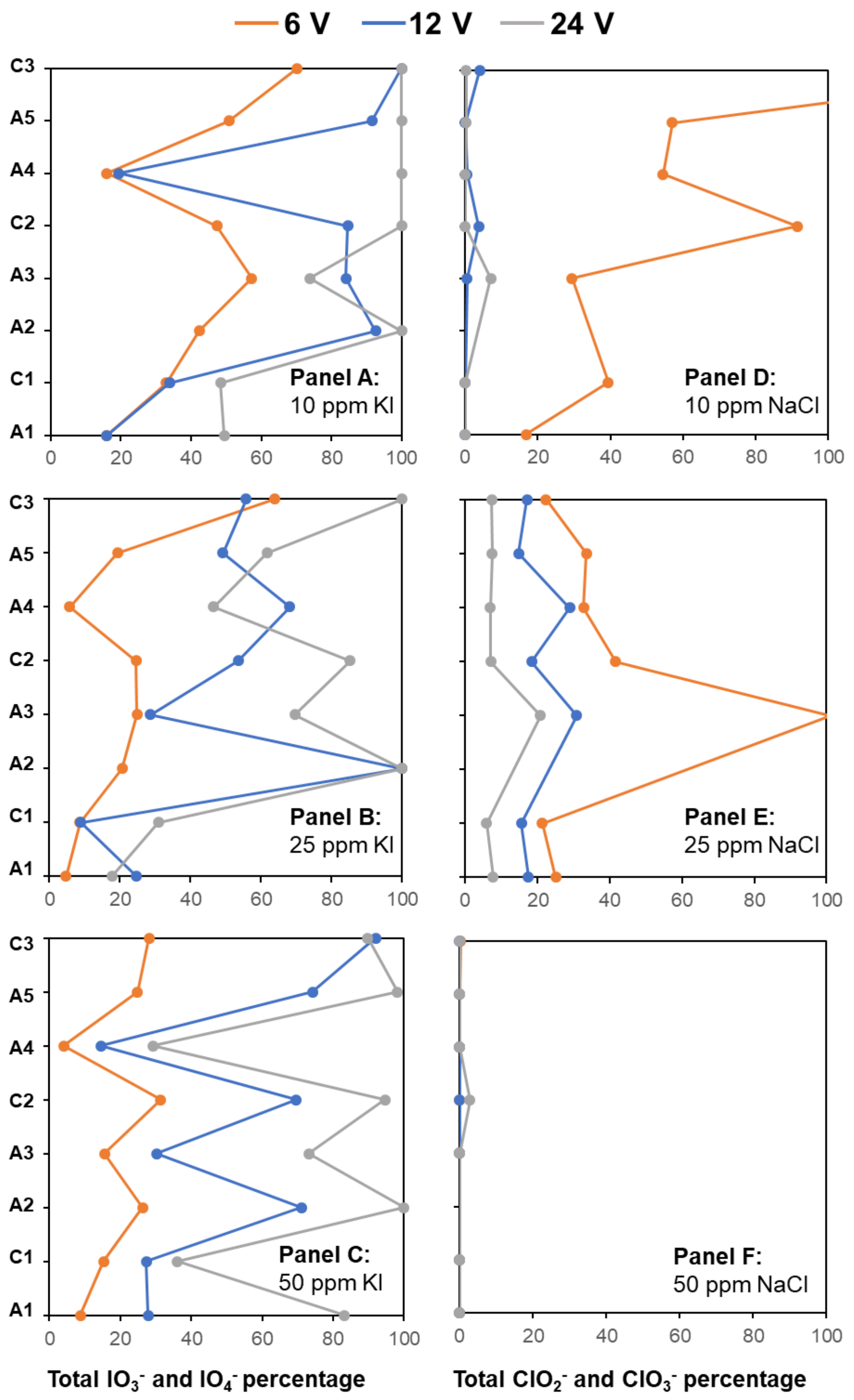

Figure 2-3: Percentage of the total oxidative iodide (Panels A, B, C) and chloride (Panels D, E, F) species present in the AOS at various KI and NaCl doses. Note that more highly oxidized species were not determined in the current study.

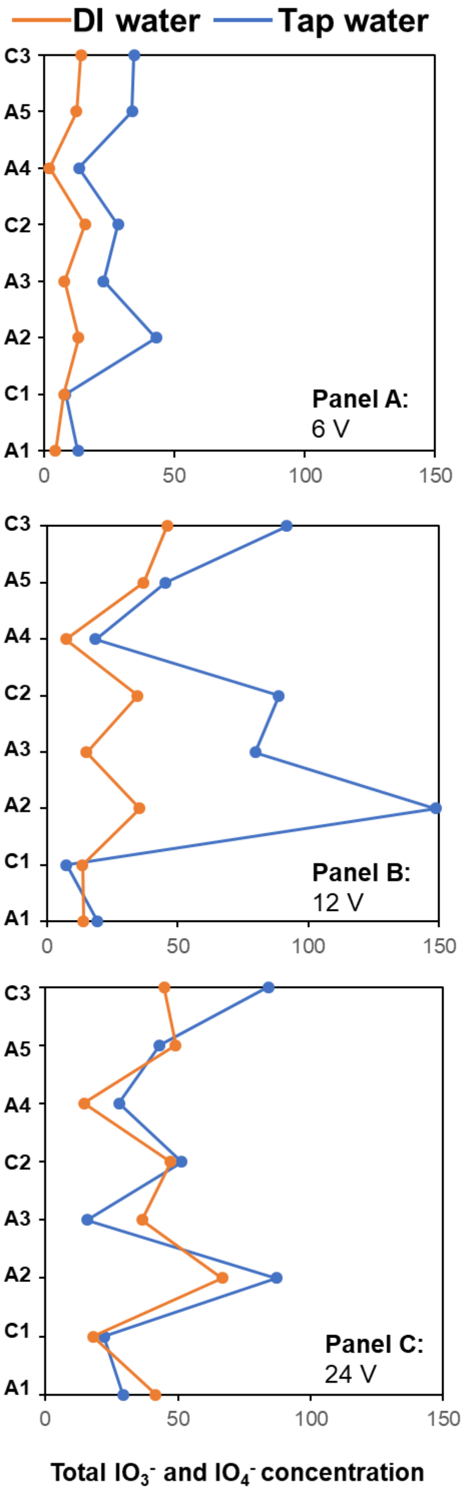

Figure 2-4: Total oxidative iodide species at 6 V (Panel A), 12 V (Panel B), and 24 V (Panel C) for distilled water (DI) and tap water samples including 50 ppm KI doses.

2.3.2 Chloride Results

The concentrations of chlorite and chlorate formed using 10, 25, and 50 ppm NaCl concentrations at various voltages are shown in Figure 2-2(Panels D, E, and F) as total oxidative chloride concentrations while concentrations of the raw data for each of the individual species are presented in Tables A-11(10 ppm), A-12 (25 ppm), and A-13 (50 ppm). As for the iodide results, the resultant current applied to the reactor for each experimental condition is shown in Table 2-3.

Overall, chlorite was the dominant oxidative species at all NaCl concentrations and applied voltages to the AOS whereas chlorate was only found in some experiments when 6 V was applied to the reactor. As for iodide, the current applied to the AOS increased with increasing NaCl concentration and applied voltage (Table 2-3). Creation of the two measured oxidative species was at a maximum at 6 V for the 10 and 25 ppm NaCl treatments and decreased with increasing voltages (Figure 2-2). The 50 ppm NaCl treatment showed negligible concentrations of both chlorite and chlorate regardless of the input voltage. As compared to KI experiments, the trends for NaCl were unexpected and some results were conflicting. For example, the concentration of the oxidative species increased at the cathodes and decreased at the anodes when 6 V and 10 ppm NaCl treatment. However, they increased at the anodes and decreased at the cathodes at all voltages for the 25 ppm NaCl treatment. The percentage of total oxidative species generated based on the total input NaCl concentration are shown in Figure 2-3 (Panels D, E, and F). The measured oxidative species were only significantly formed for the 10 ppm NaCl treatment at 6 V with totals of 20-100%. Oxidative species were formed for all voltages for the 25 ppm NaCl treatment, decreasing with input voltages with totals of 25-100%, 15-30% and 5-20% for 6, 12 and 24 V, respectively. There was a negligible concentration of chlorite and chlorate formed when 50 ppm NaCl was applied to the AOS as indicated previously. Generally, the lack of chlorite and chlorate may be due to the creation of other unmeasured oxidative species, such as perchlorate, being formed within the AOS. These species can be the result of higher currents generated in the reactor when increasing the applied voltage and/or increased the salt concentrations (Table 2-3).

Chloride is a potentially viable salt for production of oxidative species as it is commonly found in many wastewaters making addition unnecessary for treatment purposes. Chloride species that can be formed include chlorine gas (Cl_2), hypochlorous acid (HClO), hypochlorite (ClO^-), chlorite (ClO_2^-) and chlorate (ClO_3^-), with each species shown previously to be electrochemically generated (Bergmann et al., 2014; Oturan et al., 2015; Sirés et al., 2014). The HClO is the most powerful oxidant but is only formed in highly acidic conditions; it is also difficult to measure so was not included in the current species being assessed. The voltage applied to any electrochemical reactor system is important because if the anodic potential is too high, chlorate and perchlorate species can be formed. This scenario should be avoided as these species do not have any oxidation capacity and are known to be hazardous (Bergmann et al., 2014; Chaplin, 2014; Moreira et al., 2017; Radjenovic & Sedlak, 2015; Sirés et al., 2014). Thus, determination of these species currently would be a little value as they are not valuable for wastewater treatment purposes. In addition, no hypochlorite was found in any of the samples, thus, it is not included in further discussion. Clearly, the higher the applied voltage and NaCl treatment concentration applied to the AOS, the lower the formation of chlorite and chlorate, and potentially other species such as perchlorate can be created. Interestingly, Bergmann et al. (2014) used boron doped diamond (BDD) electrodes and found that chlorate is steadily formed and if the electrolysis time is long enough, all the chloride is reacted to perchlorate. Potentially using lower input voltages would lead to a decrease in applied current, or lowering the pH of the influent water below 4, which would both help to achieve lower oxidation states of chloride, such as hypochlorite, to be formed for safe and effective treatment (Cabeza et al. 2007; Juang et al. 2013). Currently, the comparison between iodide and chloride was done at three input voltages based on preliminary studies, thus lower voltage experiments were not considered.

Despite somewhat marginal result for NaCl, the optimal combination of NaCl concentration and applied voltage to create the most chlorite within the AOS for treatment purposes would be 10 ppm and 6 V, respectively. Increasing the NaCl concentration and/or the applied voltage to the AOS led to decreases in the total concentrations and percentages of chlorite and chlorate formed while increases the risk of harmful higher oxidative species, such as perchlorate, being formed within the reactor and potentially discharged the outlet of the AOS into the environment.

2.3.3 Comparing Iodide and Chloride

Overall, the concentrations of oxidative species formed for each of the various iodide and chloride treatments can be compared in Figure 2-2 and 2-3. The biggest difference between the salts is that the concentration of iodide oxidative species increases with increasing voltage, whereas the chloride species decrease with increasing voltage. In addition, the percentage of measured oxidative species is generally larger for iodide treatments in most experiments. For both salts, when the concentration of salt and/or applied voltage was increased, the resultant current also increases (Table 2-3). In addition, the higher concentration of ions in the tap water vs. DI water also resulted in an increased measured current. Typical wastewaters can contain high concentrations of ions, therefore the applied current within the AOS will be expected to be high even at low input voltages. This will make it difficult to keep the current low for real wastewater treatment, thus, it is expected that only higher chloride oxidative species will be formed for this treatment. However, the concentration of iodide oxidative species increased with increasing current making the use of iodide with the AOS being the recommended combination for consideration for the assessment of treatment for real wastewaters.

2.3.4 Synthetic Stormwater Preliminary Results

Following the assessment of the AOS for KI and NaCl concentrations, a synthetic stormwater (SSW) matrix was considered for treatment using the AOS. The optimum conditions for KI and NaCl were 10 ppm and 10 ppm, and 12 V and 6 V, respectively. Based on these results, the initial Stormwater Experiment 1 used a 10 ppm KI solution for the AOS treatment process. Given the disinfection results (see below) were successful, a 5 ppm KI solution was used for the Stormwater Experiment 2 under the assumption that the added SSW chloride (Table 2-2) would work synergistically in the treatment of the SSW. Similarly, the optimum voltage would be expected to be in the range of 6 to 12 V based on the AOS assessment experiments. The SSW experiments controlled the current at 250 mA (Experiment 1) and 40 mA (Experiment 2) rather than the voltage to account for differences between the reactors; however, the measured voltage was in the 7 to 8 V range for all experiments. Results for determination of *E. coli* reduction by the AOS including are shown in Table 2-4, while preliminary results for determination of a suite of physicochemical parameters and use of a flocculation treatment prior to the AOS are presented in Table 2-5.

The Stormwater Experiment 1 included 13 sets of treatment runs (Table 2-4). The initial untreated samples had an average *E. coli* concentration of log 6.43 (CFU/mL) with a standard deviation of log 0.44 CFU/mL. The first samples had log 3.68 (CFU/mL) with a high standard deviation of log 4.08 CFU/mL due to about half of these samples having values below the detection limit of the spiral plater (<400 cfu/ml). This variability could be attributed to the stage of cleaning

Table 2-4: Synthetic stormwater (SSW) results of stormwater experiment 1 for *Escherichia coli* reduction using 5 ppm KI and 250 mA (~7 to 8 V).

Runs	**n**	**Average (log CFU/100mL)**	**SD (log CFU/100mL)**
Initial	**13**	6.43	0.44
First sample (after 15 L)	**13**	3.68	4.08
After first sample (up to 120 L)	**13**	0.00	0.00

Table 2-5: Preliminary synthetic stormwater (SSW) results for Stormwater Experiment 2 including all physicochemical parameters using 5 ppm KI and 40 mA (~7 to 8 V). The modified SSW recipes were based on real stormwater sample data collected as part of a parallel study (Table A-15). Note: Average for each parameter shown. Duplicate samples were tested for each of COD, TOC, TSS and *E. coli*.

Experiments	EC (µS/cm)	TDS (mg/L)	pH	COD (mg/L)	TOC (mg/L)	TSS (mg/L)	*E. coli* (CFU/100mL)
30 June							
Initial	1,409	700	7.12	83.1	18.8	160	200
60 ppm Alum	1,575	784	6.10	70.2	19.2	2.5	40
AOS	1,373	680	6.15	68.0	16.8	6.5	6.5
3 July							
Initial	2,010	1,010	6.88	329	32.0	110	310
60 ppm Alum	2,090	1,058	6.18	294	30.9	3.5	15
AOS	1,825	913	5.76	228	9.60	<1.0	7.5
7 September							
Initial	511	248	6.90	39.5	7.15	110	42
60 ppm Alum	577	280	6.94	32.5	2.73	<1.0	17
AOS	318	153	5.86	17.5	0.48	<1.0	<1

Modified SSW Recipe	Sodium Nitrate (mg/L)	Glycine (mg/L)	Dibasic Sodium Phosphate (mg/L)	Calcium Chloride (mg/L)	*E. coli* (CFU/100mL)
30 June	6	12	1.8	480	200
3 July	20	40	6	600	300
7 September	2	6	0.6	120	50

or flushing of the AOS with the potential for residual iodide in the AOS leading to ‘faster’ treatment versus the need for iodide to “build up” in the reactor in the first couple minutes of treatment after cleaning. Thus, it would be expected that further improvement of the process, such as flushing the reactor with KI prior to treatment, would lead to more consistent values below the detection limit for future work. Following the first samples, the remaining samples consistently showed no presence of *E. coli* with up to 120 L of SSW and KI running through the AOS. Thus, the AOS showed a consistent 6-7 log disinfection of *E. coli* for the SSW using 10 ppm KI and 250 mA applied current indicating that this technology is well-suited to disinfection and has the promise to be successful for use in real stormwater treatment processes. This high efficiency for disinfection by the AOS is not surprising, as previous studies have shown consistent disinfection of wastewaters using other eAOPs. For example, Rajab et al. (2015) used a boron doped diamond eAOP and generated chloride oxidative species to achieve 4-8 log inactivation of *Pseudomonas aeruginosa*. Similarly, Feng et al. (2018) used a dimensional stable anode(DSA) eAOP and chloride species to achieve a 3 log (or total in this case) disinfection of *E. coli* present in both synthetic stormwater and real stormwater samples. Additionally, Cano et al. (2012) used a conductive diamond eAOP for treating a wastewater and found a greater than 4 log disinfection of *E. coli*.

Following the disinfection success of the Stormwater Experiment 1, the Stormwater Experiment 2 was used to test the ability of the AOS to provide for both disinfection and decontamination including three preliminary treatment runs. For these experiments, the KI concentration was reduced to 5 ppm in an effort to reduce the potential costs associated with addition of KI in the treatment process. In addition, results prior to these experiments suggested that higher 10 ppm KI concentration may not be necessary for treatment of more complex matrices such as the current SSW which have other salts already available for creation of oxidative species needed for treatment purposes. The *E. coli* initial concentrations were also reduced in these experiments (Table 2-5) to better represent concentrations found in real stormwater samples collected by our research team as part of a parallel study shown in Appendix A (Table A-15). In addition, the sodium nitrate, glycine, dibasic sodium phosphate, and calcium chloride concentrations added to the synthetic stormwater were varied to better represent different contaminant variations in these real stormwater (Table 2-5). Overall, the EC and TDS concentrations remained unchanged through the treatment process train and followed the added concentrations of calcium chloride and sodium nitrate which would be expected to impact these parameters. Generally, the COD, TOC, and TSS all decreased through the C/F and AOS treatment process with the TSS showing the largest reduction due to the C/F process. The initial *E. coli* concentrations were also reduced during the C/F process to a range of 17 to 40 CFU/100mL, while the AOS reduced these further to the range of <1 to 7.5 CFU/100mL.

Overall, the Stormwater Experiment 1 indicated that the AOS has a large capacity for disinfection of stormwater, or other wastewaters, having high initial *E. coli* concentrations. It would be expected that this capability would also be beneficial for reduction of other wastewater pathogens. The results for Stormwater Experiment 2 showed that the addition of the C/F step prior to the AOS provided for a large decrease in TSS and *E. coli* concentrations with the AOS process further 'polishing' the SSW for these two parameters. Assessment of the AOS for treatment of real stormwater samples is currently underway in our research labs and will be presented in a future research article. However, the results here for the SSW indicate that the treatment process train including C/F followed by the AOS shows promise for treatment of real stormwater samples.

2.4 Conclusions

Real wastewaters are complex matrices containing many compounds, such as organic matter, that could be electrochemically oxidized, potentially into hazardous compounds including halogenated disinfection by-products (DPBs) such as trihalomethanes and haloacetic acids (W. Feng, McCarthy, Henry, et al., 2018; Moreira et al., 2017; Sirés et al., 2014; Ye et al., 2012). Given this complexity, it is important to determine the oxidative species formed within eAOPs, such as the AOS, to assess if they are potentially useful for wastewater treatment (such as iodate and chlorite) or potentially hazardous species (such as perchlorate) that are not of use in the treatment process. It is also useful to know the appropriate salt concentration and applied voltage for optimized creation of oxidative species in the AOS that could result in the most effective treatment when applied to real wastewaters. Currently, it was assumed that only iodide or chloride oxidative species are created by the AOS, however, other species may be created dependent on the wastewater matrix composition. The treatment of stormwater is of interest for our research team as it is a challenging matrix given it has variable physicochemical parameters for each storm event as compared to more stable wastewater such as municipal wastewater. For example, stormwater has low chloride concentrations and conductivity which means higher voltages will be needed for effective electrochemical treatment as compared to other typical wastewaters (W. Feng, McCarthy, Henry, et al., 2018). However, as shown in the current study, the addition of salts to the stormwater can help to decrease the applied voltage needed for effective treatment.

The AOS showed excellent disinfection of synthetic stormwater including a high initial *E. coli* concentration using 10 ppm KI and a 2” 12 chamber reactor configurations. In addition, the AOS also exhibited *E. coli* disinfection of synthetic stormwater including lower initial *E.* coli concentrations using 5 ppm KI and a 1” 6 chamber reactor configuration. Additional work testing stormwater treatment in treatment train will have to be done to further test the disinfection and decontamination capability of the AOS. This could include treating real stormwater and comparing the use of iodide, chloride, and no salt added to the influent AOS water.

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Chapter 3 : Assessment of an Electrochemical Advanced Oxidation System for Stormwater Treatment

Overview

A version of this Chapter will be submitted to a journal such as the *Journal of Environmental Management* with the following details:

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Nathan's role in the research was the complete experimental design including choosing sampling locations, the coagulation/flocculation testing, and determining the water quality parameters to analyze. Nathan also was part of the stormwater collection and quality testing team that included both samples for this thesis research as well as samples for parallel research being conducted by Hayley Popick. He conducted all the stormwater treatment experiments including running coagulation/flocculation and the AOS. Nathan analyzed the results from the experiments, wrote the manuscript draft and made any necessary revisions to the paper prior to publication.

Hayley's role in research included being part of the stormwater collection and water quality testing team. She helped Nathan collect stormwater samples and performed a variety of the water quality analyses in the laboratory. Hayley will review and revise the manuscript draft prior to submission to the journal.

Kerry's role in the research was to guide the research throughout the design, operation and analyzing process. Kerry is the corresponding author and was involved in the writing and revisions of this paper prior to submission to the journal.

Abstract

Stormwater (SW) is a type of wastewater that has been of recent concern for governments and environmental agencies because it can cause large pollutant loading into water bodies if not managed properly. Stormwater management has traditionally been focused on mitigating flood and pollution risks, most commonly using natural treatment methods such as biofilters and wetlands. However, the storage and beneficial reuse of SW has become popular, especially in areas and times of water scarcity. Stormwater reuse guidelines and regulations have been developed by various municipalities in North America with SW treatment being necessary to meet water quality criteria required for reuse. There have been many technologies developed for SW treatment including electrochemical advanced oxidation processes (eAOPs) such as the currently considered Advanced Oxidation System (AOS). The AOS treatment process effectiveness for disinfection of *E. coli*, organics removal, and solids removal was compared for three treatments including: 10 ppm potassium iodide (KI); 10 ppm sodium chloride (NaCl); and no salt addition. Coagulation/flocculation (C/F) using either alum or ferric chloride was used as a pre-treatment step to the AOS for removal of solids that could negatively affect the AOS performance. Overall, the C/F was an adequate pre-treatment step, however, more effective coagulants and/or polymers should be considered to increase solids removal prior to the AOS. The AOS performed well for disinfection especially for the KI addition treatment with up to 3.5 log *E. coli* removal. However, the current AOS design and operational parameters did not provide for extensive organics removal, with the addition of KI and NaCl having similar removal efficiencies. Therefore, the design and operation of the AOS could be optimized for more effective decontamination of organics.

3.1 Introduction

Stormwater (SW) can be both a point and non-point source of municipal wastewater that results from rainfall and snowmelt runoff. This runoff water serves to collect and concentrate contaminants from a given stormwater catchment area and to potentially transfer large volumes of these polluted wastewaters into receiving water bodies if they are not managed properly (Okochi & McMartin, 2012). Common contaminants found in SW include organics, nutrients, pesticides and herbicides, pathogens, heavy metals, and polyaromatic hydrocarbons (PAHs), among others (Arora & Reddy, 2015; Aryal et al., 2010; Chong et al., 2013; Clark & Pitt, 2012; Göbel et al., 2007; Roy et al., 2008; Water Security Agency, 2015). In addition to these contaminants, other water quality parameters impacted by stormwaters may include pH, total dissolved solids (TDS). electrical conductivity (EC), turbidity (NTU), total suspended solids (TSS), fecal coliforms (including *Escherichia coli*), biological oxygen demand (BOD), and chemical oxygen demand (COD) (Aryal et al., 2010). Given their potential to negatively impact receiving waterbodies, there has been an increased focus of municipalities to responsibly manage and treat SW in order to decrease pollutant loads from SW outfalls into the environment.

Best Management Practices (BMPs) have been used worldwide to both control SW quantities (i.e., reducing potential flooding and erosion) and SW quality (i.e., reducing negative environmental impacts). However, the most common BMPs focus on the SW quantity impacts with quality typically being of secondary interest to municipalities. For example, quantitative regulations such as Stormwater Control Measures (SCMs) have been adopted by many jurisdictions in the United States (Fletcher et al., 2015). In contrast, despite the existence of various guidelines across the country there are no clear SW regulations (as of 2020) in Canada. Recently, Engineer's Canada created a seed document for consideration by Canadian municipal, provincial, and federal governments in the development of Canadian SW quality standards for release into receiving waters including suggestions of water quality targets for nutrients, suspended solids, metals, pathogens, and organic chemicals (Valley Credit Conservation & Zizzo Strategy, 2018). Alternatively, there are existing Canadian municipal wastewater effluent regulations (Government of Canada, 2016) that provide limits for effluent wastewater water quality parameters that may inform the development of potential future SW outfall water quality standards under the assumption that similar guidelines would be implemented for these two forms of municipal wastewater. Overall, all BMPs must include the implementation of one or more SW treatment technologies that are able to meet or exceed water quality regulations.

Generally, there are numerous SW treatment technologies that have been developed worldwide which can adequately treat large volumes of contaminated SW to meet various jurisdictional water quality standards. Of these, the most common technologies are focused on the more natural treatment methods including grassed swales, constructed wetlands, detention ponds, and biofilters (Begum et al., 2008; W. Feng et al., 2019; W. Feng, McCarthy, Henry, et al., 2018; Fletcher et al., 2015). However, these methods can be ineffective throughout the year in cold climates, typically require large area footprints, and are not effective for meeting water quality targets for potential beneficial reuse (Aryal et al., 2010; W. Feng, McCarthy, Wang, et al., 2018; Okochi & McMartin, 2012). For example, the Canadian prairie provinces have long durations of below-freezing weather making options such as grassed swales and biofilters ineffective. In addition, many mature municipalities in this region (including the current study City of Saskatoon) have SW conveyance from highly populated and intensive land-use areas that travels directly into receiving waterbodies, thus, these areas would not allow for the creation of large constructed wetlands or detention ponds.

Interestingly, the reuse of SW has become of greater interest in areas and/or times of water scarcity with the most common being for non-potable beneficial uses such as local or regional irrigation and toilet flushing; however, beneficial reuse may also be considered for potable water supply with consideration of proper treatment technologies (Begum et al., 2008; Chong et al., 2013; W. Feng et al., 2019; W. Feng, McCarthy, Wang, et al., 2018; Furlong et al., 2017). In general, the presence of fecal coliforms in SW are of primary concern for both non-potable and potable beneficial uses that may result in human contact and/or ingestion given the potential for negative human health impacts (Aryal et al., 2010; W. Feng et al., 2019; W. Feng, McCarthy, Wang, et al., 2018; Liu et al., 2016). Clearly, other SW treatment technologies must be implemented for use in both jurisdictions that cannot use natural treatment methodologies and/or for beneficial reuses that require more rigorous treatment to meet various non-potable and/or potable water quality reuse standards.

A successful SW treatment method must be both effective and inexpensive, while also having low energy and maintenance requirements (Arora & Reddy, 2015; Clark & Pitt, 2012; Okochi & McMartin, 2012). Electrochemical Advanced Oxidation Processes (eAOPs) are typically low cost and effective advanced treatment systems that have been used for the treatment of various wastewaters. These eAOPs have been shown to be effective in the disinfection and treatment of organics, inorganics, and micropollutants from highly polluted industrial effluents (Anawar & Ahmed, 2019; W. Feng et al., 2019; W. Feng, McCarthy, Henry, et al., 2018). However, eAOPs have not been widely assessed for treatment of SW which presents a unique challenge given its naturally high variability in flow quantity and water quality, relatively lower concentrations of salts (such as chloride) and microbes, and very low EC as compared to industrial and municipal wastewaters (Feng et al., 2018). These SW challenges do not allow for the direct adoption of existing wastewater eAOP technologies for SW treatment. Instead, existing industrial and municipal eAOP treatment processes need to be assessed and optimized for implementation of effective and efficient SW treatment.

The Advance Oxidation System (AOS) is a proprietary eAOP technology that has been optimized previously for the creation of oxidative species known to be effective in both disinfection and decontamination with the consideration of synthetic stormwater treatment (Chapter 2). In this previous study, the addition of potassium iodide (KI) and sodium chloride (NaCl) to the influent water resulted in the creation of oxidative species in the reactor including iodate (IO_3^-) and periodate (IO_4^-); and hypochlorite (ClO^-), chlorite (ClO_2^-), and chlorate (ClO_3^-), respectively. In the current study, both KI and NaCl were considered for their effectiveness in treating real SW samples taken from SW outfalls in Saskatoon, SK, Canada. In addition, the treatment efficiency with no salt added was investigated to determine if the addition of salt is necessary for real SW treatment given the availability of salts in the SW matrix without requiring their addition.

The overall objective of this study was to assess the effectiveness of the AOS for treatment of municipal SW with three treatment methods including: (a) addition of potassium iodide (KI) to each SW sample: (b) addition of sodium chloride (NaCl) to each SW sample; and (c) no additional salt added to the SW (No Salt). Municipal SW was collected from four major SW outfalls located in the City of Saskatoon (CoS) during both dry weather and storm events. The CoS has separated stormwater sewers (no connection to municipal sanitary wastewater sewers) with over 100 outfalls. Of these outfalls, there are 14 major outfalls which have catchment areas greater than 100 ha (1 km^2) that are of most interest in assessment based on their higher relative SW volumes being released into the South Saskatchewan River (SSR). A pre-treatment step consisting of coagulation/flocculation (C/F) using alum or ferric chloride was included before the AOS to reduce solids from potentially clogging the AOS or otherwise decreasing the effectiveness of the AOS due to solids loading. The expectation for scale-up would be the inclusion of the AOS in a SW treatment process ‘train’ (i.e., series of treatment processes), thus, consideration of this pre-treatment step in the current study treatment process.

3.2 Methods

The SW sampling locations and collection process is presented in Section 3.2.1. The SW treatment process train consisted of a laboratory jar test apparatus used for the preliminary C/F process followed by the AOS reactor. The C/F process methods are shown in Section 3.2.2. Figure B-1 presents the overall treatment process used and Figure B-2 shows a photo of the AOS laboratory setup and a schematic of the AOS including reactor, pump, and power supply. The AOS treatment process overview is shown in Section 3.2.3. The water quality of the samples was assessed before treatment, after C/F, and after the AOS to determine the effectiveness of each individual treatment step. The water quality analyses parameters and methods are presented in Section 3.2.4.

3.2.1 Sample Locations and Collection

The SW samples were collected from four SW outfalls including three outfalls for wet weather (WW) events and one outfall for a dry weather (DW) event. Interestingly, many SW outfalls in the CoS have significant flows even during dry weather indicating other sources of water which may include groundwater infiltration into cracked sewer pipes, potable water line leaks and infiltration, and illicit sanitary sewer connections. Thus, a DW sampling event was used to assess one of the outfalls that had consistently substantial flows throughout the warmer months even without the influence of rain events. The sampling outfall locations chosen for this study (naming convention in brackets follows CoS protocol) included outfalls at Avenue B S (Avenue B S), 17th Street West (17th St. W) and the east side of Gordie Howe Bridge (GHB) for WW sampling events and in between the 33rd Street West and CoS Weir (Weir/33rd St) for the DW event (Figure 3-1). The WW samples were collected during rainfall events using a bucket and rope to collect samples from above the outfalls, while the DW sample was similarly collected after a period of at least 48 h after the last rainfall. Two 25 L plastic containers were filled (50 L total sample volume) using the collection bucket and immediately transported back to the University of Saskatchewan Environmental Engineering Laboratories for all experiments. The SW samples collected from Avenue B S and Weir/33rd St outfalls were used for preliminary testing of the AOS in fall of 2018. Following these initial experiments, the SW collected from the 17th St. W and EGH outfalls was for more extensive experiments during the spring and summer of 2019.

Figure 3-1*:* The four City of Saskatoon stormwater sampling locations for outfalls into the South Saskatchewan River.

3.2.3 Coagulation/Flocculation (C/F)

Two known to be effective coagulants for wastewater treatment include ferric chloride and alum (Harper & Herr, 1987; Price Engineer & Yonge, 1981; Sansalone & Kim, 2008). Thus, both ferric chloride and alum were assessed individually for each sampled SW using a jar test at five different concentrations (and a blank) as shown schematically in Figure B-3. The ferric chloride and alum were purchased from Fisher Scientific (Thermo Fisher Scientific, MA, USA) and were of ACS grade purity. Ferric chloride was tested using 25, 40, 50, 60, and 70 mg/L concentrations, while alum was tested using 15, 30, 45, 60 and 75 mg/L concentrations. These concentration ranges were chosen based on their previous assessment based on both treatment and cost effectiveness in the literature (Harper & Herr, 2015; Price Engineer & Yonge, 1981; Sansalone & Kim, 2008). A jar test apparatus (Phipps and Bird, USA) was used to determine the optimal coagulant type and concentration for each collected SW before also being used for the C/F process at the optimal conditions prior to treatment through the AOS process. The mixing protocol for the jar test was based on the ASTM Standard (ASTM International, 2013) and included rapid mixing at 120 RPM for 1 min, slow mixing at 30 RPM for 20 min, and settling for 30 min. A sample of the supernatant was collected from each jar and the coagulant and concentration that resulted in the lowest residual turbidity (NTU) was used for further assessment in the treatment process train. This chosen coagulant and concentration was then used in the jar test apparatus for pre-treatment of 12 L of the collected SW using the C/F process resulting in adequate volumes for use in the AOS treatment process and all required water quality analyses as described in Section 3.2.4.

3.2.4 AOS

The AOS treatment process laboratory setup is shown in Figure B-2 and consisted of a VWR variable speed medium-high flow peristaltic pump (VWR International, AB, Canada) set at a constant pump rate (100 mL/min), a DC power supply (Newark, ON, Canada) set at a constant 40 mA current, a laboratory scale AOS reactor (BioLargo Water, AB, Canada), and storage containers for both the influent and effluent waters. The AOS reactor was rinsed prior to each SW treatment experiment to remove any impacts of previous treatment residual contamination of the reactor on the treatment of the influent SW. Ten litres of DI water (with power supply off) followed by 2 L of water with KI or NaCl (with power supply on and set at constant 40 mA current) was run through the reactor to clean and recharge the reactor. The reactor was then run through a batch cycle overnight, with the power supply on, using 5 ppm of KI or NaCl in a continuous loop through the reactor. The last two preparation steps were omitted for the no salts added experiments. The KI and NaCl were purchased from Fisher Scientific (Thermo Fisher Scientific, MA, USA) and were of ACS grade purity.

A 5 L aliquot of influent SW used for each AOS treatment experiment was decanted from the supernatant of the jars after the C/F treatment process. Three different treatments were considered including: (a) 5 ppm KI; (b) 5 ppm NaCl; and (c) no addition to the influent water. The salt (if necessary) was added to the 5 L influent SW to reach the 5 ppm concentration prior to AOS treatment. Each 5 L aliquot was treated five times (sequentially) through the reactor resulting in approximately five hours of total treatment time.

3.2.2 Water Quality Analyses

The water quality of the preliminary SW experiments in 2018 was assessed before treatment and after both the C/F and AOS treatment processes; however, for the more extensive 2019 experiments a third sample was assessed post-C/F but prior to the AOS treatment process for the determination of the effectiveness of each individual treatment process. All collected samples were analyzed for pH, TDS, EC, COD, TSS, TOC, and fecal coliforms (*E. coli*). The pH, TDS and EC were measured using their respective typical laboratory meters. The COD was determined using Hach COD digestion vials and a Hach spectrophotometer (Hach USA, CO, USA). The TSS was determined via Standard Methods 2540 ("2540 SOLIDS (2017)," 2018). A Lotix combustion TOC analyzer (Teledyne Tekmar, OH, USA) was used to measure the TOC using the instrumental method. The *E. coli* was enumerated using m-ColiBlue24 Broth PourRite Ampules (Hach USA, CO, USA) and membrane filtration using a standard method described by Hach USA, 2018.

3.3 Results and Discussion

The Results and Discussion includes two sub-sections with the first covering the Preliminary Stormwater Treatment Results (Section 3.3.1) collected in 2018 which were used for the scoping of the 2019 more extensive sampling and experimental research. Figure 3-2 and Table 3-2 present the preliminary real SW treatment results which will be discussed in this section. Note that this section will only provide an overview of the preliminary work and does not include comparison with the literature. The second sub-section includes the Full Stormwater Treatment Results (Section 3.3.2) collected in 2019. The overall results for 2019 experiments are shown in Table 3-2 with further more specific details presented in Figure 3-3 (COD Results), Figure 3-4 (TOC Results), Figure 3-5 (TSS Results), and Figure 3-6 (*E. coli* Results). This sub-section will include discussion of the current results in comparison to the relevant literature.

3.3.1 Preliminary Stormwater Treatment Results

Table 3-1 includes two preliminary SW experimental results with the Avenue B S collection occurring under dry weather (DW) conditions and Weir/33rd St. collection occurring in wet weather (WW) conditions. As mentioned previously, the Avenue B S outfall was a major outfall in which flow was substantial outside of storm events; hence, initial investigation of raw and treated SW from this outfall was considered of interest for potential future treatment needs and determination of the flow source by partners at the CoS. Interestingly, many parameters for this DW raw water were elevated as compared to the Weir/33rd St. raw water sample including EC, TDS, pH, alkalinity, and TSS. The COD was similar for both outfalls at 389 and 438 mg/L, respectively. In contrast, the *E. coli* values for the DW sample were 10 MPN/100 mL versus 290 MPN/100 mL for the WW sample. The elevated EC, TDS and alkalinity in the DW sample would indicate the impact of groundwater infiltration into the Avenue B S SW catchment area sewer pipes, while the low *E. coli* would negate the potential for illicit sanitary sewer connections into this outfall's catchment area as *E. coli* would be present in municipal wastewaters. The COD and TSS values being similar and higher, respectively, for the DW versus WW outfalls was an unexpected result but perhaps indicated that storm events may lead to dilution of suspended solids. However, both outfalls had similar dissolved organics concentrations as suggested by the COD values. Further investigation of outfalls having DW flows is being considered by the CoS, especially for determination of illicit sanitary sewer connections which would be expected to release untreated and *E. coli* wastewaters into the SSR. However, further assessment of DW flows was out-of-scope for the current study.

Interestingly, both outfalls had different optimal coagulant types with ferric chloride (30 ppm) being the best option for the Avenue B S DW sample while alum (40 ppm) was chosen for the Weir/33rd St. WW sample (Table 3-1). An example jar test result for the Weir/33rd St. sample is shown in Figure 3-2 with the optimal concentration leading to a turbidity of 20 NTU. The 2019 experiments had a similar outcome for coagulant types; thus, this inconsistency will be discussed

Table 3-1: Preliminary stormwater results for samples collected in fall 2018 and treated with 5 ppm KI solution using both C/F and AOS treatment processes. Note: Average for each parameter shown. Duplicate samples were tested for each of COD, TOC, TSS and *E. coli*.

	EC (µS/cm)	**TDS (mg/L)**	**pH**	**COD (mg/L)**	**Alkalinity (mg/L)**	**TSS (mg/L)**	***E. coli* (CFU/100mL)**
Avenue B S, October 6							
Initial	2,670	1,370	8.29	389	418	140	10
30 ppm FeCl and AOS	2,820	1,440	8.12	389	406	1.5	<1
Weir/33rd St., October 13							
Initial	1,188	586	7.87	438	219	57	290
40 ppm Alum and AOS	1,306	646	8.07	186	218	<1	19

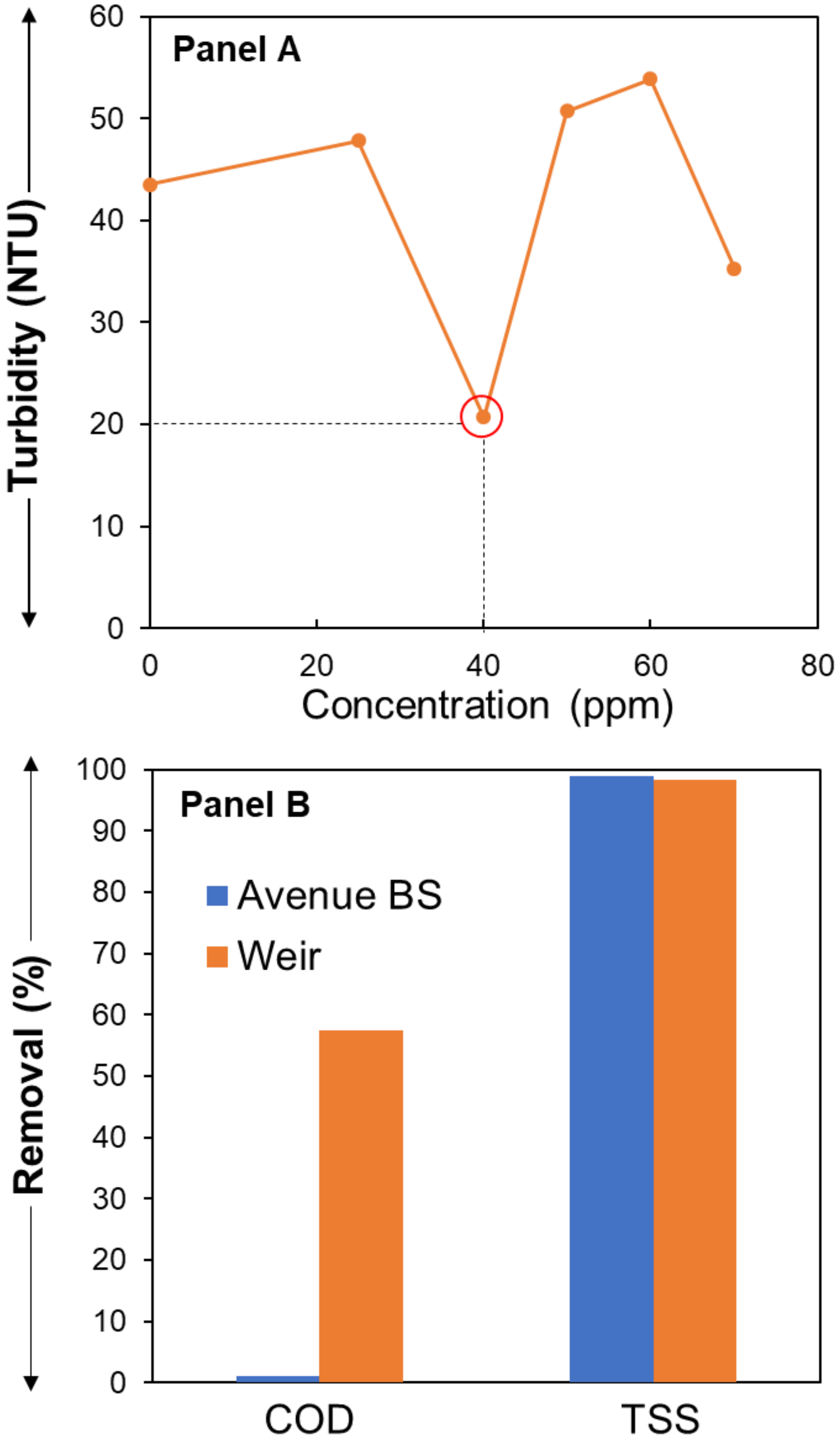

Figure 3-2: Preliminary testing including: (A) Jar test results using alum Oct 13 (B) TSS and COD percentage decrease after AOS Oct 6 and 13.

further in Section 3.3.2. In general, the AOS treatment process train had no impacts on EC, TDS, pH, and alkalinity. In contrast, the treatment resulted in substantial decreases in COD for the Weir/33rd St. with 58% removal and TSS for both outfalls at 98% (Figure 3-2). The COD for the DW Avenue B S was unchanged after treatment perhaps indicating a more recalcitrant dissolved organics matrix in this sample versus the WW Weir/33rd St. sample. Despite the combined success of the AOS train for TSS removal, the impacts of the individual processes could not be assessed given the lack of samples post-C/F but pre-AOS. The 2019 experiments included these 'middle' samples and will be discussed further below. The *E. coli* was substantially reduced for both samples indicating that the AOS train would be successful for SW disinfection purposes. However, similar to the COD and TSS, the impacts of the individual processes were not assessed.

Overall, the results of the preliminary 2018 studies allowed for the better understanding of potential differences between the DW and WW samples. This information will be useful for further assessment of DW outflows from outfalls where the source water is not known but may need to be treated in the future. The AOS treatment train was successful in treatment of two major contaminants of concern in the DW sample including *E. coli* and TSS that could potentially have negative impacts on the SSR. The WW information showed similar results for *E. coli* and TSS while also substantially reducing COD through the AOS treatment train. These results indicated that this technology has potential to be effective for SW, thus, the wider scope 2019 research was undertaken for further, more in-depth assessment of the AOS treatment train for numerous WW events for two CoS major SW outfalls.

3.3.2 Full Stormwater Treatment Results

A summary of all 2019 SW results is presented in Table 3-2. The averages and standard deviation of concentrations and percent removal are shown in Tables B-1 and B-2 respectively. Overall, each of the two outfalls, including Gordie Howe Bridge (GHB) and 17th St. W were sampled on four separate occasions for assessment of the AOS treatment train. For each outfall, three rainfall events were used to assess individual treatments including 5 ppm KI, 5 ppm NaCl, and No Salt using optimal coagulants for each event. In addition, one rainfall event for each outfall was assessed using all three treatments including 5 ppm KI, 5 ppm NaCl, and No Salt. Note that this last set of experiments included SW samples being stored at 4 °C overnight between the individual treatments given the inability to complete more than a single treatment process in one day. The temperature of the stormwater had the potential to impact the effectiveness of treatment

Table 3-2: Stormwater results for samples collected in 2019 and treated with various solutions including both post-coagulation and post-AOS analyses. Note: Average for each parameter shown. Duplicate samples were tested for each of COD, TOC, TSS and *E. coli*. Averages and standard deviations shown in Table B-1.

	EC (µS/cm)	**TDS (mg/L)**	**pH**	**COD (mg/L)**	**TOC (mg/L)**	**TSS (mg/L)**	***E. coli* (/100mL)**
5 ppm KI, Gordie Howe Bridge, May 25							
Initial	2,240	1,137	8.20	89	11.7	104	2,510
30ppm FeCl	2,180	1,098	7.91	69	10.9	12.5	280
AOS	1,797	899	7.91	54	8.8	4.5	57
5 ppm KI, 17th St. W, June 13							
Initial	694	337	7.02	334	54.7	196	2,200
70 ppm Alum	720	351	6.25	214	44.0	50	388
AOS	649	316	7.50	149	40.3	<1.0	<1
5 ppm NaCl, Gordie Howe Bridge, June 20							
Initial	1,156	570	8.13	88	14.1	84	250
60 ppm FeCl	1,119	551	7.35	51	11.6	47	100
AOS	1,018	500	7.40	52	2.8	14.5	<100
5 ppm NaCl, 17th St. W, June 28							
Initial	539	261	8.23	77	7.9	22	2,150
40 ppm Alum	543	263	8.72	56	5.2	<1.0	325
AOS	481	233	7.60	62	0.9	<1.0	12
No Salt, Gordie Howe Bridge, July 8							
Initial	1,077	530	7.59	56	12.2	2.0	160
75 ppm FeCl	1,108	545	7.11	51	6.2	<1.0	<10
AOS	967	475	7.62	49	5.2	<1.0	<1
No Salt, 17th St. W, July 17							
Initial	1,498	743	7.29	211	15.2	36	3,300
60 ppm Alum	1,502	746	7.48	112	14.3	<1.0	1,425
AOS	1,342	664	7.48	103	12.5	<1.0	675
Gordie Howe Bridge, July 22							
Initial	1140	561	7.72	75	11.1	3	75
60 ppm FeCl	1161	572	7.60	65	8.5	1.0	65
AOS 5 ppm KI	1042	512	7.75	40	3.9	<1.0	<1
AOS 5 ppm NaCl	1047	514	7.40	34.5	1.9	6	10
AOS No Salt	1030	513	7.53	47	4.9	1.5	<10
17th St. W, July 30							
Initial	425	205	7.40	124	20.3	30	<1
60 ppm FeCl	430	207	7.33	89	15.2	1.5	250
AOS 5 ppm KI	387	186	7.76	44	12.4	<1.0	<1
AOS 5 ppm NaCl	396	191	7.66	36	11.0	<1.0	7
AOS No Salt	357	172	7.69	45	5.5	<1.0	11

by the AOS. However, each of the collected stormwater samples were at room temperature (~20°C) after the coagulation/flocculation process and prior to treatment with the AOS.

3.3.2.1 Coagulant, Electrical Conductivity (EC), Total Dissolved Solids (TDS), and pH Results

Overall, the optimal coagulant varied between the two outfalls with ferric chloride being the preferred option for GHB samples at dosages between 30 and 85 ppm, and alum for 17th St. W samples at dosages for 40 to 70 ppm. The individual jar test results for experiments presented in this section are shown in Appendix B (Figure B-4). Reviewing these results, it is apparent that although each outfall's optimal coagulants differed, generally both ferric chloride and alum had similar trends in decreased turbidity for each sampling occasion. Given this outcome, it could be suggested that either ferric chloride or alum could be used as a pre-treatment process for the AOS. In addition, a dosage of 60 ppm appears to be adequate for all of the collected samples. The selection of a common coagulant and dosage for pre-treatment would greatly simplify the treatment process if multiple AOS treatment trains were applied to individual SW outfalls in a field application.

The EC and TDS are typically associated parameters so will be discussed together herein. The EC was generally higher for the GHB samples (1,000-2,240 µS/cm) than the 17th St samples (420-1,500 µS/cm), while the TDS followed the same trend at 530-1,137 mg/L and 261-743 mg/L, respectively (Table 3-2). These differences in EC and TDS may have impacted the optimal coagulant for each outfall; however, the overlap between these parameters for GHB and 17th St. W samples for collection dates for No Salt treatments indicate that there could be other water chemistry differences in these samples that may be impacting the coagulant efficiency. Overall, some samples had slightly increased EC and TDS concentrations (up to 3%) after the C/F process which could be attributed to the increase in metals the coagulant addition. For example, Pitt et al. (2002) used ferric chloride as a coagulant with concentrations of 25-75 mg/L leading to an increased EC by up to 4% for 'high conductivity' samples of 1,700 µS/cm. Interestingly, the EC of 'low conductivity' samples at 600 µS/cm was increased by 76% using a 25 mg/L ferric chloride.

3.3.2.2 Chemical Oxygen Demand (COD) Results

The results for the COD removal (%) are presented in Figure 3-3 including post-C/F and post-AOS results for the three individual treatments covering six storm events (three each for GHB and 17th St. W outfalls) (Panel A) and all three treatments used for two storm events (one for each

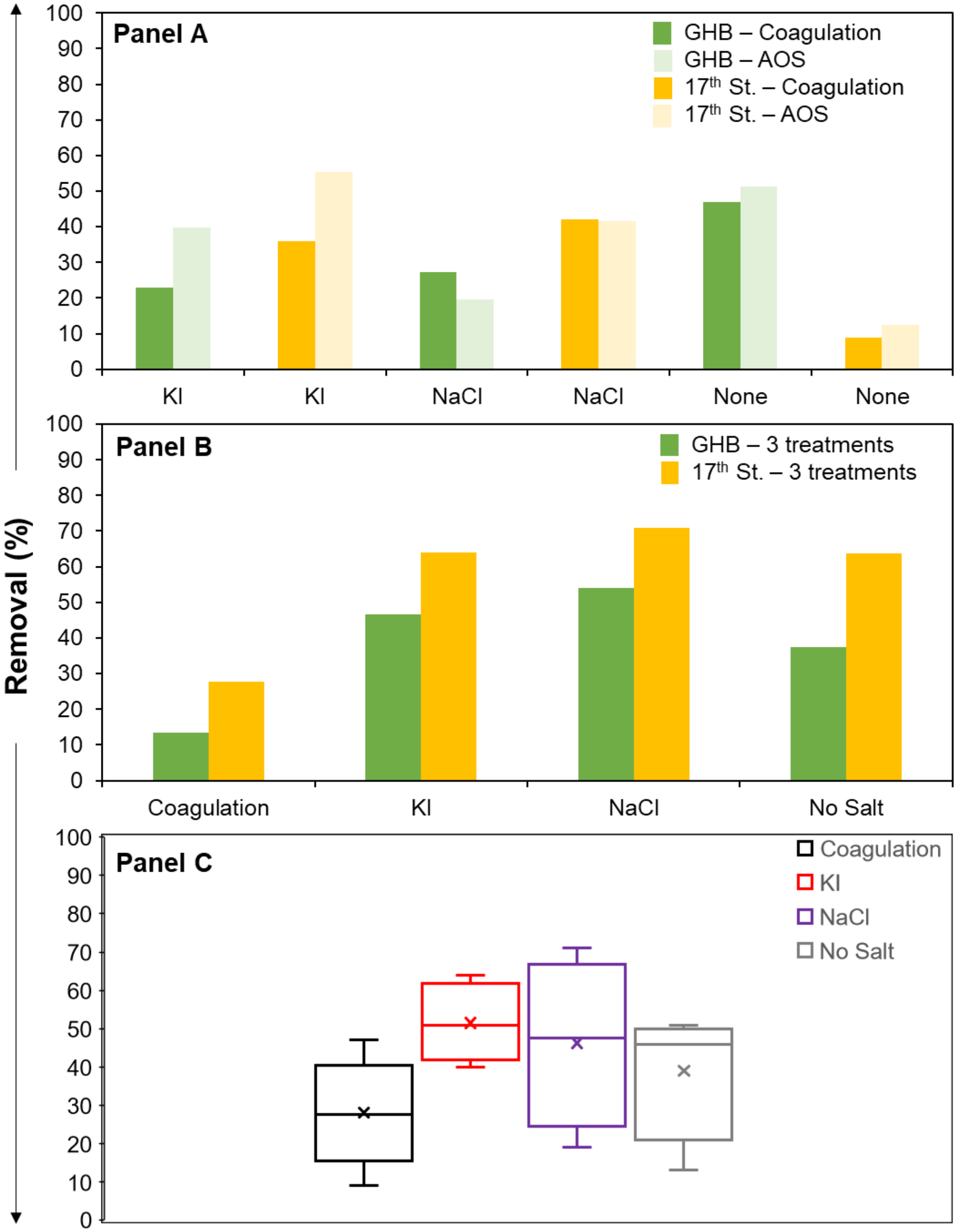

Figure 3-3: Percent removals for COD including: (A) post-coagulation and post-AOS for the GHB and 17th St. W. outfall samples collected on during separate storm events using 3 treatments; (B) post-coagulation and post-AOS for the GHB and 17th St. W. outfall sample; (C) Boxplots of all experimental combined for post-coagulation and post-treatment results.

outfall) (Panel B). The Panel C includes a set of four boxplots summarizing all post-C/F COD removal results and all individual treatment processes post-AOS COD removal results. A similar set of figures showing results for the actual COD concentrations (mg/L) are presented in Appendix B (Figure B-5).

Generally, the C/F process removed between 10 to 50% of the COD, with an average of about 25%, for all SW samples (Figure 3-3C) with the raw SW samples having COD concentrations between 56-334 mg/L (average of 143 mg/L) (Table 3-2 and Figure B-5). Following the C/F process, the complete AOS process train removed between 10 to 60% of the COD with the highest overall removal for the KI treatments (52%), followed by the NaCl (46%) and then No Salt (41%) treatments (Figure 3-3C). Interestingly, the AOS had higher COD removals for the KI and NaCl treatments of the 17th St. W samples, while for the No Salt treatment the higher COD removal was for the GHB sample (Figure 3-3A). However, the low COD removals for the 17th St. W sample were markedly lower overall versus any other samples. Reasons for these anomalous results are unknown. The results for the three treatments done for the same SW samples of each individual outfall are of most interest for direct comparisons between treatments (Figure 3-3B). Overall, all treatments (including the C/F process) had higher removal rates for the 17th St. W sample versus the GHB sample. In addition, the highest overall COD removals varied from the individual (Figure 3-3A) and summed (Figure 3-3C) results with the NaCl treatment marginally outperforming the KI treatment, followed by the No Salt treatment. Generally, it appears that either the KI or NaCl addition would be adequate for COD removal versus the No Salt treatment option.

Overall, the COD removal capability of the AOS treatment process train is consistent with other eAOPs that have been used for COD removal previously in a variety of wastewater treatment applications. The eAOP processes typically form reactive oxidative species, such as hydroxyl radicals (OH^-), active chlorine species, hydrogen peroxide (H_2O_2), which can remove COD in wastewater (Bagastyo et al., 2013; Drennan et al., 2019; Miklos et al., 2018; Radjenovic & Sedlak, 2015). Thus, the reactive iodine and chlorine oxidative species found to be formed in the AOS (Chapter 2) would also be expected to remove COD from the municipal SW samples. For example, Bagastyo et al. (2013) used an eAOP to remove up to 100% of COD from a reverse osmosis concentrate (ROC) using Si/Boron Doped Diamond (BDD) anodes with the addition of 0.05M NaCl and a current density above 3 Ah L^{-1}. In addition, Drennan et. al (2019) found that an eAOP in a divided cell configuration using a BDD or graphite cathode, and sparging of the analyte solution, was the most energy efficient for removal of COD from a greywater sample.

However, a limiting factor in using eAOPs for organics removal in wastewaters is the potential for production of halogenated organic by-products (OBPs); especially when halogens such as chloride are the active species used for treatment (Drennan et al., 2019; Miklos et al., 2018; Radjenovic & Sedlak, 2015). In addition, the application of COD removal by eAOPs is often limited by low removal efficiencies caused by low current densities and mass transfer rates (Radjenovic & Sedlak, 2015). Although higher current densities can be used to achieve COD removal, this leads to higher energy consumption and increased potential for OBP production. Currently, the AOS treatment process train removed approximately 50% of the influent COD at a current density of 2 mA/cm^2. Interestingly the current density used for this experiment is lower than the equivalent 3.6 A/cm^2 used by Bagastyo et al. to achieve 100% COD removal. The relatively low COD removal rates indicate that the AOS has not been designed to maximize COD removal through assessment of current density, treatment time, and/or electrode types. This is not surprising as the AOS treatment was initially designed for the purpose of "disinfection" rather than "decontamination". The COD removal by the AOS could also have reached a mass transfer limit when removing COD due to the relatively low SW COD concentrations as compared to other municipal and industrial wastewaters. For example, the COD removal limit for the AOS may be in the range of 30-50 mg/L (Table 3-2) regardless of the starting COD concentration in the raw SW. The AOS may potentially be optimized for better COD removal via increased current densities and/or longer treatment durations in future work.

3.3.2.3 Total Organic Carbon (TOC) Results

The results for the TOC removal (%) are presented in Figure 3-4 including post-C/F and post-AOS results for the three individual treatments covering six storm events (three each for GHB and 17th St. W outfalls) (Panel A) and all three treatments used for two storm events (one for each outfall) (Panel B). The Panel C includes a set of four boxplots summarizing all post-C/F TOC removal results and all individual treatment processes post-AOS TOC removal results. A similar set of figures showing results for the actual TOC concentrations (mg/L) are presented in Appendix B (Figure B-6).

Generally, the C/F process removed between 5 to 45% of the TOC, with an average of about 22%, for all SW samples (Figure 3-4C) with the raw SW samples having TOC

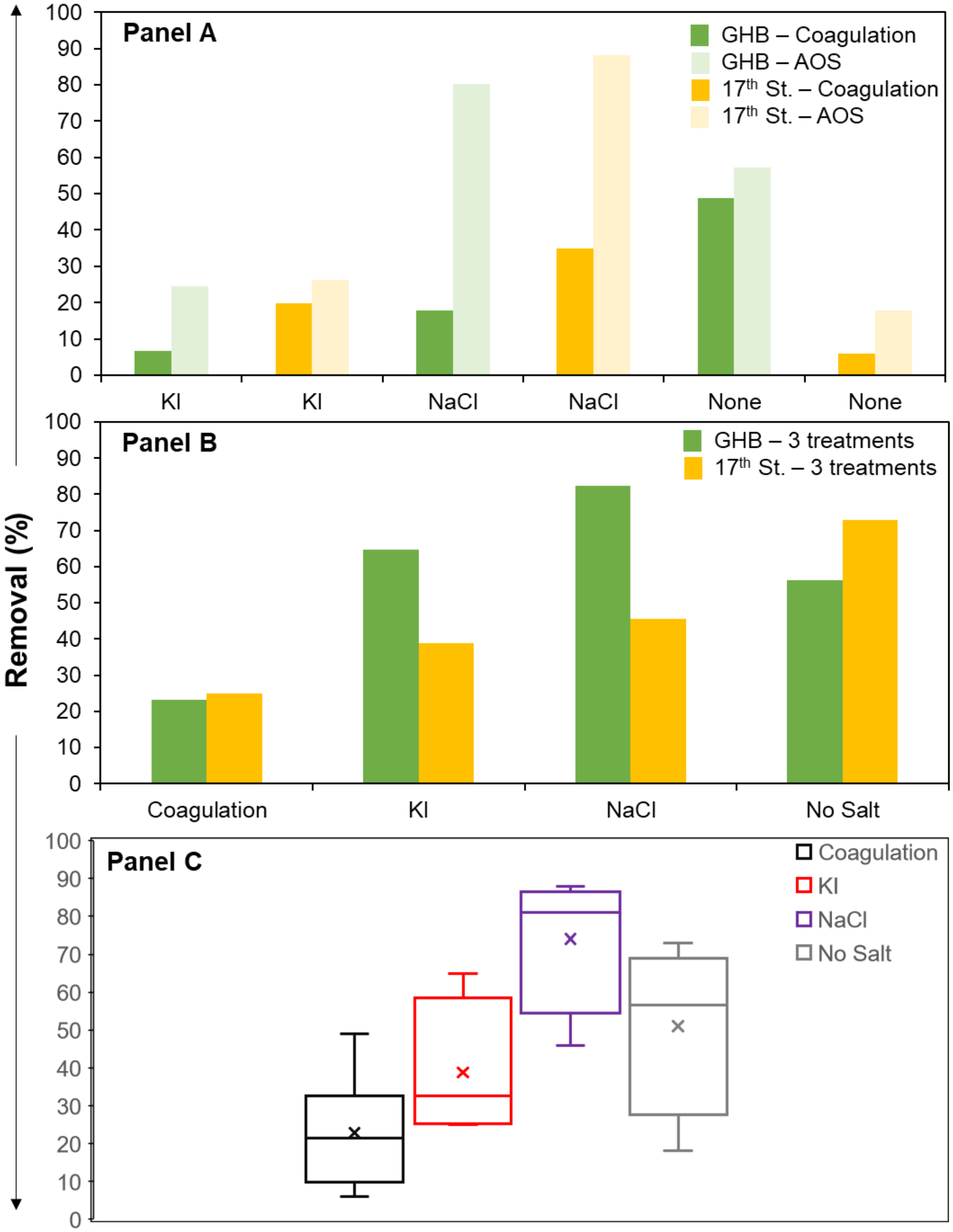

Figure 3-4: Percent removals for TOC including: (A) post-coagulation and post-AOS for the GHB and 17th St. W. outfall samples collected on during separate storm events using 3 treatments; (B) post-coagulation and post-AOS for the GHB and 17th St. W. outfall sample; (C) Boxplots of all experimental combined for post-coagulation and post-treatment results.

concentrations between 8-55 mg/L (average of 18 mg/L) (Table 3-2 and Figure B-6). Following the C/F process, the complete AOS process train removed between 20 to 85% of the TOC with the highest overall removal for the NaCl treatments (80%), followed by the No Salt (60%) and then KI (30%) treatments (Figure 3-5C). Interestingly, similar to the COD results, the AOS had higher TOC removals for the KI and NaCl treatments of the 17th St. W samples for the individual treatment experiments (Figure 3-4A). However, the GHB outfall had larger TOC removal for the No Salt added treatment versus the very low removals for 17th St. W which were a similar anomaly as for the COD results. The results for the three treatments (Figure 3-4B) showed a mixed trend as compared to the COD results with the GHB samples having larger TOC removal for KI and NaCl treatments and the 17th St. W sample having larger TOC removal for the No Salt treatment. In contrast to the COD results, both the individual (Figure 3-4A and 3-4B) and the summed (Figure 3-4C) results are in agreement indicating that the NaCl addition achieved the highest TOC removal versus the other two treatments.

Similar to COD, eAOPs such as the AOS have been shown to remove wastewater TOC due to the creation of reactive oxidative species which degrade the TOC (Bagastyo et al., 2013; Duan et al., 2015; Miklos et al., 2018; Radjenovic & Sedlak, 2015). For example, Bagastyo et al. (2013) used an eAOP under similar operating conditions as for COD presented above (i.e., Si/BDD anode, NaCl addition) but found a much lower maximum TOC removal of 40% (versus 100% COD removal) at a high current density of 5.6 Ah L^{-1}. Similarly, Duan et al. (2015) used an eAOP made from activated carbon electrodes and found 60% TOC removal at operating conditions of 2 V applied voltage, a temperature of 38 °C, and 500 ml min^{-1} oxygen flow. Additionally, Chavez et al. (2014) used a BDD anode and iron plate cathode eAOP to treat a tannery wastewater and found 48% TOC removal at a current density of 65 mA cm^{-2} and 65% removal at a higher 111 mA cm^{-2} current density.

Interestingly, the AOS treatment process train removed approximately 80% of the influent TOC at a current density of 2 mA/cm^2 which is lower than the equivalent densities of 65 mA/cm^2 - 5.6 A/cm^2 used to achieve 40-65% TOC removal in previous studies. Overall, the KI treatment results showed that the AOS removed an average of 30% TOC as compared to an average of 50% COD which is a similar result to the eAOP literature that showed lower TOC versus COD removals under the same operating conditions (Bagastyo et al., 2013). However, the AOS treatment using KI removed a lower percentage of TOC than previous studies indicating that the AOS operating parameters could be further optimized for KI treatments including potentially higher current densities and longer hydraulic residence times. Interestingly, the NaCl treatments had higher overall TOC removals than COD removals which was in contrast to other eAOP study results. Thus, the NaCl treatment was clearly the optimal treatment for TOC removal in the current study.

3.3.2.4 Total Suspended Solids (TSS) Results

The results for the TSS removal (%) are presented in Figure 3-5 including post-C/F and post-AOS results for the three individual treatments covering six storm events (three each for GHB and 17th St. W outfalls) (Panel A) and all three treatments used for two storm events (one for each outfall) (Panel B). The Panel C includes a set of four boxplots summarizing all post-C/F TSS removal results and all individual treatment processes post-AOS TSS removal results. A similar set of figures showing results for the actual TSS concentrations (mg/L) are presented in Appendix B (Figure B-7).

Generally, the C/F process removed between 50 to 90% of the TSS, with an average of 80%, for all SW samples (Figure 3-5C) with the raw SW samples having TSS concentrations between 1-200 mg/L (average of 60 mg/L) (Table 3-2 and Figure B-7). Following the C/F process, the complete AOS process train removed between 50 to 99% of the TSS with the highest overall average removal for the KI treatment (85%), followed by the No Salt (75%) and then KI (70%) treatments (Figure 3-5C). Interestingly, the No Salt and NaCl addition showed a lower TSS removal after the AOS than after C/F for the GHB 3 treatment samples. This could be due to the experimental design for these samples that included running each of the experiments on separate days and not re-analyzing the TSS after C/F for the NaCl and No Salt samples. Overall, the C/F pre-treatment step removed a majority of the suspended solids, which was goal of this process, with the AOS generally removing additional TSS following the C/F process.

Coagulation/flocculation was designed to remove solids from wastewaters such as SW, thus, its success in the current study in removing TSS was anticipated. Previously, Sansalone and Kim (2008) achieved 75% and 60-70% TSS removals for SW using dosages of 20-40 mg/L alum and 40 mg/L ferric chloride, respectively. The current average TSS removal of 80% is higher than found by Sansalone and Kim (2008) mainly due to the higher concentration of coagulants used in the current experiments at 40-70 mg/L vs. 20-40 mg/L in the previous study (Figure B-4). However, C/F has been shown to remove up to 98% of TSS from SW using commercial, synthetic coagulants and polymers while also using lower coagulant concentrations

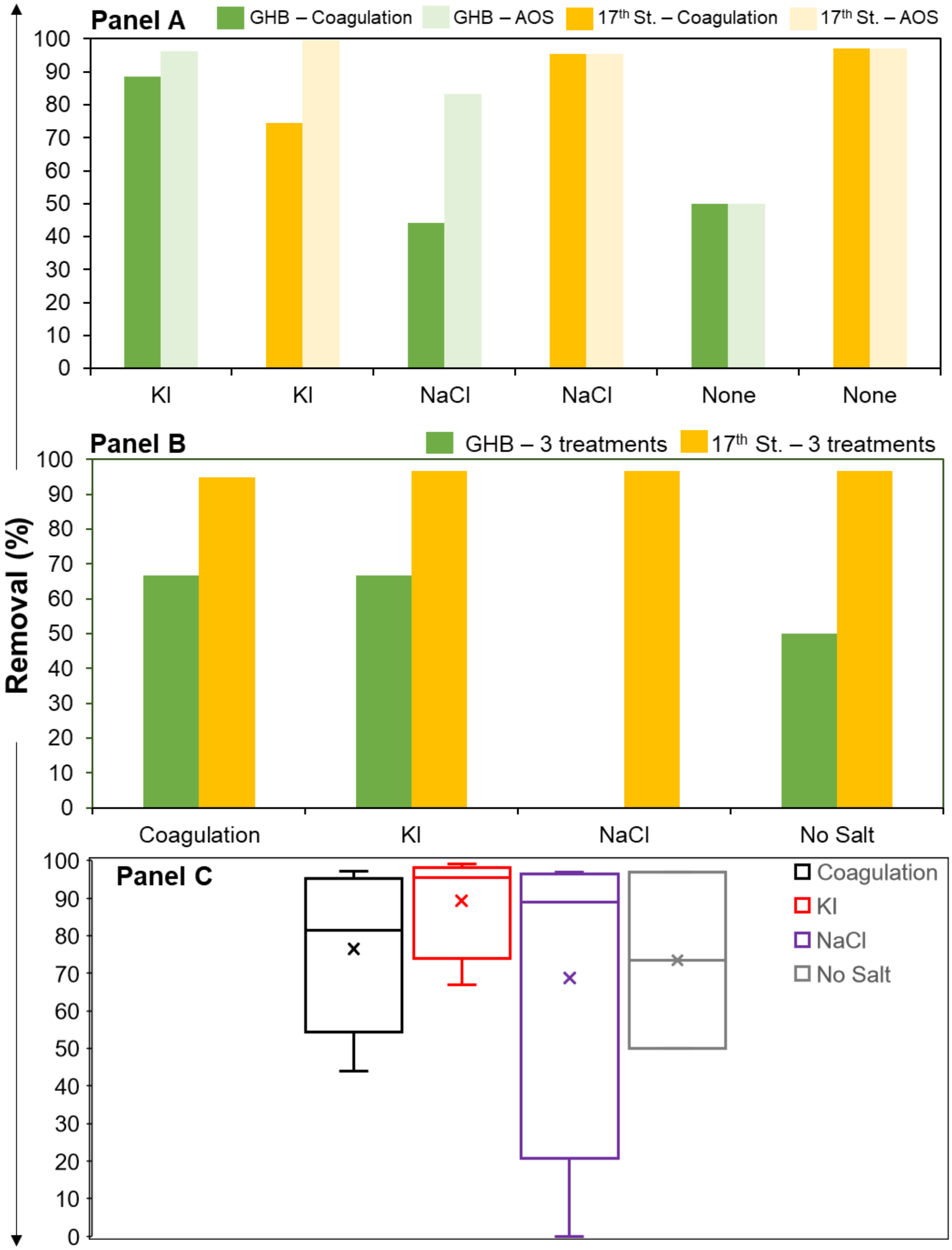

Figure 3-5: Percent removals for TSS including: (A) post-coagulation and post-AOS for the GHB and 17th St. W. outfall samples collected on during separate storm events using 3 treatments; (B) post-coagulation and post-AOS for the GHB and 17th St. W. outfall sample; (C) Boxplots of all experimental combined for post-coagulation and post-treatment results.

(Harper & Herr, 1987; Nyström et al., 2019; Sansalone & Kim, 2008). Thus, the TSS removal efficiency could be increased by using synthetic coagulants and/or polymers; however, even at lower dosages the overall costs of these more novel C/F chemicals may not be economically feasible for use in SW treatment processes.

3.3.2.5 *Escherichia coli* Results

The results for the *E. coli* removal (log removal) are presented in Figure 3-6 including post-C/F and post-AOS results for the three individual treatments covering six storm events (three each for GHB and 17th St. W outfalls) (Panel A) and all three treatments used for two storm events (one for each outfall) (Panel B). The Panel C includes a set of four boxplots summarizing all post-C/F *E. coli* removal results and all individual treatment processes post-AOS *E. coli* removal results. A similar set of figures showing results for the actual *E. coli* concentrations (log MPN/100mL) are presented in Appendix B (Figure B-8).

Generally, the C/F process was able to remove between 0 to 1.0 log of the *E. coli* with an average of 0.8 log removal for all SW samples (Figure 3-6C). Overall, the raw SW samples had *E. coli* concentrations between 1.8 and 3.5 log MPN/100ml with an average of 2.75 log MPN/100mL (Table 3-2 and Figure B-8). Following the C/F process, the complete AOS process train removed between 0.3-3.5 log *E. coli* with the highest overall removal for the KI treatments (2.3 log), followed by the NaCl (1.3 log) and then No Salt (1.0 log) treatments (Figure 3-6C). Both KI and NaCl treatments achieved markedly higher *E. coli* log removal for the 17th St. W outfall, while the No Salt treatment had higher *E. coli* log removal for the GHB outfall vs. the 17th St. W outfall. Clearly, the KI treatment achieved the highest *E. coli* removals overall having about 1 log average higher removal rate (Figure 3-6B) than the NaCl treatment making the use of KI the recommended option for maximum SW disinfection capability.

Overall, the current results are not surprising as the AOS with KI addition has previously shown excellent disinfection capabilities for synthetic SW in Chapter 2 and was initially designed for the disinfection of various wastewaters. In addition, other eAOP systems have been shown to be effective in the disinfection of various wastewaters (Cano et al., 2012; W. Feng et al., 2019; W. Feng, McCarthy, Henry, et al., 2018; Hussain et al., 2014; Rajab et al., 2015). For example, Feng et al. (2018) studied the effectiveness of an eAOP to disinfect municipal SW. Their eAOP used a BDD anode and a current density of 4.2 mA/cm^2 to achieve total disinfection (up to 4 log removal) of *E. coli*. In general, the primary eAOP disinfection mechanisms include the creation of chloride

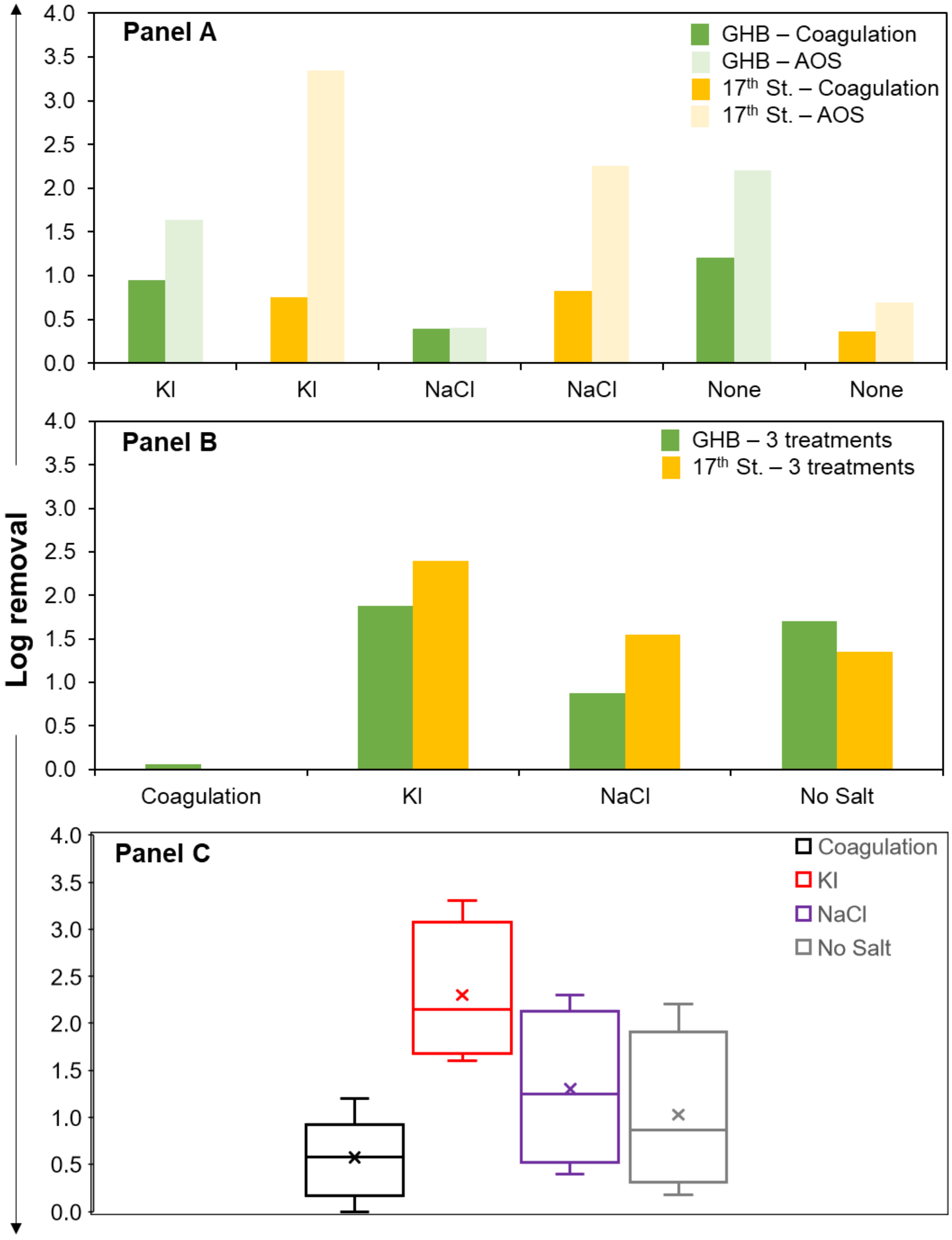

Figure 3-6: Log removals for *E. coli* including: (A) post-coagulation and post-AOS for the GHB and 17th St. W. outfall samples collected on during separate storm events using 3 treatments; (B) post-coagulation and post-AOS for the GHB and 17th St. W. outfall samples; (C) Boxplots of all experimental combined for post-coagulation and post-treatment results

oxidative species and reactive oxygen species such as hydroxyl radicals, ozone, and hydrogen peroxide (Cano et al., 2012; W. Feng, McCarthy, Henry, et al., 2018; Rajab et al., 2015).

The AOS with the KI treatment is a promising technology for use in the disinfection of SW with an almost complete removal (up to 3.5 log) of *E. coli* in the current study. In addition, the AOS achieved similar disinfection results as Feng et al. (2018) while using a lower current density (2 vs 4.2 mA/cm^2) by using KI vs. NaCl in the previous study. Thus, the iodide oxidative species created within the AOS (as shown in Chapter 2) with KI addition are likely more effective for the purposes of disinfection as compared to chloride oxidative species. Despite its success in disinfection, the creation of DBPs by eAOPs such as the AOS should be monitored in the SW treatment process in the future to ensure the AOS does not add toxicity to the SW effluents. In general, the formation of DBPs by eAOPs are of concern and can limit the use of eAOPs for disinfection purposes (W. Feng, McCarthy, Henry, et al., 2018; Rajab et al., 2015).

3.4 Conclusions

In conclusion, the optimized AOS performed well for the disinfection of SW while the AOS treatment process train also allowed for high TSS removals and adequate COD and TOC removal rates. The C/F pre-treatment step using either ferric chloride or alum primarily removed TSS from the SW prior to treatment by the AOS, while additionally removing a portion of the SW COD, TOC, and *E. coli*. In addition, the KI or NaCl salts both lead to enhanced treatment by the AOS as compared to the treatment with no salt added. The KI treatment led to the highest removal percentages for COD and *E. coli*, while the NaCl treatment had the highest TOC removal. Overall, the optimal AOS conditions for *E. coli* disinfection of SW was the use of KI with a resultant 2 mA/cm^2 current density for the 6 chamber reactor. However, under the same conditions, the AOS did not work as well for organics decontamination as indicated by COD and TOC removals. Thus, further investigation should be done in future work to optimize the AOS SW decontamination capability while maintaining its effectiveness at decontamination. For example, the AOS could be optimized for organics removal by increasing the applied current density and increasing the SW treatment time (e.g., increasing the number of reactor chambers or decreasing the flow rate). In addition, disinfection and organic by-products (DBPs and OBPs) are of concern when treating wastewaters with eAOPs so future work should include the monitoring DBPs and OBPs in the AOS effluents after the SW treatment process.

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Chapter 4 : Discussion and Future Recommendations

4.1 General Discussion

Stormwater (SW) management by water agencies has traditionally focused on water pollution and flood mitigation. However, SW storage and beneficial reuse has become of increasing interest in areas where water scarcity is an issue. The adequate reduction of common contaminants found in SW, such as fecal coliforms and organics, are required to meet the water quality criteria needed for potential SW reuse. There are many technologies that have been developed for SW treatment including wetlands and ponds, biofilters, membrane separation processes (MSPs), and electrochemical (EC) treatment processes as presented in Chapter 1 of this thesis. However, wetlands, biofilters, and MSPs are not typically designed to provide SW disinfection and/or decontamination capabilities that would be required for creating beneficial reuse waters. In addition, these technologies have limitations such as large land use area requirements, impacts of cold climates negatively affecting treatment efficiencies, and potentially labor-intensive and costly maintenance requirements.

A viable SW treatment technology must address these limitations such as being able to treat SW in a compact footprint, being versatile in a variety of operation conditions, and having low maintenance requirements. The electrochemical Advanced Oxidation Process (eAOP) technologies can have the potential to provide for an efficient, low cost treatment methodology that allows for both disinfection and decontamination capabilities of a variety of wastewaters. However, eAOPs have not been widely researched for SW treatment; thus, further research is needed to optimize and determine the treatment effectiveness of these technologies for SW treatment. An industry partner has developed an eAOP known as the Advanced Oxidation System (AOS) that was used in a laboratory scale for studies presented in Chapter 2 and 3 of this thesis. The AOS results in the creation of oxidants, such as iodide and chloride oxidative species, for the treatment of a variety of wastewaters. In this thesis, the AOS was optimized for the creation of useful iodide and chloride oxidative species for wastewater treatment (Chapter 2) and assessed for its effectiveness for treating synthetic SW (Chapter 2) and real SW (Chapter 3).

In Chapter 2, the concentrations of iodate and periodate created from iodide addition and chlorite and chlorate created from chloride addition were determined in the AOS reactor.

Operating parameters assessed included the impacts of various salt concentrations and input voltages on the creation of these oxidative species. The input salt concentrations used included 10, 25, and 50 ppm potassium iodide (KI) or sodium chloride (NaCl), while the applied voltages included 6, 12 and 24 V. The effect of tap water on the concentration of the oxidative species was also investigated. The oxidative species were determined using a UV-vis spectrophotometric method that was developed for measurement of the concentrations of both iodide and chloride species as part of this thesis. The dominant oxidative species were found to be iodate with iodide addition and chlorite with chloride addition. For iodide, the optimal conditions for creation of oxidative species was found to be 10 ppm KI and 12 V. Similarly, the 10 ppm NaCl and 6 V conditions were optimal for chloride. Overall, KI experiments resulted in the creation of a larger percentage of iodate, which has been shown to be an effective oxidant. Similarly, chlorite was formed with NaCl addition. The tap water treatment resulted in increased concentrations of both iodide and chloride oxidative species as measured using the spectrophotometric method. Chloride is typically found in detectable concentrations for the City of Saskatoon tap water, while the tap water ions results in increased conductivity for this treatment. Both of these tap water specific conditions may have led to the increased oxidative species concentrations for this treatment. Limitations for the oxidative species experiments included not repeating analysis for each operating condition due to time constraints. In addition, a larger range of applied voltage and salt concentrations could have been studied.

The treatment of synthetic SW was also assessed in Chapter 2 with two individual experiments using different AOS reactor designs and subsequent operating parameters. The first set of experiments focused on the disinfection of *E. coli* using a 2-inch, 12 chamber AOS reactor. A 10 ppm KI with a 3 mA/cm^2 current density was used to treat the synthetic SW resulting in excellent disinfection with a complete 6-7 log removal of *E. coli* after the first 15 minutes of treatment. A 1-inch, 6 chamber AOS with 5 ppm KI and a 2 mA/cm^2 current density was used for the second set of experiments where the simultaneous disinfection and decontamination (via organic removal) of the AOS was assessed. For these experiments, the AOS repeated its excellent disinfection performance for synthetic SW, while exhibiting potential for the successful removal of organics. Overall, in Chapter 2 the AOS was shown to produce oxidative species with disinfection and decontamination capabilities which indicated that it has the potential for effective SW treatment. The disinfection and decontamination capability of the AOS was assessed in the

Chapter 3 research project. Research limitations for synthetic stormwater included the development of a standard synthetic stormwater for the City of Saskatoon stormwater and additional treatment testing.

In Chapter 3, the effectiveness of the AOS for the treatment of real SW was assessed using three treatments including 5 ppm KI, 5 ppm NaCl, and no salt addition. Stormwater was collected from four outfalls in the City of Saskatoon, three during wet weather events and one during a dry weather event. The effectiveness of the AOS was assessed through determination of the disinfection of *E. coli*, the organics removal as represented by the parameters of chemical oxygen demand (COD) and total organic carbon (TOC), and solids reduction using total suspended solids (TSS) and total dissolved solids (TDS). The 1-inch, 6 chamber AOS reactor using a 2 mA/cm^2 current density was used for experiments in this study.

A C/F pre-treatment process using alum or ferric chloride was used to minimize the solids entering the AOS. Coagulation/flocculation removed an average TSS of 80% which shows that C/F was effective for suspended solids removal. The AOS further removed TSS to achieve above 90% TSS removal after AOS treatment process train. Despite the C/F process providing adequate TSS removal for real SW, previous studies have shown up to 98% TSS removal through the use of synthetic coagulants and polymers. Future work could include assessment of alternate coagulants (and potentially other pre-treatment processes) for cost-effective, increased SW TSS removal.

The AOS showed excellent disinfection of *E. coli* with an average of 2.3 log removal for the KI treatment. The NaCl and no salt treatments were not as effective with averages of 1.3 and 1.0 log removals, respectively. It should be noted that C/F removed an average of 0.5 log *E. coli*, however, the AOS reactor was the primary disinfection treatment process. The KI and NaCl treatments had similar effectiveness for the removal of COD with the AOS removing 52% with KI and 48% with NaCl. The KI treatment COD removal was lower than other eAOPs presented in literature (showing up to 100% removal) mainly due to the higher current densities used in previous studies. The AOS TOC removal was 30% and 70% for the KI and NaCl treatments, respectively. Overall, the use of NaCl is recommended for optimal organics removal using the current AOS operating conditions.

Overall, the AOS showed excellent disinfection effectiveness, as expected by the design and operating parameters of the AOS that was considered primarily for disinfection of wastewaters. However, the AOS was not designed for organics removal as indicated by the lower removal of COD and TOC. A higher current density, longer treatment time, and different electrode materials could be used to potentially increase the organic removal effectiveness by the AOS. Limitations for this chapter included further testing organic removal and different coagulation/flocculation and pre-treatment processes.

4.2 Engineering Significance

In Chapter 2, the oxidative iodide and chloride species formed in the AOS were investigated. Knowing the type of oxidative species created within the AOS was important for understanding the possible AOS treatment mechanisms and assessing the potential hazardous species formed. The determination of the species concentrations formed within the AOS anodes and cathodes was used to ensure that the AOS is functioning as designed (e.g., oxidation of salts at the anodes and reduction at the cathodes). In addition, comparing the concentration of species formed using different salt concentrations and voltage applied was used to optimize the operating parameters of the AOS. The optimal operating parameters had the highest percentage of "useful" oxidative species created, while minimizing the input salt concentrations and applied voltage to help to limit operating costs.

The treatment of synthetic SW was also assessed in Chapter 2. Synthetic SW was developed to be representative of real SW, such as having similar *E. coli* and organics concentrations. The purpose of considering synthetic SW is to have a SW for treatment testing that can be made in a laboratory setting and used to minimize the costs and logistics of real SW collection. The synthetic SW can also be used as a standard to compare different treatment systems and operating parameters between studies

The effectiveness of real SW treatment was investigated in Chapter 3. Real SW contains a variety of pollutants and is an overly complex matrix that would not be feasible to mimic in synthetic SW. In addition, real SW quality varies with outfall location, amount of rainfall and season. The use of real SW is important to assess treatment processes such as the AOS. Stormwater C/F pre-treatment was an important process to reduce the solids loading into the AOS. The C/F process was done to help to minimize clogging of the AOS and to increase the effectiveness and lifetime of the AOS reactor. Coagulation/flocculation using alum or ferric chloride was used in this thesis as it is commonly used in various wastewater treatments. However other coagulants, and other pre-treatment methods such as filtration, could be tested in future work. The AOS in the current operating parameters and design (1-inch, 6 chamber reactor, 5 ppm KI and 2 mA/cm^2 current density) worked well for disinfection but not as well for organics removal. The operating parameter AOS could be optimized for organic removal by increasing the current density (increasing current applied) and the hydraulic residence time. Lastly, the formation of disinfection and organic by-products (DBPs and OBPs) are a concern for any electrochemical treatment system, so the formation of these products by the AOS and toxicity of treated effluent should be investigated in future work.

Treated stormwater could be reused for many applications such as non-potable uses such as irrigation and toilet water. A commonly used standard used for stormwater quality required for reuse is the NSF 350 standard (Bruursema, 2011). The standard describes average and maximum allowable concentrations of contaminants for reuse, such as BOD, TSS, *E. coli*. Comparing this standard to the SW results in this thesis can be used to determine if the AOS can adequately treat SW for reuse. Chemical oxygen demand was used as an organics indicator for this thesis, however the COD/BOD ratio can be estimated to be 2-2.5 based on research by Servais et. al (1999). The average and maximum allowable BOD for reuse is 10 and 25 mg/L respectively. The AOS with KI achieved an estimated average BOD of 30-40 mg/L. This shows that the AOS does not adequately remove BOD for reuse. The allowable average and maximum TSS for reuse is 10 and 30 mg/L. The AOS treatment process with coagulation/flocculation achieved an average and maximum 0.44 and 1.76 mg/L TSS after treatment. Thus, TSS after treatment is adequate for reuse. The allowable *E. coli* concentration for reuse an average of 14 and a maximum of 240 MPN/100 mL. The treated stormwater after the AOS with KI had an average of 3 MPN/100mL and a maximum of 57 MPN/100mL. The AOS also achieved the required *E. coli* removal for non-potable stormwater reuse.

4.3 Future Work

Potential future work for treatment of stormwater with the AOS could include:

- Investigating the creation of additional oxidative species formed by the AOS such as hydroxyl radicals. This could be accomplished for both synthetic and real SW matrices.

- Development of a standard synthetic SW that can be used to compare varying operating parameters. Currently the synthetic SW recipes are variable with no definitive standard being considered in the literature.
- Using different coagulants for C/F should be investigated such as synthetic coagulants and polymers that would more effectively remove solids. However, costs for these more novel coagulants would also need to be considered for SW treatment applications.
- Assessing the use of different pre-treatment processes such as filtration. This would eliminate the costs associated with coagulant purchases and potentially limit the production of sludges which were not considered in the current thesis.
- Further assessing and optimizing the AOS for organics removal. The current AOS was designed primarily for disinfection but it is expected that disinfection would remain high even if the AOS organics removal was improved.
- Assessing the AOS for the removal of other SW contaminants such as heavy metals and polyaromatic hydrocarbons (PAHs). This was beyond the scope of the current thesis due to analytical costs, especially for PAH analyses.
- Measuring the concentration of organic and disinfection by-products in the treated SW. This was also beyond the scope of the current thesis due to the unknown nature of these by-products and the associated analytical costs for their investigation.
- Comparing the toxicity of the SW before and after treatment. Toxicity assessment is currently being considered for the real SW samples collected as part of a parallel study. However, assessment of toxicity after treatment would be important for the AOS.
- Scaling up the treatment process and the AOS to process larger volumes of SW.

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Appendix A: Chapter 2 Supplementary Information

A.1 XANES results

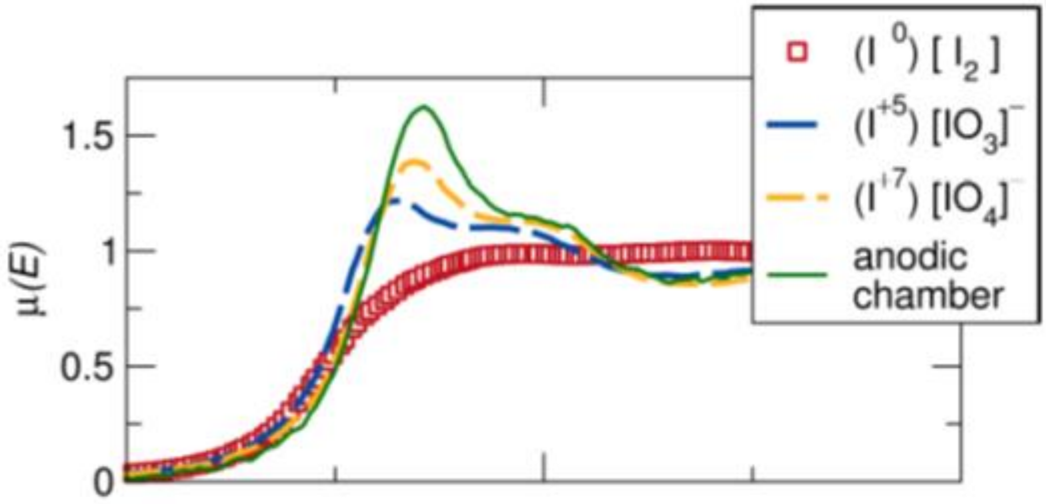

Figure A-1: K edge X-ray spectroscopy performed at the HXMA beamline at the Canadian Light Source for iodide species created in the AOS using 1,000 ppm KI solution (anodic chamber). Stock 1,000 ppm iodate (IO3-) and periodate (IO4-) solution curves are also shown while the reactor voltage was turned off. Results currently in preparation for publication as part of a parallel research study.

A.2 Buffers

Table A-1: Buffers used for pH adjustment of iodide and chloride samples.

pH	**Chemical 1**	**Amount (mL)**	**Concentration (M)**	**Chemical 2**	**Amount (mL)**	**Concentration (M)**
2	KCl	5	0.20	HCl	4.14	0.2
4	$C_8H_5KO_4$	100	0.10	NaOH	2.6	0.1
6	$Na_2HPO_4 \cdot 7H_2O$	250	0.0137	NaH_2PO_4	250	0.0863
9.7	$NaHCO_3$	50	0.14	Na_2CO_3	50	0.063

A.3 Calibration Curves

A.3.1 Iodide

For IO_4 at pH 6:

Absorbance = 0.0539 [IO_4] mg/L + 0.0349

For IO_3 and IO_4 at pH 2:

If absorbance > 0.9
Absorbance = 0.185 [IO_4] mg/L + 0.132 [IO_3] mg/L + 0.314

If absorbance < 0.9
Absorbance = 0.278 [IO_4] mg/L + 0.201 [IO_3] mg/L + 0.0322

Table A-2: Absorbances for calibration curves for iodate and periodate at pH 2.

IO_3^- (mg/L)	IO_4^- (mg/L)	Absorbance
0.88	2.68	0.894
2.65	0.89	0.756
0.88	1.34	0.532
1.33	0.89	0.488
0.88	0.89	0.342
1.33	1.34	0.605
0.44	0.45	0.18
0.22	0.22	0.083
0.09	0.09	0.022
1.33	2.678	0.963
2.65	1.339	0.918
1.33	5.355	1.612
5.3	1.339	1.383
2.21	2.231	0.909
2.65	2.678	1.135
3.54	3.57	1.337
4.42	4.463	1.759
6.63	6.694	2.372

Table A-3: Absorbances for calibration curves for iodate and periodate at pH 6.

IO_3^- (mg/L)	IO_4^- (mg/L)	Absorbance
0	0	0
0.88	0.89	0.061
1.33	1.34	0.093
2.21	2.23	0.144
2.65	2.68	0.167
3.54	3.57	0.239
4.42	4.46	0.284
6.63	6.69	0.384
8.84	8.93	0.549
22.1	22.3	1.26
44.2	44.6	2.468
0.88	2.68	0.142
0.88	4.46	0.26
0.88	6.69	0.426
0.88	8.93	0.55
0.88	22.3	1.316
0.88	44.6	2.398

A.3.2 Chloride

For ClO at pH 9.8 and 291nm:

Absorbance = 0.029 [ClO] mg/L + 0.0698

For ClO and ClO_2 at pH 4 and 381 nm:

When [ClO]> 6 mg/L
Absorbance = 0.0119 [ClO] mg/L + 0.0596 [ClO_2] mg/L – 0.0304

When [ClO] < 6 mg/L
Absorbance = 0.0596 [ClO_2] mg/L + 0.038

For ClO and ClO_2 and ClO_3 at pH 4 and 300 nm:

When [ClO] and [ClO_2] > 10 mg/L
Absorbance = 0.0182 [ClO] mg/L + 0.0137 [ClO_2] mg/L – 0.0193[ClO_3] + 0.3885

When [ClO] < 10 mg/L and [ClO_2] > 10 mg/L
Absorbance = 0.0137 [ClO_2] mg/L – 0.0193[ClO_3] – 0.2548

When [ClO] and [ClO_2] < 10 mg/L
Absorbance = 0.0825 [ClO_2] mg/L – 0.0193[ClO_3] – 0.1077

Table A-4: Absorbances for the calibration curve for hypochlorite at pH 9.8 and 291nm.

ClO^-(mg/L)	**Absorbance**
34.555	1.064
17.2775	0.584
8.63875	0.324
4.319375	0.193
3.4555	0.174
1.72775	0.113
0.6911	0.085

Table A-5: Absorbances for calibration curves for hypochlorite and chlorite at pH 4 and 381nm.

ClO^-(mg/L)	Absorbance	ClO_2^-(mg/L)	Absorbance
34.555	0.34	37.3	2.201
17.2775	0.143	18.65	1.218
8.63875	0.032	9.325	0.73
6.911	0.012	4.6625	0.295
4.319375	0	3.73	0.254
		1.865	0.096
		0.746	0.02

Table A-6: Absorbances for the calibration curves for hypochlorite, chlorite and chlorate at pH 4 and 300nm.

ClO^- (mg/L)	Absorbance	ClO_2^- (mg/L)	Absorbance	ClO_3^- (mg/l)	ClO_2^-+ ClO_3^- Absorbance	Absorbance from ClO_3^-
34.555	0.411	37.3	1.142	21.22065	0.69	-0.452
27.644	0.351	18.65	0.943	10.61033	0.606	-0.337
20.733	0.225	9.325	0.743	5.305163	0.568	-0.175
17.2775	0.122	4.6625	0.342	2.652581	0.338	-
13.822	0.044	3.73	0.25	2.122065	0.157	-0.093
10.3665	0	1.865	0.1	1.061033	0.026	-0.074
		0.746	0.054	0.424413	0.026	-

A.4 Raw Data

A.4.1 Iodide Data

Table A-7: Absorbances and corresponding concentrations of IO_3^- and IO_4^- for the 10ppm KI treatment at various voltages

Sample port	**Absorbance pH 6**	**Absorbance pH 2**	**IO_4^- (mg/L)**	**IO_3^-(mg/L)**
6V				
A1	0	0	0	1.60
A2	0	0.034	0	3.29
A3	0	0.053	0	4.24
A4	0	0.083	0	5.73
A5	0	0.063	0	4.73
C1	0	0	0	1.60
C2	0	0.07	0	5.08
Outlet	0	0.109	0	7.02
12V				
A1	0	0	0	1.60
A2	0	0.036	0	3.39
A3	0	0.154	0	9.26
A4	0	0.137	0	8.41
A5	0	0.138	0	8.46
C1	0	0.007	0	1.95
C2	0	0.152	0	9.16
Outlet	0	0.173	0	10.20
24V				
A1	0.041	0.076	1.13	3.82
A2	0.037	0.068	0.39	4.45
A3	0.104	0.724	12.81	19.92
A4	0.039	0.122	0.76	6.62
A5	0.038	0.213	0.57	11.40
C1	0.039	0.186	0.76	9.80
C2	0.039	0.221	0.76	11.54
Outlet	0.036	0.247	0.20	13.61

Table A-8: Absorbances and corresponding concentrations of IO_3^- and IO_4^- for the 25ppm KI treatment at various voltages

Sample port	**Absorbance pH 6**	**Absorbance pH 2**	**IO_4^-(mg/L)**	**IO_3^-(mg/L)**
6V				
A1	0.041	0	1.13	0.04
A2	0.046	0.027	2.06	0.10
A3	0.04	0.079	0.94	4.23
A4	0.036	0.094	0.20	6.00
A5	0.036	0.093	0.20	5.95
C1	0.037	0	0.39	1.07
C2	0.037	0.068	0.39	4.45
Outlet	0.036	0.29	0.20	15.74
12V				
A1	0.04	0.064	0.94	3.48
A2	0.042	0.133	1.31	6.40
A3	0.04	0.53	0.94	26.66
A4	0.04	0.325	0.94	16.46
A5	0.043	0.408	1.50	19.82
C1	0.04	0.209	0.94	10.69
C2	0.04	0.285	0.94	14.47
Outlet	0.042	0.582	1.31	28.73
24V				
A1	0	0.092	0.00	6.18
A2	0	0.013	0.00	2.25
A3	0.123	0.866	16.33	22.12
A4	0	0.112	0.00	7.17
A5	0	0.237	0.00	13.39
C1	0	0.31	0.00	17.02
C2	0	0.215	0.00	12.29
Outlet	0	0.248	0.00	13.93

Table A-9: Absorbances and corresponding concentrations of IO_3^- and IO_4^- for the 50ppm KI treatment at various voltages

Sample port	**Absorbance pH 6**	**Absorbance pH 2**	**IO_4^- (mg/L)**	**IO_3^- (mg/L)**
6V				
A1	0.036	0	0.20	4.16
A2	0.008	0.027	0.00	7.67
A3	0.048	0.079	2.43	10.68
A4	0.016	0.094	0.00	7.77
A5	0.055	0.093	3.72	11.97
C1	0.026	0	0.00	2.05
C2	0.036	0.068	0.20	12.21
Outlet	0.03	0.29	0.00	14.08
12V				
A1	0.11	0.202	13.92	0.00
A2	0.001	0.242	0.00	13.64
A3	0.053	0.707	3.35	32.13
A4	0	0.271	0.00	15.08
A5	0.062	0.706	5.02	29.78
C1	0	0.113	0.00	7.22
C2	0.027	0.713	0.00	37.06
Outlet	0.024	0.892	0.00	45.96
24V				
A1	0.023	0.804	0.00	41.59
A2	0	0.331	0.00	18.06
A3	0.053	1.208	3.35	63.27
A4	0	0.703	0.00	36.56
A5	0	0.936	0.00	47.31
C1	0	0.261	0.00	14.58
C2	0	0.959	0.00	49.06
Outlet	0	0.904	0.00	44.88

Table A-10: Absorbances and corresponding concentrations of IO$_3^-$ and IO$_4^-$ for the 50ppm KI using tap water treatment at various voltages.

Sample port	**Absorbance pH 6**	**Absorbance pH 2**	**IO$_4^-$ (mg/L)**	**IO$_3^-$ (mg/L)**
6V				
A1	0.017	0.231	0.00	13.09
A2	0	0.134	0.00	8.26
A3	0.047	0.843	2.24	40.43
A4	0	0.428	0.00	22.89
A5	0.007	0.54	0.00	28.46
C1	0	0.239	0.00	13.49
C2	0	0.646	0.00	33.73
Outlet	0.018	0.662	0.00	34.52
12V				
A1	0.014	0.359	0.00	19.45
A2	0	0.12	0.00	7.57
A3	0.238	2.422	37.65	107.35
A4	0	1.363	0.00	79.77
A5	0.111	1.538	14.11	73.24
C1	0	0.341	0.00	18.56
C2	0	0.883	0.00	45.52
Outlet	0.042	1.526	1.31	90.32
24V				
A1	0	0.559	0.00	29.40
A2	0	0.413	0.00	22.14
A3	0.172	1.561	25.41	59.09
A4	0	0.284	0.00	15.72
A5	0	0.99	0.00	51.41
C1	0	0.526	0.00	27.76
C2	0	0.834	0.00	43.08
Outlet	0	1.419	0.00	84.03

A.4.2 Chloride Data

Table A-11: Absorbances and corresponding concentrations of ClO^-, ClO_2^- and ClO_3^- for the 10ppm NaCl treatment.

Sample port	**Absorbance pH 9.7**	**Absorbance pH 4 381nm**	**Absorbance pH 4 300nm**	**ClO^- (mg/L)**	**ClO_2^- (mg/L)**	**ClO_3^- (mg/L)**
6V						
A1	0.069	0.048	0.034	0.00	1.68	0
A3	0.068	0.073	0.086	0.00	2.94	0
A4	0.062	0.103	0.136	0.00	5.45	0
A5	0.061	0.106	0.155	0.00	5.70	0
C1	0.062	0.085	0	0.00	3.94	0
C2	0.062	0.147	0	0.00	9.14	0
Out	0.064	0.148	0.024	0.00	9.23	7.40
12V						
A1	0.063	0.018	0.043	0.00	0.00	0
A3	0.068	0.039	0.076	0.00	0.05	0
A4	0.064	0.039	0.042	0.00	0.05	0
A5	0.061	0.019	0.021	0.00	0.00	0
C1	0.058	0.021	0.029	0.00	0.00	0
C2	0.062	0.049	0.064	0.00	0.37	0
Out	0.058	0.046	0.142	0.00	0.40	0
24V						
A1	0.004	0.014	0.019	0.00	0.00	0
A3	0	0.059	0.06	0.00	0.70	0
A4	0	0.027	0.055	0.00	0.00	0
A5	0	0.039	0.115	0.00	0.03	0
C1	0	0.027	0.067	0.00	0.00	0
C2	0	0.023	0.049	0.00	0.00	0
Out	0	0.039	0.057	0.00	0.03	0

Table A-12: Absorbances and corresponding concentrations of ClO^-, ClO_2^- and ClO_3^- for the 25ppm NaCl treatment.

Sample port	**Absorbance pH 9.7**	**Absorbance pH 4 381nm**	**Absorbance pH 4 300nm**	**ClO^- (mg/L)**	**ClO_2^- (mg/L)**	**ClO_3^- (mg/L)**
6V						
A1	0	0.225	0.163	0.00	6.28	0
A3	0	0.261	0.136	0.00	11.22	14.03
A4	0	0.201	0.31	0.00	8.20	0
A5	0	0.138	0.251	0.00	8.39	0
C1	0	0.144	0.201	0.00	5.34	0
C2	0	0.162	0.248	0.00	10.40	0
Out	0	0.205	0.261	0.00	5.60	0
12V						
A1	0	0.125	0.164	0.00	4.38	0
A3	0	0.13	0.168	0.00	7.72	0
A4	0	0.253	0.375	0.00	7.21	0
A5	0	0.148	0.266	0.00	3.69	0
C1	0	0.154	0.231	0.00	3.89	0
C2	0	0.175	0.274	0.00	4.60	0
Out	0	0.165	0.256	0.00	4.26	0
24V						
A1	0	0.095	0.11	0.00	1.91	0
A3	0	0.193	0.213	0.00	5.20	0
A4	0	0.09	0.178	0.00	1.74	0
A5	0	0.094	0.236	0.00	1.88	0
C1	0	0.082	0.096	0.00	1.48	0
C2	0	0.091	0.143	0.00	1.78	0
Out	0	0.093	0	0.00	1.85	0

Table A-13: Absorbances and corresponding concentrations of ClO^-, ClO_2^- and ClO_3^- for the 50ppm NaCl treatment.

Sample port	**Absorbance pH 9.7**	**Absorbance pH 4 381nm**	**Absorbance pH 4 300nm**	**ClO^- (mg/L)**	**ClO_2^- (mg/L)**	**ClO_3^- (mg/L)**
6V						
A1	0.051	0.012	0.00	0.00	0.00	0.00
A2	0.05	0	0.00	0.00	0.00	0.00
A3	0.054	0	0.00	0.00	0.00	0.00
A4	0.054	0.035	0.16	0.00	0.00	0.00
A5	0.053	0.041	0.00	0.00	0.15	0.00
C1	0.05	0.006	0.00	0.00	0.00	0.00
C2	0.046	0.02	0.10	0.00	0.00	0.00
Out	0.048	0.062	0.04	0.00	0.81	0.00
12V						
A1	0.00	0.00	0.00	0.00	0.00	0.00
A2	0.00	0.00	0.00	0.00	0.00	0.00
A3	0.00	0.02	0.00	0.00	0.00	0.00
A4	0.00	0.00	0.00	0.00	0.00	0.00
A5	0.00	0.00	0.01	0.00	0.00	0.00
C1	0.00	0.00	0.00	0.00	0.00	0.00
C2	0.00	0.01	0.07	0.00	0.00	0.00
Out	0.00	0.01	0.00	0.00	0.00	0.00
24V						
A1	0.00	0.00	0.00	0.00	0.00	0.00
A2	0.00	0.00	0.00	0.00	0.00	0.00
A3	0.00	0.08	0.04	0.00	1.41	0.00
A4	0.00	0.01	0.02	0.00	0.00	0.00
A5	0.00	0.00	0.00	0.00	0.00	0.00
C1	0.00	0.00	0.00	0.00	0.00	0.00
C2	0.00	0.00	0.00	0.00	0.00	0.00
Out	0.00	0.00	0.00	0.00	0.00	0.00

Table A-14 : Absorbances and corresponding concentrations of ClO^-, ClO_2^- and ClO_3^- for the tap water treatment.

Sample port	Absorbance pH 9.7	Absorbance pH 4 381nm	Absorbance pH 4 300nm	ClO^- (mg/L)	ClO_2^- (mg/L)	ClO_3^- (mg/L)
6V						
A1	0	0.004	0.00	0.00	0.00	0.00
A2	0	0	0.00	0.00	0.00	0.00
A3	0	0.022	0.00	0.00	0.00	0.00
A4	0	0.036	0.06	0.00	0.00	0.00
A5	0	0.038	0.00	0.00	0.00	0.00
C1	0	0.247	0.24	0.00	7.01	0.00
C2	0	0.036	0.05	0.00	0.00	0.00
Out	0	0.112	0.17	0.00	2.48	0.00
12V						
A1	0.00	0.00	0.00	0.00	0.00	0.00
A2	0.00	0.00	0.00	0.00	0.00	0.00
A3	0.00	0.00	0.00	0.00	0.00	0.00
A4	0.00	0.00	0.00	0.00	0.00	0.00
A5	0.00	0.00	0.00	0.00	0.00	0.00
C1	0.00	0.00	0.00	0.00	0.00	0.00
C2	0.00	0.00	0.00	0.00	0.00	0.00
Out	0.00	0.00	0.00	0.00	0.00	0.00
24V						
A1	0.00	0.08	0.13	0.00	1.51	0.00
A2	0.00	0.07	0.07	0.00	1.71	0.00
A3	0.00	0.11	0.14	0.00	2.38	0.00
A4	0.00	0.08	0.11	0.00	1.31	0.00
A5	0.00	0.09	0.00	0.00	1.78	0.00
C1	0.00	0.09	0.00	0.00	1.58	0.00
C2	0.00	0.08	0.07	0.00	1.38	0.00
Out	0.00	0.10	0.00	0.00	2.05	0.00

Table A-15: Stormwater quality data from selected outfalls in the City of Saskatoon from Summer 2018 and 2019. Note DW = dry weather and WW = wet weather; nd = no data

Outfall	Sample type	Date	TOC (mg/L)	COD (mg/L)	E. coli (MPN/100mL)	TSS (mg/L)	EC (µS/cm)	TDS (mg/L)	pH
Avenue BS	DW	June 14/2018	81	46	30	4	1,684	842	8.09
	WW	July 3/2018	93	48	2,000	6	1,420	702	8.02
	WW	July 10/2018	90	344	4,000	330	331	159	8.05
	WW	Aug 13/2018	84	51	<1	<1	1,429	708	7.94
	WW	Aug 26/2018	93	171	2,500	14	1,015	500	7.45
Weir/33rd	DW	June 14/2018	87	78	1,725	8	2,080	1,047	8.14
	WW	July 3/2018	120	68	420	18	1,768	881	8.17
	WW	July 10/2018	72	347	4,000	625	677	329	7.82
	WW	Aug 13/2018	101	123	<1	<1	1,880	942	8.11
	WW	Aug 26/2018	95	177	575	23	1,164	574	7.89
17th St W	WW	June 12/2019	55	334	<1	202	694	337	7.02
	WW	June 20/2019	13	591	850	1,045	620	301	9.14
	WW	July 25/2019	20	124	<1	55	nd	nd	nd
	WW	Aug 22/2019	378	2,711	<1	594	nd	nd	nd
GHB	WW	June 12/2019	17	118	<1	14	1,914	974	8.11
	WW	June 20/2019	14	88	250	84	1,156	570	8.13
	WW	July 25/2019	11	63	245	8	nd	nd	nd
	WW	Aug 22/2019	16	388	270	97	nd	nd	nd

Appendix B : Chapter 3 Supplementary Information

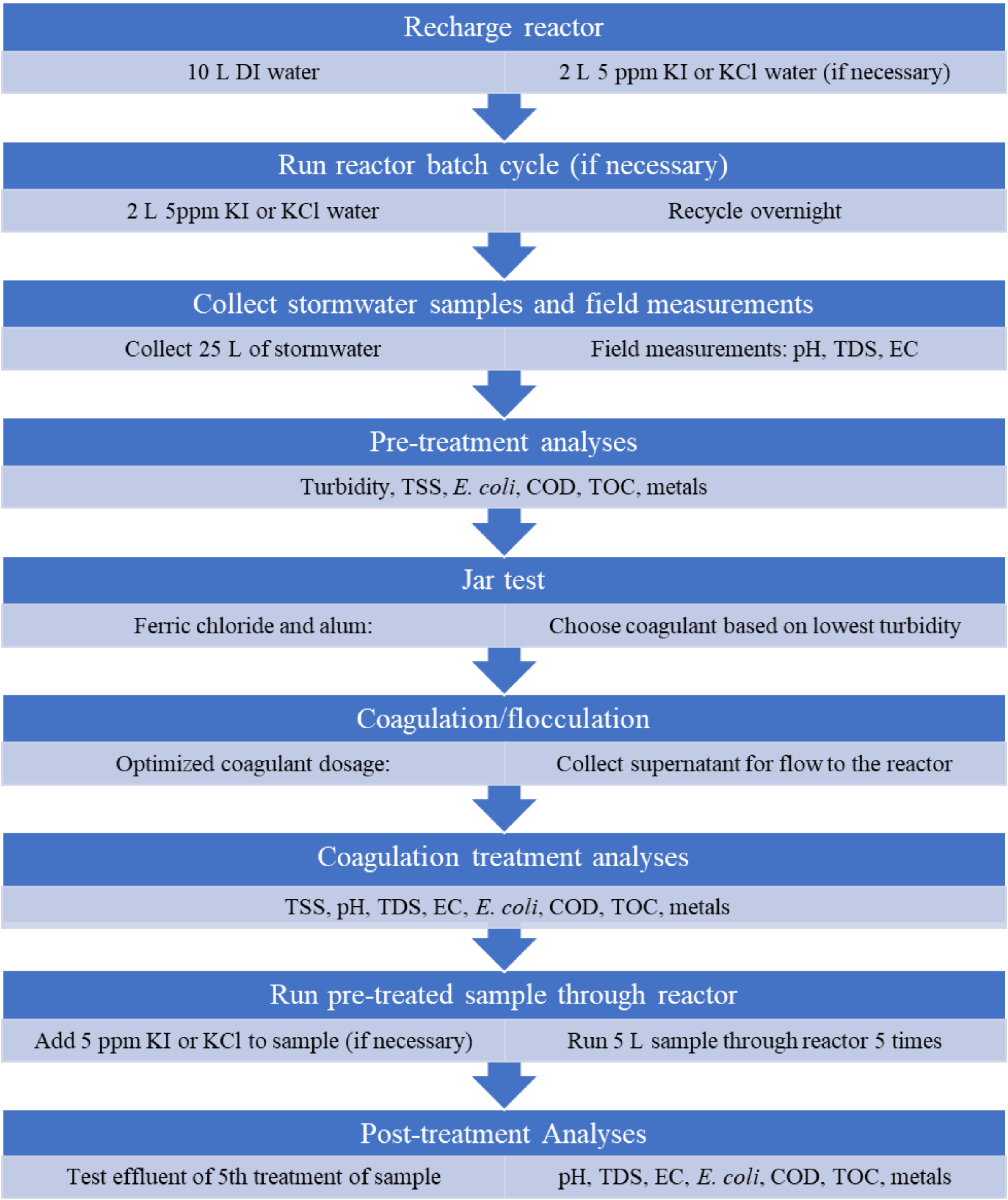

Figure B-1: Summary of the reactor preparation and stormwater treatment process

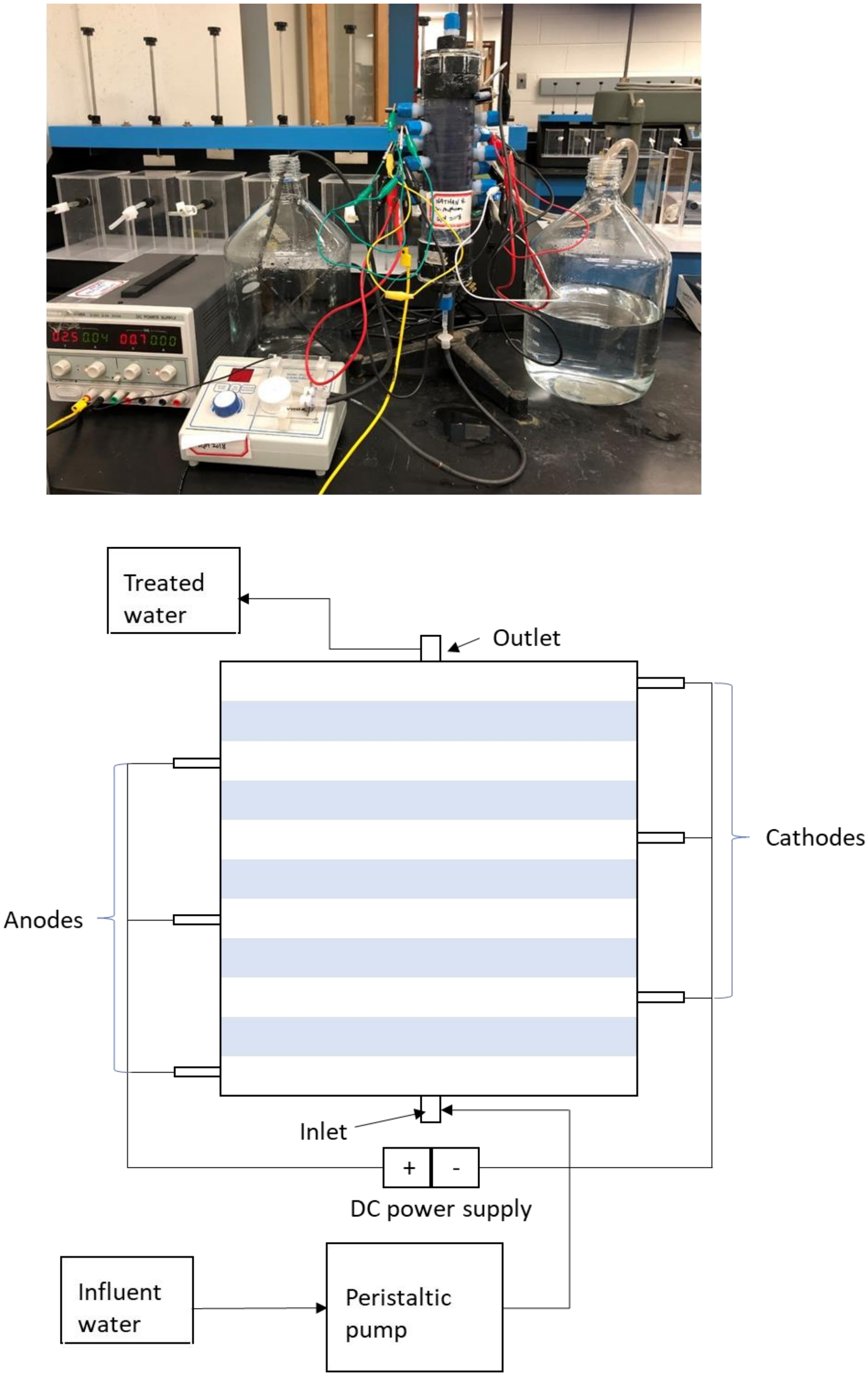

Figure B-2: Upper panel includes a picture of the laboratory apparatus; and the lower panel includes a schematic of AOS reactor.

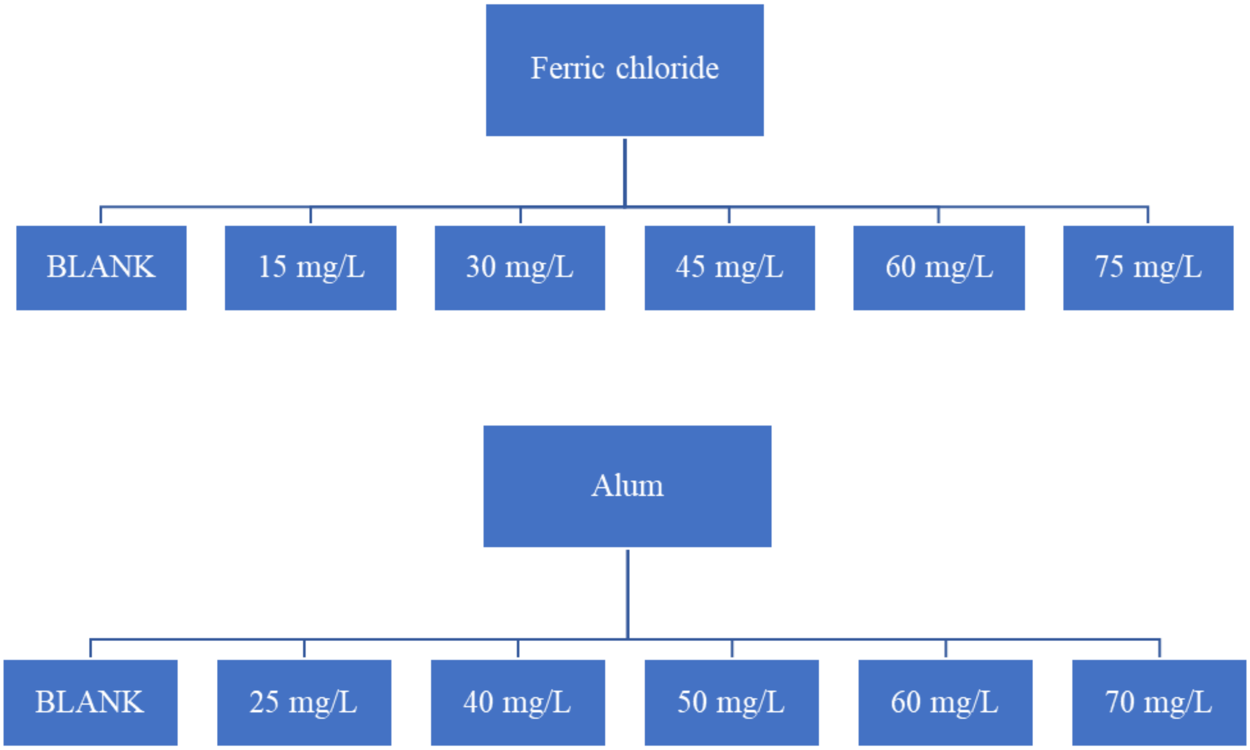

Figure B-3: Jar test parameters for ferric chloride (upper panel) and alum (lower panel).

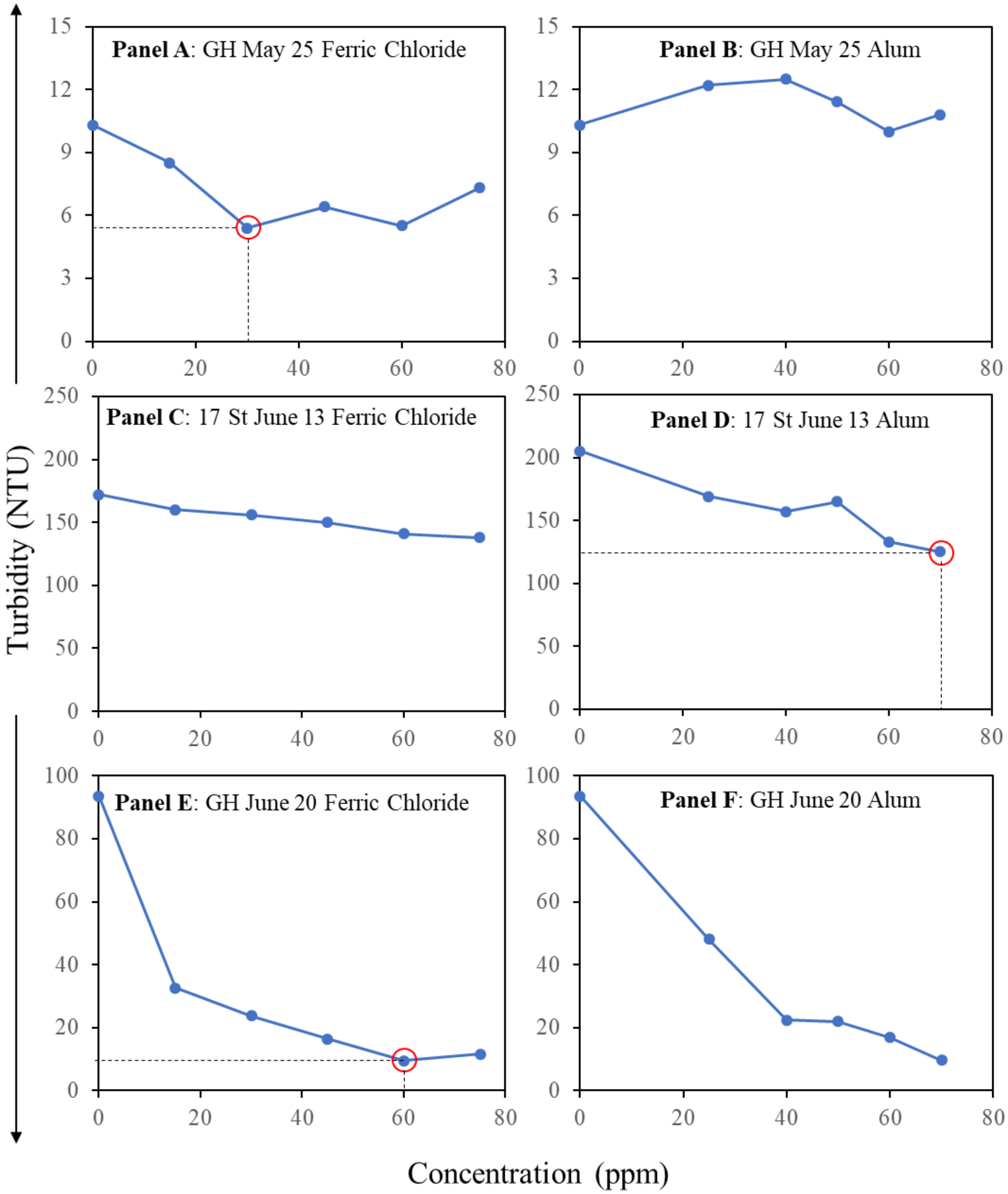

Figure B-4: Stormwater jar test turbidity results for four stormwater samples treated using ferric chloride and alum. The optimum coagulant and dosage are indicated by the red circle for each individual sampling date.

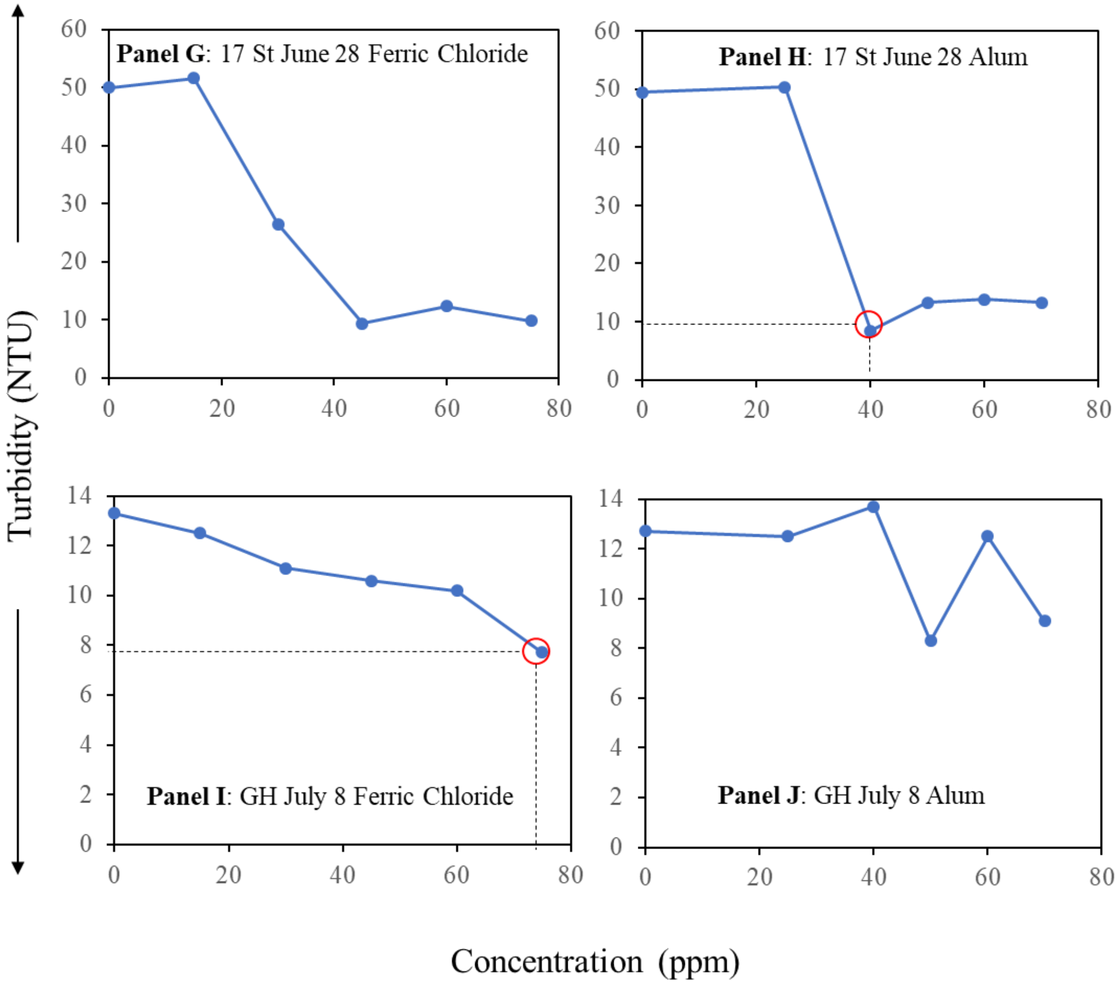

Figure B-4 (cont'd): Stormwater jar test turbidity results for four stormwater samples treated using ferric chloride and alum. The optimum coagulant and dosage are indicated by the red circle for each individual sampling date.

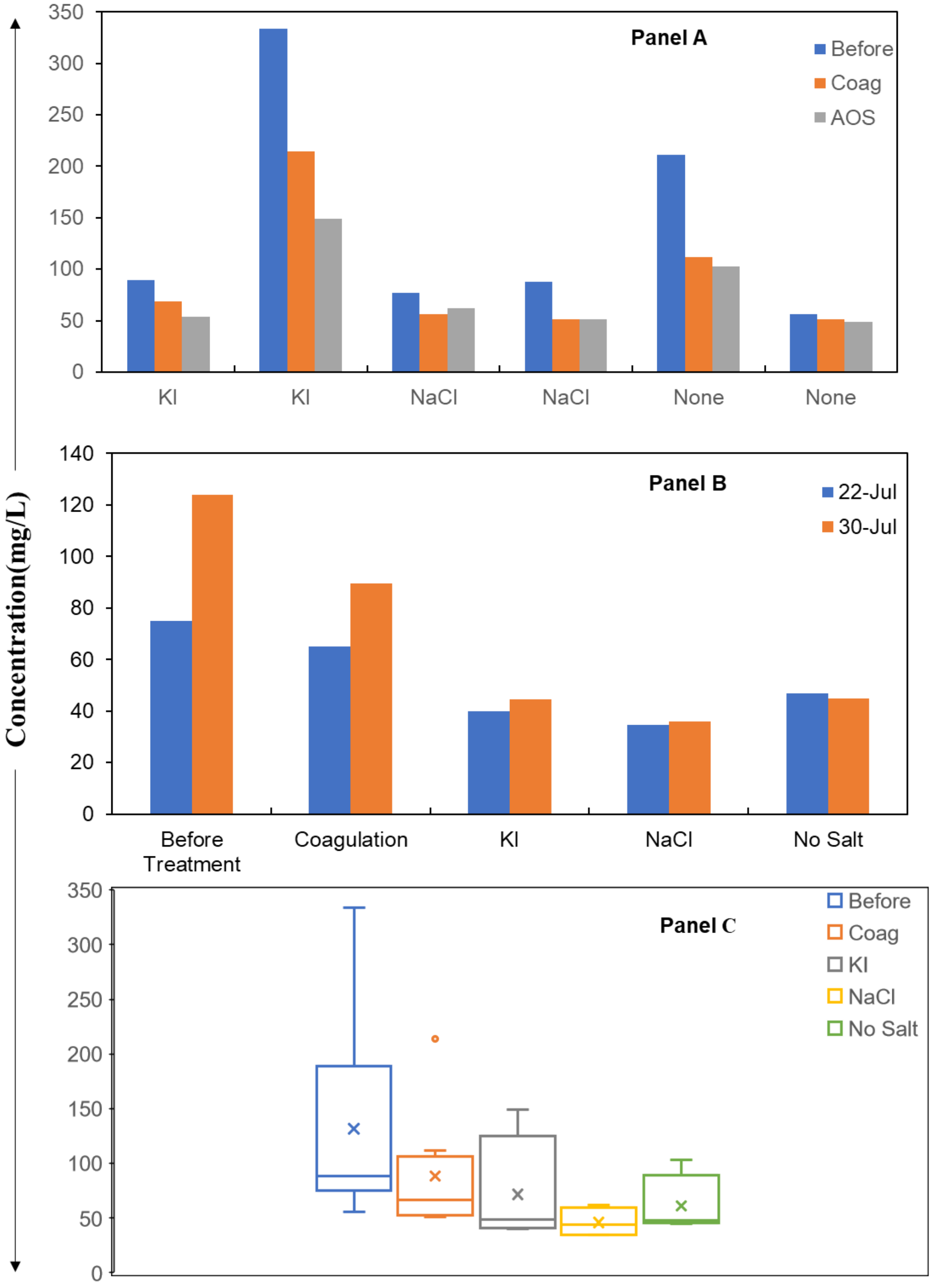

Figure B-5: COD concentrations including: (A) raw, post-coagulation and post-AOS for the GHB and 17th St. W. outfall collected on during separate storm events using 3 treatments; (B) raw, post-coagulation and post-AOS for the GHB and 17th St. W. outfall; (C) Boxplots of all experimental combined for post-coagulation and post-treatment results.

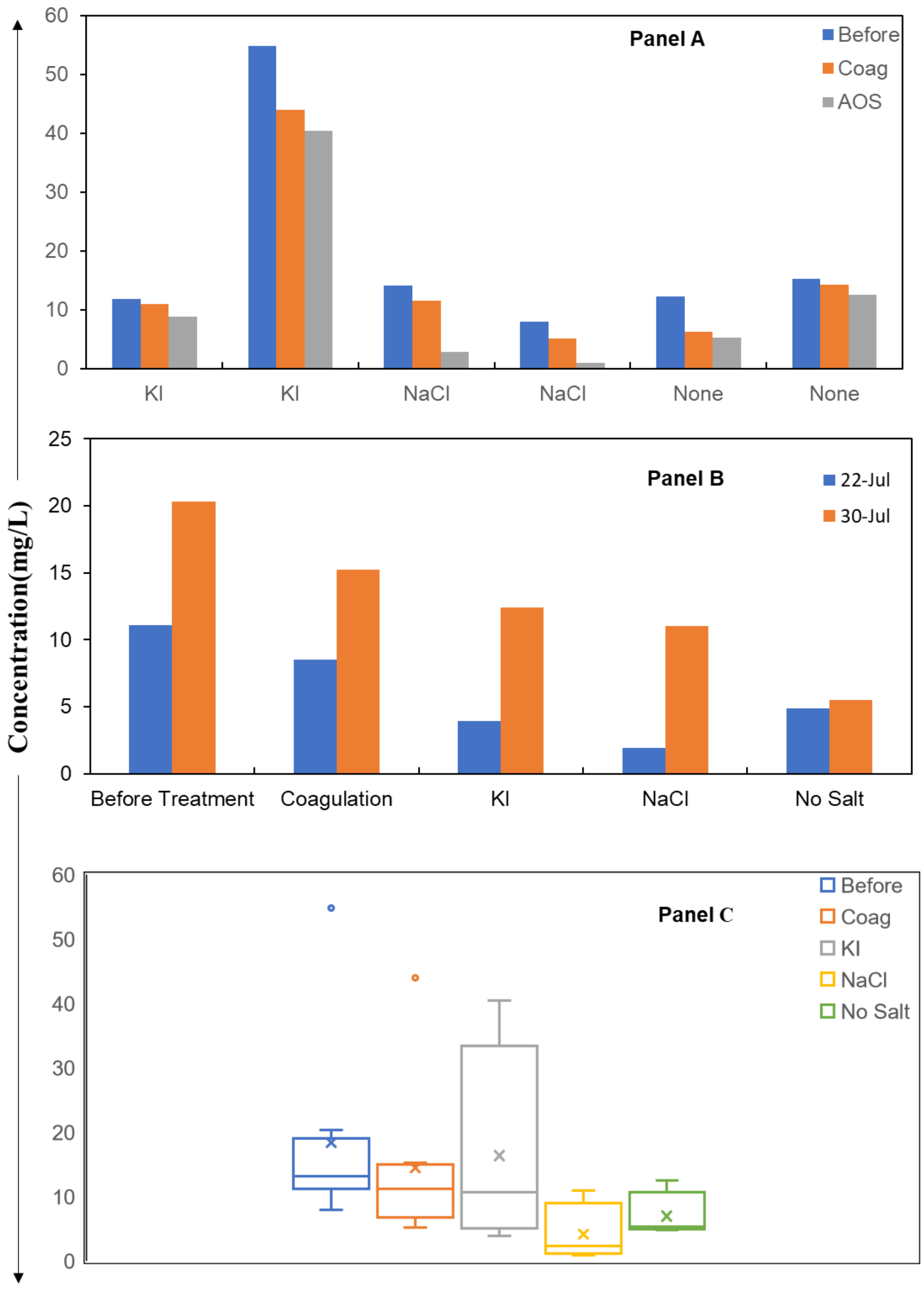

Figure B-6: TOC concentrations including: (A) raw, post-coagulation and post-AOS for the GHB and 17th St. W. outfall collected on during separate storm events using 3 treatments; (B) raw, post-coagulation and post-AOS for the GHB and 17th St. W. outfall; (C) Boxplots of all experimental combined for post-coagulation and post-treatment results.

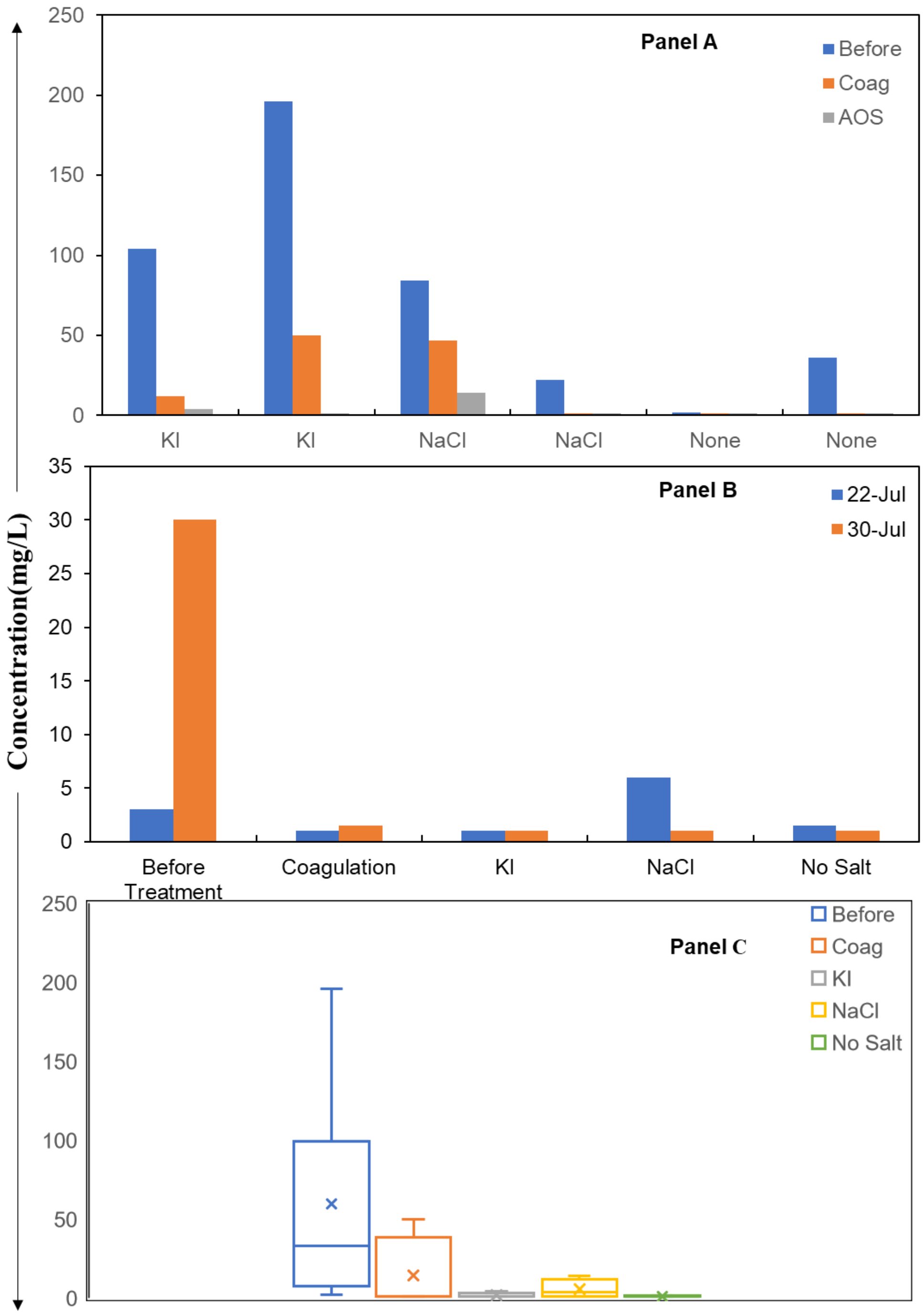

Figure B-7 : TSS concentrations including: (A) raw, post-coagulation and post-AOS for the GHB and 17th St. W. outfall collected on during separate storm events using 3 treatments; (B) raw, post-coagulation and post-AOS for the GHB and 17th St. W. outfall; (C) Boxplots of all experimental combined for post-coagulation and post-treatment results

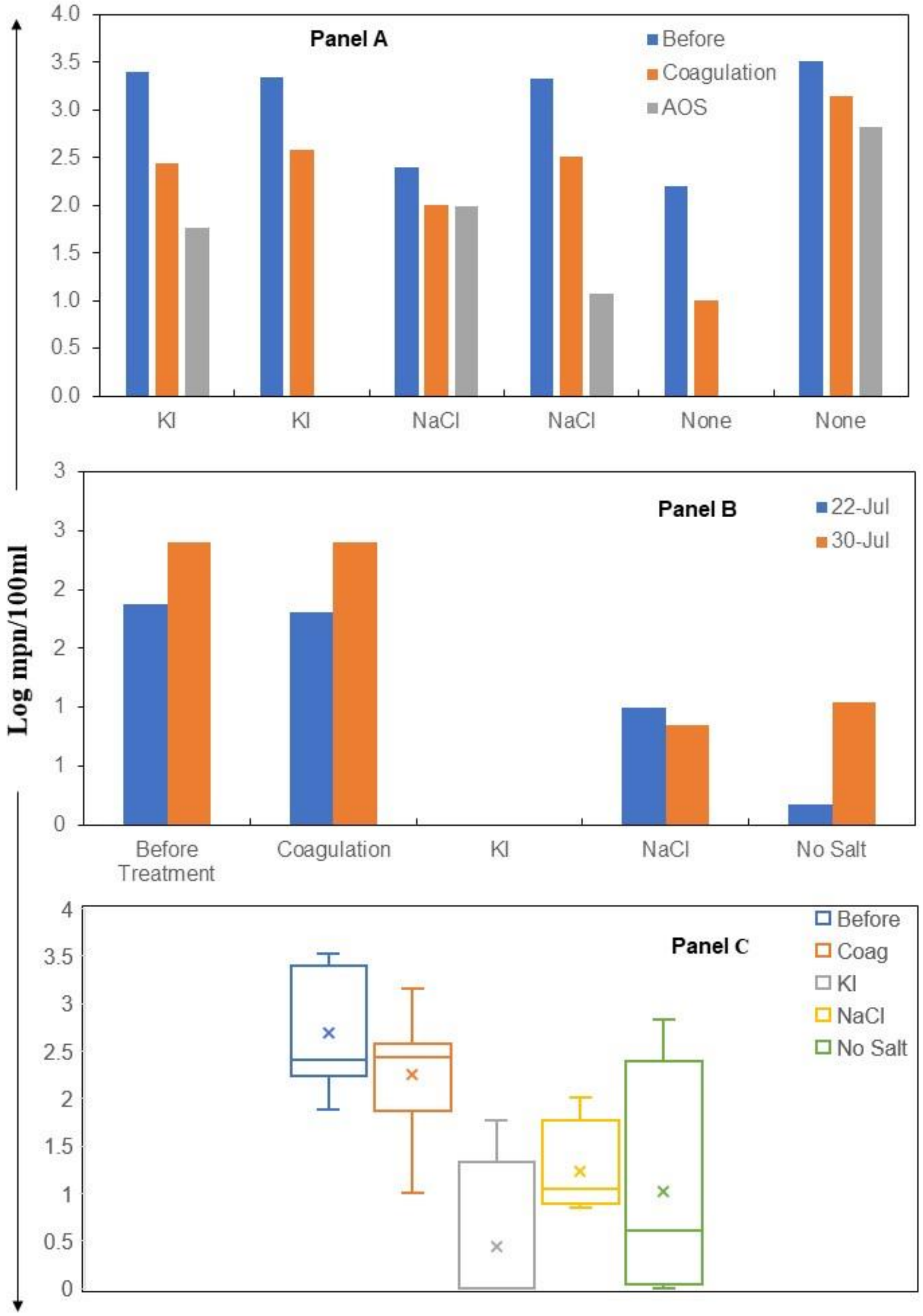

Figure B-8: *Escherichia-coli* concentrations including: (A) raw, post-coagulation and post-AOS for the GHB and 17th St. W. outfall samples collected on during separate storm events using 3 treatments; (B) raw, post-coagulation and post-AOS for the GHB and 17th St. W. outfall; (C) Boxplots of all experimental combined for post-coagulation and post-treatment results.

Table B-1: Averages and standard deviations of COD, TOC, TSS and *E. coli* concentrations for raw, post-coagulation and post-AOS samples.

			Concentration		
		n	**Range**	**Average**	**Standard deviation**
COD (mg/L)	**Raw**	8	56-334	131.8	94.8
	Coagulation	8	51-214	88.4	64
	AOS KI	4	49-149	71.8	51.8
	AOS NaCl	4	34.5-62	46	13.4
	AOS No Salt	4	45-103	61	28
TOC (mg/L)	**Raw**	8	8-55	18	15.1
	Coagulation	8	5-44	15	12.4
	AOS KI	4	4-40	16	16.4
	AOS NaCl	4	1-11	4	4.6
	AOS No Salt	4	5-13	7	3.7
TSS (mg/L)	**Raw**	8	2-196	59.6	66.1
	Coagulation	8	1-50	14.3	21.4
	AOS KI	4	1-4	1.75	1.5
	AOS NaCl	4	1-14	5.5	6.1
	AOS No Salt	4	1-1.5	1.1	0.25
***E. coli* (log MPN/100ml)**	**Raw**	8	1.88-3.52	2.68	0.63
	Coagulation	8	1-3.15	2.24	0.64
	AOS KI	4	0-1.76	0.44	0.88
	AOS NaCl	4	0.85-2	1.23	0.52
	AOS No Salt	4	0-2.83	1.01	1.29

Table B-2: Averages and standard deviations of COD, TOC, TSS and *E. coli* percentage decrease for post-coagulation and post-AOS samples

			Percentage decrease		
		n	**Range**	**Average**	**Standard deviation**
COD (%)	**Coagulation**	8	9-47	28.1	13.3
	AOS KI	4	40-64	51.5	10.3
	AOS NaCl	4	19-71	46.3	21.9
	AOS No Salt	4	13-51	39	17.5
TOC (%)	**Coagulation**	8	6-49	23	14.2
	AOS KI	4	25-65	39	18.6
	AOS NaCl	4	46-88	74	19
	AOS No Salt	4	18-73	51	23.3
TSS (%)	**Coagulation**	8	44.0-97.2	76.5	21.1
	AOS KI	4	67-99	89.25	14.9
	AOS NaCl	4	0-97	68.8	46.3
	AOS No Salt	4	50-97	73.5	27.1
***E. coli* (log MPN/100ml)**	**Coagulation**	8	0-1.20	0.57	0.42
	AOS KI	4	1.6-3.3	2.3	0.74
	AOS NaCl	4	0.4-2.3	1.3	0.83
	AOS No Salt	4	0.18-2.2	1.03	0.86