Impact of Electrocoagulation Pretreatment on E. Coli Mitigation using Electrooxidation

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IMPACT OF ELECTROCOAGULATION PRETREATMENT ON *E. COLI* MITIGATION USING ELECTROOXIDATION

By

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ABSTRACT
IMPACT OF ELECTROCOAGULATION PRETREATMENT ON *E. COLI* MITIGATION USING ELECTROOXIDATION

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Marquette University, 2019

Small drinking water systems serve approximately 20% of the US population, but they can struggle to comply with the Total Coliform Rule and the Disinfectant and Disinfection Byproduct Rule. Issues with insufficient funds to effectively treat the water and difficulties with the transportation of required chemicals can affect compliance. Electrochemical processes may offer an alternative approach for small water systems as they have demonstrated some advantages over traditional treatments, such as reduced handling and storage of chemicals and cost effectiveness. Sequential electrochemical processes have yet to be tested for the treatment of *E. coli* in drinking waters. In this study, electrocoagulation (EC) and electrooxidation (EO) were investigated using two model surface waters and two model groundwaters to determine the efficacy of sequential EC-EO for mitigating *E. coli*. At a current density of 1.67 mA/cm^2 for 1 minute, bench-scale EO alone achieved 4-logs mitigation of *E. coli* in the model shallow aquifer. Increasing the EO current density to 6.67 mA/cm^2 for 1 minute provided similar levels of *E. coli* mitigation in the model deep aquifer (characterized by lower initial chloride concentrations compared to the shallow aquifer). Using a current density of 10 mA/cm^2 for 5 minutes EC achieved 1-log or greater *E. coli* mitigation in all model waters. No additional mitigation beyond EC alone was achieved using sequential EC-EO. Reductions in the initial pH of the surface waters to target higher natural organic matter (NOM) removal did not enhance *E. coli* treatment with EC-EO compared to EC alone. In fact, an average of 64% of NOM was removed no matter the change in pH, which likely limited *E. coli* mitigation. Additional reasons for the lack of improvement in *E. coli* treatment may have included the presence of iron following EC or insufficient EO current density. Decreasing the initial water pH did improve *E. coli* mitigation using EO when pretreated by EC compared to the baseline water matrix pH. Total EC residual iron concentration also increased, and it correlated slightly with *E. coli* mitigation. This correlation and oxidation of ferrous iron may indicate that Fenton-like reactions occurred during EO after EC pretreatment.

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1. INTRODUCTION

Obtaining clean drinking water is vital to avoiding major waterborne microbial and chemical outbreaks that can cause illness or death. Drinking water treatment plants helped protect human health (Constable & Somerville, 2008) by mitigating major contaminants in water such as bacteria, viruses, and disinfection byproducts (DBPs). Public drinking water treatment plants must attain effluent standards established by the United States Environmental Protection Agency (US EPA), e.g., the Safe Drinking Water Act (SDWA) enacted in 1974. More specific regulations stemmed from the SDWA, such as the Total Coliform Rule (TCR) enacted in 1990 (revised in 2013) and the Disinfectants and Disinfection Byproducts Rule (DBPR) enacted in 1996. These rules aim to reduce drinking water concentrations of chemical and microbial contaminants such as DBPs and *Escherichia coli (E. coli),* respectively. *E. coli* is an indicator for fecal contamination due to its presence in mammals' digestive track. It is also rapidly detected, as described in the TCR.

Unfortunately, small drinking water systems (serving ≤ 10,000 people), which serve approximately 20% of the US population, can struggle to comply with the TCR and the DBPR (Allaire, Wu, & Lall, 2018; National Research Council, 1997). Small drinking water systems often have difficulties meeting standards due to lack of sufficient funding for adequate operation managers, equipment upgrades, and required upkeep (National Research Council, 1997). Furthermore, small systems may be hampered by difficulties and concerns with transporting, handling, and storing the large quantities of hazardous chemicals (e.g., oxidants) required for conventional treatment. Accessibility to chemicals following natural disasters can also impede drinking water treatment. Innovative technologies capable of overcoming the barriers to small water systems are of great interest. One potential option is electrochemical water treatment.

Electrochemical technologies may offer several advantages over conventional water treatment, making them particularly amenable to small water treatment systems. Advantages include circumventing corrosive chemicals, small footprint, no alkalinity depletion, straightforward operation and automation, and portability for water treatment during emergencies and in remote settings (Bagga, Chellam, & Clifford, 2008). Two common electrochemical treatment processes are electrocoagulation (EC) and electrooxidation (EO), which both offer possible mitigation (including both physical removal and/or inactivation mechanisms) of an array of contaminants including natural organic matter (NOM, the primary DBP precursor) and microbes like *E. coli*.

Electrocoagulation applies DC power to produce in-situ coagulants using consumable metal electrodes, typically iron or aluminum. The release of metal ions forms metal hydroxide flocs, which can subsequently be physically separated from solution using flotation, sedimentation, or filtration (Comninellis & Chen, 2010). Electrocoagulation has demonstrated removal of bacteria such as *E. coli* by the generation of *in-situ* coagulants, which then flocculate with bacteria and can be filtered from solution (Boudjema et al., 2014; Delaire, Van Genuchten, Nelson, Amrose, & Gadgil, 2015; D. Ghernaout, Badis, Kellil, & Ghernaout, 2008). Delaire et al. (2015) reported removal of 2-4 logs *E. coli* using EC with iron electrodes, with higher mitigation as coagulant dose increased or pH was adjusted. Additionally, EC can remove NOM from water, thereby mitigating the formation of harmful DBPs (Bagga et al., 2008; Dubrawski & Mohseni, 2013a; Matilainen, Vepsäläinen, & Sillanpää, 2010). To further improve NOM removal, enhanced coagulation using increased coagulant dose or decreased initial pH can help (US EPA Enhanced Coagulation Guidance Manual).

Electrooxidation uses DC power and non-reactive electrodes, such as mixed metal oxides (MMO) and boron-doped diamond (BDD), to mitigate pollutants, directly or indirectly through generation of oxidants in solution. Depending on the water matrix or electrode type, EO can oxidize chloride to form free chlorine species. Using appropriate electrodes, electrooxidation is also capable of forming reactive oxygen species such as hydroxyl radicals (Aquino Neto & de Andrade, 2009; Jeong, Kim, & Yoon, 2009). Inactivation of microbes, like *E. coli*, can occur in EO treatment through reactions with the generated oxidants in water (Jeong et al., 2009; Jeong, Kim, Cho, Choi, & Yoon, 2007; Schaefer, Andaya, & Urtiaga, 2015a). Electrooxidation, similar to traditional disinfection processes, will form DBPs when the oxidants react with NOM (Schaefer, Andaya, & Urtiaga, 2015b). While EO is a promising treatment process, the presence of DBP precursors demonstrates the need for a pretreatment process to remove NOM.

Researchers have previously investigated EC and EO treatment for both drinking water and wastewater (Anfruns-Estrada et al., 2017; Boudjema et al., 2014; Delaire et al., 2015; Jeong, Kim, & Yoon, 2006; Kerwick, Reddy, Chamberlain, & Holt, 2005). Some studies even combined electrochemical processes for the treatment of industrial and urban wastewaters (Anfruns-Estrada et al., 2017; Linares-Hernández, Barrera-Díaz, Bilyeu, Juárez-GarcíaRojas, & Campos-Medina, 2010; Llanos, Cotillas, Cañizares, & Rodrigo, 2014). However, sequential EC-EO has yet to be tested for treatment of *E. coli* in drinking waters. To address this research gap, this study investigated the efficacy of sequential EC-EO for mitigating *E. coli* in variable drinking water matrices. The first objective was to establish *E. coli* mitigation using sequential EC-EO to treat synthetic surface and ground water matrices. It was hypothesized that *E. coli* mitigation in the surface water would improve using EC-EO because surface waters contain NOM, the oxidant demand of which can interfere with disinfection processes. EC was anticipated to remove a high degree of NOM (thereby reducing oxidant demand), consequently enhancing *E. coli* mitigation by EO. The second objective was to evaluate the use of enhanced EC (using pH adjustment) as a pretreatment to EO for mitigation of *E. coli*. A lower initial pH was hypothesized to increase NOM removal by EC and further improve disinfection by yielding a higher fraction of free chlorine in the more effective HOCl form during EO. The iron added during EC was expected to consume oxidants such as free chlorine during EO, but also enhance *E. coli* mitigation via Fenton-like reactions.

2. LITERATURE REVIEW

In 1974, the United States (US) Congress passed the Safe Drinking Water Act (SDWA), which mandated that drinking water plants meet effluent standards developed by the United States Environmental Protection Agency (US EPA) (United States Congress, 1974). The intent was to produce safe public drinking water by removing major contaminants that impacted public health. For example, the maximum contaminant level goal for total coliforms, including *E. coli*, is zero. While the SDWA has been hugely successful in protecting human health, microorganisms, e.g., *E. coli* O157, and chemical contaminants in public waters have occasionally led to illness or death in the US (Heiman, Mody, Johnson, Griffin, & Hannah Gould, 2015; Ishii & Sadowsky, 2008).

2.1 Regulations

The Total Coliform Rule (TCR) ensures facilities are below the maximum contaminant level for coliform bacteria. Coliform bacteria are a group of indicator bacteria defined as “facultative aerobic, gram-negative, non-spore forming rod shaped bacteria that ferment lactose with gas formation within 48 hours at 35°C” (Madigan, Martinko, Stahl, & Clark, 2009). Fecal coliform, including *E. coli*, are bacteria that reside in human and animal intestinal systems, and are therefore indicative of fecal pollution in water (USEPA, 2013). *E. coli* is a well suited indictor of fecal contamination for several reasons: high concentrations in mammalian feces (Edberg, Rice, Karlin, & Allen, 2012; Ishii & Sadowsky, 2008), ability to survive in water for 4 to 12 weeks without a host (Edberg et al., 2012), inability to multiply in the natural environment, occurrence in nonpathogenic forms, and its quantification is quick and cost effective compared to other microorganisms (Ishii & Sadowsky, 2008).

The Disinfectant and Disinfectant By-product Rule (DBPR) was introduced into regulation as a result of growing concerns with drinking water concentrations of carcinogenic disinfection byproducts (DBPs), such as total trihalomethanes (TTHMs) and haloacetic acids (HAAs). These DBPs are formed through the reaction of natural organic matter (NOM) with oxidizing disinfectants such as chlorine (Crittenden, Trussell, Hand, Howe, & Tchobanoglous, 2012; Edzwald, 1993; Gopal, Tripathy, Bersillon, & Dubey, 2007; Matilainen et al., 2010; US EPA, 1998). All surface waters contain NOM (Matilainen et al., 2010), which is a multifaceted compound that includes hydrophobic and hydrophilic complexes (Crittenden et al., 2012; Matilainen et al., 2010). The largest fraction of NOM in most surface waters comprises humic compounds, which account for approximately half of the dissolved organic carbon (DOC) in water (Edzwald, 1993; Matilainen et al., 2010).

2.2 Conventional Treatment

A conventional drinking water treatment facility may include grit screening, coagulation, flocculation, sedimentation, granular filtration, and disinfection (Crittenden et al., 2012). While each unit process can reduce contaminants, a majority of *E. coli* mitigation typically occurs during disinfection. For example, chlorination is well documented to inactivate *E. coli* (Aieta & Berg, 1986; Crittenden et al., 2012; Rice, Clark, & Johnson, 1999). According to the US EPA's National Primary Drinking Water Regulations, a facility cannot have more than 5% positive total coliform samples in the treated effluent per month (United States Environmental Protection Agency, 2009). In order to meet this requirement, a Ct value (Concentration of disinfectant * contact time) is used to ensure that the target level for microbial disinfection is achieved. Ct values correlate to a certain extent of microbial inactivation based on the water's temperature and pH. For instance, a Ct of 15 mg-min/L free chlorine results in approximately 4-logs *E. coli* inactivation at pH 7 and 22°C (Owoseni, Olaniran, & Okoh, 2017; Tchobanoglous, Burton, & Stensel, 2003).

In addition to the targeted inactivation of pathogens, water treatment process design and operation must also consider the formation of DBPs. The US EPA Enhanced Coagulation Guidance Manual (US EPA, 1999) details how coagulation processes can be improved to decrease DBP precursors such as NOM prior to disinfection (Crittenden et al., 2012). Enhanced coagulation targets higher NOM removal by either increasing the coagulant dose or reducing the water's pH (US EPA, 1999). Particle removal processes such as coagulation can also remove some fraction of microorganisms. For example, an average of 2 logs removal of *E. coli* can be achieved during coagulation/flocculation/sedimentation under optimal conditions with an iron-based coagulant (LeChevallier & Au, 2004).

2.2.1 Challenges

Traditional treatment processes are adequate to remove an array of contaminants from drinking waters; however, conventional treatment may have risks and limitations. Chlorine disinfection affects the odor and taste of the water as well as adding corrosive chemicals, such as sodium hypochlorite, which can be dangerous to transport, handle, and store (Ghernaout, Naceur, & Aouabed, 2011a; Kraft, 2008; Martínez-Huitle & Brillas, 2008, Owoseni et al., 2017). Chlorine disinfection is also less effective against chlorine-resistant microbes, such as *Cryptosporidium* (Ireland EPA, 2013; LeChevallier & Au, 2004; Owoseni et al., 2017).

Coagulation also has some limitations. The addition of a chemical coagulant can impact overall water quality by consuming alkalinity, thereby decreasing buffering capacity, which can result in more added chemicals in downstream treatment. The sulfates and chlorides added with ferric or aluminum coagulants can also cause corrosion downstream (Matilainen et al., 2010).

Conventional multi-barrier water treatment systems may be associated with additional challenges related to operation and maintenance in small system settings.

2.3 Small Drinking Water Systems

Approximately 97% of all public water systems in the US are small drinking water systems (serving <10,000 people), which serve 20% of the US population (Latham & Impellitteri, 2016). The majority of these systems regularly meet the US EPA requirements, yet violations of both microbiological and chemical regulations can still occur. Approximately 7-8% of small water systems have at least one health-based violation per year (Allaire et al., 2018; National Research Council, 1997). Challenges with evolving source water quality and lack of sufficient funding for adequate operation, including operation managers and aging infrastructure, have contributed to facilities' difficulty in meeting US EPA standards (Latham & Impellitteri, 2016; National Research Council, 1997). Non-compliance with the TCR (USEPA, 2013) or the DBPR (US EPA,

1998) is most common, with a reported 30,000 and 20,000 health-based violations for coliforms and DBPs, respectively, between 1982 – 2015 (Allaire et al., 2018). Alternative treatment technologies, such as electrochemical processes, may overcome some of the limitations of traditional processes for small drinking water systems while still achieving equal or higher removal of contaminants.

2.4 Electrochemical Treatment Processes

Electrochemical treatment is the use of specific electrode material designed to form *in-situ* ions in the water targeting physical-chemical contaminant removal (Ghernaout et al., 2011a; Harif, Khai, & Adin, 2012; Martínez-Huitle & Brillas, 2008; Moreno et al., 2009). Electrochemical treatment processes, such as electrocoagulation (EC) and electrooxidation (EO), have several advantages over traditional treatment process. The EC process does not require handling and storage of corrosive chemicals (Bagga et al., 2008; Ghernaout et al., 2011a; Jeong et al., 2007; Kraft, 2008). Other advantages include no alkalinity consumption (Kraft, Blaschke, et al., 1999; Matilainen et al., 2010), easy availability during emergencies (Bagga et al., 2008; Mollah, Schennach, Parga, & Cocke, 2001), and lower production of DBPs compared to chlorination (Kerwick et al., 2005; Schaefer et al., 2015a). Furthermore, electrochemical treatment can be more cost effective than traditional treatment, making these processes beneficial to small drinking water systems (Bagga et al., 2008; Chen, 2004; Ghernaout et al., 2008; Ghernaout et al., 2011a; Kraft, 2008; Martínez-Huitle & Brillas, 2008). However, the increased electricity demand by electrochemical treatments must be considered. The electricity demand could be a limitation in some emergency scenarios.

Current density is a major contributor to the effectiveness of electrochemistry. It is defined as the current applied over the submerged surface area of the electrode, and is key in the rate of product formation and efficiency of the electrode (Chen, 2004; Ghernaout et al., 2011a; Holt, Barton, & Mitchell, 2005; Kraft, 2008). The reactor design can also impact functionality based on the number of electrodes or the reactor's shape (Chen, 2004; Ghernaout et al., 2011a; Holt et al., 2005). Concentrations of electrolytes like chloride in the water play major roles in whether or not the process is successful, such as determining which oxidants are likely to form, e.g., free chlorine or hydroxyl radicals (Chen, 2004; Ghernaout et al., 2011a; Kerwick et al., 2005; Kraft, 2008).

Another key aspect of electrochemical treatment is the electrode material, which determines the products generated. EC uses iron or aluminum electrodes to generate products similar to that of traditional coagulation (Chen, 2004; Gu et al., 2009; Holt et al., 2005; Matilainen et al., 2010; Mollah et al., 2004; Moussa, El-Naas, Nasser, & Al-Marri, 2017). In contrast, EO electrode materials are selected based on the oxidants needed for disinfection. For example, mixed metal oxides (MMO) promote higher free chlorine generation, whereas boron-doped diamond (BDD) are used for higher reactive oxygen species generation (Ghernaout et al., 2011a; Jeong et al., 2009; Kraft, Stadelmann, et al., 1999; Kraft, 2008; Martínez-Huitle & Brillas, 2008).

2.4.1 Electrooxidation (EO)

Electrooxidation is one disinfection process used in electrochemical treatment of water (Jeong et al., 2007; Martínez-Huitle & Brillas, 2008). There are numerous advantages of EO for small drinking water systems over traditional chlorine-based disinfection, including that it is easily operated, environmentally friendly, and cost effective (Aquino Neto & de Andrade, 2009; Jeong et al., 2007; Martínez-Huitle & Brillas, 2008). Electrolysis during EO can mitigate various biological and chemical contaminants via direct and indirect oxidation processes (Aquino Neto & de Andrade, 2009; Kerwick et al., 2005; Martínez-Huitle & Brillas, 2008). Moreover, the formation of DBPs is significantly reduced by EO since it typically produces a lower free chlorine concentration than used in conventional disinfection processes (Kerwick et al., 2005; Schaefer et al., 2015a).

2.4.1.1 Electrooxidation Mechanism

Two main mechanisms are considered to play a role in the mitigation of waterborne contaminants by EO: direct and indirect oxidation (Aguilar et al., 2018; Chen, 2004; Ghernaout et al., 2011a). Direct oxidation occurs when water adsorbs to the anode surface and is oxidized to form hydroxyl radicals (Aguilar et al., 2018; Chen, 2004). The hydroxyl radicals will directly oxidize contaminants in contact with the electrode surface (Chen, 2004; Ghernaout et al., 2011a; Jeong et al., 2007; Wu, Huang, & Lim, 2014).

Indirect oxidation occurs following electrolysis of the water at the anode and cathode (Chen, 2004; Kraft, Blaschke, et al., 1999; Kraft, 2008), described by equations 1 and 2, respectively.

$(1)\ 2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

$(2)\ 2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

A well-documented side electrolysis process during EO is the oxidation of chloride to form free chlorine, a common disinfectant (Aquino Neto & de Andrade, 2009; Chen, 2004; Kraft, Blaschke, et al., 1999; Kraft, 2008; Martínez-Huitle & Brillas, 2008). Free chlorine generation (hypochlorous acid or hypochlorite ion, based on pH) offers a similar inactivation pathway to traditional disinfection (Jeong et al., 2007; Kraft, Stadelmann, et al., 1999; Kraft, 2008; Ponzano, 2007). Other oxidants, such ozone or hydrogen peroxide could also be generated (Chen, 2004; Jeong, Kim, & Yoon, 2006; Kraft, 2008; Martínez-Huitle & Brillas, 2008). However, concentrations of these oxidants are lower, and they therefore are not considered major contributors for disinfection in comparison to free chlorine and hydroxyl radicals (Jeong et al., 2006; Kraft, 2008).

Hydroxyl radical production provides another indirect contaminant mitigation mechanism in EO, especially in waters without chloride electrolytes (Aquino Neto & de Andrade, 2009; Ghernaout et al., 2011a; Jeong et al., 2009; Kraft et al., n.d.; Schaefer et al., 2015a). Hydroxyl radicals are extremely effective in breaking down organic compounds and microorganisms (Aquino Neto & de Andrade, 2009; Jeong et al., 2009, 2006; Wu et al., 2014).

Another possible indirect oxidation process is Fenton’s reaction. Fenton’s reaction is the oxidation of ferrous iron with hydrogen peroxide at a low pH (< 4), resulting in the production of hydroxyl radicals (Anfruns-Estrada et al., 2017; Hu et al., 2018; Yeon Kim et al., 2011). However, the added pollutant of metallic salt makes this a non-ideal reaction (Chen, 2004; Ghernaout et al., 2011a; Martínez-Huitle & Brillas, 2008; Wu et al., 2014).

2.4.1.2 Anode Electrode Material

The type of metals or coated metals used in the electrode are important to the effectiveness of EO (Aguilar et al., 2018; Jeong et al., 2009; Kraft, 2008; Martínez-Huitle & Brillas, 2008). Mixed metal oxides (MMO) and boron-doped diamond (BDD) are the two most common electrode types used for EO (Ghernaout et al., 2011a; Särkkä, Vepsäläinen, & Sillanpää, 2015). MMO electrodes, typically titanium (Ti)-based, can be further categorized based on the metal coating added to the electrode's surface, such as iridium oxide (IrO_2) or ruthenium oxide (RuO_2) (Jeong et al., 2009; Wu et al., 2014). The addition of metal coating heightens the performance of the MMO electrode by increasing the surface area, therefore improving electrolysis activity and reaction rates (Wu et al., 2014). The anode material determines the main mechanism of treatment during EO (Aguilar et al., 2018; Martínez-Huitle & Brillas, 2008; Wu et al., 2014). Jeong et al. (2009) demonstrated that MMO electrodes are mainly governed by the generation of free chlorine, with the coating influencing the rate of chlorine generation (Kraft, Stadelmann, et al., 1999; Kraft, 2008). Alternately, BDD electrodes are more likely to produce reactive oxygen species (Bergmann & Rollin, 2007; Ghernaout et al., 2011a).

2.4.1.3 *E. coli* Mitigation by Electrooxidation

Inactivation of *E. coli* by EO can be achieved using either MMO (Jeong et al., 2009; Kerwick et al., 2005; Martínez-Huitle & Brillas, 2008; Schaefer et al., 2015a) or BDD (Jeong et al., 2009, 2006; Martínez-Huitle & Brillas, 2008) anodes. The main factors that influence the reduction of *E. coli* include current density, characterization of the water, and electrode material (Kraft, 2008). Numerous investigations have demonstrated that higher current densities correlate to increased rates of *E. coli* mitigation (Aquino Neto & de Andrade, 2009; Jeong et al., 2009, 2006; Schaefer et al., 2015a). Kerwick et al. (2005) used MMO platinum (Pt) electrodes to evaluate the influences of specific electrolyte on *E. coli* inactivation and determined that chloride plays a major role in disinfection. Anode material and electrolytes present will also determine the mechanisms to inactivate *E. coli* (Jeong et al. 2009). Most waters contain some chloride and numerous investigations have confirmed MMO Ir/O_2 electrodes have the highest chlorine rate generation, making them the most effective electrode for disinfection by free chlorine (Bergmann, Iourtchouk, Schöps, & Bouzek, 2002; Jeong et al., 2009; Kraft, 2008).

2.4.1.4 Limitation of Electrooxidation

Unfortunately, EO can generate DBPs from oxidation reactions with the NOM in the water (Bergmann & Rollin, 2007; Ghernaout et al., 2011a; Särkkä et al., 2015; Schaefer et al., 2015a). Särkkä et al. (2015) summarized studies on the removal of NOM by EO, finding that long treatment times or high currents were required to achieve removal. Furthermore, Schaefer et al. (2015) and Bergmann & Rollin (2007) established that both MMO and BDD electrodes generate DBPs during electrolysis. Schaefer et al. (2015) investigated the formation of DBPs by MMO electrodes and demonstrated the formation of TTHMs during disinfection of *E. coli.* Lower current densities yielded lower levels of TTHMs, as expected because less free chlorine was generated. Similarly, Bergmann & Rollin (2007) reported 30 ppm chlorate production after 10-minutes treatment using a BDD anode. The formation of DBPs by EO indicates that some pretreatment would be helpful to decrease NOM in the water prior to EO.

2.4.2 Electrocoagulation (EC)

Electrocoagulation (EC) is similar to traditional coagulation (Mollah et al., 2001). However, there are numerous advantages of EC over chemical coagulation, especially for small drinking water systems. Chemical coagulants such as aluminum sulfate and ferric chloride cause multiple issues in treatment systems. For example, chemical coagulation can decrease pH and can consume alkalinity, which results in further chemical addition to reestablish a neutral pH before distribution (Gu et al., 2009). In contrast, EC does not consume alkalinity (Matilainen et al., 2010).

Another issue with chemical coagulation is handling of the sludge waste. EC typically has lower sludge formation (Matilainen et al., 2010; Mollah et al., 2001; Moussa et al., 2017). Furthermore, EC literature suggests that it may more effectively remove smaller particles compared to traditional treatments due to electrophoretic mobility (Mollah et al., 2001; Mollah et al., 2004; Moussa et al., 2017). This could include dissolved species like hydrophilic acids (a fraction of NOM), which are difficult to mitigate by chemical coagulation (Matilainen et al., 2010). Hydrophilic acid removal can occur when the pH is acidic, favoring precipitation and charge neutralization (Vepsäläinen et al., 2009). EC also produces hydrogen gas on the cathode, which causes electrofloatation by forcing flocs to rise to the surface (Mollah et al., 2001; Moussa et al., 2017). With proper tank design, the electrofloatation layer can be removed from the treated effluent.

2.4.2.1 Electrocoagulation Mechanisms

Both chemical and physical removal mechanisms contribute to particle removal during EC, similar to conventional coagulation. The major difference is the *in-situ* addition of the coagulant metal dose during EC (Ghernaout, Naceur, & Aouabed, 2011b; Mollah et al., 2004). The concentration dosed, C (g/L) (Equation 3), can be calculated in accordance with Faraday's law (Equation 4), which establishes the dose of metal coagulant ion (M^+ [Al^{3+}/Fe^{2+}]) added to the water based on a specific current and time (Moussa et al., 2017):

$$(3)\ C = \frac{m}{V}$$

$$(4)\ m = \frac{I * t * M_w}{z * F}$$

Where m is the mass of metal dissociation (g), I is the current (A), t is the treatment time (s), M_w is the molecular weight of the metal, z is the number of electrons (in this case, $Fe^{2+} = 2$), F is Faraday's constant (96,485 C/mol), and V is the volume of the treated water (L).

Figure 1 depicts various iron and aluminum species that can form based on the pH and metal concentration. Similar to traditional coagulation and flocculation processes, the M^+ ions will react with hydroxide to form various polymeric hydroxide complexes (Ghernaout et al., 2011a; Lakshmanan, Clifford, & Samanta, 2009; Mollah et al., 2001; Moreno C et al., 2009). Depending on the pH, the polymeric hydroxides will react with negatively charged particles, like NOM and *E. coli*, through charge neutralization (Crittenden et al., 2012; Mollah et al., 2004; Moussa et al., 2017). Metal hydroxide precipitate can also be instantaneously generated, causing agglomeration of smaller particles via differential settling flocculation (Crittenden et al., 2012; Delaire et al., 2015). As the pH decreases, charge neutralization will play a bigger role, especially at lower coagulant concentrations (Crittenden et al., 2012).

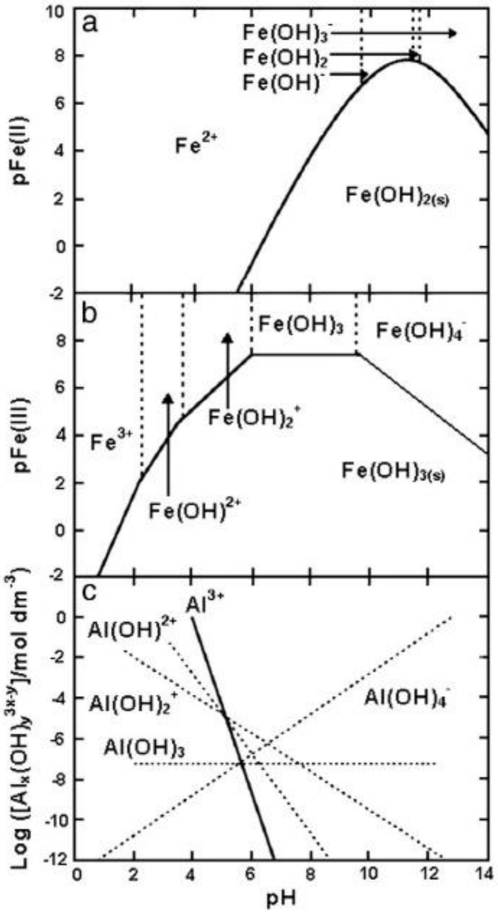


Figure 1 - The principle aqueous species diagram for (a) Fe (II) and (b) Fe (III). Below the solid line represents the insoluble iron species at equilibrium and the dotted lines represent the dominance limits of the soluble iron species. (c) Al (III) solubility versus pH diagram. Figure reproduced with publisher permission from Ghernaout et al. (2011).

Simultaneously, the cathode generates hydrogen gas and hydroxide ions, which contributes to the increase in pH by EC (Ghernaout et al., 2011a; Mollah et al., 2004; Moussa et al., 2017). Thus, the resulting precipitates will be removed either via electrofloatation or further flocculation and settling (Bagga et al., 2008; Ghernaout et al., 2011a; Moussa et al., 2017). Flocculation mechanisms like diffusion, advection, or differential settling allow EC to remove numerous particles from water including microbes, NOM, and inorganics (Arjmand, Rezaee, Nasseri, & Eshraghi, 2015; Boudjema et al., 2014; Delaire et al., 2015; Dubrawski & Mohseni, 2013a; Ghernaout et al., 2008; Moreno et al., 2009; Ricordel, Darchen, & Hadjiev, 2010; Vepsäläinen et al., 2009).

2.4.2.2 Natural Organic Matter Removal by Electrocoagulation

Särkkä et al. (2015) summarized investigations of NOM (a DBP precursor) removal by EC, finding that a majority of the studies reviewed demonstrated greater than 70% NOM removal from synthetic and natural water. Overall NOM removals are similar, albeit slightly less using EC compared to conventional coagulation (Bagga et al., 2008). Current densities equal or less than 10 mA/cm^2 offered the greatest removal of NOM, with higher current densities showing no additional improvement (Dubrawski & Mohseni, 2013b). Vepsäläinen et al. (2009) found that the electrical charge (applied current * reaction time normalized to the reactor’s volume (C/L)) and the initial pH were the crucial parameters for NOM removal.

Temperature also slightly impacted NOM removal efficiency, most likely due to the relationship with the rate formation of the metal coagulant dose (Vepsäläinen et al., 2009). A key parameter requiring further evaluation is the speciation of the metal ions in the water, especially in terms of iron EC. Dubrawski & Mohseni (2013a) established that unique iron species generated during EC can remove NOM to different extents. Ferrous or ferric iron could form complexes with NOM before forming metal hydroxides, thereby limiting ideal floc formation (Bagga et al., 2008).

2.4.2.3 *E. coli* Mitigation by Electrocoagulation

E. coli removal by EC can be equal to or greater than levels observed in traditional coagulation with settling (Delaire et al., 2015). Ghernaout et al. (2008) established that increases in current (or current density) result in higher mitigation of *E. coli*, similar to the trend exhibited for NOM removal. As shown by Faraday's law (Equation 4), current plays a vital role in the concentration of EC coagulant formed, and higher coagulation generation can form more flocs for physical removal process (Boudjema et al., 2014; Ghernaout et al., 2008). Increasing the current loading rate by adjusting treatment time may also impact the dose, even at constant current density, again enhancing mitigation of *E. coli* (Ndjomgoue-Yossa, Nanseu-Njiki, Kengne, & Ngameni, 2015). Delaire et al. (2015) further confirmed that dose plays a vital role, demonstrating improved removal of *E. coli* in a synthetic groundwater as the EC iron dose increased. A study of the Oued El Harrach River demonstrated 2.84–logs *E.coli* bacteria was removed using EC operated at 2.0 A for 10 minutes (approximately 110 mg/L Al) (Boudjema et al., 2014). However, a higher dose may impact the efficiency of EC by creating higher sludge generation and wearing the electrodes (Ghernaout et al., 2011a).

The main removal mechanism of *E. coli* removal during EC is adsorption through flocculation (Boudjema et al., 2014; Delaire et al., 2015). Additional possible mechanisms include direct damage to the cell or proteins by passage through the electrical field (Boudjema et al., 2014; Ndjomgoue-Yossa et al., 2015) or reaction with oxidants formed by electrolysis (Delaire et al., 2015; D. Ghernaout et al., 2008).

2.4.3 Electrocoagulation – Electrooxidation (EC-EO)

Both EO and EC offer advantages and disadvantages for *E. coli* mitigation. Disinfection of *E. coli* by EO is extremely effective, yet DBPs can form due to reactions between NOM and oxidants (Schaefer et al., 2015a). EC has been shown to remove NOM at rates equal to traditional coagulation and can mitigate some *E. coli* (Delaire et al., 2015). Therefore, leveraging the benefits of both processes in sequential operation, similar to that of a traditional multi-barrier treatment plant, could result in sufficient *E. coli* mitigation and adequate NOM removal to meet water quality standards (Linares-Hernández et al., 2010).

Linares-Hernández et al. (2010) implemented EC-EO in industrial wastewater, resulting in overall improved degradation of chemical oxygen demand, color, turbidity, and coliforms. The time to achieve 99% removal of these contaminants decreased from 21 hours using EO alone to 2 hours using EC-EO. Combining EC with electro-Fenton, which oxidizes ferrous iron to generate hydroxyl radicals, has also demonstrated promise. Anfruns-Estrada et al. (2017) established that the combination of iron EC and electro-Fenton with BDD electrodes plus air diffusion in an urban wastewater could achieve complete removal of numerous microbes, including *E. coli*, at a neutral pH. The study demonstrated that sequential application of EC and electro-Fenton (current densities of 20 and 33 mA/cm^2, respectively) for 30 minutes resulted in greater removal than either process alone. Other investigations utilized an integrated electrochemical cell, where both EC and EO processes occur in the same reactor. Two different studies showed that an integrated electrochemical cell could significantly reduce *E. coli* concentrations in an urban wastewater, even at current densities below 2 mA/cm^2 (Cotillas, Llanos, Cañizares, Mateo, & Rodrigo, 2013; Llanos et al., 2014).

Although integrated electrochemical treatment processes have demonstrated effective *E. coli* removal in industrial and urban wastewaters, use of sequential EC-EO for the mitigation of *E. coli* in drinking water sources has yet to be reported. Thus, the objective of this investigation was to determine the efficacy of *E. coli* mitigation by a sequential EC-EO treatment process in variable quality drinking water.

3. MATERIALS AND METHODS

3.1 *E. coli* Preparation

Log-phase stocks of *E. coli* 15597 were mixed with glycerol at 5:1 (volumetric ratio) and stored at -20°C until use. In preparation for tests, *E. coli* cells were cultured overnight at 35°C in Bacto™ Tryptic Soy Broth (TSB) (BD, Sparks, MD). On the day of each experiment, the overnight cultures were mixed with fresh TSB media (1:5 volumetric ratio), and incubated at 35°C on a shaker table (150 rpm) for 3 hours to achieve log-phase growth. The spiking concentration was determined by measuring optical density using a spectrophotometer at 520 nm. The high-organic content added by the TSB was then removed from the *E. coli* cells to decrease interference from organics during electrochemical treatments. This was done by centrifuging the *E. coli* for 10 minutes at 2000 rpm (Thurston-Enriquez, Haas, Gerba, & Jacangelo, 2003), discarding the supernatant, and resuspending the cells in an equivalent volume of Buffered Demand Free (BDF) water (0.54 g disodium phosphate, 0.88 g monopotassium phosphate and 1.0 L of Milli-Q water, pH 7). This centrifugation/re-suspension process was repeated a total of three times. The cells were spiked into synthetic drinking water matrices for electrochemistry tests at an approximate concentration of $1x10^6$ colony forming units (CFU)/mL.

3.2 Water Matrices Preparation

Four distinct synthetic waters were developed to represent characteristic alkalinity, chloride, turbidity, NOM, and pH of common natural drinking water sources.

The matrices were modeled after actual surface and groundwaters, including Lake Michigan, the Mississippi River, a sandstone aquifer, and a dolomite aquifer, as described by Heffron (2019).

Model water matrices were prepared by adding the target concentrations of alkalinity, chloride, turbidity, and dissolved organic carbon (DOC) to Milli-Q water, as shown in Table 1. The solution was rapidly mixed (≈ 400 rpm) for 20 minutes to ensure dissolution of the salts. The pH was adjusted to the target value, as shown in Table 1.

Table 1-Water quality parameters for model surface and groundwaters

Water Type		**Alkalinity (mg/L)[1]**	**Chloride (mg/L)[2]**	**Turbidity (NTU)[3]**	**DOC (mg/L)[4]**	**pH[5]**	**Approximate Conductivity (μS/cm)[6]**
Surface Waters	Model Lake Water (Lake Michigan)	95.0	13.3	0 [7]	~ 2.7	8.25	260
	Model River Water (Mississippi River)	119	11.4	5.95 [7]	~ 8.0	8.1	300
Ground Waters	Model Deep Aquifer (sandstone aquifer)	178	3.80	0	0	7.5	415
	Model Shallow Aquifer (dolomite aquifer)	226	70.4	2.00	0	7.5	775

[1] Added as $NaHCO_3$ salt
[2] Added as KCl salt
[3] Added as A2 dust
[4] Added as humic acid sodium salt
[5] 10% HCl or HNO_3 and 1M NaOH were used for pH adjustment; 1% acid was used for minor adjustments
[6] Approximate conductivity was calculated based on the added salts; pH adjustment would further affect conductivity
[7] Beyond the turbidity added as A2 test dust, humic acid also contributed to the total turbidity of the matrix waters, resulting in 3.40 NTU in the model lake water and 11.8 NTU in the model river water

3.3 Processes

3.3.1 Sampling

A schematic of the bench-scale treatment train is shown in Figure 2. *E. coli*, NOM, total iron dose, residual iron, ferrous iron, and free chlorine concentrations were sampled throughout the treatment train, as shown.

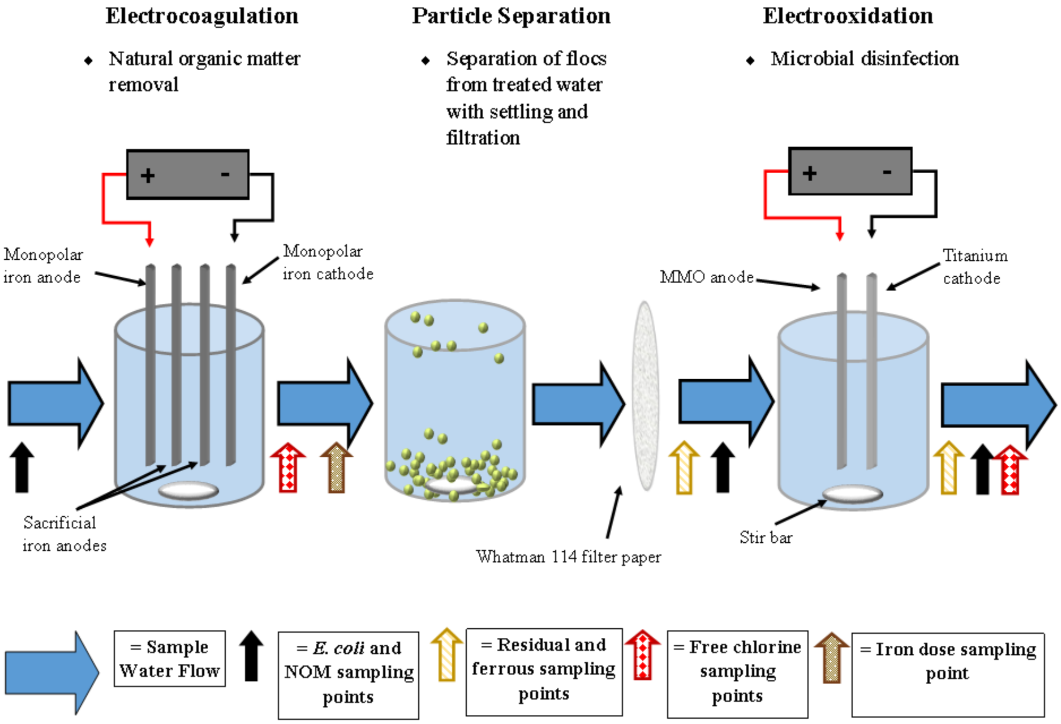


Figure 2 – Schematic of the bench-scale electrocoagulation (EC)-electrooxidation (EO) treatment process and associated sampling points. Each process was operated as a batch system.

Initial concentrations of *E. coli* and NOM were determined by sampling the water before treatment. To establish EC removal of *E. coli* and NOM, samples were collected following particle separation. Electrooxidation was conducted alone and in series (EC-EO) to determine removal of *E. coli* and NOM for the individual treatment and the overall sequence. For *E. coli* tests, immediately after completion of EC-EO and EO, 0.063 mM sodium thiosulfate per sample was used to quench oxidation reactions and halt bacterial inactivation.

3.3.2 Electrocoagulation

Steel 1020 electrodes (VMetals, Milwaukee, WI) were sanded with a finely graded sandpaper to remove corrosive iron from the electrode's surface. The electrodes were rinsed with Milli-Q water and placed under UV light for approximately 30 minutes per side to inactivate any bacteria present prior to experiments. The electrodes were connected to a switcher box, which was connected to a DC power source. The switcher box was used to reverse the cathode and anode polarity every 30 seconds. Polarity reversal was used to limit the formation of a passivation layer on the cathode, which interferes with efficiency of EC, as described by Maher et al. (2019).

The EC reactors consisted of a 250-mL polypropylene reactor filled with 200 mL water. The four electrodes were arranged as a bipolar cell in a parallel connection, as shown in Figure 2. The submerged electrode surface area was 15 cm^2 with 1 cm inter-electrode spacing. A stir rate of 200 rpm was applied with a magnetic stir bar. Prior to each EC experiment, a current density of 6.7 mA/cm^2 for 10 minutes was applied in a bacteria-free matrix to overcome the passivation layer, activate iron generation, and to polarize the electrodes (Lakshmanan et al., 2009). The electrodes were rinsed with Milli-Q to remove iron flocs formed during polarization.

3.3.2.1 Electrocoagulation Operating Parameters

In preliminary tests, a range of total iron doses was applied to the model river water (highest NOM concentration) to evaluate the total iron dose that produced the highest NOM removal. The total iron dose was estimated in accordance with Faraday's law (Equation 4). Additionally, the concentration of total residual iron after EC was considered as a secondary parameter for determining optimal dose (i.e., targeting higher NOM removal, together with lower remaining total iron concentration). Current densities ranging from 0.667– 10 mA/cm^2 (~5 – 65 mg/L Fe, as estimated by Faraday's Law) were tested. Dubrawski & Mohseni (2013b) established that no significant improvements were shown in NOM removal at current densities above 10 mA/cm^2. The best operating parameters for subsequent experiments were determined to be 10 mA/cm^2 (82.1 mg/L Fe) based on the highest NOM removal (69 ± 3.2%) and lowest total residual iron (11.2 ± 0.7 mg/L Fe) (Figure 3).

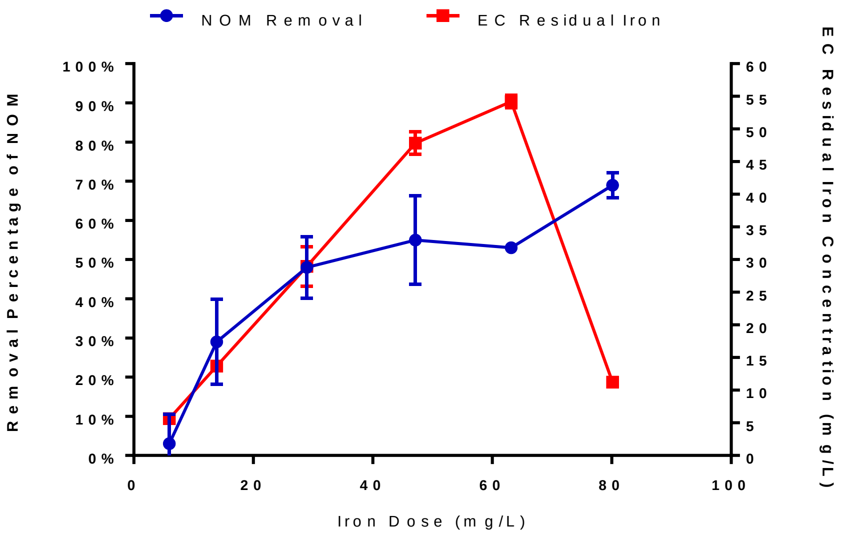


Figure 3 – Electrocoagulation operating parameters. Primary y-axis: Average natural organic matter (NOM) removal versus applied total iron dose by EC (mg/L). Secondary y-axis: EC total residual iron concentration (mg/L) (passed through particle separation) versus applied total iron dose by EC (mg/L). Points show averages of triplicate tests ±1 standard error.

Measured total iron concentrations were higher than the estimated values from Faraday's law. On average, the actual total iron doses were 1.3 times greater than that of the estimated values, similar to findings by Gu et al. (2009). The difference was attributed to the dissolution of iron in water without an applied current (Gu et al., 2009; Sasson, Calmano, & Adin, 2009).

3.3.3 Particle Separation

Following EC, the electrodes were removed and flocculation, settling, and filtration were implemented to separate the iron flocs. The process was modified from Vepsäläinen et al. (2009) to include 10-minutes flocculation at 60 rpm with a magnetic stir bar followed by 15-min sedimentation with no mixing. Approximately 150 mL was pipetted from the center of the reactor to avoid collecting flocs and was subsequently passed through Whatman 114 filter paper (pore size = 25 μm) via vacuum filtration. The filtrate was transferred to a sterile reactor for EO treatment, and the pH was measured.

3.3.4 Electrooxidation

For EO, a titanium cathode was used in combination with a non-reactive thin-film iridium coated dimensionally stable anode (mixed metal oxide; MMO; Ti/IrO_2+TaO_2) (Ti Anode Fabricators Pvt. Ltd, Chennai., India). Prior to EO experiments, the anode was conditioned by polarization using electrolysis in strong acid (0.2 M HCl or 0.25 M HNO_3) at 7.4 mA/cm^2 for 10 minutes (modified from Devilliers & Mahé (2010) and Jeong et al. (2006)). Between trials, the electrode was re-submerged in acid for sterilization, and electrolysis was performed at 7.4 mA/cm^2 for 5 minutes followed by a rinse with Milli-Q water.

3.3.4.1 Electrooxidation Operating Conditions

EO experiments were performed in 200-mL polypropylene reactors with 1-cm electrode spacing. Preliminary tests were conducted to determine the EO operational parameters. These tests were performed in the model shallow aquifer water, which was anticipated to offer the highest bacterial inactivation due to generation of free chlorine based on the high chloride concentration of 70.4 mg/L. A range of currents (20, 25, 30, or 35 mA) was applied for 1-minute periods to identify the condition leading to the highest quantifiable *E. coli* inactivation (countable plates between 30 – 300 CFUs). The highest quantifiable inactivation was achieved using 25 mA (1.67 mA/cm^2), which was then used in all subsequent EO experiments. The submerged surface area was adjusted to achieve a consistent current density of 1.67 mA/cm^2 for all EO tests.

3.4 Analysis

The pH and conductivity were determined using a VWR symphony Benchtop B40PCID meter.

3.4.1 E. coli

E. coli was analyzed using the standard membrane filtration method 9222 (APHA, WEF, & AWWA, 1999) with Difco™ m Endo Broth MF™ (BD, Sparks, MD). Samples were diluted with 10-fold serial dilutions in BDF, and 2 mL of the relevant dilution was pipetted onto GN-6 Metricel® MCE Membrane Disc Filters (Pall Corporation) for vacuum filtration. A BDF-only (negative) sample was also processed to ensure that no contamination occurred. After incubation for 22 – 26 hours at 35°C, the colonies were counted.

3.4.2 Total Iron Concentrations

Bacteria-free matrices were used to evaluate 1) the total iron dose remaining in solution immediately following EC, 2) EC total residual (in solution after particle separation), and 3) EC-EO total residual iron concentrations (in solution after EC-EO treatment and 15-min settling). The EC-EO with settling sample was included to determine if the total residual iron concentration could be decreased through settling after the sequential electrochemical process. Independent tests were conducted to determine the total iron dose generated during EC, where the reactor contents were rapidly mixed to ensure homogeneous iron distribution before sampling.

In accordance with EPA method 3050B (US EPA, 1996), water samples were acid digested in 2% nitric acid and 0.5% hydrochloric acid. Total iron was then analyzed using a 7700 series inductively coupled plasma mass spectrometer (ICP-MS) (Agilent Technologies, Santa Clara, CA).

3.4.3 Natural Organic Matter Concentration

NOM experiments were conducted in the surface waters without the presence of *E. coli* to avoid sample interference. Analysis of NOM was conducted in accordance with Standard Method 5310 – Total Organic Carbon (TOC) (APHA, WEF, & AWWA, 1999). A standard curve was developed using 850 mg/L potassium hydrogen phthalate (KHP), where 1.0 g of KHP is equivalent to 0.47 g of total organic carbon. Samples were filtered through PTFE 0.45 µm syringe filters to analyze the dissolved organic content (DOC) (Agela Technologies, Torrance, CA), acidified to pH 3, and analyzed with an ASI-V autosampler and TOC-V_{CSN} analyzer (Shimadzu).

3.4.4 Free Chlorine Concentration

Hach Method 8021 was used to quantify the free chlorine generated during EC, EC-EO, and EO alone. The standard curve was developed using NaOCl and a spectrophotometer (Genesys 20 Thermo Scientific, Waltham, MA) at wavelength 530 nm (curve shown in Appendix A, Figure A1). The method limit of detection was 0.02 mg/L Cl_2.

3.4.5 Total and Ferrous Iron Concentrations

Hach Methods 8008 and 8146 were used to quantify total and ferrous iron, respectively. A standard curve was developed using ferrous chloride and a spectrophotometer at wavelength 510 nm (Appendix A, Figure A2). Total iron samples were diluted in Milli-Q water at 1:20 and ferrous samples were diluted 1:10 and 1:1 after EC and EC-EO, respectively, to ensure concentrations in the relevant analytical range. The method detection limit was 0.02 mg/L Fe.

3.5 Electrical Energy Efficiency

The electrical energy efficiency for *E. coli* mitigation using each electrochemical treatment was analyzed using the electrical energy per order magnitude reduction (EEO) metric (Bolton, Bircher, Tumas, & Tolman, 1996). EEO is the amount of energy required to mitigate one log of a contaminant per volume of water. The power (P) for each treatment was estimated using the equation: $P = V*I$, where the current (I) is multiplied by the voltage (V) input. Voltage varied throughout the testing and was calculated as the average of the initial and final values for every test.

3.6 Data Analysis and Quality Control

All experiments were performed in triplicate. Statistical analyses were conducted using GraphPad Prism version 7 at a significance level of $\alpha=0.05$ for t-test, two-way ANOVA, and Tukey’s post hoc. Linear regression analysis was performed to determine Pearson’s R^2 correlation factor. Full statistics are summarized in Appendix B.

Positive controls (no power applied) were conducted for *E. coli*, iron, DOC, and free chlorine generation, each demonstrating that the target constituent did not change in the absence of electrochemical treatment. The maximum loss of *E. coli* was 0.04 ± 0.03 logs, illustrating that no significant losses occurred in the system in the absence of applied current. Full data for the *E. coli* controls are shown in Appendix C.

4. RESULTS AND DISCUSSION

4.1 Impact of Water Quality on *E. coli* Mitigation

4.1.1 E. coli Mitigation by EC

E. coli mitigation was evaluated in the four water matrices for electrocoagulation alone (EC), electrooxidation alone (EO), and the two treatments in sequence with particle separation (EC-EO). EC reduced *E. coli* concentrations in every water matrix (Figure 4). The model groundwaters experienced higher *E. coli* mitigation (greater than approximately 2 logs) than both surface waters (approximately 1-log reduction). The model deep aquifer offered statistically greater *E. coli* mitigation than the model lake water and model river water ($p = 0.0043$ and 0.0167, respectively). The limited removal of *E. coli* in the two surface waters could be attributed to competition between the natural organic matter (NOM) and *E. coli*. Table 2 shows that NOM removal occurred in both surface waters, with significantly more removal in the model river water compared to the model lake water ($p < 0.0001$). This could be a result of the higher initial concentration of NOM in the model river water.

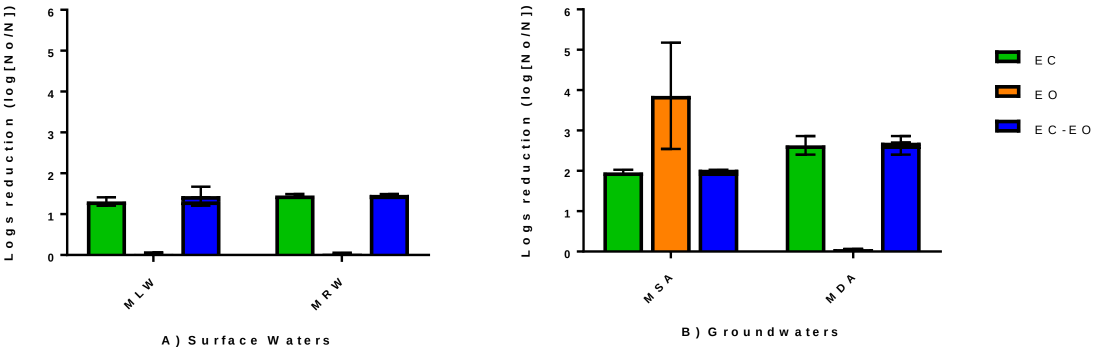


Figure 4 –*E. coli* mitigation by electrocoagulation (EC), electrooxidation (EO), and sequential EC-EO in A) model surface and B) model groundwaters. MLW = model lake water, MRW = model river water, MSA = model shallow aquifer, and MDA = model deep aquifer. Operating parameters: EC at 10 mA/cm^2 for 5 minutes and EO at 1.67 mA/cm^2 for 1 minute. Each bar represents the average of triplicate tests, with ±1 standard deviation shown by the error bars.

Despite the different characteristics of the two groundwaters in this investigation, *E. coli* mitigation was not statistically different between them using EC (p = 0.5858). However, *E. coli* removals in the two groundwaters were slightly lower than the approximately 3-log removal reported by Delaire et al. (2015) when applying a similar EC dose (1.5 mM Fe) to a synthetic groundwater. Variances in water parameters could explain this difference, especially the 320 mg/L of chloride added to the groundwater by Delaire et al. (2015). High chloride has the ability to limit the impact of ions like carbonate or sulfate, which can form an insulating layer on the electrode's surface, thereby decreasing current efficiency (Chen, 2004). Additionally, Delaire et al. (2015) flocculated for 90 to 120 minutes and then settled overnight, which could allow more *E. coli* to settle compared to the 10-min flocculation and 15-min settling periods used here.

Table 2 - Final water quality parameters for each treatment process (EC, EO and EC-EO) in each of the model drinking water matrices. Values represent averages from triplicate tests ±1 standard deviation.

Water Matrix		Model Lake Water	Model River Water	Model Shallow aquifer	Model Deep Aquifer
EC	Final pH	9.59 ± 0.13	9.55 ± 0.07	8.93 ± 0.14	9.13 ± 0.07
	NOM Removal %	8.2 ± 4.1%	61.7 ± 7.8%	N/A	N/A
	Free Chlorine (mg/L)	BDL	BDL	BDL	BDL
	Total Residual Iron (mg/L)	12.61 ± 0.79	11.24 ± 0.71	17.14 ± 0.76	15.20 ± 4.02
EO	Final pH	8.01 ± 0.03	7.98 ± 0.07	7.78 ± 0.02	7.77 ± 0.01
	NOM Removal %	14.1 ± 0.9%	2.2 ± 1.7%	N/A	N/A
	Free Chlorine (mg/L)	BDL	BDL	0.074 ± 0.008	BDL
EC - EO	Final pH	9.53 ± 0.09	9.47 ± 0.03	8.90 ± 0.15	9.02 ± 0.07
	NOM Removal %	9.1 ± 5.4%	64.8 ± 8.6%	N/A	N/A
	Free Chlorine (mg/L)	BDL	BDL	0.010 ± 0.014	BDL
*BDL = Below detection limit of Hach Method 8021 (0.02 mg/L) N/A = Not applicable since NOM was not added to model groundwaters					

4.1.2 E. coli Mitigation by EO

An EO current density of 1.67 mA/cm^2 was insufficient to reduce *E. coli* concentrations in the model waters, with the exception of the model shallow aquifer (Figure 4). High *E. coli* mitigation in the model shallow aquifer was most likely due to the high chloride concentration (70.4 mg/L Cl^-), which was five times greater than the other waters. The higher chloride concentration resulted in higher free chlorine generation, as shown in Table 2.

To assess the impact of increased free chlorine generation in the other waters, higher current densities were tested. Doubling the current density to 3.34 mA/cm^2 significantly increased *E. coli* mitigation in the model lake water ($p = 0.0164$) (Figure 5). However, there was no improvement in *E. coli* mitigation in the model river water or the model shallow aquifer. Again, low free chlorine generation (Figure 6) was likely responsible for the lack of *E. coli* mitigation at 3.34 mA/cm^2. Using the highest EO current density tested of 6.67 mA/cm^2, there were significant differences in *E. coli* mitigation among the three model waters tested ($p < 0.011$).

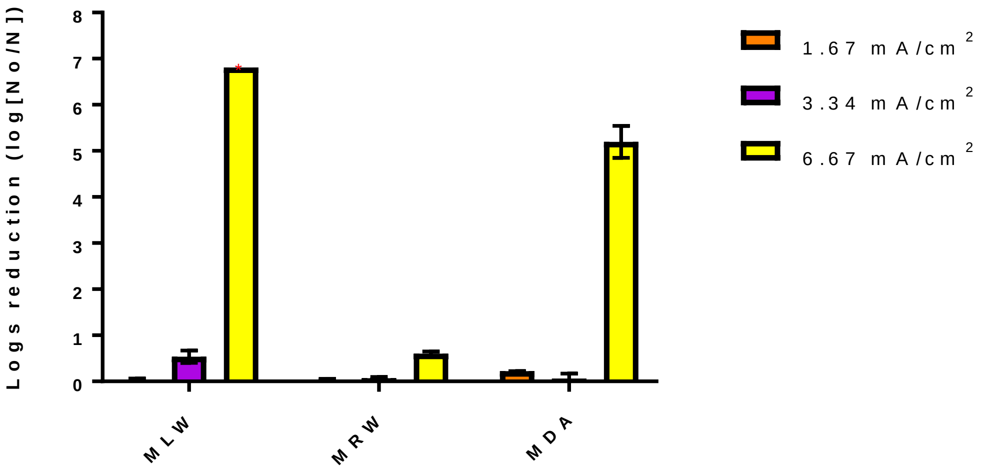


Figure 5 – *E. coli* mitigation by electrooxidation (EO) as a function of current density. MLW = model lake water, MRW = model river water, and MDA = model deep aquifer. The model shallow aquifer was not tested as the limit of *E. coli* detection (maximum assessable removal) was reached at 2.0 mA/cm^2, as discussed in the section 3.3.4.1. Each bar represents the average of triplicate tests, with ±1 standard deviation shown by the error bars. *Indicates that colony counts were below the quantifiable detection limit, so the bar is shown at the limit.

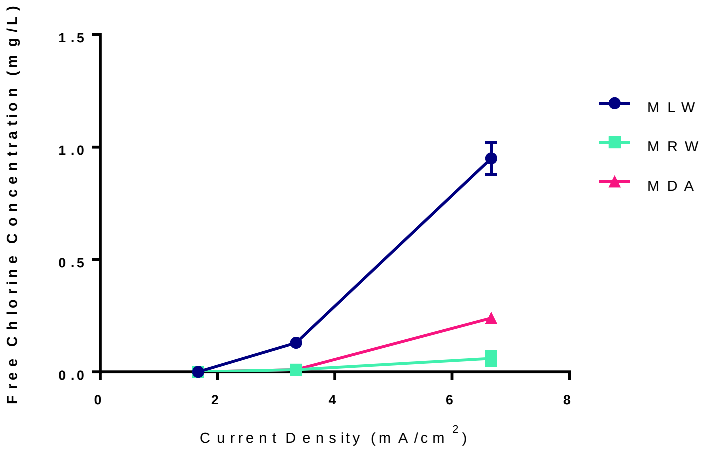


Figure 6 – Free chlorine generated as a function of electrooxidation current density in the model lake water (MLW), model river water (MRW), and model deep aquifer (MDA). Points represent average of triplicate tests, with ±1 standard deviation shown by the error bars.

The presence of NOM in the surface waters could be a limiting factor for *E. coli* inactivation, as NOM consumes oxidants. This is illustrated when comparing the free chlorine generation between the two surface waters at the increased current densities (Figure 6). The model lake water and the model river water had similar initial chloride concentrations (13.3 mg/L Cl^- and 11.4 mg/L Cl^-, respectively), yet significantly different final concentrations of free chorine ($p < 0.01$). The high concentration of NOM in the model river water (8 mg/L) likely consumed the free chlorine, which limited the removal of *E. coli*. For comparison, the model lake water contained 2.7 mg/L DOC. Moreover, the presence of NOM would contribute to greater DBP formation. Therefore, a pretreatment ahead of EO is recommended to remove NOM and improve overall treatment of surface waters. Since NOM is not present in the groundwaters and EO alone produced greater *E. coli* mitigation, this pretreatment is not required.

4.1.3 E. coli Mitigation by EC-EO

Sequential EC-EO did not improve *E. coli* mitigation beyond EO alone in any of the water matrices (Figure 4). This may stem from the increase in pH inherent to EC treatment (Table 2), which would influence oxidant speciation. For example, hypochlorous acid (HOCl) has a pKa of 7.54, so higher pHs will shift the free chlorine toward the conjugate base form (OCl^-). While either form can inactivate *E. coli*, HOCl is a much more effective disinfectant (Crittenden et al., 2012).

Another possible reason for ineffective mitigation of *E. coli* was the presence of total residual iron that passed through particle separation following EC treatment. Table 2 shows that more than 10 mg/L of total iron was present during EO after EC pretreatment.

Kraft et al. (1999) noted that dissolved iron species can consume free chlorine. At a high pH, dissolved iron may be present, although most of the total iron will be insoluble (Sasson, Calmano, & Adin, 2009). However, even small concentrations of dissolved iron could be sufficient to consume the small amount of free chlorine generated by EO under these operating conditions. Indeed, a lower concentration of free chlorine was measured in the EC-EO treated water compared to the EO-only treatment for the model shallow aquifer (Table 2). Enhanced NOM removal during EC, improved total iron removal following EC, or higher EO current densities may improve free chlorine generation and the concurrent mitigation of *E. coli*.

4.1.4 EEO for E. coli Mitigation

Figure 7 shows the electrical energy per order magnitude mitigated (EEO) for each process tested in the different water matrices. A lower EEO values demonstrates that lower energy input was required per log of *E. coli* mitigation. The EEO for EO alone was lower in all four waters than EC and the sequential process. This demonstrates that EO’s tradeoff in lower *E. coli* mitigation, but lower energy input yielded more efficient treatment of *E. coli* compared to EC. The results further illustrate that EC pretreatment did not improve the efficacy of *E. coli* mitigation by EO.

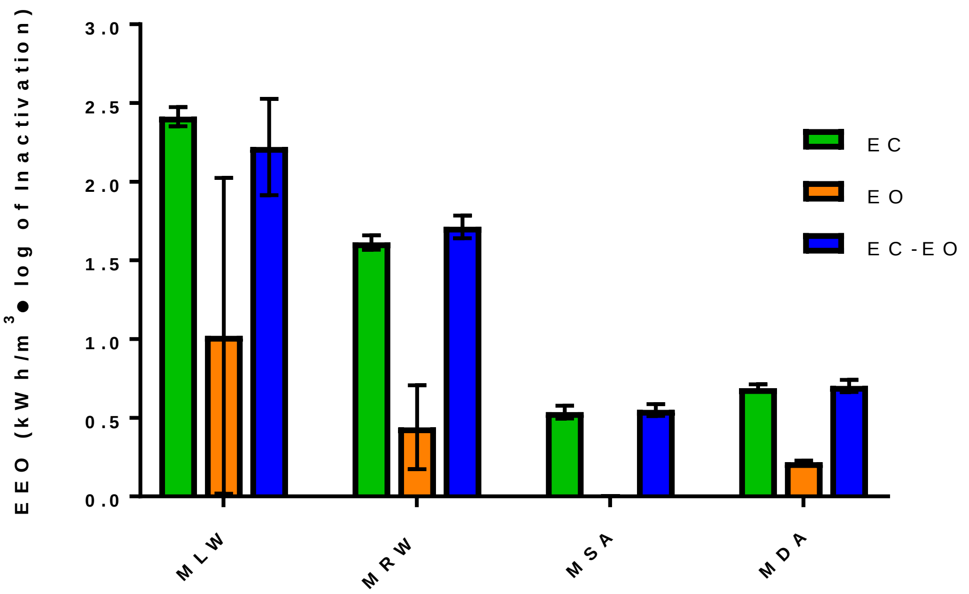


Figure 7 – Electrical energy per order magnitude (EEO) for *E. coli* mitigation in each water using electrocoagulation (EC), electrooxidation (EO), and sequential EC-EO in MLW = model lake water, MRW = model river water, MSA = model shallow aquifer, and MDA = model deep aquifer. Each bar represents the average of triplicate tests, with ±1 standard deviation shown by the error bars.

Figure 8 shows EEO values for increased EO current densities. The power applied increased with increased current density, yet at 6.67 mA/cm^2 the lowest EEO was established. Thus, increased current density not only improved the mitigation of *E. coli*, but also improved the energy efficiency for *E. coli* mitigation. This suggests that increased current density may be required to enhance the efficacy of the sequential process.

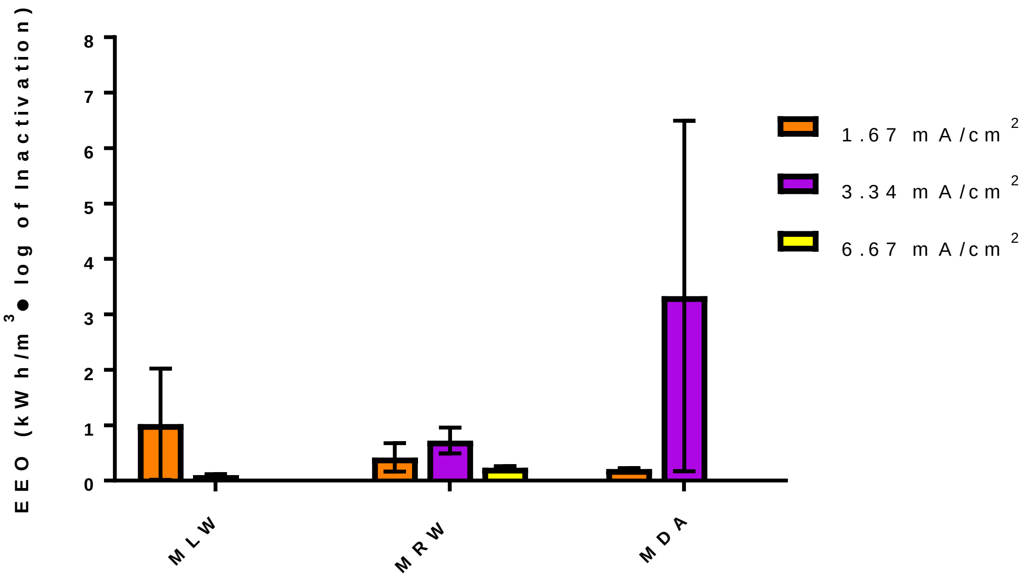
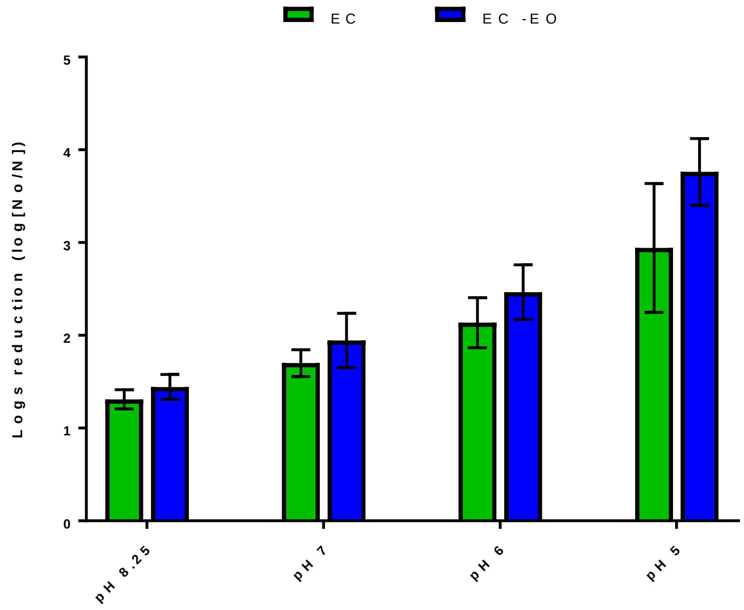


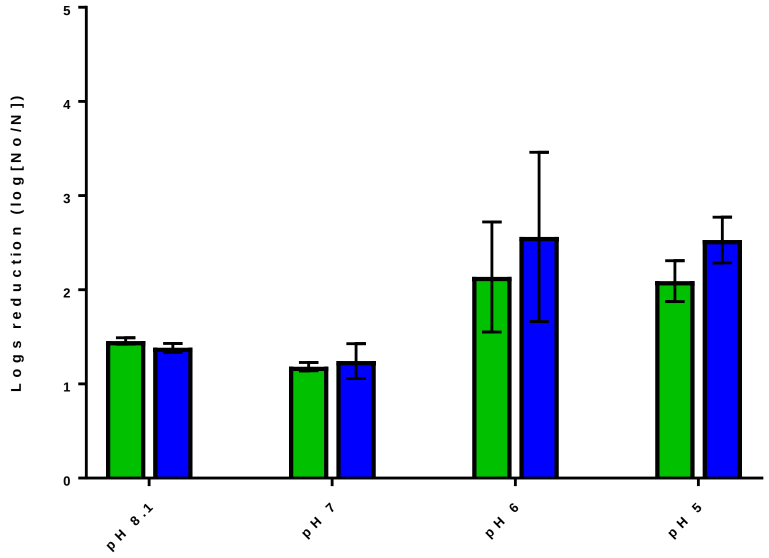
Figure 8 – Electrical energy per order magnitude (EEO) associated with *E. coli* mitigation by electrooxidation (EO) as a function of current density. MLW = model lake water, MRW = model river water, and MDA = model deep aquifer. Each bar represents the average of triplicate tests, with ±1 standard deviation shown by the error bars.

4.2 Impact of Enhanced EC-EO for *E. coli* Mitigation

Electrochemical treatment studies have shown that a lower initial pH benefits both EC and EO (Delaire et al., 2015; Koparal, Yildiz, Keskinler, & Demircioğlu, 2008; Vepsäläinen et al., 2009; Wu et al., 2014). The degree of improvement in *E. coli* mitigation using lower initial pHs for sequential EC-EO has yet to be reported in drinking waters. Thus, the influence of pH adjustment for the two surface waters using EC-EO treatment was evaluated (Figure 9). The groundwaters were not included as EO alone was sufficient to achieve greater *E. coli* mitigation than EC or EC-EO in these waters (section 4.1.2).



A) Model Lake Water



B) Model River Water

Figure 9 – *E. coli* mitigation by electrocoagulation (EC) and sequential EC-EO as a function of initial pH conditions in A) model lake water and B) model river water. Operating parameters: EC at 10 mA/cm^2 for 5 minutes, EO at 1.67 mA/cm^2 for 1 minute. Each bar represents the average of triplicate tests, with ±1 standard deviation shown by the error bars.

Improvements in *E. coli* mitigation were observed using EC alone for initial pH values of 6 or lower, similar to reports by Delaire et al. (2015). A possible reason for the improved *E. coli* mitigation at lower pH levels is that a higher concentration of soluble ferrous iron would form (Figure 1), which could shift the mechanism of physical removal (e.g., charge neutralization vs. sweep flocculation). Additionally, the oxidation rate of ferrous to ferric iron is slower at a lower pH, causing more ferrous hydroxide flocs to form (Bagga, Chellam, & Clifford, 2008; Sasson et al., 2009). Ferrous hydroxide flocs are smaller than ferric hydroxide flocs (Bagga et al., 2008), and flocs that are smaller than *E. coli* cells are more effective for removing *E. coli* (Delaire et al. 2015). Notably, only *E. coli* mitigation in the model lake water for pH 5 versus the baseline pH (8.25) was statistically different; in all other cases, slight but not significant improvements were observed.

Using pH adjusted sequential EC-EO treatment, slight improvements (≥0.3 logs) in *E. coli* mitigation were achieved compared to EC alone. However, the improvements were not significant for either surface water. Decreased pH was hypothesized to increase *E. coli* removal using EC-EO as NOM removal was expected to increase as pH decreased (Vepsäläinen et al., 2009). However, approximately 64% NOM removal was consistently achieved regardless of initial pH in this investigation ($p > 0.84$, Figure 10).

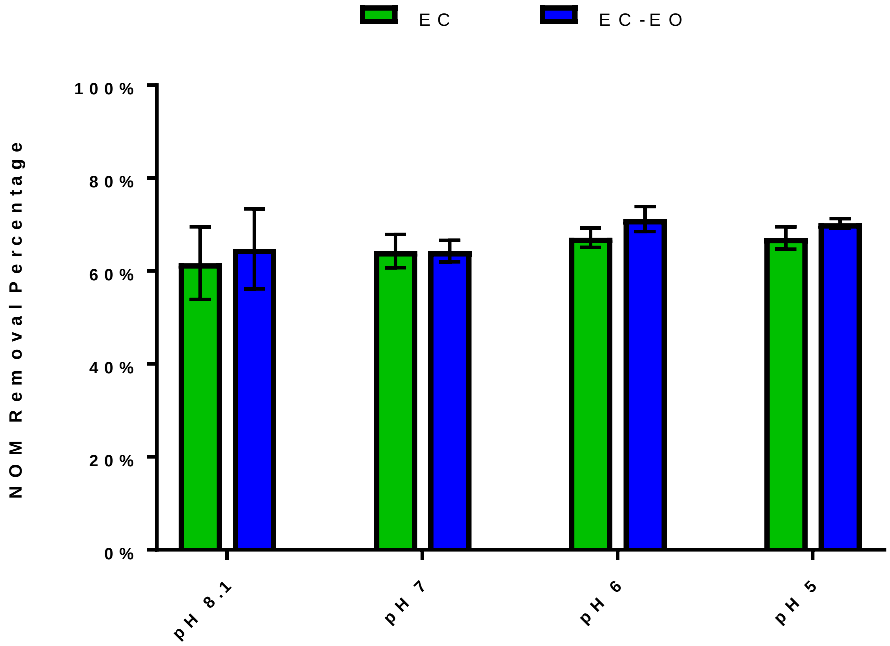
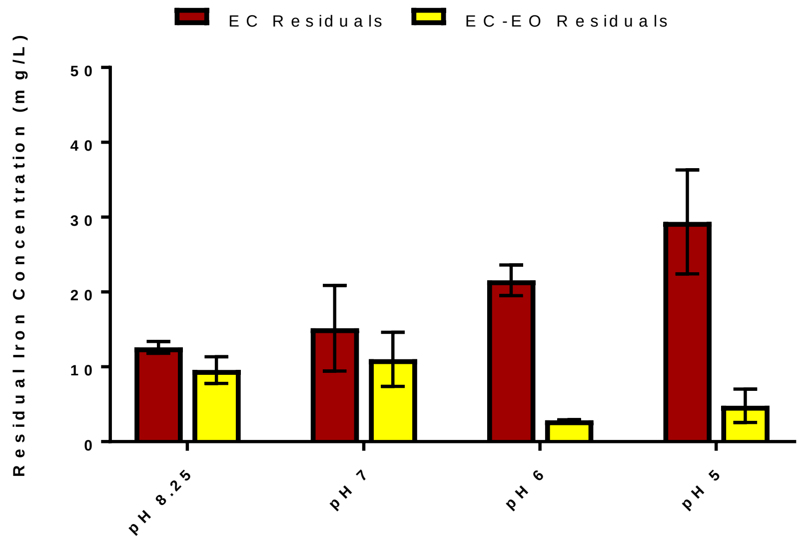


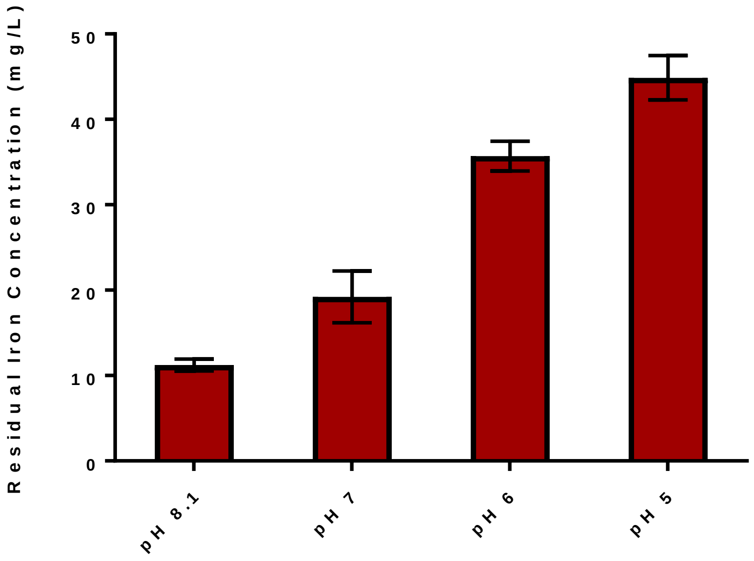
Figure 10 – Natural organic matter (NOM) removal in the model river water by electrocoagulation (EC) and electrocoagulation-electrooxidation (EC-EO) as a function of pH. Bars demonstrate average values for triplicate test with ±1 standard deviation shown by the error bars. The influence of pH on NOM removal was only assessed in the model river water as it had the highest initial NOM concentration.

The NOM concentration in the model river water did not drop below 1.9 mg/L after EC treatment, regardless of pH. This lack of improvement in NOM removal possibly explains the lack of improved *E. coli* mitigation by EC-EO, since the remaining NOM could consume the oxidants formed during EO. The applied total iron dose (82 mg/L Fe) may have reached the point of diminishing return (PODR), as described in the US EPA’s Enhanced Coagulation and Enhanced Precipitative Softening Guidance Manual. If this was the case, lower total iron doses together with pH adjustment may better optimize NOM removal. Vepsäläinen et al. (2009) showed similar changes in percent NOM removal as a function of initial pH using the highest specific charge, which correlates to the highest coagulant dose.

Lack of improvement in *E. coli* mitigation by EC-EO with pH adjustment could also stem from high total residual iron concentrations. Ferrous iron is more soluble at a lower pH; as such, it may pass through the filter during particle separation and increase EC total residual iron (Lakshmanan, Clifford, & Samanta, 2009; Sasson et al., 2009). As expected, Figure 11 shows that total residual iron concentrations increased with decreasing pH. Ferrous iron concentrations were measured after particle separation in the model lake water (this matrix contained limited turbidity to minimize interference). At pH 6 and 8.25, the fraction of total iron in the ferrous iron form was 40 ± 5% and 7 ± 1%, respectively. These higher ferrous levels at lower pH may have contributed to increased consumption of free chlorine during EO, which would detract from *E. coli* mitigation. This may help to explain why EC-EO did not significantly increase bacterial loads beyond EC alone.



A) Model Lake Water

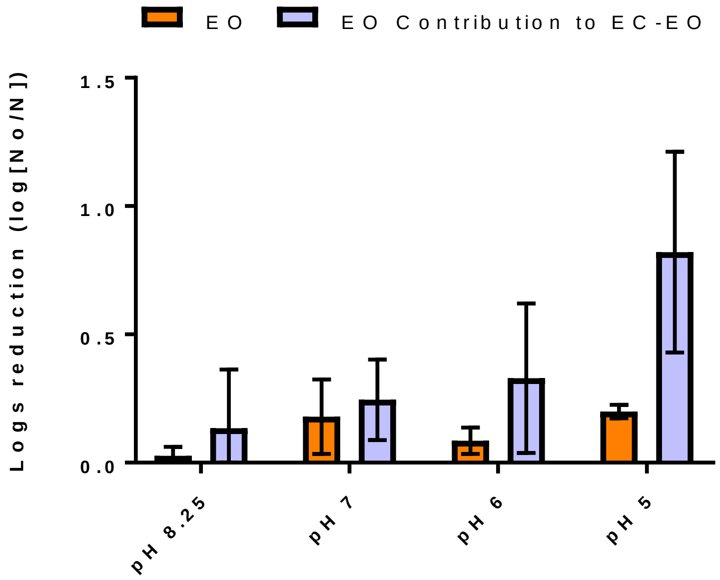


B) Model River Water

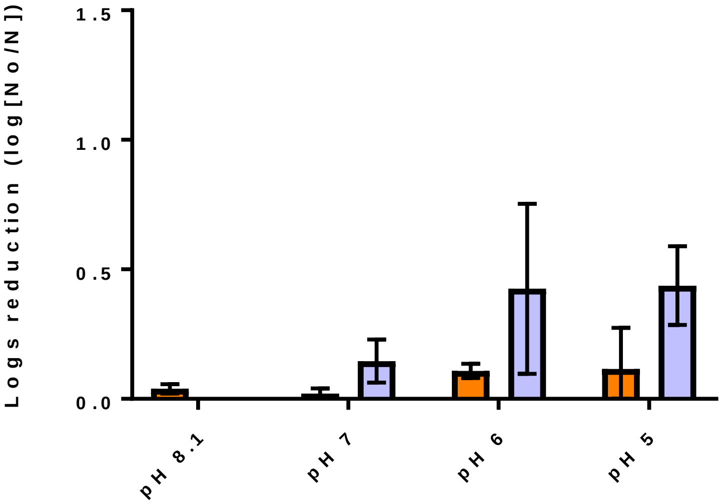
Figure 11 –Total residual iron concentrations after electrocoagulation (EC) and particle separation as a function of pH in the surface waters: A) model lake water and B) model river water. Total residual iron concentrations were also quantified in the model lake water after electrocoagulation-electrooxidation (EC-EO) with an additional 15-minute settling period to assess further the potential for further decreasing total residual iron levels (A).

4.2.1 E. coli Mitigation by the EO Contribution to EC-EO

Figure 12 shows that with EC pretreatment, *E. coli* mitigation increased 4 times during EO (shown as EO's contribution to EC-EO) at pH 6 and 5 compared to pH 8.1 (baseline) in the model river water. Similarly, the model lake water demonstrated 3 and 8 times greater *E. coli* mitigation by EO following EC at pH 6 and 5, respectively, compared to the baseline pH (8.25). There was no significant improvement by EO alone with pH adjustment for either surface water ($p > 0.9999$).



A) Model Lake Water



B) Model River Water

Figure 12 - *E. coli* mitigation by electrooxidation (EO) and EO's contribution to electrocoagulation-electrooxidation (EC-EO) as a function of initial pH conditions in A) model lake water and B) model river water. Operating parameters: EO at 1.67 mA/cm^2 for 1 minute. Each bar represents the average of triplicate tests, with ±1 standard deviation shown by the error bars.

As shown in Table 3, pH increased by about 1 to 1.5 pH units following EC. This indicates that the final pH after EC pretreatment may have impacted the removal of *E. coli* during EO. The pH heavily impacts water parameters, e.g., speciation of free chlorine. For initial pHs of 5 and 6, the final pH following EC-EO remained below the pKa of HOCl (7.54), which would shift free chlorine toward the more effective HOCl form. However, the shift in speciation may not have improved *E. coli* mitigation as low levels of free chlorine were measured in all cases (Table 2).

Table 3 - Final pH after each treatment process in the surface waters. Values are averages of triplicate tests ±1 standard deviation.

Initial pH	Model Lake Water			Model River Water		
	EC	EO	EC-EO	EC	EO	EC-EO
Baseline	9.59 ± 0.13	8.01 ± 0.03	9.53 ± 0.09	9.55 ± 0.07	7.98 ± 0.07	9.47 ± 0.03
7	9.23 ± 0.09	7.23 ± 0.03	9.10 ± 0.17	8.75 ± 0.18	7.21 ± 0.02	8.69 ± 0.20
6	7.11 ± 0.01	6.29 ± 0.04	6.93 ± 0.01	7.06 ± 0.02	6.29 ± 0.03	6.80 ± 0.06
5	6.88 ± 0.03	5.49 ± 0.03	6.65 ± 0.08	6.82 ± 0.04	5.34 ± 0.04	6.40 ± 0.04

Other species impacted by pH include iron. Lower pH leads to higher ferrous iron concentrations, which are not as easily oxidized to ferric iron because the conversion is directly correlated to the hydroxide ion concentration (i.e., pH), as shown by Equation 5 (Lakshmanan et al., 2009; Morgan & Lahav, 2007; Sasson et al., 2009; Stumm & Lee1, n.d.).

$$(5)\ \frac{d[Fe^{2+}]}{dt} = -k[Fe^{2+}]P_{O_2}[OH^-]^2$$

Where $[i]$ represent the molar concentration, k is the rate constant, and P_{O2} is the partial pressure of oxygen.

The formation of orange flocs was observed after EO when pretreated by EC at pH 5 and 6 (Figure 13). Based on the coloring, these flocs were most likely ferric-based. During EO, water undergoes electrolysis, where the anode produces oxygen while the cathode produces hydroxide ions. Both dissolved oxygen and hydroxide accelerate the conversion of ferrous iron to the ferric form (Equation 5). Figure 14 shows conversion of ferrous by EO in the model lake water at pH 8.25 (baseline) and pH 6. In both cases, 95% of the ferrous iron was converted during EO. While the conversion percentage was similar for both pH, the magnitude of the concentrations was noticeably different. At pH 6 the ferrous iron concentration was 5 times greater than the baseline pH. Ferrous conversion with EO was 6.8% higher than without EO (pH 6 w/o EO) ($p = 0.012$). This oxidation of ferrous iron during EO (following EC pretreatment) could indicate that Fenton’s reaction occurred.

Figure 13 - Orange flocs after EC-EO plus an additional settling period.

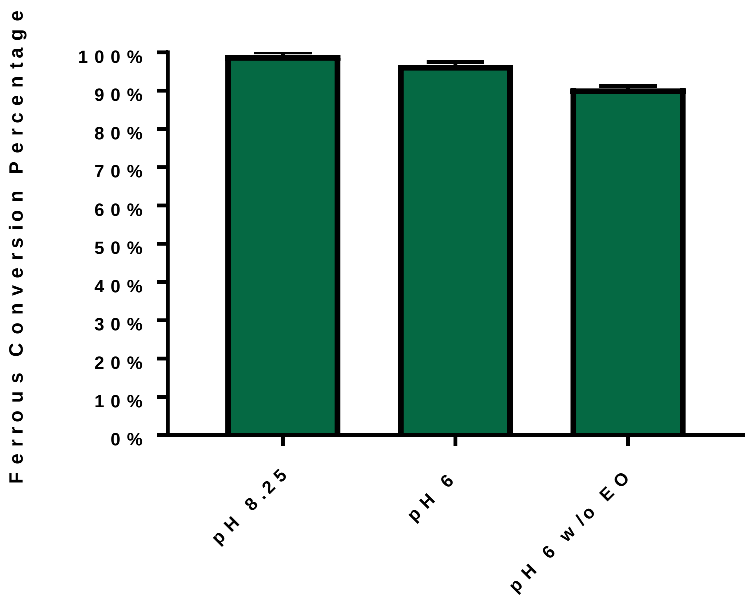


Figure 14 – Percent of ferrous iron oxidized during electrooxidation (EO). Initial ferrous concentrations were measured immediately after particle separation. The control (pH 6 w/o EO) represents the conversion of ferrous without an applied EO current. Each bar represents the average of triplicate tests, with ±1 standard deviation shown by the error bars.

Oxidation of ferrous iron causes Fenton's reaction (Anfruns-Estrada et al., 2017; Hu et al., 2018; Yeon Kim et al., 2011). Fenton reactions occurs when ferrous is oxidized by hydrogen peroxide to form hydroxyl radicals and ferric iron (Yeon Kim et al., 2011). Hydrogen peroxide can either be directly added or can be generated during EO, e.g., through a two-electron transfer of oxygen and zero valent iron (ZVI), as shown in equation 6.

$$(6) \quad Fe^{0}_{(s)} + O_2 + 2H^+ \rightarrow Fe(II) + H_2O_2$$

Zero valent iron is formed when iron is reduced at the cathode (Hu et al., 2018; Yeon Kim et al., 2011). Fenton's reaction typically occurs at low pH, yet Anfruns-

Estrada et al. (2017) demonstrated that electro-Fenton reactions, with *in-situ* formation of hydrogen peroxide, can inactivate *E. coli* in wastewater at a neutral pH. Electro-Fenton's reaction could explain the 3.8 times greater *E. coli* mitigation by EO following EC pretreatment (EC's contribution to EC-EO) at pH 5 and 6 compared to EO operated independently (Figure 12). To further investigate whether electro-Fenton reactions may have contributed to *E. coli* mitigation, correlation analysis was performed using *E. coli* data and EC total residual iron concentrations for all surface water experiments (Figure 15). Figure 15 suggests that a correlation between these two variables may exist (R^2 = 0.4469 p = 0.07), but future direct examination of the role of Fenton's reactions in EO when pretreated by EC in surface waters is needed.

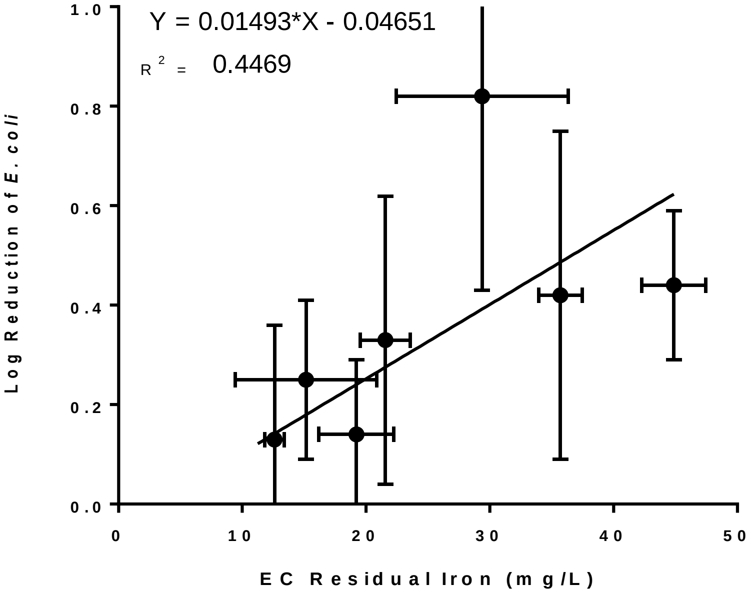


Figure 15 –*E. coli* mitigation versus electrocoagulation (EC) total residual iron concentration (mg/L) during electrooxidation (EO) following EC pretreatment. Data is the average of triplicate tests for all surface water experiments. Error bars show ±1 standard deviation.

4.2.2 EEO for E. coli Mitigation with pH Adjustment

Figure 16 shows the EEO for treating model lake and model river water using each electrochemical process with the pH adjustment. When the initial pH was decreased to 6 or 5, the EEO for all processes decreased in both surface waters, demonstrating that the energy efficiency improved as the pH decreased. Two factors likely played a role in the improvement. First, the nitric acid added to decrease the pH also increased the water's conductivity, which resulted in a lower voltage. Additionally, as shown in Figures 9 and 12, there was a slight improvement in *E. coli* mitigation, therefore, less power and greater *E. coli* mitigation led to a lower EEO.

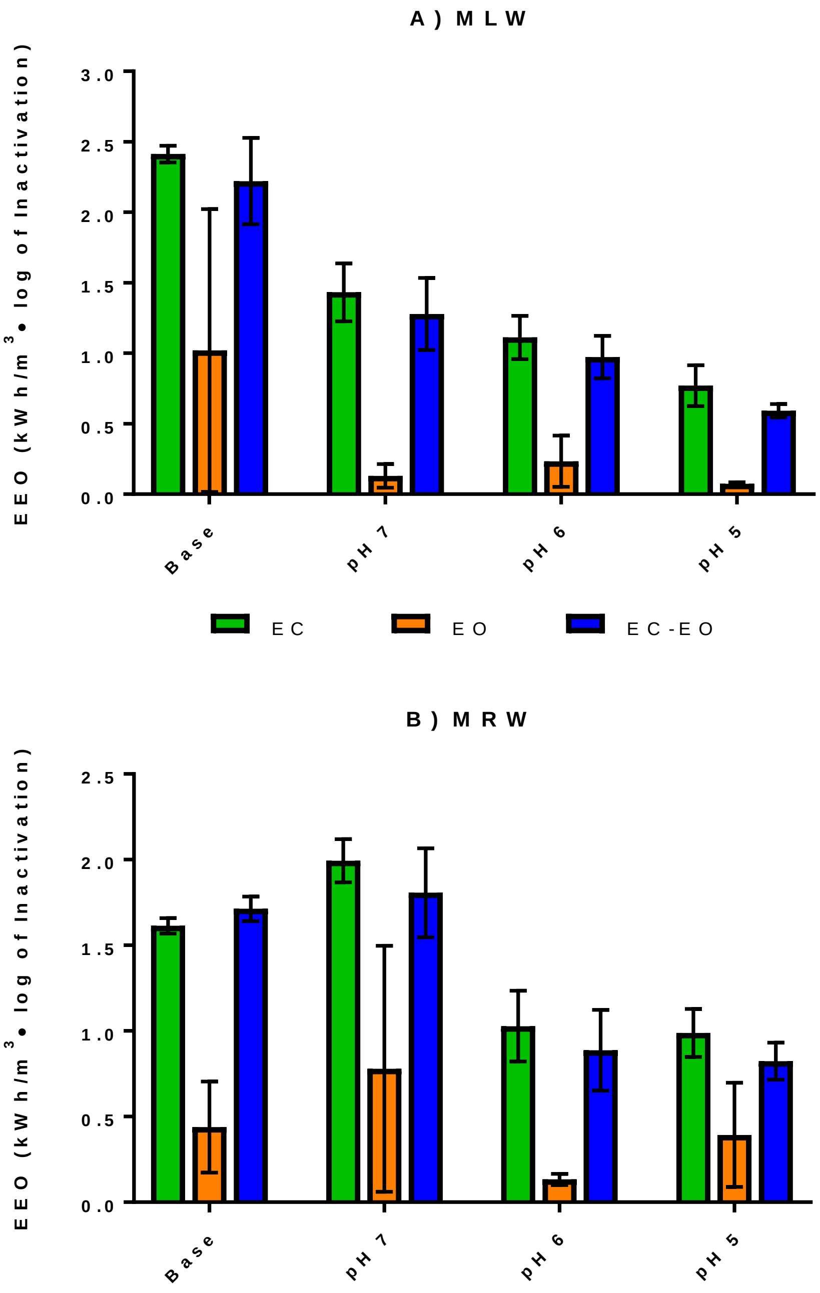


Figure 16 – Electrical energy per order magnitude (EEO) for *E. coli* mitigation using electrocoagulation (EC), electrooxidation (EO), and sequential EC-EO as a function of initial pH conditions in A) model lake water (MLW) and B) model river water (MRW). Each bar represents the average of triplicate tests, with ±1 standard deviation shown by the error bars.

5. CONCLUSIONS

Sequential EC-EO was evaluated for mitigation of *E. coli* in four model drinking waters. The results indicated that EC was not an effective pretreatment process for EO for mitigation of *E. coli* in groundwaters. The addition of iron by EC likely limited improvements in groundwater due to the consumption of oxidants and high total residual iron concentrations after filtration. Alternately, EO alone was sufficient for *E. coli* mitigation in groundwaters, providing 4-logs and 5-logs mitigation in the model shallow and model deep aquifer, respectively, using current densities less than those required for EC. The energy efficiency per order (EEO) of *E. coli* mitigation for EO alone was less than the EEO of either EC or the sequential process.

EC removed 64% of NOM from the model river water, which is important as NOM is a DBP precursor. However, removal of NOM by EC did not increase *E. coli* mitigation by EO. Possible reasons for the lack of improved *E. coli* mitigation were a high final pH, consumption of free chlorine by iron, or insufficient applied EO current density.

Further investigation using enhanced EC-EO with pH adjustment to treat surface waters showed that a lower pH for EC-EO slightly improve *E. coli* mitigation, but not significantly. Slight improvements in NOM removal at pH 6 or below were shown for both surface waters, but the remaining NOM would scavenge oxidants, thereby limiting improvements in *E. coli* mitigation by EC-EO. While further optimization of NOM removal is needed, the EEO for E. coli mitigation using each process improved when the initial pH was below 6, demonstrating the benefit of pH adjustment.

Decreasing the initial pH increased EC total residual iron concentrations, which would also consume free chlorine. However, the total residual iron concentrations following EC-EO decreased, likely due to oxidation of ferrous to ferric hydroxides, which offered more efficient floc settling. The oxidation of ferrous iron can also cause Fenton’s reaction. A slight correlation was shown between EC total residual iron concentrations and *E. coli* mitigation during EO (following EC pretreatment). Ferrous iron was also converted to ferric during EO, demonstrating that Fenton-like reactions could have occurred, resulting in the increased *E. coli* mitigation. While decreased initial pH improved *E. coli* mitigation for EO following EC, the difference was not significant for any case. This indicates that the EO current density was too low to generate the oxidants required for increased *E. coli* mitigation.

5.1 Future Work

This study showed that EC-EO did not improve *E. coli* mitigation beyond EC alone. Future process optimization may yield improvements. For example, optimizing the iron dose for NOM removal would limit the impact of oxidant scavengers. Furthermore, a more effective filtration process such as granular filtration would reduce NOM and total iron concentrations in EO influent, which would decrease consumption of free chlorine due to these constituents. Higher EO current densities should be applied to the sequential treatment to enhance mitigation of *E. coli*. Improved *E. coli* mitigation would be expected based on greater oxidant formation as a function of current density.

Beyond optimizing the system, further investigation is needed to determine the specific mechanisms of *E. coli* mitigation in drinking waters during EO when high concentrations of iron are present. This requires consideration of iron speciation as well as electrostatic interactions between the iron and microbes.

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APPENDIX A – STANDARD CURVES

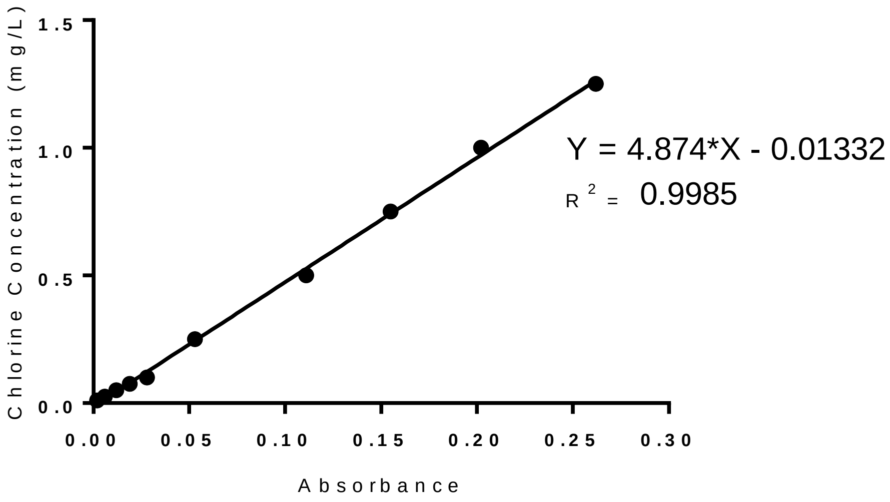


Figure A 1 – Standard curve developed for Hach Method 8021 using NaOCl. Points represent single data points.

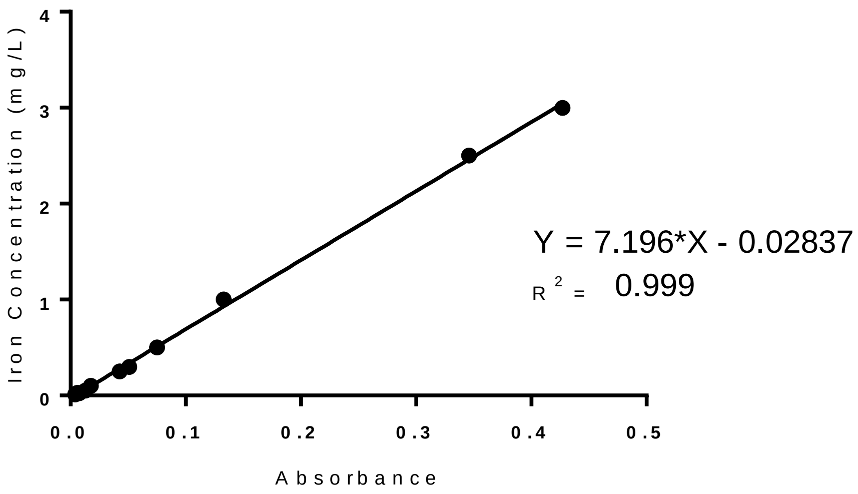


Figure A 2 - Standard curve developed for ferrous and total iron concentrations using ferrous chloride. Points represent single data points.

APPENDIX B – STATISTICAL ANALYSIS

Table B 1 – Statistics for *E. coli* mitigation by each treatment process for the model waters conducted in baseline conditions (as defined in Table 1). EO* = EO's contribution to EC-EO. Light green = statistically different, Red = not statistically different. MLW = model lake water, MRW = model river water, MSA = model shallow aquifer, and MDA = model deep aquifer.

Water		MLW				MRW				MSA				MDA			
	Treatment	EC	EO	EC-EO	EO*	EC	EO	EC-EO	EO*	EC	EO	EC-EO	EO*	EC	EO	EC-EO	EO*
MLW	EC																
	EO	0.0062															
	EC-EO	>0.9999	0.0017														
	EO*	0.0166	>0.9999	0.0048													
MRW	EC	>0.9999	0.0015	>0.9999	0.0042												
	EO	0.0069	>0.9999	0.0019	>0.9999	0.0017											
	EC-EO	>0.9999	0.0031	>0.9999	0.0084	>0.9999	0.0034										
	EO*	0.0024	>0.9999	0.0006	>0.9999	0.0006	>0.9999	0.0012									
MSA	EC	0.6184	<0.0001	0.8835	<0.0001	0.9016	<0.0001	0.7813	<0.0001								
	EO	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001							
	EC-EO	0.6758	<0.0001	0.916	<0.0001	0.9307	<0.0001	0.8283	<0.0001	>0.9999	<0.0001						
	EO*	0.0038	>0.9999	0.001	>0.9999	0.0009	>0.9999	0.0018	>0.9999	<0.0001	<0.0001	<0.0001					
MDA	EC	0.0043	<0.0001	0.0148	<0.0001	0.0167	<0.0001	0.0086	<0.0001	0.5858	0.0104	0.5277	<0.0001				
	EO	0.0086	>0.9999	0.0024	>0.9999	0.0021	>0.9999	0.0043	>0.9999	<0.0001	<0.0001	<0.0001	>0.9999	<0.0001			
	EC-EO	0.0055	<0.0001	0.0189	<0.0001	0.0213	<0.0001	0.0111	<0.0001	0.6492	0.0081	0.5912	<0.0001	>0.9999	<0.0001		
	EO*	0.0037	>0.9999	0.001	>0.9999	0.0009	>0.9999	0.0018	>0.9999	<0.0001	<0.0001	<0.0001	>0.9999	<0.0001	>0.9999	<0.0001	

Table B 2 - Statistics for NOM removal for the model surface waters conducted in baseline conditions (see description in Table 1). Light green = statistically different, Red = not statistically different. MLW = model lake water and MRW = model river water.

Water		MLW			MRW	
	Treatment	EC	EC-EO	EO	EC	EC-EO
MLW	EC					
	EC-EO	>0.9999				
	EO	0.7861	0.8707			
MRW	EC	<0.0001	<0.0001	<0.0001		
	EC-EO	<0.0001	<0.0001	<0.0001	0.9795	
	EO	0.7594	0.6574	0.1636	<0.0001	<0.0001

Table B 3 - Statistics for *E. coli* mitigation by electrooxidation (EO) as a function of current densities for model lake water (MLW), model river water (MRW), and model shallow aquifer (MSA) in baseline conditions (see description in Table 1). Light green = statistically different, Red = not statistically different.

Water		MLW			MRW			MDA		
	Current density (mA/cm^2)	1.67	3.34	6.67	1.67	3.34	6.67	1.67	3.34	6.67
MLW	1.67									
	3.34	0.0164								
	6.67	<0.0001	<0.0001							
MRW	1.67	>0.9999	0.02	<0.0001						
	3.34	>0.9999	0.0326	<0.0001	>0.9999					
	6.67	0.0053	0.9997	<0.0001	0.0064	0.0106				
MSA	1.67	0.8254	0.2836	<0.0001	0.8682	0.9471	0.1124			
	3.34	>0.9999	0.0296	<0.0001	>0.9999	>0.9999	0.0096	0.935		
	6.67	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	

Table B 4 - Statistics for *E. coli* mitigation by each treatment process with pH adjustment for the model lake water. EO* = EO's contribution to EC-EO. Light green = statistically different and Red = not statistically different.

Initial pH		pH 8.25 (Baseline)				pH 7				pH 6				pH 5			
	Treatment	EC	EO	EC-EO	EO*	EC	EO	EC-EO	EO*	EC	EO	EC-EO	EO*	EC	EO	EC-EO	EO*
pH 8.25	EC																
	EO	0.0003															
	EC-EO	>0.9999	<0.0001														
	EO*	0.0011	>0.9999	0.0002													
pH 7	EC	0.9287	<0.0001	0.9984	<0.0001												
	EO	0.002	>0.9999	0.0004	>0.9999	<0.0001											
	EC-EO	0.3247	<0.0001	0.6902	<0.0001	0.999	<0.0001										
	EO*	0.0043	0.9997	0.0009	>0.9999	<0.0001	>0.9999	<0.0001									
pH 6	EC	0.061	<0.0001	0.2096	<0.0001	0.852	<0.0001	>0.9999	<0.0001								
	EO	0.0006	>0.9999	0.0001	>0.9999	<0.0001	>0.9999	<0.0001	>0.9999	<0.0001							
	EC-EO	0.0015	<0.0001	0.0071	<0.0001	0.1102	<0.0001	0.6394	<0.0001	0.9815	<0.0001						
	EO*	0.0115	0.9916	0.0024	>0.9999	0.0001	>0.9999	<0.0001	>0.9999	<0.0001	0.9991	<0.0001					
pH 5	EC	<0.0001	<0.0001	<0.0001	<0.0001	0.0005	<0.0001	0.0095	<0.0001	0.0745	<0.0001	0.7576	<0.0001				
	EO	0.0025	>0.9999	0.0005	>0.9999	<0.0001	>0.9999	<0.0001	>0.9999	<0.0001	>0.9999	<0.0001	>0.9999	<0.0001			
	EC-EO	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	0.0003	<0.0001	0.0644	<0.0001		
	EO*	0.7253	0.0844	0.3553	0.219	0.0351	0.3104	0.0021	0.4803	0.0002	0.1464	<0.0001	0.719	<0.0001	0.3579	<0.0001	

Table B 5 - Statistics for *E. coli* mitigation by each treatment process with pH adjustment for the model river water. EO* = EO’s contribution to EC-EO. Light green = statistically different and Red = not statistically different.

Initial pH		pH 8.1 (Baseline)				pH 7				pH 6				pH 5			
	Treatment	EC	EO	EC-EO	EO*	EC	EO	EC-EO	EO*	EC	EO	EC-EO	EO*	EC	EO	EC-EO	EO*
pH 8.1	EC																
	EO	0.0002															
	EC-EO	>0.9999	0.0005														
	EO*	<0.0001	>0.9999	0.0002													
pH 7	EC	0.984	0.0118	0.9984	0.0035												
	EO	0.0002	>0.9999	0.0005	>0.9999	0.011											
	EC-EO	>0.9999	0.0026	>0.9999	0.0007	>0.9999	0.0024										
	EO*	0.0007	>0.9999	0.0017	>0.9999	0.0327	>0.9999	0.0078									
pH 6	EC	0.3492	<0.0001	0.2103	<0.0001	0.0163	<0.0001	0.0643	<0.0001								
	EO	0.0005	>0.9999	0.0012	>0.9999	0.0238	>0.9999	0.0055	>0.9999	<0.0001							
	EC-EO	0.0077	<0.0001	0.0035	<0.0001	0.0002	<0.0001	0.0007	<0.0001	0.9284	<0.0001						
	EO*	0.0166	0.9657	0.0344	0.8046	0.3522	0.9608	0.1244	0.998	<0.0001	0.9941	<0.0001					
pH 5	EC	0.4568	<0.0001	0.291	<0.0001	0.0258	<0.0001	0.0965	<0.0001	>0.9999	<0.0001	0.8603	<0.0001				
	EO	0.0006	>0.9999	0.0013	>0.9999	0.0256	>0.9999	0.006	>0.9999	<0.0001	>0.9999	<0.0001	0.9953	<0.0001			
	EC-EO	0.0109	<0.0001	0.005	<0.0001	0.0002	<0.0001	0.0011	<0.0001	0.9612	<0.0001	>0.9999	<0.0001	0.9131	<0.0001		
	EO*	0.0187	0.9563	0.0387	0.7781	0.3796	0.9505	0.1375	0.9969	<0.0001	0.9915	<0.0001	>0.9999	<0.0001	0.9932	<0.0001	

Table B 6 – Statistics for NOM removal by each treatment process with pH adjustment for the model river water. Light green = statistically different and Red = not statistically different.

Initial pH		pH 8.1 (Baseline)			pH 7			pH 6			pH 5		
	Treatment	EC	EC-EO	EO	EC	EC-EO	EO	EC	EC-EO	EO	EC	EC-EO	EO
pH 8.1 (Baseline)	EC												
	EC-EO	0.9968											
	EO	<0.0001	<0.0001										
pH 7	EC	0.9992	>0.9999	<0.0001									
	EC-EO	0.9995	>0.9999	<0.0001	>0.9999								
	EO	<0.0001	<0.0001	>0.9999	<0.0001	<0.0001							
pH 6	EC	0.8431	0.9997	<0.0001	0.9987	0.9982	<0.0001						
	EC-EO	0.1757	0.6895	<0.0001	0.5988	0.5791	<0.0001	0.9769					
	EO	<0.0001	<0.0001	0.9982	<0.0001	<0.0001	0.9995	<0.0001	<0.0001				
pH 5	EC	0.8526	0.9998	<0.0001	0.9989	0.9985	<0.0001	>0.9999	0.974	<0.0001			
	EC-EO	0.285	0.8431	<0.0001	0.7685	0.751	<0.0001	0.9968	0.751	<0.0001	0.9962		
	EO	<0.0001	<0.0001	>0.9999	<0.0001	<0.0001	>0.9999	<0.0001	<0.0001	0.9995	<0.0001	<0.0001	

APPENDIX C – *E. COLI* CONTROLS

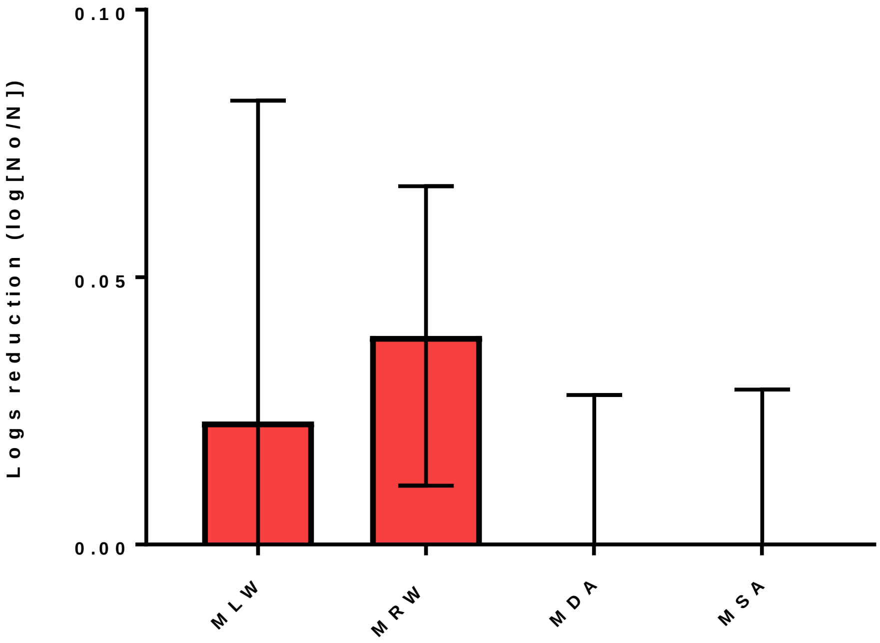
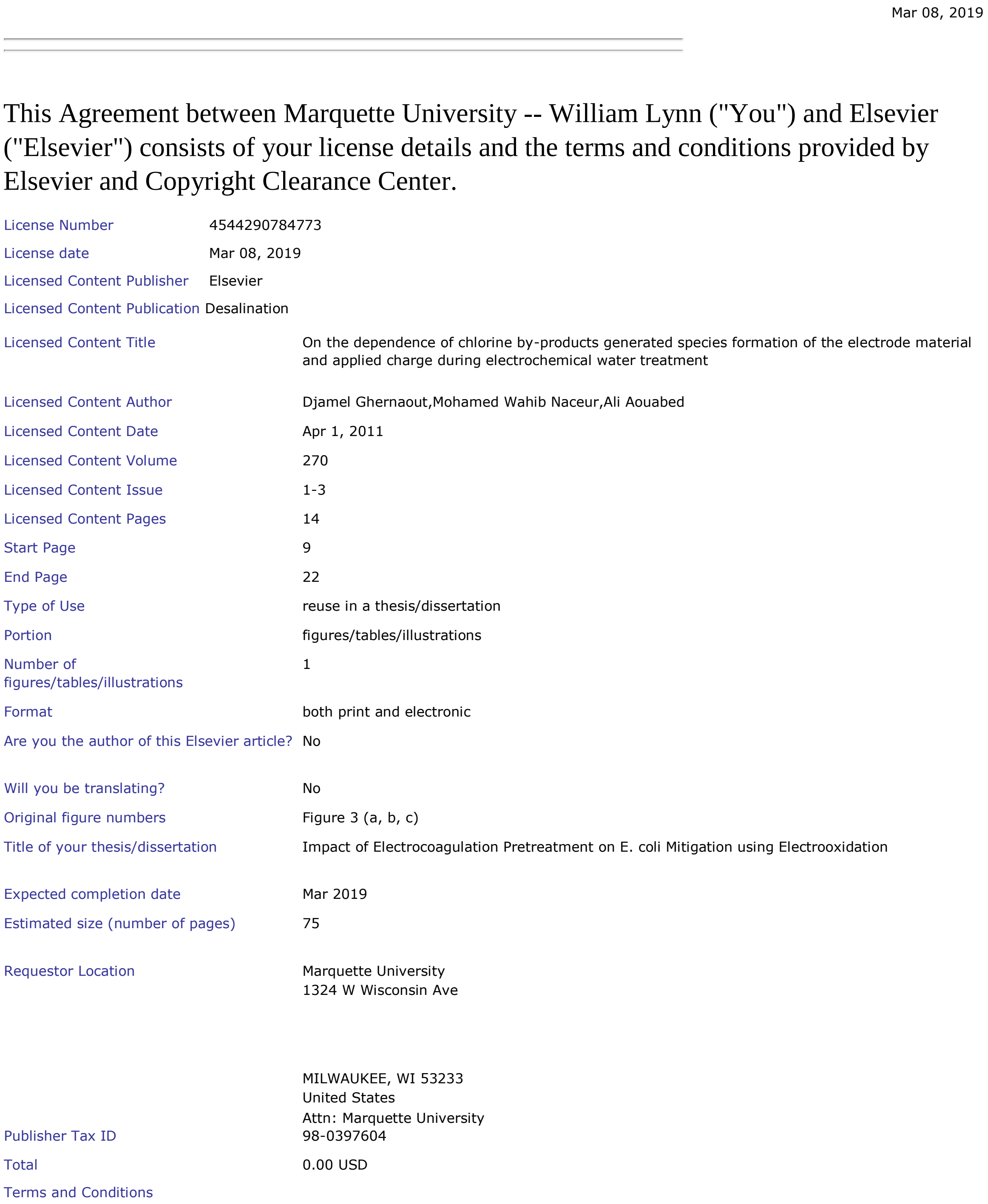


Figure C 1 – Control test conducted in each model water for *E. coli* mitigation using the sequential electrocoagulation-electrooxidation (EC-EO) system without power applied. MLW = model lake water, MRW = model river water, MSA = model shallow aquifer, and MDA = model deep aquifer. Operating parameters: EC at 0 mA/cm^2 for 5 minutes and EO at 0 mA/cm^2 for 1 minute. Each bar represents the average of triplicate tests, with ±1 standard deviation shown by the error bars.

APPENDIX D – PUBLISHERS CONSENT

Included below is the publisher’s consent to use Figure 1 in this thesis.



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