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Electrocoagulation-Electrooxidation for Mitigating Trace Organic Compounds in Model Source Waters

by

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ABSTRACT

ELECTROCOAGULATION-ELECTROOXIDATION FOR MITIGATING TRACE ORGANIC COMPOUNDS IN MODEL SOURCE WATERS

Donald Rockwood Ryan

Marquette University, 2019

Conventional coagulation and oxidation are well suited for many drinking water operations to meet regulatory requirements for safe drinking water. However, these processes require auxiliary chemicals and materials that must be transported from off-site, which increases complexity of operations, and can pose difficulties for small treatment systems. Electrochemistry offers an innovative method to induce coagulation and oxidation processes for water treatment. Electrocoagulation (EC) together with electrooxidation (EO) is an attractive option for drinking water treatment systems because these processes generate iron coagulants using iron EC electrodes and oxidants (e.g., free chlorine and reactive oxygen species) using boron-doped diamond EO electrodes. This research evaluated the performance of combined EC-EO as a water treatment process for mitigating trace organic compounds in model groundwaters and surface waters. The trace organic compounds evaluated were acyclovir, trimethoprim, and benzyldimethyldecylammonium chloride (BAC-C10). These compounds represent different classes of trace organics found in source waters for drinking water treatment facilities. EO-only removed greater than 70% of acyclovir and trimethoprim in model groundwater matrices, but negligible BAC-C10 was removed relative to control experiments. Alternately, in surface waters, EO-only treatment was effective for BAC-C10 removal, but not for acyclovir and trimethoprim removal. EC-EO for model surface water treatment removed 73.5 ± 1.25% of dissolved organic carbon and improved downstream EO treatment of acyclovir, trimethoprim, and BAC-C10 by factors of 3.4, 1.7, and 1.4, respectively based on mean removal. However, EC-EO of model groundwater improved removal for only BAC-C10 (factor of 5.2 improvement), whereas ACY and TMP removal did not improve. BAC-C10 removal via EC-EO in groundwater was attributed to the particle separation step. EO was generally more energy efficient in treating model groundwaters than model surface waters. EC-EO improved the energy demands for treating model river water.

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DEDICATION

I would like to dedicate this work to my parents, DeAnna and Chuck West for their continued love and support throughout my academic journey. In addition I would like to dedicate this thesis to my friends both new and old, from my friends back home in Oklahoma, to newer friendships that have developed in Wisconsin. To my friends back home, thank you for always being a source of support since I've made the move up north and also for staying in touch to see how this new chapter has gone. To my newer friendships in Milwaukee, thank you for making Milwaukee feel like home.

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1. INTRODUCTION

This work focused on a combination of physicochemical water treatment processes, electrocoagulation-electrooxidation, to mitigate trace organic compounds. These technologies were analyzed with respect to their trace organic compound removal capabilities in varying source waters, each with different challenges. The concomitant energy demand required for operation was also assessed.

1.1 Motivation for Work

Trace organic compounds (TOrCs) include a wide range of compound classes such as pharmaceuticals and personal care products, industrial products, hormones, and pesticides (Bieber et al., 2018; Kolpin et al., 2002; Schwarzenbach et al., 2006). TOrCs, particularly personal care products, have been measured in receiving waters downstream of water resource reclamation facilities (WRRFs) since as early as 1977, when metabolites of aspirin and clofibrate were measured in WRRF effluent (Hignite and Azarnoff, 1977). Advances in analytical chemistry have further highlighted the prevalence of TOrCs in water by offering more thorough quantification of the waterborne occurrence of common compounds found in commercial and personal care products (Kolpin et al., 2002). The extent of impacts on organisms in waters affected by TOrCs is unknown as there are many synthetic compounds used each day that may contribute to the ambiguous mélange of compounds present in aquatic systems. These compounds are not reported as acutely toxic to human health at concentrations present in surface waters; however, the chronic toxicity of these compounds may indirectly impact human health via avenues including endocrine disruption, increased cancer rates, antibiotic resistance, and antiviral resistance (Jain et al., 2013; Kolpin et al., 2002).

Drinking water treatment plants (DWTPs) are responsible for treating water before public distribution, and WRRFs are critical in mitigating waste and pollution before release into ecosystems. Hence, optimization of TOrC mitigation technologies is an important task for both DWTPs and WRRFs to combat potential exposure to these contaminants. Rising demands for clean water in response to stressors such as increasing population, increases in drought frequency, and global climate change (Vörösmarty et al., 2000) may drive utilities to rely on TOrC-laden water sources, such as reclaimed water, to enhance existing supplies of clean drinking water (USEPA, 2012a).

Unfortunately, conventional treatment processes used by both DWTPs and WRRFs do not completely remove TOrCs (Kolpin et al., 2002; Schwarzenbach et al., 2006; Westerhoff et al., 2005). The recalcitrant nature of TOrCs requires advanced water treatment regimes such as advanced oxidation processes (AOPs), granular activated carbon (GAC), or membrane filtration (MF) to minimize TOrC occurrence in water. AOPs are physicochemical treatment processes that employ highly reactive hydroxyl radical species (HO•) to treat waters at ambient temperatures (Crittenden et al., 2012). AOPs offer a promising alternative to conventional treatment processes and advanced separation processes such as GAC and MF as AOPs can transform contaminants into mineralization products such as carbon dioxide.

Electrochemical water treatment can be used as an AOP and also provides a multi-barrier physicochemical water treatment approach for TOrC mitigation by combining coagulation, flocculation, and chlorination. In electrochemical water treatment, electrodes are employed to produce water treatment chemicals *in-situ* via electrolysis of different electrode materials. Electrocoagulation (EC) can be used to dose common coagulants such as iron and aluminum by the anodic dissolution of sacrificial electrodes. Electrooxidation (EO) uses non-sacrificial electrode materials, such as boron-doped diamond, to promote water oxidation through homogeneous and heterogeneous reaction pathways. EC and EO may provide an effective combined treatment process capable of mitigating TOrCs. Specifically, EC could be used as a preliminary treatment process to remove common oxidant scavengers, such as dissolved organic carbon (DOC), thereby improving subsequent downstream treatment of TOrCs via EO.

1.2 Objectives

The main objective of this work was to assess the efficacy of combined EC-EO water treatment in mitigating TOrCs in model source water matrices. The first objective was to evaluate the performance of EO as a sole treatment process in model source waters. This objective included two components, the first of which was to test source water constituents (HCO_3^-, Cl^-, and DOC) at a range of concentrations relevant to natural water to elucidate the impact of each parameter on TOrC removal. The second component focused on assessing the performance of EO in more complex mixtures modeled after real surface and groundwater sources. It was hypothesized that ions such as Cl^- would improve TOrC removal in EO via electrochemical conversion to oxidants, such as free chlorine, while HCO_3^- and DOC would inhibit removal due to oxidant scavenging.

The second objective focused on the combined EC-EO treatment process for TOrC removal to assess if preliminary EC treatment improved removal during EO. It was hypothesized that preliminary EC would remove oxidant scavengers such as DOC, and improve downstream treatment by EO by decreasing the oxidant demand of the EO influent, thus providing a cleaner matrix for active oxidants to target TOrCs. The electrical energy demand was evaluated to assess these hypotheses.

2. LITERATURE REVIEW

2.1. Trace Organic Compounds

TOrCs are increasingly recognized as emerging contaminants due to the recent rise in antibiotic resistance, antiviral resistance, and potential for endocrine disruption (Daughton and Ternes, 1999; Jain et al., 2013; Jones et al., 2003). TOrCs generally enter aquatic systems due to incomplete removal during WRRF processes (Kolpin et al., 2002). After TOrCs enter aquatic systems, they can potentially enter drinking water sources (Furlong et al., 2017). Although the low concentrations of individual TOrCs (low ng/L) may assuage concerns, when the total TOrC mass is considered, potential risks and unknown impacts cannot be discounted as a possible chronic problem for public health (Daughton and Ternes, 1999; Schwarzenbach et al., 2006). For example, Wang et al. (2017) used advanced MS techniques for non-targeted analysis to gain greater understanding of the molecular composition of the complex mixture of organic compounds in source waters. They reported 2452 different molecular formulas across 20 different source waters, with 1092 of the molecular formulas present in 90% of the samples. The USGS conducted a nationwide study of 25 different source waters before and after drinking water treatment (Furlong et al., 2017). Their targeted analysis detected 118 pharmaceuticals, where 47 pharmaceuticals were common across each source. The samples collected following drinking water treatment generally showed reduction of the parent compounds; however, reduction of the parent compound does not negate concerns over transformation products. The most frequently detected TOrCs that passed through drinking water treatment were bupropion, metoprolol, carbamazepine, and cotinine (Furlong et al., 2017).

Westerhoff et al. (2005) assessed the impact of simulated drinking water treatment processes (coagulation, powdered activated carbon, chlorination, and ozonation) in mitigating 62 different TOrCs. Coagulation experiments removed only a fraction of TOrCs, with more than 75% of TOrCs being removed less than 20% via alum coagulation. The addition of powdered activated carbon to coagulation improved removal of more volatile TOrCs, potentially due to higher octanol-water partition coefficients associated with different compounds. The process that generally had the largest contribution to TOrC abatement was ozonation (although TOrCs such as iopromide were recalcitrant). Westerhoff et al.'s (2005) findings suggest that TOrCs may generally be recalcitrant to conventional treatment processes unless advanced treatment processes such as ozone or powdered activated carbon are employed. In addition to this study, Ternes et al. (2002) investigated the impact of conventional drinking water treatment and found that granular activated carbon may also be a generally effective option for TOrC mitigation.

This thesis focuses on three TOrCs from three different compound classes: acyclovir (ACY, an antiviral), trimethoprim (TMP, an antibiotic), and benzyldimethyldecylammonium chloride (BAC-C10, an antimicrobial). These compounds feature a variety of physicochemical properties with respect to their acid-base character, charge, log K_{ow}, K_H, and reactivity with different oxidants (Table 1).

Table 1: Summary of physicochemical properties of TOrCs in this study.

	Trace Organic Compound (TOrC)		
Parameter	Trimethoprim	Acyclovir	Benzyldimethyldecyl ammonium chloride (BAC-C10)
pK_a	7.21 (cation at pH < 7.21, otherwise neutral molecule)	2.27, 9.25 (cation at pH < 2.27, zwitterion at pH 2.27-9.25, anion at pH > 9.25)	(cation at all pH levels)
Acid base properties	Weak base	Amphoteric	-
log K_{ow} [a]	0.91	-1.56	1.95(est)
$K_{H,}$ atm-m^3 mol^{-1}	2.39E-014[a]	3.18E-022 [a]	4.32E-012 [a]
$k_{HO\bullet}$, M^{-1} s^{-1}	1.22×10^{11} [a] 8.7×10^{9} [b]	4.78×10^{10} [a] 5×10^{9} [d]	2.29E+10 [a]
k_{O3}, M^{-1} s^{-1}	4.3×10^{5} (apparent) at pH = 7.7 [b]	2.5×10^{2} (anion) – 3.4×10^{6} (cation) [c]	Not available
k_{HOCl} at pH = 8, M^{-1} s^{-1}	1.1×10^{1} (± 2%) [d]	9.9×10^{0} (± 24%)[d]	Not available

[a] Values from EPI SUITE V. 4.1 (USEPA, 2012b).
[b] Values from Dodd et al. (2006).
[c] Values from Prasse et al. (2012).
[d] Values from Barazesh et al. (2016).
Trace organic compound structure provided in Figure A1.

ACY was the most commonly detected antiviral in a nationwide survey of 25 different waters, where it was detected in 44% of source waters and 8% of treated potable waters (Furlong et al., 2017). ACY is a nucleoside analog, which is a compound that can be used to treat a variety of viral infections, e.g., herpes simplex virus and varicella zoster virus (Jain et al., 2013). Based on the frequent occurrence of antivirals such as ACY, there may be concerns of antiviral resistance due to chronic exposure and pseudo-persistence in source waters (Jain et al., 2013). For example, environmentally relevant concentrations (1 μg/L) of oseltamivir (Tamiflu ®) were associated with antiviral resistance in mallards. The development of antiviral resistance in wild birds may raise concerns of anti-viral resistant influenza mutations that may cross species (Järhult et al., 2011). To date, no studies have been conducted on environmental antiviral resistance due to ACY.

Physicochemical properties of nucleoside analogs may be important to consider in studies focused on TOrC abatement as these compounds have unique properties like high water solubility and zwitterionic character over a range of pH conditions (Table 1). Zwitterions can bear both a positive and negative charge as a function of pH. ACY has a zwitterionic fraction between pH = 2.27 and 9.25, where the compound will predominantly be cationic in acidic conditions and anionic in basic conditions; the combined charges in the zwitterion will make the compound neutral. This unique characteristic impacts ACY reactivity with different oxidants. For example, Prasse et al. (2012) found that the second order rate constant for ACY with ozone varied 4-orders of magnitude between pH 1.7 and 8.5. The cationic form of ACY was most amenable to ozonation.

Following sulfamethoxazole, TMP was the second most commonly detected antibiotic in the USGS study (Furlong et al., 2017). This high occurrence of TMP makes sense as TMP and sulfamethoxazole are generally prescribed in the same mixture due to their synergetic antibiotic impact (Bushby, 1975). Nationwide, TMP was qualitatively detected (present, but below the limit of quantification) in 28% of water sources, and 8% of treated potable water (Furlong et al., 2017). TMP is a commonly studied antibiotic for assessing advanced treatment process performance (Barazesh et al., 2016; Garcia-Segura et al., 2015; González et al., 2011; R. Zhang et al., 2016; Y. Zhang et al., 2016), so existing TMP removal data may be compared to other work. TMP can have a range of reactivity with different oxidants utilized during water treatment (Dodd et al., 2006; Dodd and Huang, 2007). Dodd and Huang (2007) investigated the reactivity of TMP with HOCl and found that TMP can react with HOCl between pH 3 and 9, but reactions were most likely at neutral pH. The moiety oxidized by chlorine shifts as a function of pH, leading to different chlorinated transformation products depending on the part of the compound that is oxidized. TMP was also highly reactive with ozone as a function of pH, where the second order rate constants were higher between pH 7 and 8 (Dodd et al., 2006), Accordingly, TMP may be most reactive with conventional oxidants at neutral pH conditions, typical of drinking water treatment.

Benzalkonium chlorides (BAC) are mixtures of quaternary ammonium antimicrobial compounds commonly used as hospital disinfectants. The antimicrobial properties of BAC may lead to it being increasingly incorporated into antimicrobial products labeled “triclosan-free” following the ban on triclosan usage in “consumer antiseptic washes” in September 2017 (Food and Drug Administration, 2017). Consequently, BAC compounds may enter source waters where they could potentially inhibit cellular function such as cholesterol biosynthesis (Herron et al., 2016) or confer other indirect impacts such as antimicrobial resistance (Kümmerer, 2009; Langsrud et al., 2004), However, little research is available regarding BAC removal during conventional drinking water treatment processes. BAC also exhibits unique properties with respect to other TOrCs because it is a surfactant that can form micelles, and it is a permanent cation across all pH conditions due to the quaternary ammonium moiety (Smith et al., 2002). The micellar properties of this compound may enhance its removal by physicochemical processes such as adsorption due to the large spheres formed (Baek et al., 2006). Adsorption and oxidation mechanisms are likely to remove BAC based on studies focusing on activated carbon cloth (Duman and Ayranci, 2010) and ozonation (Hernández-Leal et al., 2011). Hernández-Leal et al. (2011) reported 98% removal of BAC following 45 minutes of ozone treatment in Milli-Q water. In real grey water matrices, ozonation removed BAC to below the limit of quantification.

2.2. Physicochemical Drinking Water Treatment for Trace Organic Compound Mitigation: Conventional Treatment and Advanced Oxidation Processes

Coagulation is a common physicochemical drinking water process in which metal salts, typically aluminum-based or iron-based, are added to water to remove contaminants. During this process, metals destabilize colloidal matter. Particles then aggregate together to form flocs during flocculation (Crittenden et al., 2012). Enhanced coagulation targets removal of natural organic matter (e.g., dissolved organic carbon [DOC]) rather than solely turbidity and color. Improved DOC removal is achieved by increased coagulant doses or improved charge neutralization resulting from lowering the pH to influence the surface charge and solubility of large organics comprising natural organic matter (Edzwald and Tobiason, 1999; Kastl et al., 2004; Volk et al., 2000).

AOPs are physicochemical drinking water processes that generate HO• to degrade large organics as well as refractory trace organics. HO• are nonselective oxidants with a higher oxidizing potential ($E^0 = 2.73$ V) compared to common disinfectants like chlorine ($E^0 = 1.36$ V) (Copeland and Lytle, 2014; Pignatello et al., 2006; Rush et al., 1990; Westerhoff et al., 1999). These strong oxidants are an alternative for drinking water treatment because they are able to convert recalcitrant contaminants (e.g., TOrCs) to mineralization products ($CO_2 + H_2O$) when they are effectively implemented. AOPs offer a different removal mechanism compared to processes such as coagulation-flocculation-sedimentation and GAC, which physically remove compounds, but do not degrade them.

2.2.1 Electrical Energy Inputs

Electrical energy per order (EEO) is a quantitative assessment that can be used to evaluate the efficacy of a physicochemical treatment process, such as AOPs, in mitigating contaminants (Bolton et al., 2001). EEO is generally expressed as the energy input per cubic meter of water treated to achieve 1 order of magnitude reduction (kWh/m^3). Here, EEO will be referred to as "electrical energy demand".

Conventional treatment (coagulation + flocculation + sedimentation + filtration) has energy consumption ranging from 0.05 – 0.15 kWh/m^3 overall (Howe et al., 2012). Advanced water treatment processes, particularly AOPs and reverse osmosis, are generally more energy intensive than conventional treatment processes. Energy consumption for AOPs depends on the process employed (Howe et al., 2012; Vince et al., 2008), e.g., O_3 and O_3/H_2O_2 range from 0.05 – 0.125 kWh/m^3, whereas UV/H_2O_2 can range from 0.06 – 1 kWh/m^3. At this time, reverse osmosis is generally the most energy intensive treatment process, depending on the water matrix. Brackish water reverse osmosis requires 0.6 – 1.7 kWh/m^3 and sea water reverse osmosis requires 3.5 – 7 kWh/m^3 (Howe et al., 2012; Vince et al., 2008). Based on these values, the energy consumption for advanced treatment technologies used for TOrC mitigation should not exceed 7 kWh/m^3 in a scaled up process for it to be a favorable competitor with existing advanced water treatment technologies.

2.2.2 The Impact of Initial Water Quality on Contaminant Mitigation by Physicochemical Water Treatment Processes

Natural organic matter (NOM) is ubiquitous in natural waters. NOM cannot be expressed by a single molecular structure because its structure is a function of biogeochemical processes that occur in each unique ecosystem. NOM is generally defined as a bulk parameter describing a complex system of conjugated aromatics with differing polar functional group content (e.g., carboxylic acids and phenols) (Leenheer, 1981; Thurman, 1985a). These macro-organic compounds are of interest in drinking water treatment because they can hinder the efficacy of treatment processes such as filtration, scavenge oxidants, and serve as precursors to chronically toxic disinfection byproducts. In particular, the high concentration of NOM relative to TOrCs (typically mg/L versus ng/L, respectively) may strongly inhibit TOrC degradation via oxidation processes.

Bulk parameters are often used to broadly characterize NOM in order to assess how it is removed or transformed in physicochemical treatment processes. Dissolved organic carbon (DOC) is often used to quantify NOM and UV_{254} is commonly used to assess structural characteristics of NOM, i.e., the degree of aromatic structures. DOC is a measure of the oxidizable carbon present in water samples containing no inorganic carbon that have passed through a 0.45 µm filter. UV_{254} is used to assess the degree of NOM aromaticity in a water sample. High aromaticity may exert a higher oxidant demand due to the high electron density, which may be selectively oxidized by electrophilic oxidants such as ozone. In addition, UV_{254} has been used as a parameter to assess the possible formation of disinfection byproducts (Edzwald et al., 1985).

Water quality parameters have a large impact on AOP effectiveness. Alkalinity and DOC can greatly hinder AOP performance by scavenging HO•. Due to the deleterious impacts of oxidant scavengers, a multi-barrier water treatment approach is needed to ensure that upstream processes, like coagulation and flocculation, will provide sufficient pretreatment to advanced water treatment processes such that AOPs, for example, can better target more recalcitrant contaminants such as TOrCs.

2.3. Electrochemistry

Electrochemistry is a field of chemistry focused on the flow of electrons that cause electrical energy in a system due to the electromotive force, or cell potential (E^0_{cell}). The electrical energy produced or required enacts chemical change through a series of redox reactions. These reactions consist of two half reactions, where one cell reaction is an oxidation and the other is a reduction. In order for these reactions to occur, the thermodynamic conditions must be met by the E^0_{cell} resulting from the electrochemical cell configuration. When E^0_{cell} is positive, it is indicative of a spontaneous reaction. Examples of half-cell reactions relevant to electrochemical treatment are provided in Table 2.

Table 2: Electrochemical half reactions relevant to water treatment

Half Reaction	E^0 (Volts) (vs. Standard Hydrogen Electrode)	Electrochemical Reaction
$2Cl^- \leftrightarrow Cl_2 + 2e^-$ [a]	-1.358	Anode oxidation
$Fe \leftrightarrow Fe^{2+} + 2e^-$ [a]	0.441	Anode oxidation
$Fe^{3+} + e^- \leftrightarrow Fe^{2+}$ [a]	0.771	Cathode reduction
$H_2O \leftrightarrow (1/2)\, O_2 + 2H^+ + 2e^-$ [a]	-1.229	Anode oxidation
$H_2O \leftrightarrow H_2O_2 + 2H^+$ [b]	-1.763	Cathode reduction

[a] Provided in Bagotsky (2005).
[b] Provided in Fan et al. (2017).

Electrochemical systems are further subdivided into two different categories: galvanic cells and electrolytic cells. An electrochemical cell consists of three parts: conductive electrode materials (anodes and cathodes), an electrolyte solution to carry the flow of electrons, and electrical contact where the electrodes are connected by the electrolyte solution. In a galvanic cell, E^0_{cell} is a result of the electrode configuration, and the potential difference between the electrodes drives the reaction. Galvanic cells take multiple forms in real world systems, such as batteries that provide electrical energy based on the potential difference between electrode materials, or corrosion in water distribution systems between metals in electrical contact. Alternately, in an electrolytic cell the potential is provided from an external battery to supply the electromotive force for the reaction, making nonspontaneous reactions possible, e.g., iron dissolution via anodic oxidation (Table 2). In an electrolytic cell, oxidation half reactions occur at the anode, and reduction half reactions occur at the cathode. Electrochemical water treatment processes are carried out in electrolytic cells. Electrocoagulation (EC) is a result of the electrolytic dissolution of sacrificial iron anode materials. In an EC reactor, the iron is oxidized to ferrous iron (Fe^{2+}) and enters the solution as a coagulant. Electrooxidation (EO) processes do not utilize sacrificial anode material; rather, inactive electrode materials undergo electrolysis.

2.3.1 Electrochemical Water Treatment

Electrochemistry also serves as an emerging method for physicochemical water treatment processes wherein electrodes are employed to produce water treatment chemicals *in-situ* via electrolysis of different electrode materials. EC doses common coagulants such as iron and aluminum by anodic dissolution of sacrificial electrodes. EO uses non-sacrificial electrode materials, such as boron-doped diamond, to promote oxidation reactions. Electrochemical water treatment may facilitate multi-barrier physiochemical water treatment processes capable of mitigating TOrCs by a combination of processes: coagulation, flocculation, sedimentation, advanced oxidation, and chlorination. Flotation due to bubble generation at the cathode may also be a potential removal pathway in electrochemical treatment for volatile TOrCs; however, the TOrCs in this assessment have low Henry's constant ($10^{-12} – 10^{-22}$ atm-m^3-mol^{-1}) (Table 1) and are not expected to be removed via volatilization.

Current density and charge loading rate are metrics used to estimate the electrochemical dose applied to a system. Current density is a measure of the charge applied to the system relative to the submerged surface area facing the cathode in solution (mA/cm^2). Charge loading rate is a measure of the charge applied to a liter of solution per unit time (Coulomb/L-time). Current density may also be used to estimate the amount of coagulant added via EC using Faraday's Law (equation 1 in *Section 3.2.1.1*). These values can be used as a means of comparing electrochemical doses among electrochemical processes employed in other studies.

2.3.1.1 Electrocoagulation

EC is highly similar to conventional coagulation, with the primary difference being that iron or aluminum coagulants are generated *in-situ*. *In-situ* generation gives EC a competitive advantage over conventional coagulation because less auxiliary chemicals are required as the primary chemicals are generated within the reactor.

EC has demonstrated efficacy in treating a range of wastewaters such as municipal wastewater, tannery wastewater, and textile effluent (Chen, 2004; Emamjomeh and Sivakumar, 2009). In the early 1980s, Weintraub et al. (1983) demonstrated that EC was effective in treating oily wastewater. The treatment was ascribed to a combined mechanistic process in which electro-generated coagulant destabilized oily emulsions and encouraged metal-hydroxide precipitation and corresponding flocculation. The electrogenerated bubbles provided additional separation by inducing an electroflotation process. EC decreased the emulsion concentration from 300 – 7000 mg/L to less than 10 mg/L of effluent oil. Khandegar and Saroha (2013) reviewed the use of EC as an alternative treatment process for textile industry effluent. Conventional industrial water treatment may utilize biological treatment or AOPs, which may be hindered either by excessive amounts of oxidant scavengers or toxicity to biological treatment's active microbial communities. Of note, the dyes present in these effluents are of particular concern due to their associated toxicity and the resulting color of the effluent. EC offers a promising alternative to biological treatment and AOPs for textile industry effluent due to dye decolorization resulting from *in-situ* coagulation processes wherein the metal hydroxides are capable of agglomerating various solids present as well as adsorbing hydrophobic wastewater constituents (Khandegar and Saroha, 2013).

Beyond demonstrating viability as a competitive technology for treatment of wastewaters, EC has shown promise as a treatment technology for drinking waters from both groundwater and surface water sources. EC has been investigated as a means for implementing coagulation for treating surface water since the early 1980s (Nikolaev et al., 1982; Vik et al., 1984). Vik et al. (1984) compared aluminum EC to conventional coagulation dosed by aluminum salts as a treatment technique for producing potable water and found that EC generally performed the same in removing aquatic NOM, but EC-treated water did not have extra salts that are concomitantly added with aluminum coagulants. Nikolaev et al. (1982) investigated aluminum EC in tandem with two-stage filtration (filtration-EC-filtration) as a treatment technique for small, rural water systems, and found that this treatment approach removed 90-92% of suspended solids and 85-90% of color. These early studies provide ground work for studies investigating the use of EC as a means of generating coagulant *in-situ* for producing potable water.

Another criterion that demonstrates the potential of EC to treat source water is its effectiveness in removing DOC. For example, Ulu et al. (2014) reported approximately 87% removal of humic acid ($DOC_{initial}$ = 16.2 mg-C/L) following EC at pH 4 for 25 minutes. Dubrawski and Mohseni (2013) investigated parameters used in EC reactor design with respect to NOM removal using iron-EC. They found that optimum NOM removal was the result of using a current density of approximately 10 mA/cm^2, leading to 73% DOC removal ($DOC_{initial}$ =13.8 mg-C/L). In addition to these studies, Särkkä et al. (2015b) reviewed the efficacy of EC and EO in mitigating NOM. Generally, DOC or humic acid removal of 70 – 95% was reported (Table 3). These studies demonstrate that EC may be a competitive treatment technology for mitigation of NOM in source water matrices.

Table 3 Studies reviewed by Särkkä et al. (2015b) focused on iron electrocoagulation for NOM mitigation.

$DOC_{initial}$	Removal	Reference
500 mg Humic/L	92.7%	(Evki Yildiz et al., 2007)
10 mg-C/L	80%	(Ben-Sasson et al., 2013)
10 mg Humic Acid/L	95.3%	(Ghernaout et al., 2014)

Additional studies have focused on the use of EC in removing trace metal contaminants such as arsenic and chromium VI (Heffron et al., 2016; Li et al., 2012; Mohora et al., 2012). Mohora et al. (2012) found that EC was effective in removing 85% of arsenic from raw groundwater using a continuous flow aluminum-EC process. Heffron et al. (2016) investigated the removal of a suite of trace metal contaminants (arsenic, cadmium, chromium, lead, and nickel) using iron and aluminum EC and found that EC paired with filtration (0.45 μm) was effective in removing trace metals from synthetic groundwaters.

As described in this section, EC is capable of treating a wide range of common waterborne contaminants from wastewater as well as source water-relevant contaminants like NOM and trace metals. Accordingly, EC may mitigate oxidant scavengers like NOM and colloidal matter, thereby serving as a promising pretreatment technology ahead of downstream processes targeting TOrC abatement of source waters.

2.3.1.2 Electrooxidation

Electrode materials can be classified as active or inactive electrodes. Active electrodes generate HO•, and these radicals react with the electrode surface (M) to form a metal-oxide (Reaction 1). Inactive electrodes are electrode materials that do not react with electro-generated HO• (Reaction 2) (Marselli et al., 2003). Reaction 1 is characteristic of inactive higher-oxide electrodes like mixed metal oxides, whereas Reaction 2 is typical for electrodes like BDD. In Reaction 2, HO• does not react with M, and M is left over in the products while HO• participates in intermediate reactions to form oxygen. In comparison, in Reaction 1, M is oxidized to MO and oxygen (and corresponding reactive oxygen species) are not formed.

$$M(\mathrm{HO}\bullet) \rightarrow \mathrm{MO} + H^{+} + e^{-}\ (Reaction\ 1)$$

$$M(\mathrm{HO}\bullet) \rightarrow \mathrm{M} + \frac{1}{2}O_2 + H^{+} + e^{-}\ (Reaction\ 2)$$

BDD are inactive electrodes with high anode stability, which allows high oxygen overpotentials (Chaplin, 2014; Chen, 2004; Marselli et al., 2003). High oxygen overpotentials are required in order to produce HO•, as HO• are an intermediate produced prior to oxygen evolution (Chaplin, 2014). Due to these novel electrode properties, BDD have recently gained more attention for electrochemical water treatment via EO processes.

BDD-EO is an oxidation process capable of producing a myriad of oxidant species. Electrochemical-based oxidation methods, such as BDD-EO, are complex, featuring a variety of homogeneous oxidants in solution and heterogeneous reactions occurring on the electrode surface. Potential homogeneous oxidation pathways may include reactive oxygen species (ROS), such as O_3, H_2O_2, $^1O_2$, and HO•. Others include activated electrolytes such as sulfate species (sulfate radicals, peroxodisulfate), carbonate species (carbonate radicals, peroxycarbonates), phosphate species (monoperoxy phosphoric acid), chloride-derived species (Cl•, HOCl, perchlorate, chlorate), and potentially ferrate (Cañizares et al., 2009; Hu et al., 2009; Jeong et al., 2006; Marselli et al., 2003; Michaud et al., 2003; Rajab et al., 2015; Sáez et al., 2008; Saha et al., 2003).

Heterogeneous oxidation reactions occur in EO on or near the electrode surface by a combination of direct electron transfer reactions with the anode material, surface sorbed HO•, and surface sorbed chlorine radicals (Barazesh et al., 2016; Bejan et al., 2012; Marselli et al., 2003). Oxidation reactions can occur on the electrode surface as HO• form there due to water oxidation, but HO• have also been shown to dissociate from the electrode surface and act as homogeneous oxidants (Bejan et al., 2012).

The role of ROS is another unclear, yet relevant, mechanism associated with EO. Jeong et al. (2006) investigated the role of ROS in chloride-free waters in microbial disinfection and found that HO• were the primary oxidant responsible for inactivation. Jeong et al. (2006) speculated that H_2O_2 formation was due to HO• recombination/dimerization ($HO• + HO• \rightarrow H_2O_2$) because H_2O_2 formed during electrolysis, but did not form under conditions in which HO• were quenched with tert-butyl alcohol. The prospect of O_3 production via BDD electrolysis is also unclear. Jeong et al. (2006) did not measure detectable O_3 at the current densities tested (33 – 83 mA/cm^2). However, other studies measured 0 – 0.62 mg- O_3/L production using the indigo method (Bader and Hoigne, 1982) in high current density conditions above 42 mA/cm^2 (Rajab et al., 2015; Ureña de Vivanco et al., 2013).

HOCl production has also been demonstrated in studies focused on disinfection of chloride-containing waters (Boudreau et al., 2010; Jasper et al., 2017; Kraft et al., 1999; Pérez et al., 2010; Polcaro et al., 2009; Särkkä et al., 2015a; Schmalz et al., 2009). Although the prospect of *in-situ* free chlorine generation is an attractive option for water treatment processes, the true extent of chlorine generation may be difficult to quantify. Conventional chlorine quantification methods such as DPD use probe compounds, and other oxidants produced via EO, such as O_3 and H_2O_2, can interfere with accurate quantification of HOCl (EPA, 2009).

The identity of active oxidants during EO remains a challenge in water treatment research because oxidants can interact with contaminants either via homogeneous or heterogeneous pathways. Additionally, oxidants can be formed as a function of innate electrolytes in solution as well as the applied current density and the cell potential of the system. The presence of varying electrolytes in natural waters (e.g., Cl^-, CO_3^{2-}, SO_4^-, and PO_4^{2-}) may quickly complicate predicted EO processes, as the removal ascribed to one electrolyte, such as Cl^-, may not be accurate if other electrolytes are present that can be transformed into oxidants. This ambiguity may present a problem in real systems as each oxidant exerts a different reactivity with different contaminants. For example, O_3 is selective and highly electrophilic, whereas HO• are generally considered nonselective. Other oxidants, e.g., HOCl and H_2O_2, are capable of microbial disinfection and provide a residual disinfectant, but generally have low reactivity with TOrCs.

The electrical energy demands for TOrC mitigation via EO processes have been less studied than conventional AOPs. Lanzarini-Lopes et al. (2017) investigated the impact of different current density and organic loading on EO process efficiency by quantifying mineralization current efficiency, EEO, and first order rate constants to assess efficiency. As the applied current density increased, the first order rate constant of para-chlorobenzoic acid improved. However, the resulting EEO increased and mineralization efficiency decreased. A current density of 16.6 mA/cm^2 resulted in an EEO of 39.3 kWh/m^3-order, a mineralization current efficiency of 30.8%, and a first order rate constant of 7.64 $*10^{-5}$ s^{-1} for para-chlorobenzoic acid removal. Values associated with a higher current density of 100 mA/cm^2 were 331.8 kWh/m^3-order, 4.8%, and 1.07$*10^{-4}$ s^{-1}. These data suggest that a higher current density may improve the kinetics of organic compound degradation, however, the increased energy demands and hindered mineralization current efficiency may hurt overall process efficiency in scaled up systems (Lanzarini-Lopes et al., 2017).

BDD-EO has demonstrated removal of organics in a variety of wastewaters and some studies have also investigated EO for TOrC mitigation (Särkkä et al., 2015a). For example, Chaplin et al. (2010) demonstrated that BDD-EO was an effective process for removing N-nitrosodimethylamine (NDMA) from RO concentrates. Garcia-Segura et al. (2015) investigated the use of BDD-EO in tertiary wastewater by evaluating the removal of DOC, chemical oxygen demand (COD), and 29 target TOrCs. DOC and COD were effectively mineralized after 2 hours using 196 A/m^2 (19.6 mA/cm^2) at pH = 3. TOrCs were generally removed after 2 hours of electrolysis; however, more recalcitrant TOrCs, such as atrazine and iodinated x-ray contrast media, required as much as 24 hours of electrolysis to be fully removed. The concentration of bulk organics relative to TOrCs may have greatly hindered removal due to oxidant scavenging because each TOrC was present at 100 μg/L whereas bulk organics were present at 21 ± 2 mg-O_2/L COD, and

22.7 ± 0.5 mg-C/L DOC. In addition to these studies, Table 4 summarizes other studies that investigated the efficacy of BDD-EO in TOrC mitigation. These studies were generally conducted in simple electrolyte solutions and exhibited high TOrC removal over different electrolysis times and current densities.

Table 4: Summary of different studies utilizing BDD-EO for TOrC removal

TOrC	C_i	Current Density mA/ cm^2	Time	Removal	Matrix	Reference
Estrone	500 ug/L	10	10 minutes (with NaCl) 30 minutes (w/o NaCl)	85 – 98%	0.1 M Na_2SO_4 or 0.1 M Na_2SO_4 +0.36mM Cl^-	Brocenschi et al., (2016)
E2	500 ug/L	12.5 – 50	30 – 40 minutes	100%	0.1 M Na_2SO_4	Murugananthan et al., (2007)
BPA	20 mg/L	25-35.7	5 – 9 hours	100%	0.1 M Na2SO4	Yoshihara and Murugananthan, (2009)
Sulfamethoxazole (SMX) + Trimethoprim Mixture	50 mg/L SMX + 11.1 mg/L TMP	33.3	160 minutes (TMP) – 360 minutes (SMX)	100%	0.05 M Na2SO4	Murillo-Sierra et al. (2018)

2.3.1.3 Combined Electrocoagulation-Electrooxidation

Electrochemical pretreatment has been used in prior studies in which EC was utilized to pretreat water before a downstream process. For example, EC has shown promise as a pretreatment to membrane filtration for NOM mitigation (Ben-Sasson et al., 2013; Dubrawski et al., 2013). EC has also been paired with EO for treating different wastewater matrices such as municipal wastewater (Cotillas et al., 2013); industrial wastewater (Linares-Hernández et al., 2010); and other high COD wastewater such as dairy, gelatin, and coffee effluent (Belaid et al., 2017; Ibarra-Taquez et al., 2017;

Kruthika et al., 2013). In these studies, combined treatment was either conducted in the same reactor or as a sequential system in which EC was followed by EO. Linares-Hernández et al. (2010) studied the impact of EC, using iron electrodes, as a pretreatment to downstream EO for industrial wastewater using BDD electrodes. In their study, EO required up to 21 hours at a current density of 80 mA/cm^2 in order to mineralize persistent organics. However, when preliminary EC was employed for 30 minutes, the treatment time needed for mineralization of organics decreased to 90 minutes, or less than 10% of the original EO-only electrolysis time. This synergy was attributed to EC's efficacy in removing 52% of the initial 890 mg/L COD; here, the COD was attributed to large organics (suspended particles, colloids). Following mitigation of large organics and particles, EO was more effective in targeting persistent organics for mineralization. These studies focused on wastewaters indicate that combined EC-EO may have synergy in a variety of matrices due to EC's capability in removing a wide range of oxidant scavenging contaminants, which subsequently allows oxidants produced via EO to better target contaminants such as microbes and organics.

2.4. Summary of Research Needs

The studies described in this review suggest that advanced water treatment processes are needed to mitigate TOrCs, as these compounds are generally resistant to conventional treatment processes. Prior studies have demonstrated that EO may be an effective treatment for TOrC mitigation in a range of water matrices due to *in-situ* oxidant generation. However, the presence of bulk organics generally increased the required treatment times substantially, alluding to a need for preliminary treatment, such as EC, to maximize removal efficiency. Combined EC-EO has demonstrated synergy in high-strength wastewater matrices due to the removal of bulk organics that inhibit EO processes. However, research is lacking that focuses on using EC-EO for treating drinking water source matrices with respect to the removal of TOrCs

2.5. Research Objectives

This thesis research focused on using combined EC-EO as a method of TOrC mitigation in model groundwater and surface water matrices. The efficacy of this treatment train was assessed by investigating the removal of three TOrCs as a function of source water quality. Additionally, the electrical energy demand required for TOrC mitigation was evaluated, which may prove useful in comparing electrochemical treatment to other processes with respect to associated energy demands for operation.

Objective 1: Evaluate the performance of EO as a sole treatment process in TOrC mitigation in model source waters.

Hypothesis: Source water constituents such as Cl^- will improve TOrC removal in EO via electrochemical conversion to oxidants, such as free chlorine, while HCO_3^- and DOC will inhibit removal by scavenging oxidants produced by EO. HCO_3^- and DOC are prominent oxidant scavengers in water because they are present at concentrations orders of magnitude higher than TOrCs.

Objective 2: Evaluate the performance of combined EC-EO in TOrC mitigation in model source waters.

Hypothesis: EC will remove oxidant scavengers such as DOC, and improve downstream TOrC treatment by EO by decreasing the oxidant demand of the EO influent.

3. METHODOLOGY

3.1 Electrooxidation Experiments

Boron-doped diamond electrodes (BDD/Nb substrate) (Fraunhofer, Lansing, MI) were used for this study. Before conducting EO experiments, the electrodes were cleaned and polarized by electrolysis in a 0.2 M HCl solution at a current density of 3.70 mA/cm^2 for 5 minutes, as recommended by the manufacturer. EO experiments were conducted at a current density of 14.8 mA/cm^2 (i =200 mA, A=13.5 cm^2, inner electrode distance = 1 cm), which is a mid-range value relative to other EO studies using BDD (Garcia-Segura et al., 2015; Murillo-Sierra et al., 2018; Zhang et al., 2016). Tests were run for 5 minutes for experiments focused on the impact of innate water quality, and 20 minutes for those focused on source water quality. An extended EO electrolysis time of 20 minutes was used in experiments conducted in model source water matrices to assess the extent of removal in more realistic water matrices. The stir rate for all EO experiments was 200 rpm to simulate a rapid mixing phase. Batch reactors were 250-mL Berzelius beakers without a spout that were fitted with 3D printed electrode caps. Electrodes were arranged in the caps to provide a submerged surface area of approximately 13.5 cm^2 and an inner-electrode distance of 1 cm. The applied charge per volume of water was 83.3 and 333 mA-h/L for 5 minutes and 20 minutes, respectively. Preliminary tests were conducted to evaluate whether thiosulfate quenching was needed to stop TOrC reactions following EO. Results showed that quenching had no impact on TOrC removal (Figure A2), so subsequent samples were not quenched prior to LC-MS analysis.

3.2 Electrocoagulation-Electrooxidation Sequence Experiments

3.2.1.1. EC Procedure

Prior to EC experiments, iron electrodes (Vmetals, Milwaukee, WI) were sanded with 320 grit silicon carbide sandpaper to remove rust and corrosion products. The electrodes then underwent electrolysis at 7.4 mA/cm^2 for 10 minutes in the test water matrix to pretreat the iron electrodes to the test water matrix conditions, and simulate continual use during a conventional process. This iron electrode cleaning method may better simulate EC in real water treatment systems as the iron electrode does not undergo extensive treatment such as acid polarization. After iron electrode preparation, the electrodes were rinsed with deionized water and placed in the EC reactors.

The same beakers and electrode caps used for EO were also used for EC reactors. The electrodes had a submerged surface area of 13.5 cm^2 with an inner-electrode distance of 1 cm. EC experiments were conducted in batch conditions to simulate conventional coagulation jar tests. In these experiments, iron electrolysis was operated with rapid mixing at 200 rpm. During electrolysis, a polarity reversal time of 30 seconds was used to prevent electrode passivation by preventing the buildup of excess ferrous ions on the anode surface. This time was selected based on previous studies analyzing EC reactor performance (Maher et al., 2018). The current applied to the system varied between 1.85 and 11.1 mA/cm^2 depending on the iron dose used for the experiment. After iron-electrolysis, electrodes were removed from the solution, and the solution was flocculated for 10 minutes at 60 rpm. Following the flocculation phase, the samples settled for 15 minutes to separate the agglomerated flocs from the bulk solution. For enhanced coagulation, adjustments to pH were made using HCl in order to match the supporting electrolyte. The final chloride concentration resulting from pH adjustment was approximately 60 mg-Cl^-/L (measured with Hach model 8-P chloride test kits), which may slightly increase downstream TOrC removal during EO based on free chlorine generation.

3.2.1.2. Iron dose and Faraday's Law

In these experiments, iron was dosed into the solution by varying the current and maintaining a consistent electrolysis time. The theoretical electrolysis time required to achieve the desired iron dose was calculated using Faraday's Law (Equation 1), as described by Gu et al. (2009).

$$Dosing\ rate\ \left(\frac{mmol}{cm^2 min}\right) = \frac{i}{F \cdot z} \times \frac{60s}{min} \quad \text{Equation 1}$$

where i represents the current density in mA/cm^2, F represents the Faraday's constant (9648 Coulomb/mol), and z is the number of electrons transferred via the electrochemical reaction.

Here it was assumed that $z = 2$ based on work showing that Fe^{2+} is the iron species initially generated via electrocoagulation (Lakshmanan et al., 2009). The faradaic yield of iron with respect to current density is discussed in Appendix 6.2. The electrodes used for this study were faradaic efficient, meaning that they delivered the anticipated iron dose to the solution.

3.2.1.3. EC-EO Procedure

After the settling phase of EC, 150 mL was transferred from the reactor using a 50-mL sterile pipette and was vacuum filtered through Whatman (Maidstone, United Kingdom) 114 filter paper (pore size = 25 μm). A filtration step followed EC to remove large agglomerated iron flocs that did not settle during the settling phase. After filtration, the water was added to the EO batch reactor, where the samples underwent electrolysis at 14.8 mA/cm^2 (i = 145 mA, A = 9.8 cm^2) for 20 minutes. In EC-EO experiments, the EO current was adjusted to maintain the applied current density accounting for changes in solution volume and submerged electrode depth.

3.2.1.4. Control Experiments

Control tests were conducted in the reactor without electricity to assess potential TOrC losses due to the reactor setup, such as glass adsorption. Controls for EO-only tests were run in *model lake water* for 20 minutes under the same conditions detailed in *Section 3.1*, but without electricity. Three technical replicates of each control were used to assess variance in the experimental methods. BAC-C10 had the most removal from glassware, with 15 ± 5%. ACY and TMP had less removal in the controls, at -0.7 ± 1.9% and 3.6 ± 0.8%, respectively.

Control tests without electricity were also conducted to determine TOrC losses due to the EC-EO sequence in *model river water* and *model shallow aquifer* (Table 6). In addition, a particle separation control test was conducted to determine losses due to the 25 µm filtration step in *model river water* (Table 7).

Table 5 Percent removal due to full EC-EO controls in *model river water* and *model shallow aquifer*; Data reported are from single experiments

Compound	Model River Water	Model Shallow Aquifer
BAC-C10	19.6	31.4
TMP	7.55	2
ACY	0.03	-10

Table 6 Percent removal from filtration controls in *model river water*. Data shown are the average of quadruplicate tests.

	Average	Standard deviation
BAC-C10	21.2	6.66
TMP	13.8	11.7
ACY	2.50	1.01

3.3 Synthetic Water Matrices

All experiments were conducted in synthetic waters to either simulate weak electrolyte solutions, or model source waters. Experiments were performed in simple electrolyte solutions in order to determine the contribution of different source water constituents to the overall removal of TOrCs. These experiments supplemented analysis of the model source waters in order to better understand the specific contribution of each water constituent. In these experiments, an electrolyte concentration and pH were fixed, and the parameter of interest was varied (Table 8). Following the experiments to assess the impact of individual water constituents, experiments were conducted in model source water matrices by varying multiple parameters simultaneously to determine the efficacy of EO in different challenge waters (Table 8). Model surface water matrix composition was designed according to Mississippi River and Lake Michigan water quality data, and model groundwater matrix composition was designed according to groundwater quality data from Kewaunee and Waukesha Counties (Heffron, 2019).

Table 7: Water Matrices.

Test	Alkalinity, mg/L as $CaCO_3$	Chloride, mg/L	DOC, mg-C/L	pH initial	Conductivity, µS/cm
Simple Electrolyte Waters					
Bicarbonate Buffer Matrix (HCO_3^-B)	179	0	0	7.75	315
Low Chloride	179	5	0	7.5	335
Mid Chloride	179	20	0	7.5	400
High Chloride	179	40	0	7.5	475
No DOC	95.2	13.3	0	8.1	250
Low DOC	95.2	13.3	2	8.1	250
High DOC	95.2	13.3	8	8.1	250
Low Alkalinity	100	16.6	0	7.5	255
Mid Alkalinity	200	16.6	0	7.5	432
High Alkalinity	300	16.6	0	7.5	584
Synthetic Source Waters					
Model lake water (MLW)	95.0	13.3	1.5	8.25	250
Model river water (MRW)	119	11.4	8.0	8.1	300
Model shallow aquifer (MSA)	178	3.80	0	7.5	360
Model deep aquifer (MDA)	226	70.4	0	7.5	690

The synthetic waters were adjusted to target levels using A2 fine test dust (Powder Technology Inc, Arden Hills, WI), humic acid sodium salt (technical grade, Sigma Aldrich, St. Louis, MO), potassium chloride (ACS grade, FisherScientific, Hampton, NH), and sodium bicarbonate (ACS grade, FisherScientific). The TOrCs included acyclovir (ACY; reference grade, Sigma Aldrich), trimethoprim (TMP; Tokyo Chemical Industry, Tokyo, Japan), and benzyldimethyldecylammonium chloride (BAC-C10; >97%, Sigma Aldrich).

After preparation of synthetic water matrices, bulk solutions were spiked with TOrCs to achieve a concentration of 200 µg/L of each TOrC. BAC-C10 and TMP were dissolved in HPLC-grade methanol, and ACY was dissolved in Milli-Q water. The BAC-C10 and TMP were added as methanol solutions for a final methanol concentration of 0.05% v/v. This small volume of methanol relative to bulk solution volume is expected to minimize co-solvent effects attributed to methanol (Tong et al., 2016). ACY was dissolved in a separate stock solution because ACY is insoluble in methanol at high concentrations, and BAC-C10 and TMP are insoluble in water at high concentrations (Table 1).

3.4 Analytical

3.4.1 Trace Organic Compound Quantification Using LC-MS

All TOrC samples were filtered through a 0.22-µm PTFE syringe filter (Agela Technologies, Wilmington, DE) and blended with HPLC-grade methanol (80% sample, 20% methanol) prior to analysis. TOrCs (ACY, TMP, and BAC-C10) were quantified using a Shimadzu (Kyoto, Japan) Liquid Chromatography Mass Spectrometer (LC-MS

2020). For these analyses, 0.1% formic acid served as the mobile phase (Pump A) and HPLC-grade methanol served as the organic phase (Pump B). The pump flow rate was 0.2 mL/min. The chromatographic conditions are provided in Table 9.

Table 8: LC-MS 2020 information for method utilized to quantify TOrCs.

Time, Minutes	Organic Phase Percent of Flow (%)
0	15
8	50
12	50
14	100
16	50
18	15
25	15
26	End of run

Ten-point standard curves were used with concentrations ranging from 4 µg/L to 400 µg/L to capture a range of TOrC concentrations. Each standard curve was prepared in the respective water matrix to normalize LC-MS response to the ionic interference present in each unique matrix. Concentration data was determined via LC-MS spectral data to calculate percent removal relative to the initial concentration.

3.4.2 Total Organic Carbon Analysis

All DOC samples were filtered through a 0.45-µm PTFE syringe filter (Agela Technologies, Wilmington, DE) and acidified with HCl to pH 3 before analysis. DOC was measured using a Shimadzu TOC-V_{CSN} equipped with a Shimadzu ASI-V autosampler. All sample bottles used for TOC analysis were prepared to eliminate organic demand by steeping them in a 5% HCl acid bath solution for a minimum of 12 hours. Following acid washing, bottles were triple rinsed with deionized water, and baked at 550 ^{o}C for one hour.

3.4.3 Iron Quantification

Iron produced via EC was measured to assess the faradaic efficiency of the iron electrodes. Additionally, the residual iron (iron remaining in solution after EC and particle separation) was quantified. All iron samples were measured using a 7700 series ICP-MS (Agilent Technologies, Santa Clara, CA) following acid digestion in a solution containing 4% HNO_3 and 1% HCl. Information regarding faradaic efficiency of iron electrodes in delivering iron dose is shown in Figure A4.

3.5 Electrical Energy Demand Analysis

Electrical energy per order of magnitude reduction (electrical energy demand) was analyzed as a quantitative figure of merit to assess the energy demands associated with electrochemical treatment (Bolton et al., 2001). During each test, the voltage reading on the power supply was used to assess the power demand for each water matrix. Power was calculated using $P = VI$ and the electrical energy demand (kWh/m^3) for batch processes was estimated using Equation 2 (Radjenovic and Sedlak, 2015).

$$EEO = \frac{Pt}{V\, log\frac{C_0}{C}} \quad \text{Equation 2}$$

where P represents the power required for treatment (kW), t represents the duration of treatment (hours), V is the volume of the water in batch conditions (m^3), and C and C_0 are units of concentration (e.g., mg/L).

3.6 Statistical Analysis

Statistical analyses were performed using the Microsoft Excel statistics package and GraphPad Prism 7 software. GraphPad Prism 7 was used to estimate Pearson correlation coefficients in order to assess the impact of specific water quality parameters on TOrC removal and electrical energy demand, and also to conduct ANOVA, t-test, and Grubbs test for outliers analyses ($\alpha=0.05$ for all statistical analyses).

RESULTS & DISCUSSION

4.1 The Impact of Water Quality on Boron-Doped Diamond Electrooxidation

EO experiments were conducted in simple electrolyte solutions and model water matrices. The simple electrolyte experiments provide data on the specific impacts of each electrolyte on TOrC removal, and the model water data detail the performance of EO in TOrC mitigation in representative source waters.

4.1.2 The Impact of Water Matrix Constituents: Chloride, Alkalinity, and Dissolved Organic Carbon

4.1.2.1. Chloride

. Without chloride, TMP removal was approximately 12.3 ± 2.0%, whereas removal improved to 48.5 ± 1.0% after five minutes of BDD-EO in waters with as little as 5 mg-Cl^- /L(Figure 1). However, beyond 5 mg-Cl^-/L, greater chloride additions (20 and 40 mg-Cl^-/L) did not significantly enhance TOrC removal ($p=0.137$). Pearson correlation analysis showed a statistically significant positive relationship between background chloride concentration and TMP removal ($p=0.0001$) (Table A1). However, increased chloride did not statistically increase removal of ACY and BAC-C10 in any scenario ($p=0.250$ and 0.308, respectively) (Table A1).

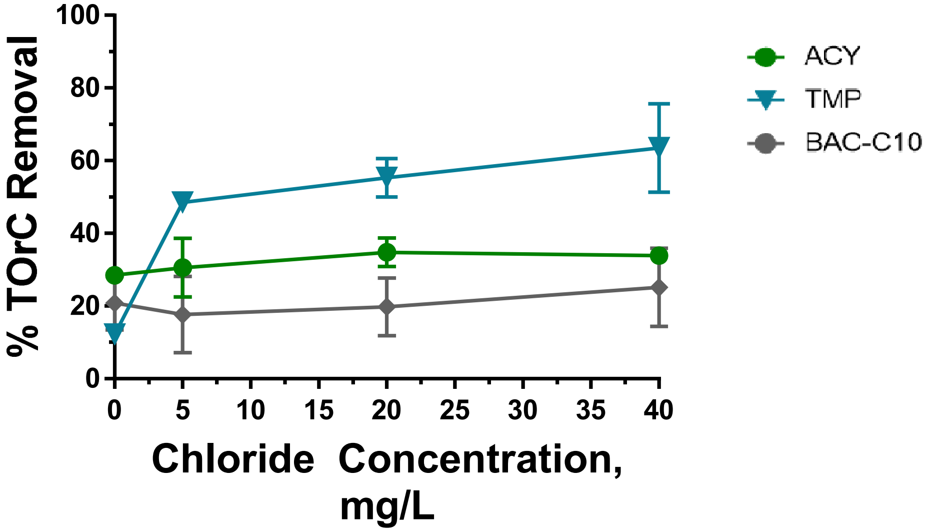

Figure 1: The impact of chloride on electrooxidation of ACY, TMP, and BAC-C10 using boron-doped diamond electrodes at 14.8 mA/cm^2 for 5 minutes. Tests were conducted in 3.5 mM HCO_3^- electrolyte solution. The symbols represent mean values of triplicate experiments. Error bars show ± 1 standard error.

TMP was generally removed to a greater extent than ACY and BAC-C10. Reported rate constants indicate that TMP is generally more reactive with electro-generated oxidants (HO•, O_3, and HOCl) than ACY (Table 1). Activity of these oxidants may support why TMP had the largest removal. The presence of H_2O_2 (Figure A5) may indicate the dimerization of electrochemically produced HO• (HO• + HO• → H_2O_2) (Jeong et al., 2006), although HO• production was not assessed in this thesis. Additionally, O_3 was measured at very low concentrations (Figure A5). These oxidants are continually produced at low concentrations via electrolysis, and may react at a rate similar to the rate at which they are produced. Therefore, the primary oxidant generated in EO cannot be verified in this study.

Chloride was negatively correlated to electrical energy demand for ACY and TMP ($p<0.05$) (Table A1). These data support claims that groundwaters, which typically have higher chloride concentrations than surface waters, may be more amenable to electrochemical treatment with respect to energy demands. However, risks regarding inorganic chlorinated byproducts should be considered in higher chloride conditions (Jasper et al., 2017).

4.1.2.2. Alkalinity

Alkalinity (primarily HCO_3^- and CO_3^{2-}) is a significant oxidant scavenger in AOPs used in drinking water treatment as these ions are generally present in waters at concentrations orders of magnitude higher than the target contaminants (Crittenden et al., 2012). Increased alkalinity significantly decreased the mean removal of TMP ($p=0.001$), but did not impact ACY or BAC-C10 ($p = 0.158$ and 0.258, respectively) (Figure 2). These different TOrC removal trends may suggest that TMP is susceptible to electrochemically generated homogeneous oxidants (O_3, HO•, and HOCl) that are impeded by alkalinity, whereas ACY and BAC-C10 may be removed by oxidation on the anode surface.

The insignificant impact of alkalinity for removal of some TOrCs may be a unique phenomenon in electrochemical systems. Chaplin et al. (2010) focused on the impact of ions during BDD-EO of RO concentrates. They suggested that the scavenging effect of carbonate system ions may not be as deleterious to electrochemical AOPs as they are to conventional AOPs (e.g., UV/H_2O_2, O_3, and UV/TiO_2) because HCO_3^- did not inhibit removal until concentrations exceeded 5 mM HCO_3^- (Chaplin et al., 2010). A primary difference between conventional AOPs and electrochemical AOPs is the impact of anode surface oxidation occurring during EO. Chaplin et al. (2010) speculated that the acidic character of the diffuse layer on the anode surface will protonate carbonate ions near the surface into carbonic acid (H_2CO_3). The HO• rate constant with H_2CO_3 ($<1 \cdot 10^6$

L/mol-s) is lower than the rate constants for HCO_3^- (8.5•10^6 L/mol-s) and CO_3^{2-} (3.9•10^8 L/mol-s) (Buxton et al., 1988; Chaplin, 2014; Crittenden et al., 2012). Accordingly, protonation of carbonate ions near the anode surface will decrease reactivity of carbonate species with the surface-sorbed HO• that may be present during EO.

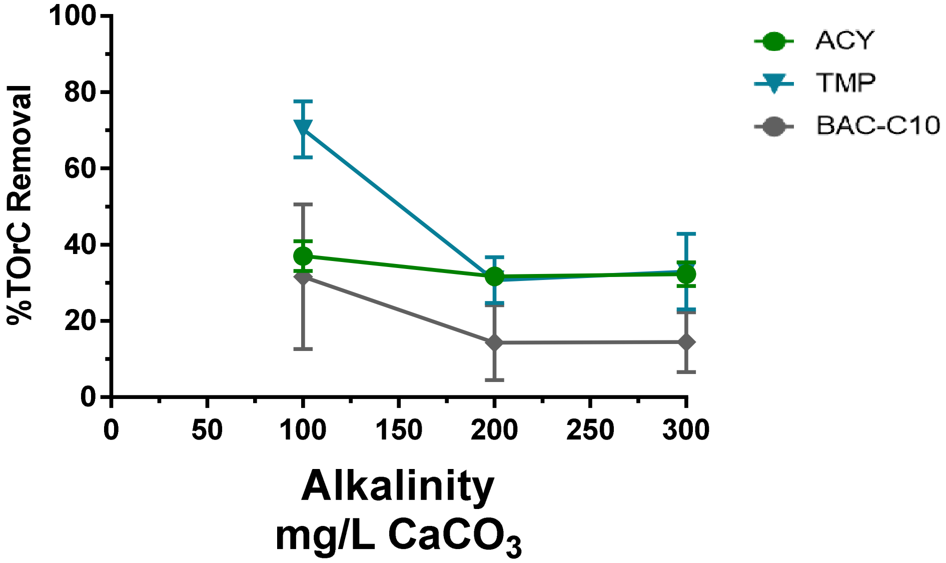

Figure 2: The impact of alkalinity on electrooxidation of ACY, TMP, and BAC-C10 using boron-doped diamond electrodes operated at 14.8 mA/cm^2 for 5 minutes. Tests were conducted in 0.375 mM chloride electrolyte solution. The symbols represent mean values of triplicate experiments. Error bars show ± 1 standard error.

Alkalinity had a mixed impact on electrical energy demand. The electrical energy demand required for TMP treatment increased with increasing alkalinity ($p = 0.0055$) (Table A1), possibly due to homogeneous oxidant quenching via carbonate species. On the other hand, the ACY electrical energy demand had a negative correlation with alkalinity addition ($p=0.0026$), and the electrical energy demand associated with BAC-C10 treatment was not significantly impacted by varying alkalinity ($p=0.847$) (Table A1).

4.1.2.3. Dissolved Organic Carbon

The impact of DOC on TOrC removal during EO was investigated by analyzing the overall removal of TOrCs in model surface water matrices containing 0 – 8 mg-C/L. These values are expected to be in the moderate to high ranges quantified in surface waters (Thurman, 1985a). Pearson correlations indicated a negative correlation with DOC for removal of ACY, TMP, and BAC-C10, but the strengths of correlation were only statistically significant for ACY and TMP (p= 0.0273 and 0.01, respectively) (Table A1). DOC concentrations as low as 2 mg-C/L DOC significantly inhibited removal of TMP and ACY relative to source waters containing no DOC (Figure 3, p =0.015, 0.0002, respectively). These data align with previous studies that suggest that DOC can greatly inhibit oxidative water treatment processes (von Gunten, 2018). DOC had a negative impact on the electrical energy demand of ACY and TMP, which resulted in the highest electrical energy demands for TMP and ACY relative to each water constituent assessed here (Table A1; Table A3). TMP required a significantly higher electrical energy demand (p=0.0050), but ACY's electrical energy demand was not statistically significant.

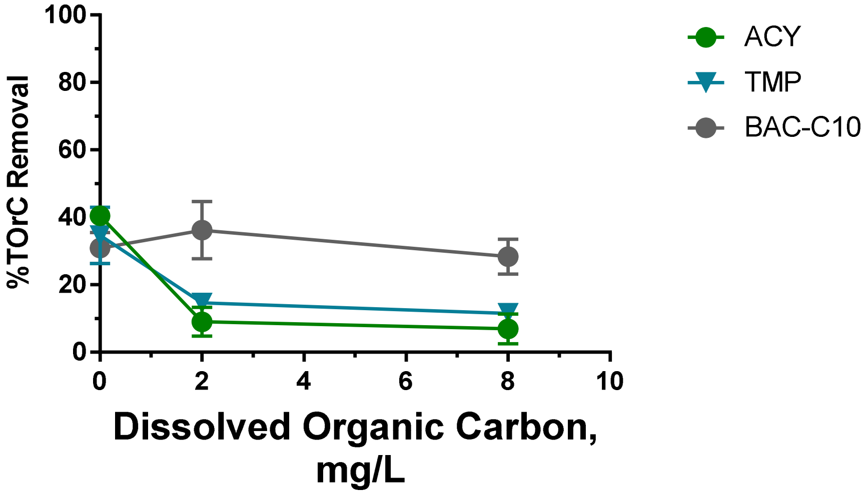

Figure 3: The impact of dissolved organic carbon on electrooxidation of ACY, TMP, and BAC-C10 by boron-doped diamond electrodes at 14.8 mA/cm^2 for 5 minutes. The symbols represent mean values of triplicate experiments. Error bars show ± 1 standard error.

The presence of DOC did not statistically impact removal of BAC-C10 after 5 minutes of EO ($p = 0.368$) (Figure 3). As such, the electrical energy demand for BAC-C10 treatment was not significantly impacted (Table A1; Table A3). The negligible impact of DOC contrasts with other AOP-based work as increased concentrations of a notorious oxidant scavenger had no impact on the oxidative removal of BAC-C10 during EO. This phenomenon is discussed in greater detail in *Section 4.1.4*.

4.1.3. The Efficacy of Boron-Doped Diamond Electrooxidation in Varying Water Quality Surface Waters and Groundwaters

Following the experiments to assess the impact of individual water constituents, EO experiments were conducted in model source water matrices by varying water constituents simultaneously (Figure 4). For all of the different source water matrices, water quality parameters significantly impacted removal of all TOrCs ($p<0.05$, ANOVA). In the model surface waters, approximately 20 – 75% removal was observed for all TOrCs. TMP and BAC had the greatest removal following 20 minutes of EO in model surface waters. ACY and TMP generally had the least removal in *model river water* while BAC-C10 had a contrasting trend with the greatest removal in *model river water*.

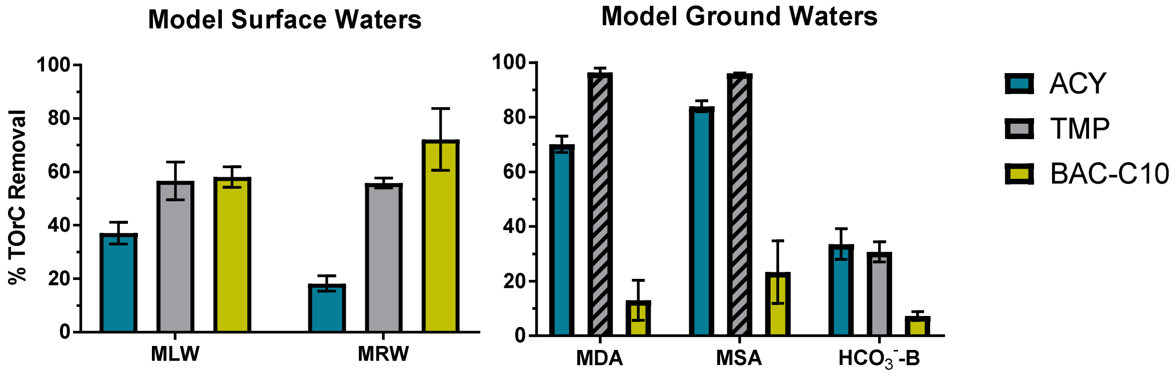

Figure 4: Electrooxidation of trace organics using boron-doped diamond electrodes at 14.8 mA/cm^2 for 20 min in varying water matrices. MLW = *model lake water*, MRW = *model river water*, MDA = *model deep aquifer*, MSA = *model shallow aquifer*, and HCO_3-B = 3.5 mM bicarbonate buffer. Striped bars indicate removal beyond the quantifiable limit of the LC-MS method (~4 µg/L for each compound), in which case the quantifiable limit was used for statistical analyses. The bars show mean values of triplicate experiments and error bars show ± 1 standard deviation.

For model groundwater matrices, ACY and TMP were removed to a greater extent in the *model deep aquifer* (approximately 70 and 95%, respectively) compared to the *model shallow aquifer* (84 and 95%, respectively) (Figure 4). Of the TOrCs, BAC-C10 was removed to the least extent with less than 20% removal in both model groundwaters. This level of removal was similar to removal in the no electricity controls described in *Section 3.2.1.4*, indicating that EO treatment of groundwaters did not remove BAC-C10.

There was a stark difference in removal between model groundwater matrices containing chloride ions (*model shallow aquifer* and *model deep aquifer*) and the matrix without chloride (HCO_3-B). Amongst the matrices tested, HCO_3-B offered the lowest removal for all TOrCs with the exception of ACY's low removal in the *model river water*.

Relative rate reduction is a quantitative parameter used to assess the impact of water quality on the HO• rate constant of different TOrCs (Chaplin, 2018; Crittenden et al., 2012). Although HO• were not verified as the primary oxidant in this work, relative rate reduction calculations were used to aid in analyzing trends associated with homogeneous oxidants in solution. The estimated scavenging trend based on relative rate reduction was: *model river water, model shallow aquifer, model lake water, model deep aquifer,* and *bicarbonate buffer;* where *model river water* has the most scavengers and *bicarbonate buffer* has the least. A more detailed description of relative rate reduction calculations is provided in Appendix 6.6. The results in Figure 4 do not align with the expected trends based on relative rate reduction values for the TOrCs in each water matrix (Table A4). For example, TMP had the greatest removal in the *model shallow aquifer* water matrix and the least removal in the HCO_3-B (Figure 4). However, the *model shallow aquifer* matrix theoretically had more scavengers and the HCO_3-B was expected to have the least scavenging. These data suggest that oxidation in EO systems may proceed via different mechanisms than conventional AOPs, such as surface oxidation or the generation of conventional oxidants. For example, Barazesh et al. (2016) observed that the presence of 100 mM chloride in electrochemical systems enhanced the rate of removal for ACY and TMP by a factor of 2 relative to a 10 mM chloride solution. These differences in removal between chloride-containing waters and chloride-free waters may stem from the production of homogeneous and heterogeneous chloride-derived oxidants.

As shown in Figure 4, the removal behavior of BAC-C10 was quite different relative to TMP and ACY. In water matrices with DOC, ACY and TMP had the lowest removal, whereas BAC-C10 had the greatest removal by EO. The ionic character of each compound likely influenced removal by EO processes. ACY and TMP are neutral compounds in the pH conditions tested. Alternately, BAC-C10 is a permanent cation at all pH conditions. In an electrolytic cell, the anode bears a positive charge due to the production of protons in the diffuse layer, and the cathode is negatively charged. Thus, it is possible that the positively charged BDD surface repels BAC-C10 due to electrostatic repulsion, thereby preventing BAC-C10 from being removed by surface oxidation on the anode surface. Electrostatic repulsion between anode materials and the cationic TOrCs atenolol and metroprolol was also shown by Barazesh et al. (2016).

Although electrostatic repulsion may hinder BAC-C10 treatment, DOC may serve as a transport mechanism to make BAC-C10 more susceptible to surface oxidation by mitigating electrostatic repulsion between BAC-C10 and the anode, as illustrated in Figure 5. The DOC compound in this study was humic acid sodium salt, which is characterized by high aromaticity (UV_{254} =0.65 ± 0.036 cm^{-1} when DOC = 8.5 mg-C/L), resulting in a strong net negative surface charge due to high electron density in aromatic ring systems. The higher BAC-C10 removal in model surface water relative to model groundwater may indicate that the net negative charge of DOC may neutralize BAC-C10 and cause BAC-C10 to co-dissolve or sorb in the electronegative portions of DOC. Once BAC-C10 is sorbed/dissolved in DOC, it may be more vulnerable to anodic surface oxidation.

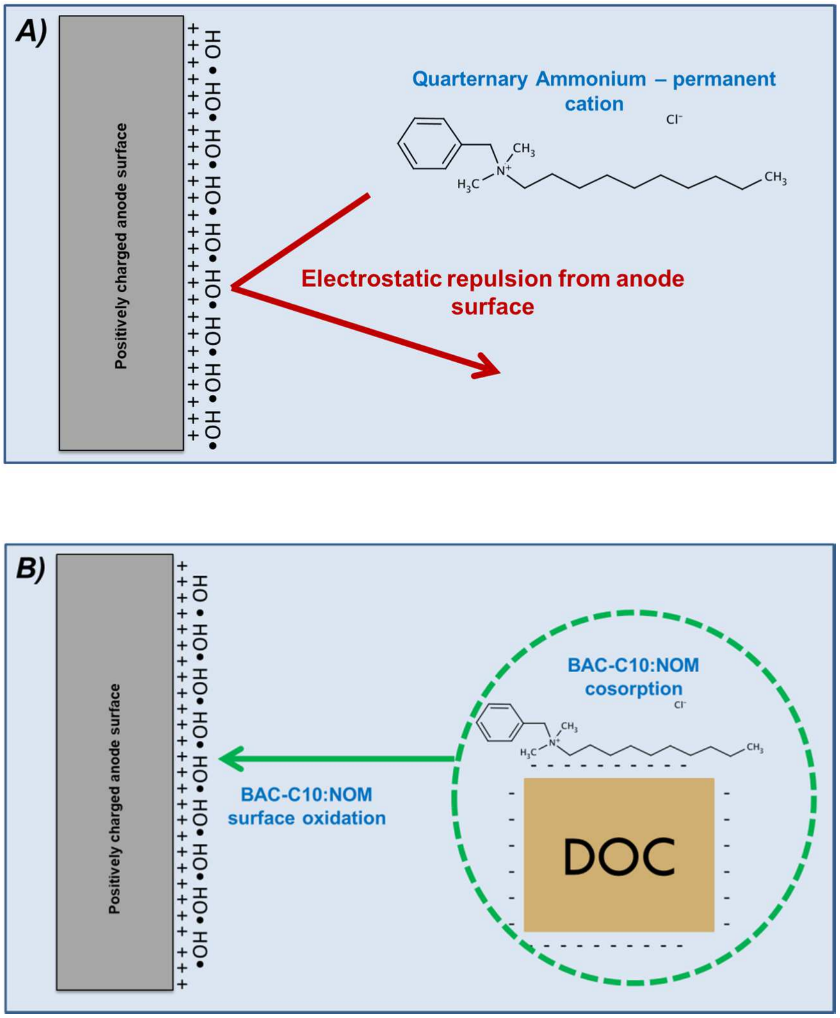

Figure 5: The speculated mechanism of BAC-C10 removal via surface oxidation. A) Electrostatic repulsion between the positively charged anode surface and the cationic BAC-C10. B) Charge neutralization of BAC-C10 via co-dissolution in DOC. Following co-dissolution, BAC-C10 is susceptible to oxidation at the anode surface and inhibitory effects due to electrostatic repulsion are mitigated.

4.1.4. The Impact of Source Water Quality on Electrical Energy Demand

Water quality had a major impact on the electrical energy demand for each TOrC ($p<0.05$ for all). Model groundwaters generally had a lower electrical energy demand for ACY and TMP, potentially due to the higher matrix conductivity and absence of oxidant scavengers (Figure 6). The *model shallow aquifer* required the lowest electrical energy demand for mitigation of ACY and TMP (6.2 ± 0.43 and 3.5 ± 0.06 kWh/m^3, respectively).

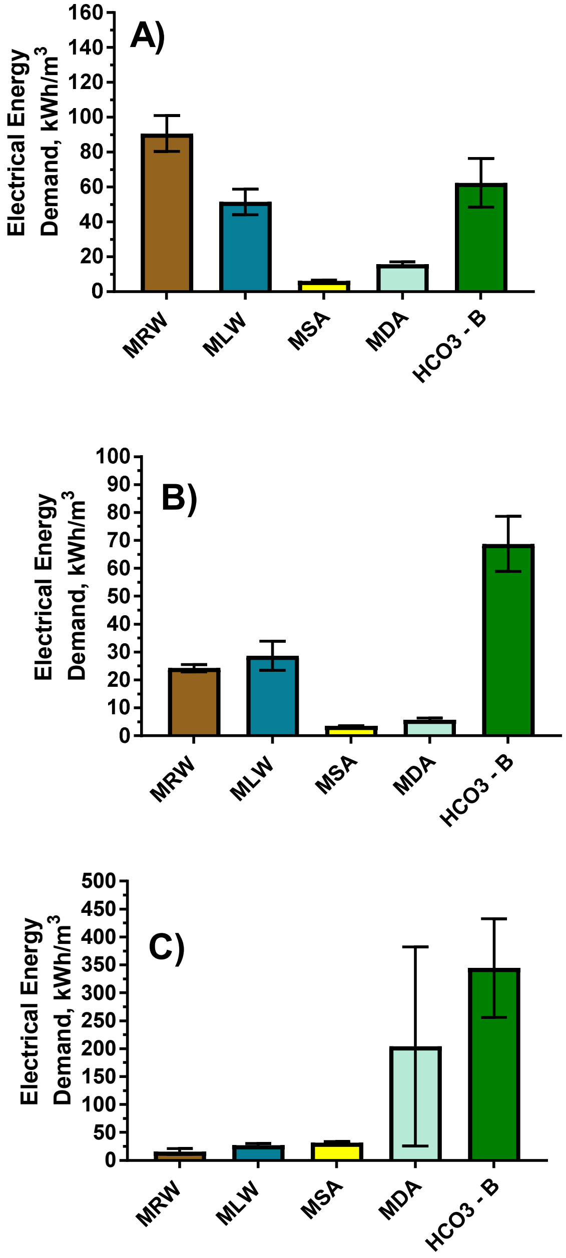

Figure 6: Electrical energy demand after 20 minutes of electrooxidation at 14.8 mA/cm^2 for each model source water. The bars show mean values of triplicate experiments and error bars show ± 1 standard deviation. MRW = *model river water*, MLW = *model lake water*, MSA = *model shallow aquifer*, MDA = *model deep aquifer,* and HCO_3-B = 3.5 mM bicarbonate buffer. A) acyclovir, B) trimethoprim, and C) BAC-C10.

The model surface water matrices generally had higher electrical energy demands for ACY and TMP treatment due to lower TOrC removal, higher amount of oxidant scavengers, and lower solution conductivity. A contrasting trend was observed for electrical energy demand for BAC-C10 treatment, primarily due to higher removal of BAC-C10 in surface water matrices relative to groundwater matrices.

4.2 The Impact of Electrocoagulation Pretreatment on Boron-Doped Diamond Electrooxidation

EO may be an effective oxidative treatment process for mitigation of TOrCs in groundwater matrices based on the high removal of ACY and TMP. However, EO may not serve as an effective process for surface water treatment due to the strong inhibitory impact of DOC. Therefore, pretreatments to remove DOC, such as EC, may improve subsequent removal of TOrCs by EO. The model source water experiments showed that DOC may be a large impediment to EO because DOC was negatively correlated to ACY and TMP removal (p=0.02 and 0.01, respectively). Thus, EC was investigated as a pretreatment to EO to determine the efficacy in sequential electrochemical processes in removing DOC from water to improve downstream TOrC removal.

Sequential EC-EO tests were performed in *model river water* due to the high DOC content in the matrix. The model groundwater matrices generally had similar removal due to EO treatment, whereas removal in the *model deep aquifer* was slightly lower for ACY and BAC-C10 (TMP was approximately 95% removed in both water matrices). Therefore, the *model deep aquifer* was selected as the model groundwater for EC-EO studies. Although the groundwater matrices generally had high removal of ACY and TMP, removal of BAC-C10 was generally poor, so the role of EC in removing BAC-C10 was also studied.

4.2.1. Impact of Electrocoagulation on Dissolved Organic Carbon

Before conducting EC-EO experiments, EC conditions were tested with respect to DOC removal to gain an understanding of iron doses and water quality parameters for pretreatment of DOC in order to minimize potential oxidation scavengers that can inhibit EO.

4.2.1.1 The Impact of pH on Dissolved Organic Carbon Removal

The first parameter examined for EC pretreatment for DOC removal was the initial solution pH. Tests were performed at pH = 8.1 (the initial pH of *model river water*) and pH = 6. Prior studies showed that enhanced coagulation for DOC mitigation is generally effective in an acidic pH range (5.5 – 6.0) (Mayer et al., 2008; Volk et al., 2000). In these experiments, a mid-range EC generated iron dose of approximately 35 mg-Fe/L was selected.

As pH decreased, DOC removal significantly improved using EC ($p < 0.05$) (Figure 7). NOM is generally composed of acidic functional groups, the most common of which is carboxylic acid, which generally has a pKa of 4 -5 (Thurman, 1985b). At pH = 8, the NOM functional groups are in their anionic state and are highly soluble in water; accordingly, NOM is less likely to sorb to flocs during coagulation and flocculation. Decreased pH ostensibly led to protonation of NOM’s functional groups, thus decreasing its solubility in water, and making NOM more prone to removal via EC.

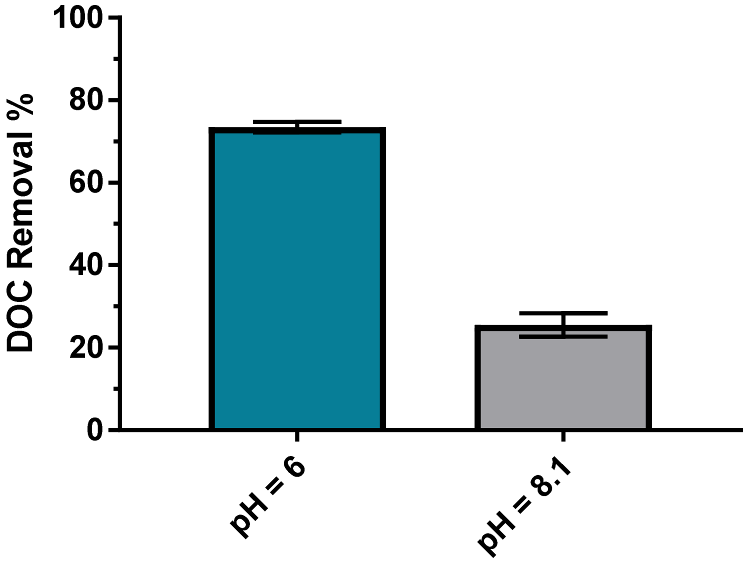

Figure 7: Electrocoagulation (EC) of dissolved organic carbon (DOC) in the model river water matrix at pH 8.1 (as defined for the matrix) versus pH 6 (reflecting enhanced coagulation conditions). Tests were performed using a current density of 5.5 mA/cm^2 for 5 min to dose approximately 35 mg/L Fe. EC was followed by a 10-min flocculation period at 60 rpm (no electricity) and 15 min of settling. The bars show mean values of triplicate experiments and error bars show ± 1 standard deviation.

Due to significantly improved DOC removal at pH = 6 ($p < 0.0001$), pH = 6 served as the initial pH for EC-EO tests focused on improving treatability of model source waters. This result aligns with studies using EC as a pretreatment for membrane processes, where EC at pH = 6 optimized process operation (Ben-Sasson et al., 2013). Other studies have also shown that EC is more effective for NOM and DOC mitigation at pH = 6 compared to neutral pH conditions (Dubrawski and Mohseni, 2013).

4.2.1.2 Point of Diminishing Return Analysis of System Parameters: DOC removal, Iron Dose, UV_{254} Reduction, and Residual Iron

After establishing an operating pH, additional parameters were evaluated to select the operating conditions for electrochemical experiments, including DOC removal, iron dose, UV_{254} absorbance, and residual iron. DOC was used as the primary parameter to assess the smallest iron dose that removed the largest amount of DOC. UV_{254} reduction was used to assess the smallest iron dose that decreased the aromaticity and therefore the potential for disinfection byproduct formation. Iron dose was considered to assess the amount of coagulant required for DOC removal, while residual iron was used to assess the amount of iron remaining in solution following the EC-EO sequence. When the EC generated iron dose was approximately 35 mg-Fe/L, the slope of DOC removal vs. iron dose began to decrease, and the corresponding residual iron and UV_{254} also decreased relative to other iron doses (Figure 8).

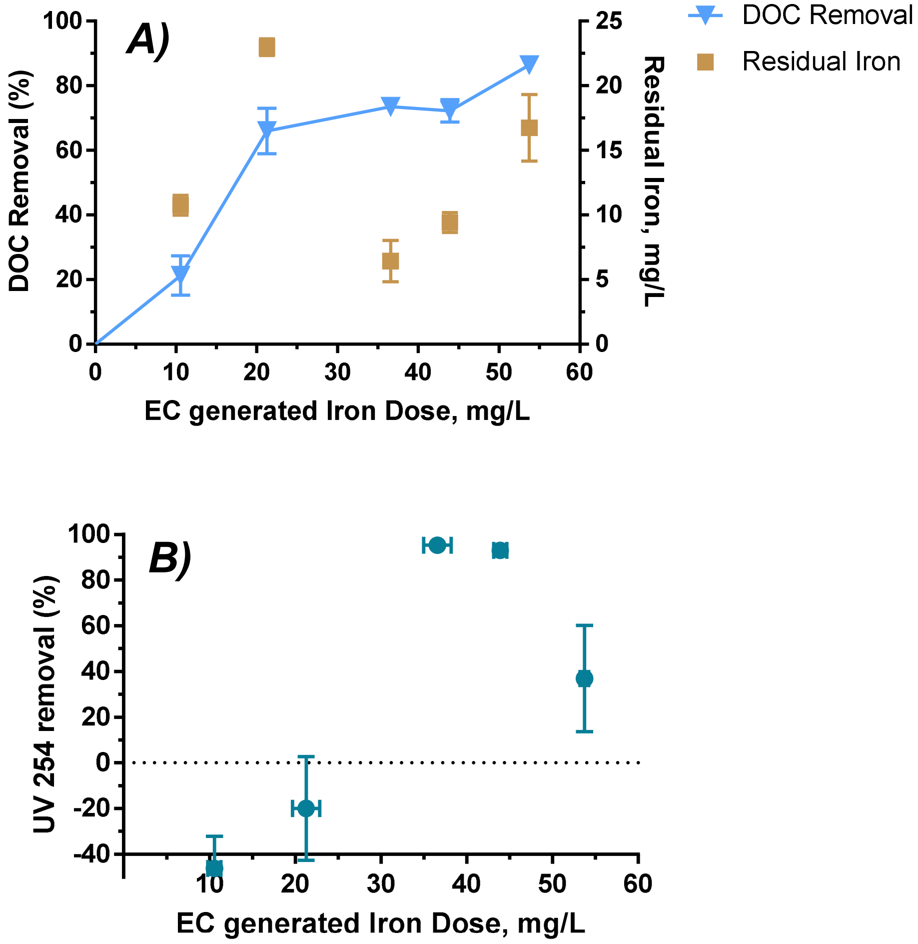

Figure 8: A) Dissolved organic carbon (DOC) removal using electrocoagulation (EC). Iron was dosed via electrolysis at varying current densities (1.85 – 11.1 mA/cm^2) to provide 10 – 55 mg-Fe/L after 5 minutes of electrolysis. Residual iron represents the iron passing through the Whatman filtration step following EC. B) Removal of UV absorbance at 254 nm using EC. The symbols show mean values of triplicate experiments and error bars show ± 1 standard deviation.

Flocs were not formed for EC generated doses of less than approximately 35 mg-Fe/L. The lack of floc formation corresponds to the point at which the residual iron dose was not statistically different than the applied iron dose ($p > 0.05$, t-test for EC iron dose = 10, and 20 mg-Fe/L). Although DOC was well removed in these scenarios, DOC was suspected to sorb to fine iron particles that were not able to agglomerate during the flocculation phase. Based on these data, an EC generated iron dose of approximately 35 mg-Fe/L was selected for EC-EO experiments as it was the lowest iron dose with high

DOC removal (74 ± 7%), the greatest UV_{254} reduction (95 ± 1%), and the least residual iron (6 ± 2 mg-Fe/L) following EC-EO (Figure 8).

Although the residual iron levels do not meet the secondary standards (0.3 mg-Fe/L) for iron in drinking water, the residuals resulting from a dose of approximately 35 mg-Fe/L were the lowest observed for the conditions tested in this project. The high residuals were primarily an artifact of the EC-EO lab-scale testing sequence because the transfer step between the EC and EO processes likely disrupted buoyant flocs in the floatation layer of the reactor. Iron generated during EC has different properties from conventional coagulants, which may affect the ease of flocculation and particle agglomeration. For example, EC-generated iron is dosed as Fe^{2+}, which is more soluble than Fe^{3+}, and requires additional hydrolysis to fully form insoluble complexes that will flocculate and precipitate (Lakshmanan et al., 2010). Ben-Sasson et al. (2013) overcame the residual iron problem using microfiltration; however, this optimized filtration step was not included here as this study primarily focused on the influence of EC pretreatment on EO for TOrC removal. Accordingly, future work should focus on EC process optimization, such as longer flocculation times, to improve particle separation.

4.2.2 Electrocoagulation-Electrooxidation Removal of Trace Organic Compounds

Overall, EC pretreatment ahead of EO improved removal of all TOrCs in the *model river water*. Relative to removal by EO only, sequential EC-EO removal of ACY, TMP, and BAC-C10 increased mean removal by a factor of approximately 3.4, 1.7, and 1.4 respectively (Figure 9). The improved removal may be due to enhanced DOC removal in the preliminary EC step. Less DOC entering EO may cause the target TOrCs to be more readily oxidized as there are less oxidant scavengers in the matrix.

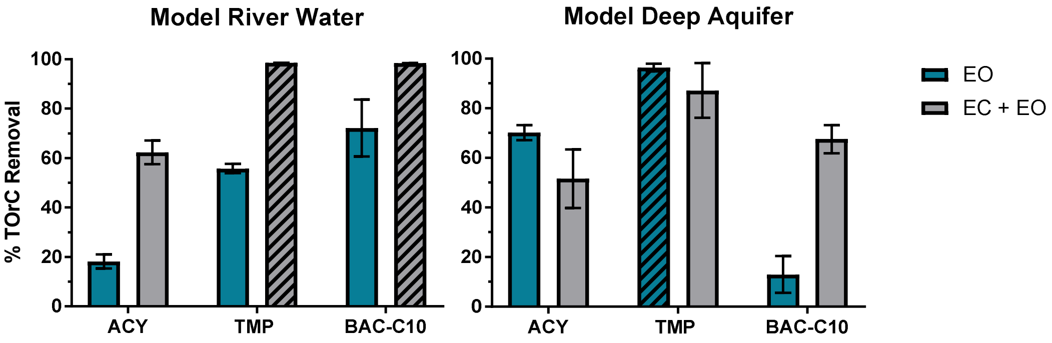

Figure 9: Effect of electrocoagulation (EC) pretreatment ahead of electrooxidation (EO) in variable water matrices. EC was run at a current density of 11.1 mA/cm^2 for 5 min to dose approximately 60 mg/L Fe (based on DOC tests). EO was performed at a current density of 14.8 mA/cm^2 for 20 min. Striped bars indicate removal beyond the quantifiable limit of the LC-MS method (~4 µg/L for each compound), and are shown at the quantifiable limit. The bars show mean values of triplicate experiments and error bars show ± 1 standard deviation.

In the *model deep aquifer* matrix, however, EC pretreatment hindered the mean removal of ACY and TMP, although not significantly. Alternately, EC pretreatment significantly improved removal of BAC-C10 in the *model deep aquifer* by a factor of 5.2 ($p = 0.0036$, t-test). The BAC-C10 removal in *model deep aquifer* was greater than the no electricity EC-EO controls in Table 6.

4.2.2.1. Relative Contribution of Electrocoagulation and Electrooxidation Processes

To provide a measure of the impact of each individual process during the EC-EO sequence, samples were collected at the following points: initial sample, post-EC, post filtration, and post-EO. EO was the predominant contributor to removal of ACY and TMP (Figure 10). However, EC provided the largest contribution to BAC-C10 removal in the *model river water*, and particle separation (rather than EC or EO) was a large contributor to BAC-C10 removal in the *model deep aquifer*.

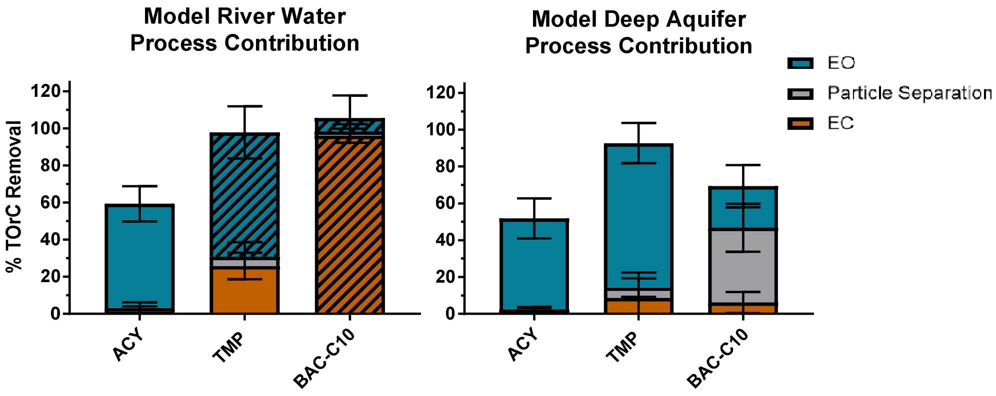

Figure 10: Process contribution of TOrC mitigation using sequential electrocoagulation (EC)-electrooxidation (EO) in *model river water* and *model deep aquifer*. EC was run at a current density of 5.5 mA/cm^2 for 5 min to dose approximately 35 mg/L Fe (based on DOC tests). EO was performed at a current density of 14.8 mA/cm^2 for 20 min. Striped bars indicate removal beyond the quantifiable limit of the LC-MS method (~4 µg/L for each compound), and are shown at the quantifiable limit. The bars show mean values of triplicate experiments and error bars show ± 1 standard deviation.

As noted previously, BAC-C10 was removed to the greatest extent during EC treatment of the DOC-containing water matrices (Figure 10). However, low BAC-C10 removal was observed using EC to treat *model deep aquifer* (no DOC content). This data further supports speculations that BAC-C10 may adsorb to, or dissolve into, large aromatic organics and subsequently be oxidized with them during treatment.

The impact of each process on the solution pH was also determined by measuring pH initially, after EC, and after EO. For each experiment, EC increased the pH and EO decreased the pH (data shown in Appendix 6.7). EO may have decreased the pH due to the oxidation of organics present in NOM as the general scheme of oxidation of organics via AOPs is organic compound (NOM or TOrC) → aldehyde→ carboxylic acid → carbon dioxide or mineral acid (Bolton and Carter, 1994; Crittenden et al., 2012; Mayer and Ryan, 2017).

4.2.2.2. Impact of Electrocoagulation Pretreatment on Electrical Energy Demands: The Prospect of Electrochemical Process Synergy

Combined EC-EO improved the mean electrical energy demand in *model river water*, by a factor 4.2 for ACY and 4.4 for TMP relative to EO alone (Figure 11) (p = 0.017 and 0.001, respectively). Although mean electrical energy demand improved for BAC-C10 by 2.8, the difference was not significant (p=0.0692). These findings demonstrate combined process synergy in surface waters from an energy demand perspective.

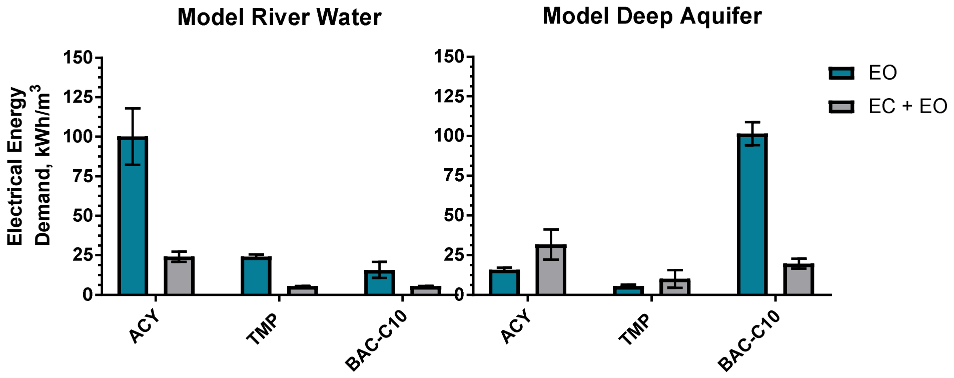

Figure 11: Electrical energy demand of electrocoagulation-electrooxidation (EC-EO) treatment compared to EO-only treatment. The bars show mean values of triplicate experiments, with the exception of EO BAC-C10, which is the result of duplicate experiments. Error bars show ± 1 standard deviation.

The electrical energy demand of EC-EO of the *model deep aquifer* was not statistically different than EO-only treatment for TMP and ACY. The electrical energy demand for BAC-C10 statistically improved following EC-EO (p=0.0036). Accordingly, EC-EO decreased energy demands for all TOrCs in the *model river water*, but not in the *model deep aquifer*.

The electrical energy demands were generally higher than the maximum electrical energy input to conventional systems (3.5 – 7 kWh/m^3 for RO treatment), with the exception of TMP and BAC-C10 treatment following combined EC-EO treatment in *model river water*. It is important to note that these experiments were conducted at a lab-scale in reactors that were not optimized for energy demands.

5. CONCLUSIONS

5.1. Key Findings

The main objective of this work was to assess the efficacy of combined EC-EO water treatment in mitigating TOrCs in model source water matrices. This objective was investigated by conducting experiments to assess the performance of EO in different electrolyte solutions followed by experiments in model source water matrices to evaluate the efficacy of treatment in more authentic water matrices. After EO experiments, combined EC-EO treatment was investigated to understand a multi-barrier water treatment process in overall mitigation of each TOrC. The key findings were:

1. EO was effective as a standalone treatment for ACY and TMP (greater than 70% removal), but not BAC-C10 in groundwater matrices (less than 30% removal). The effectiveness of EO treatment of ACY and TMP in model groundwater matrices was attributed to the absence of oxidant scavengers, which may have promoted oxidation.
2. EO was not effective in treating ACY and TMP in the model surface waters (less than 60% removal), but it was promising for treatment of BAC-C10 in the *model river water* (greater than 60% removal). Lower TOrC removal in the model surface waters was primarily due to the presence of oxidant scavengers. Additionally, lower matrix conductivity hindered the overall treatment effectiveness of ACY and TMP, and increased the energy demands for treatment.
3. Combined EC-EO was generally effective in mitigating challenges innate to the *model river water*. Improved treatment was demonstrated by greater removal of each TOrC (and associated decreases in electrical energy demand). Combined

EC-EO offered improved treatment of BAC-C10 mitigation in the *model deep aquifer,* primarily due to particle separation rather than electrochemical treatment, although EO-only treatment already yielded high removal of ACY and TMP.

4. EC was an effective DOC mitigation technique at pH 6 and offered a high contribution to overall BAC-C10 removal in the *model river water*. EC improved treatment via downstream EO due to oxidant scavenger mitigation.
5. EO offers both homogeneous and heterogeneous oxidation pathways as plausible removal mechanisms. However, TOrC physicochemical properties (e.g., compound charge) may inhibit their removal efficacy in an electrochemical system. In this work, BAC-C10 was not well removed by EO in model waters without DOC. This hindered removal was attributed to electrostatic repulsion between BAC-C10 and the anode surface, where oxidation reactions may occur.
6. Electrical energy demand was evaluated for EO-only and combined EC-EO treatment. EO-only treatment was generally more energy efficient in model groundwaters, and EC-EO improved the energy demands associated with treatment of *model river water*.

The findings from this study demonstrate that combined EC-EO may serve as a promising advanced water treatment process for TOrC mitigation in different source waters.

5.2. Future Work

Electrochemical water treatment processes may serve as a potential treatment approach for mitigating TOrCs in drinking water source matrices due to the high TOrC removal resulting from combined EC-EO. However, future work is needed to understand many process factors such as oxidation mechanisms, disinfection byproduct formation, electrical energy demand optimization, and reactor design.

As mentioned in *Section 2.3.1.2*, EO is a unique AOP capable of generating numerous oxidants depending on multiple factors that can either be manipulated by electrical energy or chemical inputs. For example, the presence of Cl^- in solution may produce HOCl. However, EO simultaneously forms ephemeral ROS that are highly reactive such that they cannot be accurately measured with conventional methods like DPD or the indigo method. Although the oxidants may not be quantified, their activity cannot be fully ruled out if they are in solution long enough to react. In addition to these homogeneous reactions, the anode surface also plays a role in overall compound oxidation via direct electron transfer or surface-sorbed oxidants. Future work is needed to assess the impacts of different oxidants suspected to occur during electrochemical treatment. The use of molecular probes such as para-chlorobenzoic acid, or selective quenchers such as tert-butyl alcohol, methanol, and terephtalic acid, in tandem with cyclic voltammetry may be useful in understanding which oxidants are most active during different electrochemical treatment conditions (Jing and Chaplin, 2017; Pi et al., 2005; Tai et al., 2004).

A comprehensive study of disinfection byproducts (DBPs) resulting from EO of source waters is also needed to more fully vet electrochemical water treatment. The different reactivity associated with each oxidant may promote different routes of DBP formation. For instance, halogenated oxidants may promote formation of classical DBPs (e.g., trihalomethanes and haloacetic acids), whereas ROS may lead to the production of low molecular weight organics (e.g., aldehydes and organic acids) as a result of incomplete oxidation, which may also complicate downstream processes (Mayer and Ryan, 2017). In addition, electrochemical processes can result in a separate suite of inorganic chlorinated DBPs such as chlorate and perchlorate (Bergmann et al., 2009; Jasper et al., 2017; Radjenovic and Sedlak, 2015). While organic chlorinated byproducts are regulated, inorganic byproducts (e.g., chlorate and perchlorate) are only beginning to be regulated. The heightened formation of these inorganic byproducts may potentially serve as an additional barrier to the implementation of electrochemical processes as a drinking water treatment technology (Radjenovic and Sedlak, 2015).

Future work is also needed to optimize EO process design and operation. Differences between flow-through systems and batch-scale processes may have a major impact on removal mechanisms occurring in EO, such as surface oxidation. Results from this work and others suggest that the surfaces of BDD electrodes may have a major contribution to TOrC abatement (Barazesh et al., 2016; Radjenovic and Sedlak, 2015). A benefit of batch-scale processes may be the heightened opportunity for TOrC contact with the electrode surface for oxidation, where this contact time may not be as feasible in a flow-through system processing larger volumes of water. EO reactor characteristics to consider in future studies may focus on the impact of surface-to-volume ratio on EOmediated removal to determine if increased surface area provides more surface oxidation and oxidant production. Work in reactor configuration will also inform design optimization to decrease the overall electrical energy demand of electrochemical systems. For example, electrode configuration parameters such as inter-electrode spacing, submerged electrode depth, connectivity (bipolar vs. monopolar), and number of electrodes can impact required voltage.

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6. APPENDIX

6.1 Trace Organic Compound Molecular Structure

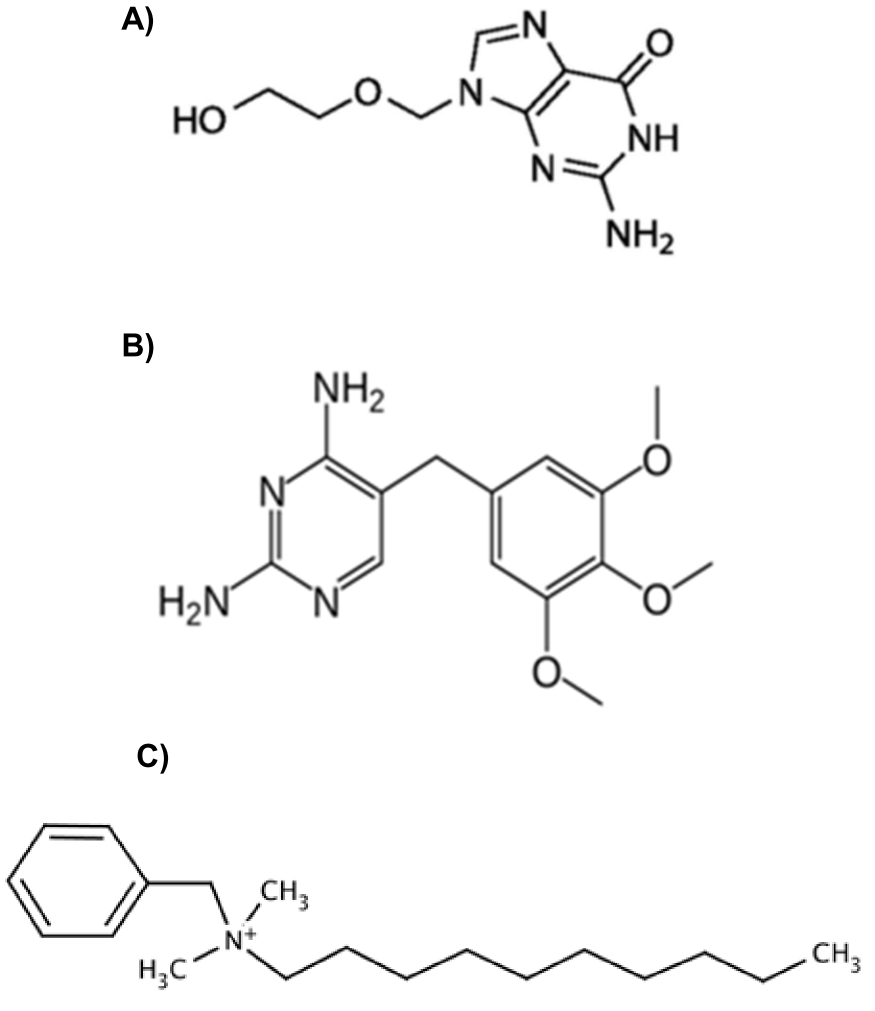

Figure A1: Trace organic compound molecular structure. A) Acyclovir, B) Trimethoprim, C) Benzyldimethyldecylammonium Chloride

6.1. Sample Quenching

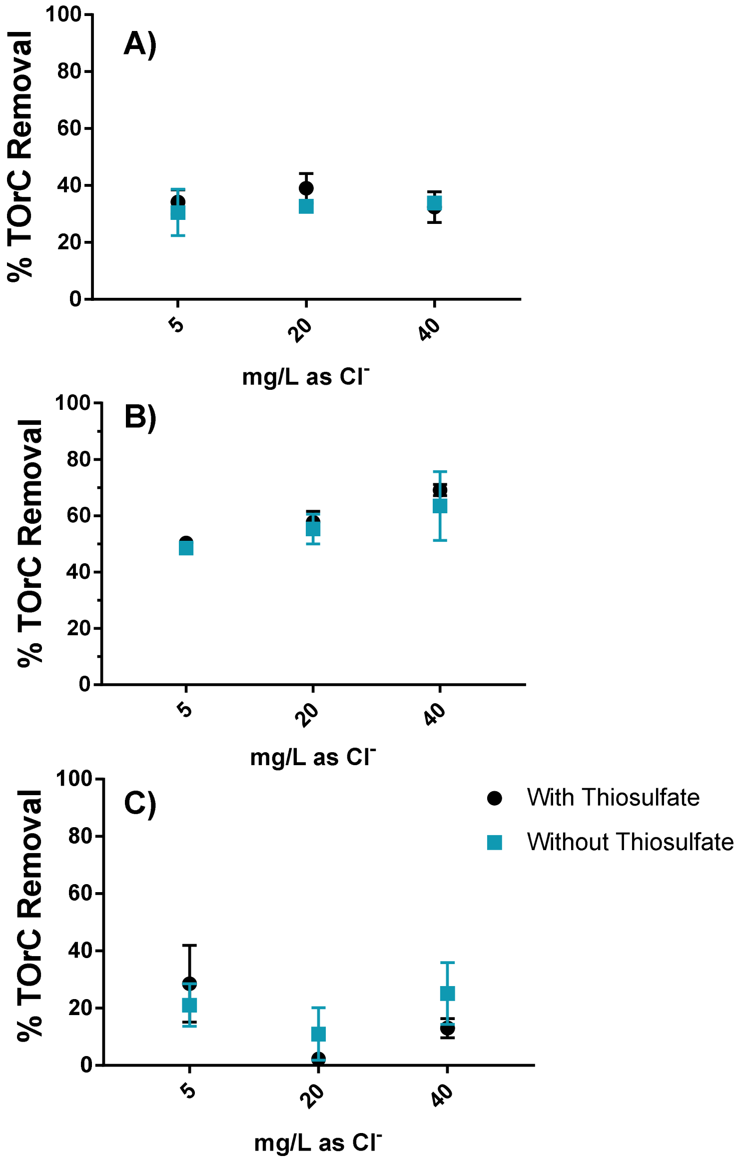

Figure A2: The impact of thiosulfate quenching (0.2 M $S_2O_3^-$ per 1 M ClO^-, as suggested by Boal and Patsalis (2017)) in simple electrolyte matrices with varying chloride concentrations following electrooxidation for 5 minutes at 14.8 mA/cm^2. A) acyclovir, B) trimethoprim, and C) BAC-C10. The data show mean values of triplicate experiments and error bars show ± 1 standard deviation.

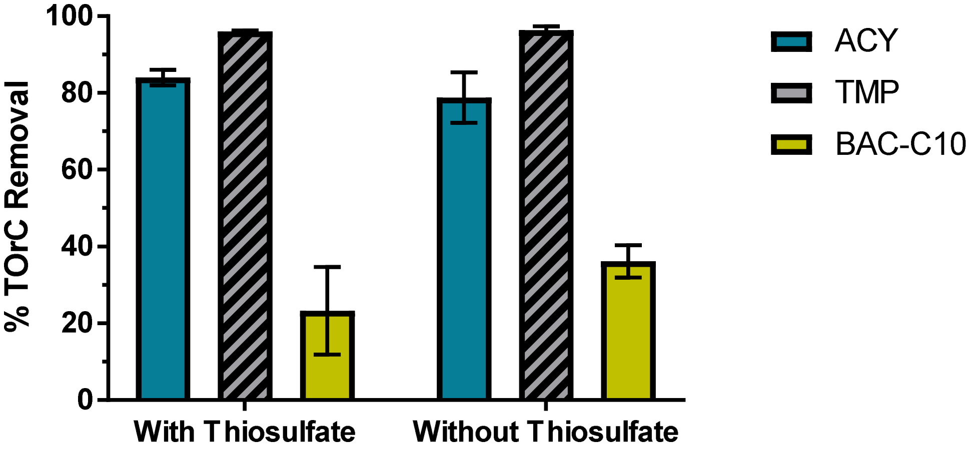

Figure A3: The impact of quenching the *model shallow aquifer* with sodium thiosulfate following electrooxidation for 20 minutes at 14.8 mA/cm^2. Striped bars indicate removal beyond the lowest standard, and are shown at the limit of quantification (~4 µg/L for each compound). The data show mean values of triplicate experiments and error bars show ± 1 standard deviation

6.2. Faradaic Efficiency

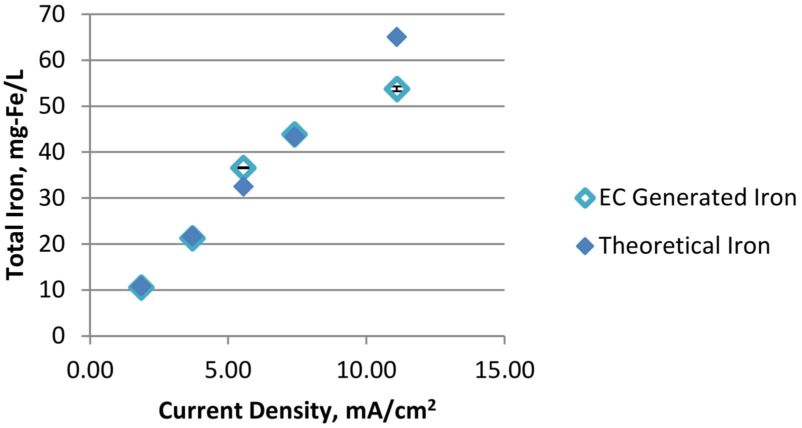

Figure A4: Experimental versus theoretical iron generation as a function of electrocoagulation current density. Experiments were conducted in batch conditions where electrolysis was run for 5 minutes. n = 6 for 3.7 mA/cm^2, n = 4 for 11.1 mA/cm^2, n =3 for the remaining current densities.

6.3. Pearson Correlation of Simple Electrolyte Matrices

Table A1: Pearson correlation analyses of TOrC removal and the electrical energy demand resulting from electrooxidation for 5 minutes at a current density of 14.8 mA/cm^2 in simple electrolyte water matrices. The r coefficient represents the strength of correlation, and a p value less 0.05 demonstrates statistical significance.

		% TOrC Removal			Electrical Energy Demands		
Parameter	TOrC	r coefficient	p value	Significance	r coefficient	p value	Significance
Chloride	ACY	0.377	0.091	×	-0.6987	0.0115	✓
	TMP	0.579	0.005	✓	-0.6559	0.0209	✓
	BAC-C10	0.1187	0.608	×	-0.09378	0.7719	×
Alkalinity	ACY	-0.157	0.497	×	-0.8646	0.0026	✓
	TMP	-0.538	0.012	✓	0.8315	0.0055	✓
	BAC-C10	-0.1053	0.649	×	0.07526	0.8472	×
Conductivity	ACY	-0.010	0.963	×	-0.6667	0.0010	✓
	TMP	-0.188	-0.414	×	-0.2469	0.2806	×
	BAC-C10	-0.208	0.364	×	0.04549	0.8448	×
Dissolved Organic Carbon	ACY	-0.7244	0.0273	✓	0.422	0.296	×
	TMP	-0.753	0.01	✓	0.6985	0.0050	✓
	BAC-C10	-0.2965	0.4386	×	0.1154	0.7676	×

6.4. Reactive Oxygen Species Generation

Ozone and hydrogen peroxide were measured during EO treatment of HCO$_3$-B to assess their potential roles. Hach Method 8311 was used to measure O$_3$ production with a DR3900 Hach spectrophotometer. Hach Model HYP-1 test kit was used to measure hydrogen peroxide using a titrimetric method. Figure A3 shows that H$_2$O$_2$ and O$_3$ were generated over the course of electrolysis.

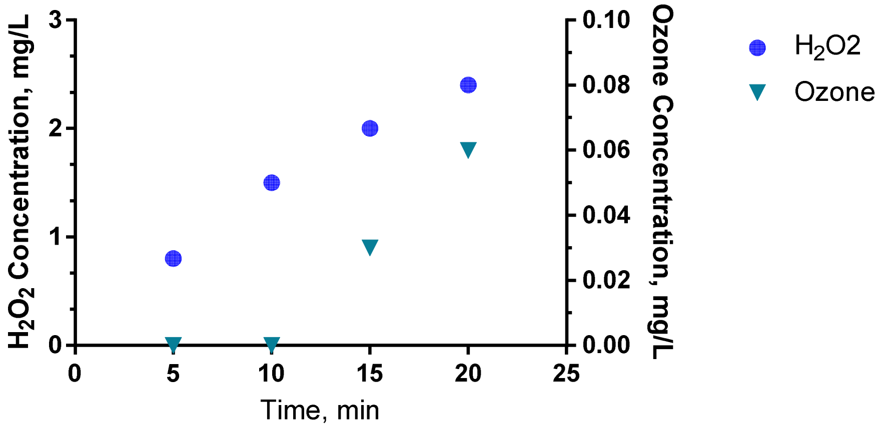

Figure A5: H_2O_2 and O_3 produced during boron-doped diamond electrooxidation of chloride free bicarbonate buffer at a current density of 14.8 mA/cm^2. The data shown are from single experiments.

6.5. Electrical Energy Demand Analysis

The energy demand for electrochemical cell operation ranged from 5.0 to 10.3 kWh/m^3 as a function of water quality and the electrochemical reactors. These values are above the range of conventional treatment discussed in *Section 2.2.3*. These values are only for the electrochemical cell (Table A2), and all other electrical energy demands are normalized to the order of magnitude reduction of each respective TOrC (Table A3 represents simple electrolyte waters and A4 represents model source waters).

Table A2: Energy demands associated with electrochemical cell operations. These values are not normalized to TOrC removal and reflect only the energy demand per volume of water treated.

	Cell Energy Demand (kWh/m^3)	
Water Matrix	EO	EC-EO
Model river water	8.6	10.2
Model lake water	10.3	-
Model shallow aquifer	5.0	-
Model deep aquifer	8.3	9.6

MRW = *model river water*, MLW = *model lake water*, MSA = *model shallow aquifer*, MDA = *model deep aquifer,* and HCO_3-B = 3.5 mM bicarbonate buffer

Table A3: Electrical energy demands resulting from electrooxidation for 5 minutes at a current density of 14.8 mA/cm^2 in simple electrolyte water matrices. * indicate outliers relative to other replicates, according to Grubb's test for outliers, and were not used in subsequent analyses.

	Electrical Energy Demands, kWh/m^3								
Water Matrix	ACY			TMP			BAC-C10		
No Chloride	18.1	19.7	18.0	43.2	43.3	59.6	46.2	24.1	19.8
Low Chloride	12.1	13.8	23.1	8.1	8.6	8.5	60.6	35.0	16.1
Mid Chloride	10.1	9.9	10.9	4.1	3.7	3.4	45.9	11.9	7.2
High Chloride	9.8	8.9	13.3	3.3	3.6	3.6	42.4	26.3	24.3
No DOC	13.3	15.2	14.1	25.3	15.6	13.9	16.4	22.9	21.5
Low DOC	41.7	125.0	56.9	34.3	35.3	41.2	10.4	18.7	11.6
High DOC	342**	65.4	60.4	71.2	45.4	44.6	24.7	16.0	17.8
Low Alkalinity	16.3	12.5	14.1	5.6	4.3	6.5	8.7	22.6	36.0
Mid Alkalinity	10.3	11.0	9.3	10.3	8.6	13.8	14.5	98.4	22.8
High Alkalinity	7.8	9.9	8.9	13.4	11.1	11.5	25.2	13.0	43.2

Table A4: Electrical energy demands resulting from electrooxidation for 20 minutes at a current density of 14.8 mA/cm^2 in model source water matrices. * indicate outliers relative to other replicates according to Grubb's test for outliers, and were not used in subsequent analyses.

	Electrical Energy Demands, kWh/m^3								
Water Matrix	ACY			TMP			BAC-C10		
MRW	83.5	119	98.0	25.0	25.0	22.8	15.8	21.0	10.8
MLW	44.7	59.2	50.6	22.7	32.3	31.1	30.6	24.8	26.7
MSA	6.1	6.7	5.9	3.6	3.5	3.5	31.3	33.9	30.8
MDA	17.4	15.0	15.2	6.5	5.4	5.2	410*	96.3	107
HCO3 - B	57.3	78.2	51.9	69.4	78.3	58.6	311	445	278

6.6. Relative Rate Reduction

Equation 3 was used to estimate the impact of scavenging ions on the efficacy of EO in degrading TOrCs (Chaplin, 2014; Crittenden et al., 2012). Values for the second order rate constant of HO• with different compounds (Cl^-, HCO_3, DOC, and TOrCs) were taken from Buxton et al. (1988) or estimated using EPIWEB 4.1 EPISUITE.

$$Relative\ rate\ reduction\ (R_r) = \left(\frac{k_{\mathrm{R,HO\bullet}} \cdot C_R + \sum k_{i,\mathrm{HO\bullet}} \cdot C_i}{k_{\mathrm{R,HO\bullet}} \cdot C_R}\right) \text{ Equation 3}$$

where, $k_{R,\mathrm{HO}\bullet}$ represents the second order rate constant of the target compound, $k_{i,\mathrm{HO}\bullet}$ represents the second order rate constant of a HO• scavenging compound, and C_i and C_R represent the concentration (M) of the scavenger and target compound, respectively. The average molecular formula of humic acid was assumed to be $C_{187}H_{186}O_{89}N_9S$ based on Anjan et al. (2005).

The corresponding relative rate reduction value can be used to assess the general impact of scavenging ions on the theoretical rate constant of HO• with each ion. As relative rate reduction increases, HO• scavenging increases. As shown in Table A4, the relative order of the waters with respect to scavenger content was: *model river water* > *model shallow aquifer* > *model lake water* > *model deep aquifer* >HCO_3-B. Based on the estimated scavenging, the matrices hypothesized to have the highest removal of target compounds by HO• (least interference from scavengers) were the HCO_3-B and *model deep aquifer*.

Table A4: Relative rate reduction values (unitless) for each model water matrix.

Water Matrix	ACY	TMP	BAC-C10
Model lake water	20.2	13.2	30.5
Model river water	24.3	15.8	36.6
Model deep aquifer	18.3	11.9	27.6
Model shallow aquifer	23.0	15.0	34.7
Bicarbonate Buffer (HCO_3-B)	18.0	11.8	27.2

Table A5: Rate constants used for calculation of relative rate reduction.

Compound	k $_{HO•}$, $M^{-1} s^{-1}$
HCO_3^-	8.50E+06 [a]
Cl^-	4.30E+09 [a]
DOC	4.50E+08 [b]
ACY	4.78E+10 [c]
TMP	1.23E+11 [c]
BAC	2.29E+10 [c]

[a] From Buxton et al. (1988), as reported by Crittenden et al. (2012).
[b] From Chaplin (2014).
[c] Values from EPI SUITE V. 4.1 (USEPA, 2012b).

6.7. The Impact of Electrochemical Treatment on pH

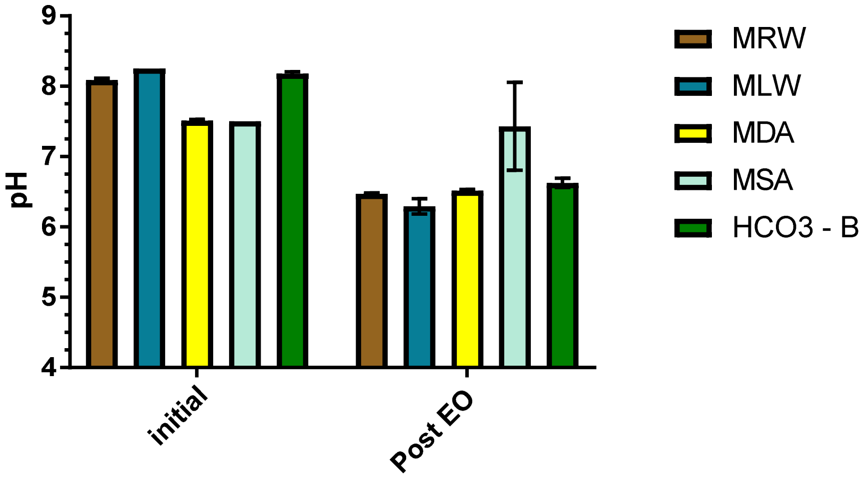

Figure A6: pH before and after electrooxidation. The bars show mean values of triplicate experiments and error bars show ± 1 standard deviation.

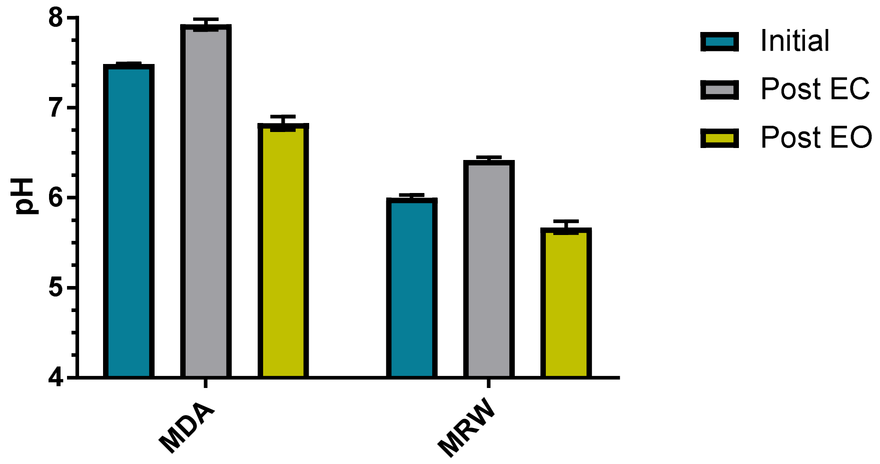

Figure A7 Initial pH, post-electrocoagulation (EC) pH, and post-electrooxidation (EO) pH. The bars show mean values of triplicate experiments and error bars show ± 1 standard deviation.