

**Application of Electrochemical Processes in Onsite Wastewater Systems:
Electrocoagulation and Hypochlorite Production**

by

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ABSTRACT

APPLICATION OF ELECTROCHEMICAL PROCESSES IN ONSITE WASTEWATER SYSTEMS: ELECTROCOAGULATION AND HYPOCHLORITE PRODUCTION

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Ineffective treatment of decentralized wastewater by septic systems contribute to both the spread of pathogens and increased nutrient loading in ground and surface waters. These nutrients and pathogens create economic, ecological, and public health consequences for society at large. This thesis is comprised of two studies investigating the applicability of electrochemical technologies to these problems. In the first study, a continuous manifold electrocoagulation system was used to treat representative synthetic onsite wastewater with the goal of removing nutrients.

Maximally, more than 95% reduction in orthophosphates and 20% reduction in ammonia was observed at a current density of 2.8 mA/cm^2 , however, reduction in chemical oxygen demand was not observed. The second study was a bench scale analysis of an electrochemical cell to produce hypochlorite disinfectant tested at several operational parameters. It was found that the greatest disinfectant yields were achieved using an aluminum cathode and at low cathode to anode surface area ratio (0.5:1). This research suggests that these electrochemical techniques could be used in tandem with existing septic tank systems to improve effluent quality.

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ABBREVIATIONS

BOD	Biological Oxygen Demand
BDD	Boron Doped Diamond
COD	Chemical Oxygen Demand
CBOD	Carbonaceous Biological Oxygen Demand
CFU	Coliform Units
CMECR	Continuous Manifold Electrocoagulation Reactor
DC	Direct Current
EC	Electrochemical Coagulation
ED	Electrochemical Disinfection
HRT	Hydraulic Retention Time
MMO	Mixed Metal Oxide
OBC	Ontario Building Code
PSU	Power Supply Unit
PVC	Polyvinyl Chloride
TSS	Total Suspended Solids

1 - Introduction

Decentralized wastewater treatment systems, otherwise known as onsite wastewater treatment systems, service over 1 million people in Ontario. The most common decentralized wastewater treatment systems used in North America is the septic system. This system is used widely for its simplicity, inexpensiveness, and the ability to remove total suspended solids (TSS) and biological oxygen demand (BOD) from wastewater streams (Tilley et al. 2014; Lourenço et al., 2020). The effectiveness of these systems is important to preserve ecosystems, especially in rural areas, where decentralized systems are the predominant wastewater treatment method. Septic systems in Ontario are regulated under the Ontario Building Code (OBC), which sets limits for effluent water quality, however, these standards are limited (O. Reg. 312/12). Under the current building code, there are only requirements for TSS content as well as BOD and carbonaceous biological oxygen demand (CBOD). It is well understood that septic systems are limited in the removal of other forms of water pollution (Nasr and Mikhaeil, 2013).

In the case of domestic wastewater, the primary source of water pollution aside from TSS, BOD and CBOD is the nutrient content of the wastewater. Nutrients include phosphates, nitrates, nitrites, and ammonia. These chemicals are used in biological processes and promote the growth of both flora and fauna (National Research Council, 2000). High nutrient content in septic tank effluent increases the nutrient content in both surface and ground water supplies. Groundwater aquifers are often used for drinking water sources in the rural communities, where onsite wastewater treatment is common. Excess nutrients in drinking water must be treated, especially nitrates where exposure can lead to methemoglobinemia, a harmful condition which primarily harms infants (Fewtrell, 2004; United States and National Research Council, 1995). In surface water, increased nutrient content results in eutrophication. This is the result of rapid growth in

algae due to the abundance of nutrients like phosphorous which sustain them (Karydis and Kitsiou, 2019). The result of these algal blooms has both ecological and economic consequences. Algal blooms block sunlight at the surface of the water, preventing subsurface aquatic plants and animals that rely on sunlight from getting exposure. Due to this effect, algal blooms are hysteretic and upset the homeostasis of a surface water ecosystems (National Research Council, 2000; Reynolds, 2002). Economically, algal blooms lower the aesthetic quality of lakes and rivers, devaluing lakefront properties as well as the recreational quality of the lakes (Dodds et al., 2009). In addition, the eutrophication of larger lakes such as the Great Lakes have unique economic and public health implications. These lakes are used as source water for drinking water supplies in municipalities surrounding the lake. Certain algae produce cyanotoxins such as microcystin which is toxic to humans. The drinking water plants which purify water from these lakes are burdened with removing these compounds from lake water to make it safe for consumption (Singh, 2018). Algae will also foul mechanical screens at the head of the treatment plants which require cleaning and replacement (Howell and Benoit, 2021). Measures to counter obstruction due to algae require greater upkeep than standard mechanical screening. In addition, the presence of algae in lakes which are used as a drinking water supply lowers the aesthetic quality of the drinking water produced. Geosmin, a terpene produced by cyanobacteria which is known colloquially as blue-green algae, has been associated with unpleasant odor in drinking water in the Great Lakes region (Ridal et al., 2000; Rao et al., 2003). For these ecological and economic reasons, nutrient management from wastewater effluents has come under increased scrutiny in recent years. Standard decentralized treatment methods such as the septic systems have proven to be inadequate at substantially removing nutrients from wastewater (Nasr and Mikhaeil, 2013; Tilley et al. 2014).

Pathogenic contamination of onsite wastewater effluents is another cause for concern.

Conventionally, onsite septic treatment systems in Ontario are comprised of just a septic tank and a leaching bed system. These systems alone have been found to be inconsistent in the removal of pathogens such as viruses, bacteria, and parasites (Wang et al., 2021; Tilley et al., 2014). Conventional systems offer 1-log to 2-log removal depending on the design of the system and the environmental circumstances (Wang et al., 2021). In more robust filtration systems that have been deployed in onsite treatment applications, removal of pathogens is sensitive to temperature. This is due to the increase in microbial predation and die-off rates of bacteria and viruses (Wang et al., 2021). Coliform removal as high as 4-log in summer with coliform removal as low as 0.5-log in winter have been observed with septic tank treatment. The primary goal of onsite wastewater disinfection is to prevent public exposure to pathogens both in groundwater and surface water. Insufficient groundwater treatment has historically led to significant outbreaks in the US and Canada, including the well-known Walkerton Disaster (Craun et al., 2002; Clark et al., 2003). According to the most recent data available, groundwater source contamination has resulted in 33% of waterborne illness outbreaks in 2014-2015 (Benedict et al., 2017). The need for consistent year-long disinfection is particularly important in coastal areas and areas, where there is significant mixing of ground and surface water supplies. In these areas, pathogens may be transported to surrounding lakes more easily through ground water flow (Tufenkji and Emelko, 2011). As such, inadequate pathogen removal from traditional septic systems has become a public health interest.

The problem of insufficient onsite wastewater treatment has brought about research into a variety of treatment methods. Among these new methods are electrochemical treatment technologies. These technologies have emerged as a viable solution to a wide range of organic and inorganic

water contamination issues (Barrera-Díaz et al., 2018; Groenen Serrano, 2018). The advantage of electrochemical technologies is that they use simple equipment, are easily automated, are energy efficient in many applications, and with the exception of certain systems like the electro-Fenton process, they do not require the use and handling of additional chemicals (Brillas and Martínez-Huitle, 2015). These advantages are particularly valuable in an onsite wastewater setting, where skilled operators are unavailable and dangerous chemicals cannot be handled safely. Of particular interest is the electrocoagulation and electrochemical disinfection processes.

Electrocoagulation involves the use of an electrochemically produced coagulant to flocculate contaminants which may then be settled or removed via flotation (Barrera-Díaz et al., 2018). In previous research, this has been shown to effectively remove phosphorous, nitrogen and chemical oxygen demand (COD) from wastewater sources (Brillas and Martínez-Huitle, 2015; Sahu et al., 2014). This technology presents a promising opportunity to solve the problems with high nutrient concentration in septic tank effluent. Electrochemical disinfection involves the onsite generation of free chlorine, usually in the form of hypochlorite, a broad-spectrum disinfectant that is effective against viruses, bacteria, and parasites (Groenen Serrano, 2018). The advantage of this method of production is it only requires a source of chloride salt as an input to produce the hypochlorite. This process is commonly applied to applications requiring the decentralized production of hypochlorite including use on ballast water and for marine sewage treatment (Nanayakkara et al., 2011). Electrochemical disinfection provides an opportunity for chemical disinfection of septic tank effluent without requiring storage and handling of dangerous chemicals.

1.1 - Research Objectives

The overall goal of this research work is to provide a research basis for the further development of electrochemical treatment technologies for septic tank effluents. For nutrient removal, this work will build on previous research in the development of a continuous electrocoagulation system for the removal of phosphorous in septic wastewater (Hayden, 2020). The aim of this work is to better understand the capabilities and limitations of Hayden's design in the treatment of nutrients and contaminants other than phosphorous which are found in septic tank effluent. In addition, this work will investigate the influence of these other contaminants on phosphorous removal efficiency. In a separate study, the suitability of electrochemical disinfection of septic tank effluent is explored. The objective of this work is to determine an optimal design and operational configuration for an electrochemical disinfection unit in an onsite wastewater application.

1.2 - Thesis Structure

The present thesis is comprised of two studies investigating the use of electrochemical technologies in onsite wastewater treatment. The dissertation has been divided into five chapters. The first chapter introduces the topic of research by identifying the limitations of existing septic tank systems and proposing electrochemical solutions: electrocoagulation and electrochemical disinfection. The second chapter is a literature review to provide background knowledge for each of these technologies. This chapter is broken into three sections, the first section is dedicated to the septic tank systems and regulation, whereas sections 2 and 3 are on electrocoagulation and electrochemical disinfection, respectively. Chapter 3 contains the investigation of the potential of using electrocoagulation in the removal of nutrients and COD from synthetic wastewater using a

continuous manifold reactor. The second study, found in Chapter 4, is a bench scale investigation of the operational and design parameters of an electrochemical disinfection system tailored for use in onsite wastewater treatment. Finally, Chapter 5 goes over the major finding of this research endeavor as well as recommendations for future research.

2 - Literature Review

2.1 - Onsite Wastewater Treatment

On-site wastewater treatment or decentralized wastewater treatment is necessary in cases where there centralized treatment solutions are not possible. In Ontario, 10% of the population or approximately 1.5 million citizens rely on on-site systems for their wastewater treatment (Ontario Ministry of Environment and Climate Change, 2018). These systems are designed to remove organics and solids from wastewater in rural or temporary developments to promote environmental sustainability (Hlavinec, 2011). As with other wastewater and drinking water treatment standards, the decentralized treatment systems in Ontario are regulated at the provincial level. Specifically, Ontario Building Code (OBC) Division B, Part 8 sets regulations pertaining to the treatment of sewage effluents up to 10,000 L/day (O. Reg. 312/12). Other portions of the building code are referenced in this section as well such as the Building Code Act and Supplementary Standard SB6. These regulations pertain to sewage and not any industrial wastewater effluents.

2.1.1 - Ontario Building Code Act (O.Reg 312/12) Division B Part 8

The requirements for a particular decentralized wastewater solution are dependent on the classification of the system. In total, there are 5 classifications for an on-site sewage treatment system, which are as follows (O. Reg. 312/12):

Class 1 - Portable toilets, incinerating toilets, composting toilets, chemical toilets and all manners of privy

Class 2 – Grey water systems

Class 3 – Cesspools

Class 4 – Septic tank - Leaching bed systems

Class 5 – Systems requiring a holding tank for the retention of hauled sewage at the site where it was produced prior to its collection by a hauled sewage system

Each class of sewage treatment system has different requirements detailed in sections 8.3 – 8.8 of O.Reg 312/12 Division B. Class I – III and V are sewage systems where the goal is collection of black water, whereas Class IV sewage systems have built in treatment systems for environmental discharge. The primary treatment method for standard Class IV systems is sedimentation and digestion in a septic tank followed by filtration and absorption through a leaching bed (O. Reg. 312/12). Septic tanks separate 60-80% of insoluble materials from the septic tank effluent through sedimentation. They can also remove up to 50% of BOD through partial anaerobic digestion based on a 48-hour detention time (Adhikari & Lahani, 2019). This process also removes nutrients from the wastewater biologically, which can be reused in the form of fertilizer from sludge at the bottom of the tank. Due to anaerobic digestion, methane and carbon dioxide are produced and must be vented (Adhikari & Lahani, 2019). Regulation 350/06 outlines septic tank treatment standards for BOD, CBOD, and suspended solids and provides guidance for tank design. This guidance includes items such as an audio or visual alarm alerting at malfunction for tanks with mechanical components, a filter at the effluent, and that the treatment unit allows sampling at the effluent (O. Reg. 312/12). Typical design of a septic tank features two or more chambers separated by a baffle wall in order to prevent hydraulic short circuiting. Septic tanks effectively work as a pretreatment for the leaching bed, which filters remaining insoluble materials and biologically and physically absorbs pathogens and nutrients from the wastewater stream (Tilley, 2014). Leaching beds are subject to a great deal more regulation in their design. O. Reg. 312/12 specifies the graduation of septic stone used, the

distance and length requirements for a distribution pipe based on percolation time, the slope of the ground and distance from water sources.

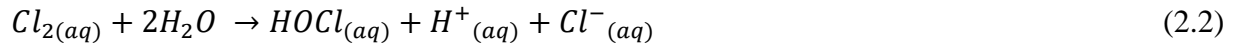
Despite existing regulations, problems with on-site wastewater treatment effluents persist. Septic tanks are ill equipped to remove dissolved nutrients and pathogens and are a source of groundwater pollution (Meuler et al., 2008). In terms of total nitrogen removal, complete Class IV systems only remove an estimated 21 – 25% of the applied nitrogen loading, the majority of which is removed by the leaching bed (Costa et al. 2002). For phosphorous, only 31-36% of phosphorous is removed in an on-site treatment process. In addition, currently septic tanks offer little in the way of pathogen removal and require additional components to meet regulations in some areas (Capodaglio et al., 2017). It is estimated that over half of onsite treatment systems in the US are over 30 years old and may be performing even worse than expected (US EPA, 2003). Pathogenically, septic tank systems also do not provide adequate disinfection. In a typical septic tank system, only a 2-log removal of coliform can be expected (Tilley, 2014). These shortcomings have led to a growing number of research papers into alternative methods of treating nutrients and pathogens to supplement traditional Class IV sewage treatment systems. In this research work, two methods are investigated: electrochemical disinfection and electrochemical coagulation.

2.2 - Electrochemical Disinfection (ED) Unit

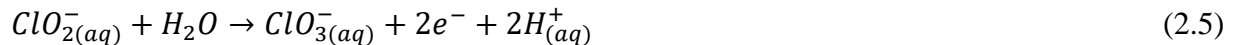
Electrochemical disinfection is the use of an electrolytic cell to remove pathogens within a water source. Free chlorine may be electrochemically produced through the oxidation of chloride ions within an electrolytic cell (Groenen Serrano, 2018). In most cases, this free chlorine takes the form of hypochlorite. This so called indirect electrochemical oxidation process is well

understood and has been applied commercially for decades (Martínez-Huitle & Brillas, 2009). This method of free chlorine production is well suited for on-site generation because it only requires a supply of chloride salt and electricity. Other methods of producing free chlorine require the application of chlorine gas which is extremely toxic or the availability of steady supply of hypochlorite salt. Using these methods in on-site wastewater applications is therefore not always feasible.

The reaction mechanism of the electrochemical disinfection process involves the donation of electrons from chloride ions near the anode. This oxidation reaction yields dissolved chlorine, which then hydrolyzes with water to form hypochlorous acid. At higher pH levels, protonated hypochlorite is formed. However, the degree of dissociation is a function of pH and temperature.



Formation of chlorite, chlorate and perchlorate as by-products is well documented in studies of this process (Sánchez-Carretero et al., 2011). The formation of these unwanted disinfection by-products is a result of uncontrolled oxidation of hypochlorite at the anode (Cheong et al., 2010),



Chlorite, chlorate and perchlorate are undesirable as they have lower oxidation potential than hypochlorite and are therefore weaker disinfection agents (Sánchez-Carretero et al., 2011). More importantly, these compounds are ecotoxic and pose a risk to human health. Perchlorate is noted for its thyroid and lung toxicity in the event of chronic exposure (Cheong et al. 2010). The World Health Organization (WHO) recommends a maximum drinking water concentration of ClO_2 , ClO_3 and ClO_4 to be 0.2 mg/L, 0.7 mg/L and 0.07 mg/L, respectively (Groenen Serrano, 2018). Anode materials with high oxygen overpotential such as boron doped diamond and antimony-tin oxide coated electrodes are more effective at oxidation, and therefore, produce chlorite, chlorate and perchlorate more quickly (Mostafa al., 2018; Sánchez-Carretero et al., 2011). However, anode materials with low stability will preferentially oxidize dissolve metal ions over the chloride ions. Operational controls for the formation of chlorite, chlorate and perchlorate include retention time, water pH and current density (Groenen Serrano, 2018). Other process by-products such as chlorine gas and volatile chlorine oxides have also been studied (Mostafa et al., 2018). These by-products represent energy inefficiency for an electrochemical disinfection process as well as potential hazards for owners of the disinfection units.

Operational cost efficiency of the process is determined both by the unit's longevity and energy efficiency. Energy efficiency is dependant on electrode material, electrode spacing, conductivity of the chloride solution and any other resistances between the power source and the electrolytic cell (Martínez-Huitle & Brillas, 2009). Electrode materials should be selected to prevent leaching of metal ions from the anode or cathode into the disinfectant solution, therefore dimensionally stable anode materials (DSAs) are favoured (Yang et al., 2000). As previously stated, anode materials with high oxygen over potential are more suited for perchlorate production processes than hypochlorite production. Other DSA materials like ruthenium oxide coated titanium or

graphite are better suited for this application (Yang et al., 2000). Typical electrode assembly designs for this process feature tightly packed electrodes with spacing as low as 0.3 cm.

The effectiveness of an electrochemical process like ED is primarily driven by the current density of the electrolytic cell and the mass transport of the contaminants to the electrode (Spasojević et al., 2015). The current density is defined as the current through the electrolytic cell divided by the surface area of the working electrode. This variable is therefore directly proportional to the electrical energy supplied to the system provided the influent wastewater maintains constant conductive properties. Reactions such as in Equation 2.1 is generally current limited, meaning the supplied current limits the rate of the reaction (Spasojević et al., 2015). In other reactions, such as those described in Equations 2.4 to 2.6, the rate is limited by mass transport (Spasojević et al., 2015). The mass transport to the electrode is achieved via three modes, convection diffusion and migration (Cheng & Kelsall, 2007). The convection in a unit with out mechanical agitation is comprised of hydrodynamic transport. Hydrodynamic transport is influenced by the geometry of the electrolytic cell, the geometry of the electrodes, the fluid properties of the influent as well as the flow rate of the influent (Hibbert, 1993). Diffusion is a mode of transport which is influenced by the concentration gradient of a species within the electrolytic cell as well as the diffusion coefficient. Finally, migration is the movement a charged body that is caused by the influence of an electrical field. The degree of migration in an electrolytic cell is dependant on the charge of the charged body, the operating temperature of the unit, the diffusion constant and electric potential gradient (Hibbert, 1993). The mass transfer to an electrode of a chemical species i in an electrolytic cell is mathematically represented by the Nernst-Planck equation (Cheng & Kelsall, 2007; Hibbert, 1993),

$$J_i(x) = -D_i \frac{\delta C_i(x)}{\delta x} - \frac{z_i F}{RT} D_i C_i \frac{\delta \phi(x)}{\delta x} + C_i v(x) \quad (2.7)$$

In the design of continuous reactor systems, it is important to consider the hydrodynamics of the reactor. Some common methods of arriving at the hydrodynamic properties of the reactor such as the Sherwood number and mass transfer coefficient are through computerized fluid dynamics analysis.

2.3 - Applications of Electrochemical Disinfection

There are several existing applications of electrochemical disinfection processes. One such application is for automatically cleaning pools by producing and dosing hypochlorite. There are several brands which provide products using this technology such as De Nora, Hayward and Pentair (Chen et al., 2017; Stewart et al., 2019; Doyle & Schulte, 2019). These chlorinators represent the closest comparison to the application of electrochemical disinfection to onsite wastewater treatment. These are designed using tightly packed dimensionally stable electrodes, generally titanium coated with a mixed metal oxide layer (MMO) in a flow through electrolytic cell (Doyle & Schulte, 2019; Chen et al., 2017). These units generate hypochlorite then continuously dose hypochlorite into the pool. Smaller scale models of these chlorinators exist as products for cleaning aquariums. At the industrial scale, hypochlorite has been used on oil rigs to remove unwanted aquatic wildlife from intake lines and other instruments (De Nora, 2018). In this case, ocean water is used as an input and therefore there is no need to ship hypochlorite salts to the oil rig on a regular basis.

2.4 - Design and Operational Parameters of ED Units

2.4.1 - pH

The pH of the produced disinfectant solution is important to the functionality of the electrochemical disinfection unit. When pH is greater than the pK_a of hypochlorous acid then

most of the hypochlorous acid is protonated (Black and Veatch, 2009; Groenen Serrano, 2018). In an electrolytic cell, the volume of solution surrounding the anode becomes increasingly acidic closer to the anode surface (Hibbert, 1993). This is important in divided cell designs, where a salt bridge carries current from one half cell to the other. In the anode half cell where the hypochlorous acid is formed, pH of the solution is depressed resulting in an inferior product, therefore the dividing membrane must be permeable to hydroxide ions (Krstajić et al., 1991). It is also important that the input chloride solution is not overly acidic for the same reason. Under acidic conditions the predominant free chlorine species is dissolved chlorine gas, which is a much weaker disinfectant (Black and Veatch, 2009).

2.4.2 - Electrode Material and Size

While oxidation occurs close to the anode in an electrolytic cell, reduction occurs near the cathode (Krstajić et al., 1991; Spasojević et al., 2015; Khelifa et al., 2004). This reduces hypochlorite and reverses the hypochlorite production mechanism occurring at the cathode. To maximize the total hypochlorite that may be produced, the rate of reduction at the cathode must be minimized while the rate of oxidation at the anode must be maximized. The properties of the electrodes used is important to the rates of electrochemical reactions at the anode and cathode. At the anode, materials with high oxygen overpotential is desirable to produce hypochlorite (Shao et al., 2014; Bergmann, 2012; Qing et al., 2021; Jeong et al. 2009). A high oxygen overpotential represents a large difference in the potential that is required thermodynamically to produce oxygen at the anode and the experimentally observed potential (Hibbert, 1993). High oxygen overpotential means less of the available current is going towards the production of oxygen and more of it is going into the other electrochemical activities occurring within the electrolytic cell (Raut et al., 2019; Jeong et al., 2009). For the purposes of the electrolytic cell used to produce

hypochlorite, oxygen is not a necessary by-product. More of the available current going into oxygen production therefore represents inefficiency in the system (Raut et al., 2019; Shao et al., 2014). At the cathode, hydrogen is produced instead of oxygen (Hibbert, 1993). Theoretically, more hydrogen production at the cathode would represent less hypochlorite reduction occurring at the cathode. This is a desirable outcome as a lower amount of energy is being used to reverse the hypochlorite production reaction, however research directly comparing cathode materials for hypochlorite production suitability is scarce. Furthermore, a product of hypochlorite reduction is chlorine gas (Spasojević et al., 2015). This gas is dangerous even at low concentrations and has special storage and handling requirements. A drawback of using materials with high oxygen over potential is that disinfection by-products such as perchlorates are produced more quickly and in greater number (Bergmann, 2012). This is because there is more energy available at the anode to further oxidize hypochlorite and less energy available at the cathode to reduce perchlorates, chlorates and chlorites.

The size and shape of the electrodes has a great influence on the efficiency of any electrochemical process. Surface area increases the rate of electrochemical reactions that occur close to the surface of the electrode (Cheng & Kelsall, 2007; Khelifa et al., 2004). The only chemically available molecules on the electrode reside on the very surface at the electrolyte solution-electrode interface. Greater surface area results in greater amount of available electrode molecules to exchange electrons with the electrolyte solution (Cheng & Kelsall, 2007). In the case of the electrochemical disinfection process, a larger electrode surface area is beneficial at the anode and detrimental at the cathode. The surface area of an electrode is dependant on both the size and shape of the electrode, however increasing the size of an electrode increases production costs. Shape, specifically surface geometry, is therefore particularly important when

it comes to optimal electrode selection and design (Khelifa et al., 2004; Spasojević et al., 2015). Research into porous and 3D electrodes shows promise for improving reaction rates of electrochemical processes such as direct and indirect electrochemical oxidation (Cheng & Kelsall, 2007).

2.4.3 - Influent Sodium Chloride Concentration

The influent concentration of sodium chloride is an important design consideration for electrochemical disinfection units. Sodium chloride and water are the initial reagents in the hypochlorite production mechanism, therefore increasing sodium chloride concentration improves the rate of reaction and increases the steady state concentration in a batch system (Spasojević et al., 2015; Khelifa et al., 2004). Conversion rates for the sodium chloride should be considered, particularly for a wastewater treatment system. Unreacted sodium chloride can pose a hazard to freshwater ecosystems as well as increased corrosion on plumbing equipment.

2.4.4 - Detention Time & Current Density

With longer detention times there is more opportunities of chloride to be oxidized at the anode of the electrolytic cell. Simultaneously, there are more opportunities for hypochlorite to be further oxidized into perchlorate, chlorite, and chlorate (Bergmann, 2012). As the amount of hypochlorite rises, the rate of hypochlorite reduction occurring at the cathode also rises. This results in diminishing returns for a single cell unit as detention time increases. Past research has observed decreasing hypochlorite concentration at extreme detention times up to 300 minutes (Khelifa et al., 2004).

2.5 - Electrochemical Coagulation System

Electrochemical coagulation (EC) is a relatively more complicated process than ED. The removal of contaminants in this process begins with liberation of cations from the anode due to electrochemical oxidation (Barrera-Díaz et al., 2018). The process by which this occurs is known as anodic dissolution and involves the transfer of electrons from an electrolyte solution to the surface of the anode. This occurs through three distinct mechanisms (Keddam, 2002),

1. *The aquo-ligand mechanism:*



2. *The hydroxo-ligand mechanism*



3. *The aniono-ligand mechanism*



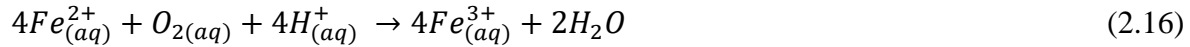
Where M is the metal of the electrode used

z is the charge of the dissolved metal M

And A is the anion of the electrolyte used in the electrolytic cell

Of these mechanisms, the aquo-ligand mechanism and hydroxo-ligand mechanism are the most important to the formation of coagulant in the electrocoagulation process. The most common

electrode coagulants used in electrochemical coagulation are iron and aluminum (Barrera-Díaz et al., 2018; Cañizares et al., 2007; Nidheesh et al., 2021). In the case of iron, dissolved iron from the aquo-ligand mechanism is first realized as cation in its ferrous oxidation state, Fe^{2+} . In more acidic media it is oxidized into its ferric oxidation state, Fe^{3+} , via dissolved oxygen in the electrolytic cell (Jiménez et al., 2012). Finally, it is hydrolyzed to form polymeric ferric hydroxide which is capable of forming flocs,



After hydration, the iron hydrolyzes under the right pH conditions to precipitate various ferrous hydroxides and poly-hydroxides. These hydroxides form polymeric iron complexes with contaminants in the water due to the surface charge of the molecule. The hydroxo-ligand mechanism results in a ferric hydroxide molecule desorbing from the surface of the electrode. Similarly, this ferric hydroxide will further hydrolyze depending on the pH into polymeric iron complexes which act as a coagulant. At lower pH, the iron ions do not typically hydrolyze and are in a simple cation form. The window for which this is true is different between Fe(II) and Fe(III), where Fe(III) has a much smaller pH window where it is present in simple cationic form (Barrera-Díaz et al., 2018). As the simple cation form does not produce the desired coagulation effect, the pH where iron begins to hydrolyze represents the minimum pH for operation. In the case of Fe(II), this minimum pH is 5.5 where Fe(II) hydrolyzes into $Fe(OH)_2$. For ferric iron, the minimum pH for hydrolyzing into $Fe(OH)_3$ is just 1 (Barrera-Díaz et al., 2018). Since surface complexation occurs on the precipitated iron hydroxide, the ferric iron has a much greater operational window (Barrera-Díaz et al., 2018). It is therefore preferable to have sufficient dissolved oxygen in the electrolytic cell, so that ferrous iron may oxidize into ferric iron

(Jiménez et al., 2012; Önder et al., 2007). Polymerization of dissolved iron hydroxide is particularly pronounced for ferric iron between the pH of 3.5 and 7 (Jiménez et al., 2012).

A similar process occurs for aluminum, where dissolved aluminum from the aquo-ligand mechanism hydrolyze in water to form aluminum hydroxide. Through further hydrolysis and polymerization more complex aluminum precipitates may form dependant on the pH of the electrolytic cell. These complex and polymer compounds may be single core or multicore, meaning they contain a single aluminum or multiple aluminum atoms (Jiménez et al., 2012). In the pH range of 4-9, aluminum hydroxides such as $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_2^+$, $\text{Al}_2(\text{OH})_2^{4+}$, $\text{Al}(\text{OH})_3$ and $\text{Al}_{13}(\text{OH})_{32}^{7+}$ can be found (Barrera-Díaz et al., 2018; Jiménez et al., 2012). These species of aluminum are well suited for coagulation making this pH range the best for EC systems. At pH below 4, the dominant species of aluminum that is dissolved in the electrolytic cell is Al^{+3} , which has no coagulation capability. At a pH of 10 and above, the dominant species is $\text{Al}(\text{OH})_4^-$ and continuously coagulation becomes less effective with rising pH (Barrera-Díaz et al., 2018).

Removal of the formed flocs can be done in various ways. In some designs, the oxygen evolution at the anode and hydrogen evolution at the cathode are leveraged to create flotation (Barrera-Díaz et al., 2018). Flocs which are hydrophobic in nature will cling to the rising bubble close to the anode and are removed at the top of the electrolytic cell. Other designs include a settling tank at the outlet of the cell such that coagulated contaminants can accumulate at the bottom of the tank due to gravity (Cañizares et al., 2007). Figure 2.1 shows a simple electrolytic cell design demonstrating potential removal methods for the reactor. In either case, a scraping mechanism is required to remove the accumulation of flocs.

Electrochemical coagulation is like the traditional chemical coagulation in many ways. Both utilize metal hydroxides to amalgamate contaminants into large, precipitated colloids, which are

more easily removed via filtration, flotation or settling (Cañizares et al., 2007; Barrera-Díaz et al., 2018). There are, however, several advantages to using electrochemical coagulation over more traditional methods. Conventional coagulation treatments are limited in that they require more control over the pH of the treated water (Barrera-Díaz et al., 2018). In an EC unit, the pH range for effective production of coagulants is 4-9, whereas traditional alum coagulation is limited to a pH of 6-7. In addition, flocs created from EC are larger and more stable, typically containing less water in their complexes. This results in flocs that are easier to de-water and is better in low turbidity conditions as the flocs are initially larger (Ilhan et al., 2008).

Electrocoagulation is known for its ease of operation and low operating costs especially in situations with lower throughput (Mamelkina et al., 2020). One of the major disadvantages of the system is the required sacrificial anode. The anode will naturally corrode and passivate through continuous operation which will impact the rate at which flocs are produced and impact water quality (Barrera-Díaz et al., 2018). At some point, the anode will need to be replaced due to loss of effectiveness in the system. In addition, the system's energy efficiency and suitability are dependant on wastewater conductivity. In some cases, electrolyte must be dosed to maintain a high enough conductivity (Barrera-Díaz et al., 2018). Electrochemical coagulation systems also require a source of electricity, whereas other coagulation methods theoretically do not. The

applications of EC that make the most use of these advantages are decentralized water treatment applications (Nawarkar and Salkar, 2019).

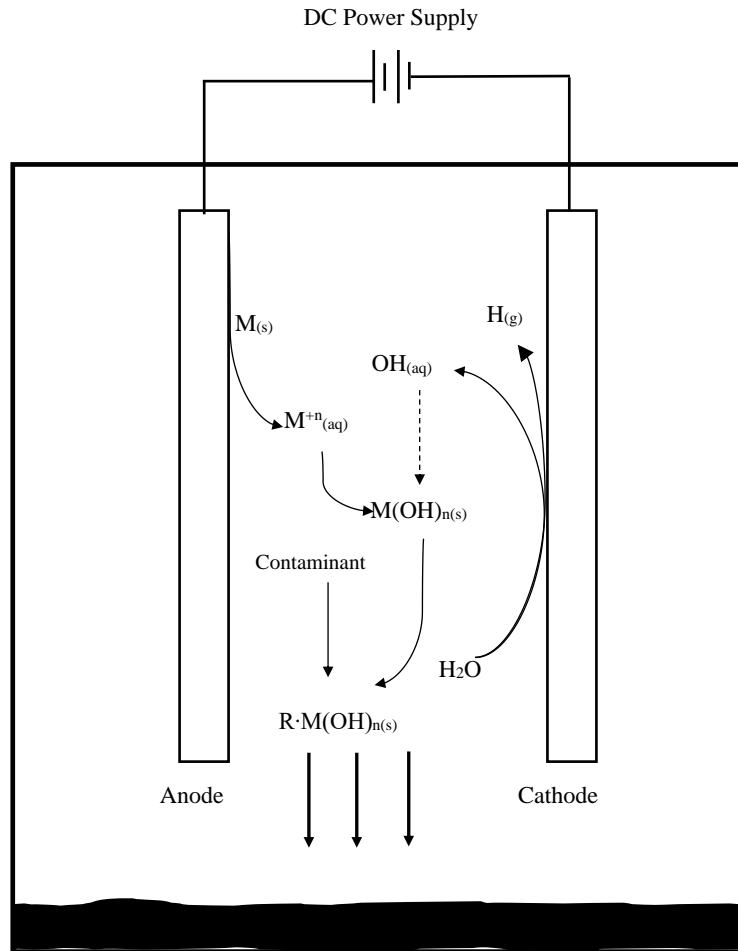


Figure 2.1: EC Schematic Diagram

2.6 - Applications and Design of Electrochemical Coagulation Units

There are many applications for electrochemical coagulations which have been investigated. Electrochemical coagulation has been studied for use in both drinking water and wastewater treatment. In wastewater treatment, EC system have been effective in treating a variety of

industrial sources such as textile wastewater, mining wastewater, pharmaceutical wastewater, landfill leachate and agricultural wastewater (Zeboudji et al., 2013; Panizza & Cerisola, 2010; Ilhan et al., 2008; Mamelkina et al., 2019; Ensano et al. 2019). Common contaminants removed using electrochemical coagulation include heavy metals, phosphorous, organics and chemical oxygen demand (Arambarri et al. 2019; Swain et al., 2020; Potrich et al., 2020; Zeboudji et al., 2013; Panizza & Cerisola, 2010). For all purposes, the general design principles for an electrochemical coagulation system remains the same. That is two or more parallel electrodes with alternating charges similar to the schematic given in Figure 2.1. An EC unit may be batch or continuous depending on the application and treatment requirements. Continuous designs are either done with parallel flow through multiple electrode pairs or through a single series of electrode pairs. The difference is primarily in the flow rates and the reaction time for the system. In a parallel system, lower potential differences are found as the current is split between each of the electrode pairs. However higher electrolytic cell flow rates in series designs can improve ion diffusion rates due to turbulence. At extremely high electrolytic cell flow rates, the flocs may lose stability and break down due to turbulence (Sahu et al., 2014).

2.7 - Electrochemical Coagulation Operational Parameters

2.7.1 - Electrode Material

The two most typically used electrode materials for the sacrificial anode are aluminum and iron (Cañizares et al., 2007). This is due in part to the abundance and low cost of the materials as well as their effectiveness in forming well understood coagulants at low current densities. Iron electrodes are cheaper but heavier than aluminum electrodes though the most important difference between electrodes is the coagulants produced. In certain applications, aluminum

tends to perform better than iron in terms of removal of contaminants at a particular current density and detention time. Applications such as COD removal from pulp and paper mill wastewater, boron removal from aqueous solutions, landfill leachate COD removal were better performed by aluminum electrodes (Zeboudji et al., 2013; Ilhan et al., 2008). In other applications iron electrodes yielded better removal percentages. Oil and grease removal from carwash wastewater, oil grease and COD removal from slaughterhouse wastewater and sulfate removal from mining wastewater were found to be better applications for iron electrodes (Mamelkina et al., 2019; Potrich et al., 2020; Panizza & Cerisola, 2010). Similar results have been noted for various other contaminants such as colour removal from azo dye contamination, nutrient (nitrogen and phosphorous) removal from slaughterhouse wastewater and fluoride removal (Potrich et al., 2020; Bazrafshan et al., 2012; Cañizares et al., 2007). Due to the variability, it is important to pilot test different electrodes to determine which electrode is best suited for a particular application.

In addition to these two electrode materials, other alloys and electrode materials have been studied. Zinc alloys have been studied for their application in electrochemical coagulation units and have had promising results in the removal of perfluoroalkyl acids and boron (Barrera-Díaz et al., 2018). Copper has been combined with hydrogen peroxide to create a dual disinfection and electrocoagulation system where COD and pathogens have been removed.

2.7.2 - Cell pH

The cell pH is a very important parameter when operating an electrocoagulation unit. This determines hydroxide species that may be formed as a result of hydrolysis of the dissolved metal ions. As stated in section 3.2, aluminum electrode systems operate best under neutral conditions in the pH range of 4 to 9 (Barrera-Díaz et al., 2018; Jiménez et al., 2012). This is where the best

hydroxide coagulants are formed for the process. In the case of iron electrodes, the minimum operating pH is just 2 provided there is sufficient dissolved oxygen to raise the oxidation state of ferrous ions (Barrera-Díaz et al., 2018). Under low oxygen conditions, a minimum pH of 5.5 is required in order to produce ferrous hydroxide (Jiménez et al., 2012). For the greatest effectiveness, the pH of an iron electrocoagulation system should be maintained from 3 to 12 for ferric ions and 8 to 14 for ferrous ions (Barrera-Díaz et al., 2018; Jiménez et al., 2012). At pH beyond this, the predominant form of monomeric iron hydroxide is dissolved. Under operation, the pH of the solution will decrease with the production of coagulants (Demirci et al., 2015). This is due to the protons liberated from water as a result of equation 2.17. However, electrolysis occurring simultaneously at the cathode neutralize the acid produced at the anode. As a result, pH control is frequently unnecessary when using an EC system. (Martínez-Huitle & Brillas, 2009). It has been observed in some cases that pH will trend towards acidity throughout the detention time of an EC reactor. pH maintenance is therefore necessary under some operational conditions (Demirci et al., 2015).

2.7.3 - Current Density & Detention Time

Current density affects the rate at which coagulants are dosed into the electrolytic cell (Sahu et al., 2014). Higher current densities therefore result in greater coagulant concentrations at a given detention time and therefore more removal (İrdemez et al., 2006; Kim et al., 2015; Vázquez et al., 2014). A higher current density at a lower detention time differs from a lower current density at a higher detention time due to cell hydrodynamics. Turbulence increases the convective mass transport of coagulant from the surface of the anode to the rest of the electrolytic cell, however increased turbulence may result in crumbling flocs (Sahu et al., 2014).

3 - Removal of Nutrients from Onsite Wastewater Using Electrocoagulation Manifold System

Abstract

High nutrient content in septic tank effluent is damaging to the watersheds which they are released to. This study investigates a continuous manifold electrocoagulation treatment system in purifying a synthetic wastewater designed to accurately emulate dissolved contaminants in onsite wastewater. Particularly, the removal rates for orthophosphates, ammonia and chemical oxygen demand were observed. This study also assesses the settleability of electrochemically produced flocs using a baffled settling tank by tracking total suspended solids throughout the settling tank. It was found that under low phosphate loading, over 95% removal of orthophosphates could be achieved in 15 minutes using current densities as low as 2.0 mA/cm². Under high phosphate loading, 88% could be removed in 30 minutes at 2.8 mA/cm². Up to 20% of ammonia was removed using a current density of 2.8 mA/cm² and a retention time of 30 minutes. Chemical oxygen demand generated solely by glucose was not significantly reduced in this study. Total suspended solids were reduced to below 15 mg/L after the first settling chamber in all test cases. It is recommended that further research be conducted to determine the effectiveness of the continuous manifold electrocoagulation system in the removal of nutrients found in real septic tank effluent.

3.1 - Introduction

Decentralized wastewater treatment involves the collection, treatment, and disposal of small quantities of wastewater at or near the wastewater source. Despite the commonality of centralized sewage systems in the developed world, decentralized sanitation solutions are the

most widely implemented water treatment technology. This is because decentralized systems offer a low cost, simple, reliable, and low energy consuming alternative to centralized systems for the developing world (Oladoja, 2017). As a result, there are currently 2.7 billion people globally who are served by decentralized wastewater treatment technologies. This amount is expected to increase to 5 billion people by 2030 as access to sanitation has become a global priority (Strande, 2014). These treatment systems are not limited to rural areas with over one billion on-site treatment systems operating in urban areas worldwide. Though decentralized systems are up to five times less expensive than centralized sewer systems, in developed nations centralized sewers are common in urban areas (Strande, 2014). In the developed world, on-site wastewater treatment is primarily used for temporary settlements and areas that are sparsely populated due to economic and practical reasons (Laurenco et al. 2020). The performance of these technologies is important in the maintenance of the watersheds and local ecosystems of remote settlements in the developed world. This is why decentralized wastewater treatment is a growing area of concern in the water treatment industry.

Currently, there exist many different methods of treating wastewater using decentralized methods. These methods can be divided into two primary groupings, wet methods, and dry methods (Laurenco et al. 2020). In developing countries, the majority of decentralized wastewater treatment is done using dry treatment methods, however in the developed world wet treatment methods are more common. The most common of these wet treatment methods is the septic system (Laurenco et al. 2020). This is because the septic system is considered one of the simplest and most reliable decentralized treatment methods (Schaidler et al. 2017). Septic systems are currently used by approximately 20% of the population of North America and are growing in popularity outside of the developed world (Strande, 2014). These systems consist of a septic tank

buried underground which collects and settles solids out of wastewater effluents. Larger particulate matter sinks to the bottom of the settling tank throughout the retention time while scum formed from oils and other lighter organics float to the top (Tilley et al., 2014). Baffles prevent this scum and sludge from flowing into a secondary chamber from which septic tank effluent is drawn out. Within the tank, anaerobic digestion occurs eliminating BOD and nutrients within the wastewater, however the tank must periodically be emptied to dispose of the accumulated sludge and scum (Laurenco et al. 2020). The effluent of the tank is piped to a leaching bed or soaking pit, where further treatment occurs via filtration and adsorption through a porous medium. Though these systems have proved to be cost effective and reliable, they have been shown to provide only partial treatment of wastewater. Typically, a septic tank system removes only 30 - 40% of BOD, and about 50% of total suspended solids (Tilley et al., 2014). For nutrient removal, a septic tank system removes 18 – 34% of total nitrogen and 26 – 36% of total phosphorous (Nasr and Mikhaeil, 2013). Nutrients remaining in effluent from septic systems have been shown to be damaging to watersheds, particularly those in coastal regions (Laurenco et al. 2020). Various post-treatments for septic system effluents have been investigated for their ability to limit this environmental damage. One such post-treatment is the electrochemical coagulation process.

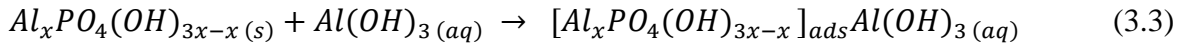
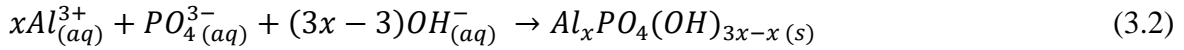
Electrochemical coagulation (EC) is the process of coagulating and removing contaminants using metal hydroxides formed as by-product of electrolysis (Barrera-Díaz et al., 2018). It has been studied as a primary treatment, pre-treatment, and post-treatment within a variety of applications. EC has been applied in many different industrial settings including mining, agricultural, textile, oil and landfilling industries. Within these industries, it has been used to remove a wide variety of contaminants ranging from pathogens to heavy metals, organics

including pharmaceuticals, nutrients, and particulates (Al Jaryan et al., 2021; Hai et al. 2015; Nawarkar and Salkar, 2019; Mollah et al. 2001). EC has also been studied extensively for its use in treating municipal wastewater effluents (Koyuncu & Arıman, 2020; Symonds et al., 2015; Omwene & Kobya, 2018). In this application, EC has been primarily used to treat phosphorous contamination, but COD, BOD and nitrogen removal have also been studied (Yehya et al. 2014). EC has continuously demonstrated many benefits including effectiveness, simple and compact equipment requirements, simple set up and automation (Mollah et al., 2001).

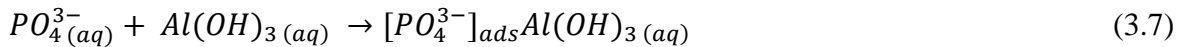
In the treatment of municipal wastewater, EC has shown some great promise as an alternative to chemical coagulation. Aside from an electrolyte in the case of a low conductivity wastewater, EC does not require any chemical additive to function (Koyuncu & Arıman, 2020). This is particularly useful in the case of decentralized wastewater systems, where proper storage and regular purchasing of coagulant chemicals is expensive and dangerous. The coagulant used to remove nutrients and organic contaminants from domestic wastewater in the EC process is primarily monomeric or polymeric iron or aluminum hydroxide species (Mollah et al., 2001). Due to electrolysis, metal ions originating from the anode dissolve into electrolytic cell then hydrolyze into metal hydroxide species.

The specific removal process for an EC system is dependent on the contaminant being removed but is functionally very similar as it revolves around the adsorption of contaminants to positively charged hydrolysis products (Zhou et al., 2021). Charge surrounding a contaminant and the hydrolysis products are neutralized due to collisions between them (Mollah et al., 2001). Once the charge is neutralized, van der Waals forces become dominant allowing the contaminant to adsorb to the surface of the electrochemically produced coagulant (Hakizimana et al., 2017). Hydrolysis products present in the solution are dependent on the pH of the electrolytic cell.

Insoluble aluminum hydroxide is most common at intermediate pH levels in an electrolytic cell with aluminum electrodes (Mollah et al., 2001; Barrera-Díaz et al., 2018). In the removal of phosphorous, two major coagulation mechanisms have been identified: (1) the formation of metal-hydroxo-phosphate complexes which then adsorb to the surface of metal hydroxides; (2) adsorption of phosphate ions directly to the metal hydroxide precipitate (Omwene & Kobya, 2018; Zhou et al., 2021). With aluminum electrodes, the first of these mechanisms is represented in equation 3.1 to 3.4.



The second of these mechanisms is represented in equations 4.5 to 4.7.



A similar mechanism exists for nitrogen species, including nitrates, nitrites, nitrous oxide and ammonia. It should be noted though that reduction of nitrates and nitrites may occur at the cathode of the electrolytic cell (Amarine et al., 2020). The product of this reduction is nitrogen gas, ammonia and nitrous oxide.

EC processes have been studied for application to municipal wastewater extensively but have not been thoroughly investigated as a post-treatment for a septic tank system. In previous work done

by colleagues at the University of Guelph, a novel EC treatment system was proposed as to treat septic tank effluent prior to disposal through a leaching bed (Hayden, 2020). This work investigated the effectiveness of a continuous manifold electrocoagulation reactor (CMECR) in removing dissolved ortho- and polyphosphates. The results of this study indicated that over 95% removal of phosphate can be achieved at current densities lower than 2.8 mA/cm^2 at a 15-minute retention time using aluminum electrodes (Hayden, 2020). These results show promise for a post-treatment system designed to remove phosphorous, however, it remains unclear how well this system would remove other nutrients and organic contamination. The aim of the present study is to investigate the suitability of a CMECR system for the removal of nutrients and COD in representative synthetic onsite wastewater. This investigation will explore the effects of variation in initial phosphorous concentration as well as the influence of current density and retention time on treatment outcomes. In addition, this study will evaluate the settleability of CMECR effluent and compare the water quality of the CMECR and settling tank effluent.

3.2 - Materials

3.2.1 - Synthetic Wastewater

Genuine wastewater could not be used at this stage of development due to biohazardous risk. Instead, synthetic wastewater was used in this study to represent typical aqueous conditions in an onsite wastewater treatment application. The concentrations of the various chemicals were determined in a previous work conducted in affiliation with the University of Bremen (Abbassi et al., 2000). This work found the aqueous composition of raw, untreated municipal wastewater. The aqueous chemical composition of this synthetic wastewater is detailed in Table 3.1.

Table 3.1: Chemical Composition of Synthetic On-site Wastewater

<i>Component</i>	<i>Concentration (mg/L)</i>
<i>Glucose (C₆H₁₂O₆)</i>	1000
<i>NH₄Cl</i>	200
<i>MgSO₄ · 7H₂O</i>	100
<i>FeCl₃</i>	0.5
<i>KH₂PO₄</i>	52.7
<i>K₂HPO₄</i>	107
<i>CaCl₂</i>	7.5

In this synthetic wastewater composition, glucose is the sole organic compound creating chemical oxygen demand. The glucose acts a stand-in representation of the more varied and complex carbon species that would be present in real wastewater.

To evaluate the effect of influent phosphorous concentration, a second synthetic wastewater composition was used. This wastewater composition lowers the total amount of dissolved phosphate to 20 mg/L while maintaining the same ratio of potassium phosphate dibasic and potassium phosphate monobasic. The composition of this synthetic wastewater is given in Table 3.2.

Table 3.2: Chemical Composition of Synthetic On-site Wastewater (Low PO4)

<i>Component</i>	<i>Concentration (mg/L)</i>
<i>Glucose (C₆H₁₂O₆)</i>	1000
<i>NH₄Cl</i>	200
<i>MgSO₄ · 7H₂O</i>	100
<i>FeCl₃</i>	0.5
<i>KH₂PO₄</i>	11.1
<i>K₂HPO₄</i>	22.5
<i>CaCl₂</i>	7.5

3.2.2 - Treatment Unit

To conduct experiments on the removal of nutrients from synthetic wastewater, a parallel pipe electrocoagulation reactor was employed. This reactor's design details are given in previous work done by Hayden in a master's dissertation (Hayden, 2020). It features a manifold, which contains three electrolytic cells within two-inch (5.08 cm) diameter polyvinyl chloride (PVC) pipes. These pipes channel wastewater vertically from an inlet header towards the outlet header. These headers are also comprised of PVC pipes and fittings. Within the cells, two parallel aluminum 6061 electrodes are used interchangeably as the anode and cathode. This alloy is more than 95% pure aluminum with impurities including magnesium, silicon, iron, and copper. The electrodes span the entire electrolytic cell, extending to a length of 78.5 cm with a width of 2.5 cm and a thickness of 2 mm. Of this length, 63.5 cm of the electrodes are submerged in the cell allowing for the electrode to protrude beyond the top of the manifold. This amounts to a total

electrode surface area of 161 cm², amounting to a total anodic surface area of 484 cm² and complete electrode surface area of 968 cm². The volume of one electrolytic cell is 0.93 L, with a total volume for the system of 2.79 L the surface-area-to-volume ratio for each electrolytic cell is 17.2 m⁻¹. In these electrolytic cells a distance of 3.5 cm was used between electrodes and was fixed using a rubber stopper. The portion of the electrode that protrudes beyond the manifold reactor is used to connect the power supply unit to the electrodes. The power supply used was a B&K Precision 9111 180W Multirange 60V/8A Direct Current (DC) Power Supply. A peristaltic pump feeds the bottom header of the reactor and controls the flow rate of wastewater through the treatment unit. This pump connects a 67 L plastic tub to the inlet header at the bottom of the manifold unit. The vinyl tube that runs through the pump and into the inlet port of the manifold reactor has an internal diameter of 4.76 mm. At the top of the unit, the outlet header connects the three-pipe manifold and directs the flow of wastewater to an outlet port.

The outlet of the electrocoagulation unit connects to a 1.5 cm vinyl tube which connects the manifold reactor to the settling tank. The settling tank is divided into four chambers which are separated by two over-under baffles each. These baffles are meant to decrease hydraulic short circuiting of settleable aluminum hydroxide flocs. The settling tank has 3 front facing sampling ports at the outlets of the first three internal chambers and an outlet valve beyond the fourth chamber. At the outlet is a bucket is used to collect and dispose of treated wastewater.

3.3 - Methods

3.3.1 - Experimental Plan

To evaluate the performance of the CMECR and the settling tank combination in the treatment of synthetic wastewater, four key water quality parameters were tracked: phosphorous

concentration, ammonia concentration, chemical oxygen demand and total suspended solids. Four current densities, two hydraulic retention times and two synthetic wastewater compositions were compared. Table 4.3 shows the test configurations for each of the tests carried out as part of this study.

Table 3.3: Experiment Configurations

<i>Exp. Number</i>	<i>Hydraulic Detention Time (min)</i>	<i>Initial Phosphate Concentration (mg/L PO₄³⁻)</i>	<i>Current Density (mA/cm²)</i>	<i>Exp. Number</i>	<i>Hydraulic Detention Time (min)</i>	<i>Initial Phosphate Concentration (mg/L PO₄³⁻)</i>	<i>Current Density (mA/cm²)</i>
1	15	96	0.7	9	30	96	0.7
2	15	96	1.4	10	30	96	1.4
3	15	96	2.0	11	30	96	2.0
4	15	96	2.8	12	30	96	2.8
5	15	20	0.7	13	30	20	0.7
6	15	20	1.4	14	30	20	1.4
7	15	20	2.0	15	30	20	2.0
8	15	20	2.8	16	30	20	2.8

3.3.2 - Experimental Procedure

To begin the experiment, a 1 L synthetic wastewater stock solution was created to accommodate 60 L of the wastewater detailed in Table 4.1 or 4.2 depending on the experiment. This was done by weighing each of the chemicals on a Denver Instruments APX-100 analytical balance and adding it to a 1 L volumetric flask which was subsequently filled with deionized water. The mass of the constituent chemicals was determined to three decimal places. No additional electrolytes were added to the stock solution to improve conductivity. To create the influent synthetic

wastewater, this 1 L stock solution was added to 59 L of deionized water within the 67 L wastewater tub. The 59 L of deionized water was verified gravimetrically using a balance capable of measuring mass in grams to one decimal place. The synthetic wastewater was then briefly mixed before pH and conductivity measurements were taken. The initial pH measurements were then taken using a Thermo Scientific™ Orion Star™ pH probe and electrical conductivity was measured using an Oakton TDS 6+ conductivity meter. The 67 L tub was then placed close to the CMECR manifold body as well as the peristaltic pump.

The CMECR was assembled from 5 previously built components: the three electrode pairs, pipe manifold body and the inlet cap. Each of the electrode pair was dropped down to the bottom of the manifold reactor through the ports at the top of the manifold body and were screwed into the top of the reactor. The inlet cap was hammered into open pipe at the bottom of the reactor assembly. Situated on this inlet cap is a port, where the vinyl inlet tube was attached. This inlet tube runs through the peristaltic pump and into the 67 L synthetic wastewater tub. At this point, the power supply unit was powered on and set to the appropriate current as detailed for the experiment as detailed in Table 4.4. These currents were calculated based on the surface area of the electrodes in a previous work (Hayden, 2020). For the purposes of these experiments the power supply unit was operated in a constant current variable voltage mode. This allows for the maintenance of a constant current density throughout the test period.

Table 3.4: Constant Current Settings for Test Current Density (Hayden, 2020)

<i>Current Density (mA/cm²)</i>	<i>Constant Current Setting (mA)</i>
0.7	333
1.4	655
2.0	982
2.8	1310

The outlet of the CMECR reactor was then piped to the inlet of the settling tank using a 1.5 cm diameter vinyl tube. An 18.9 L bucket was placed at the outlet of the settling tank to collect treated wastewater. Once in place, the peristaltic pump was turned on and the CMECR began to fill with synthetic wastewater. Once the synthetic wastewater level reaches approximately 1/4th up the height of the manifold, the power supply unit was switched on allowing current to flow. The CMECR continues to fill until the water level reaches the top of the reactor unit. At this point, the treated synthetic wastewater flows through a vinyl tube and into the settling tank.

Once the settling tank is filled and begins to overflow into the outlet bucket, a timer begins for 30 minutes to allow the unit to reach steady state operation. Once the timer expired, four 50 mL sample vials were filled with treated wastewater, two at the inlet of the settling tank and two at the outlet. This was done in order to compare treated water quality prior to and after the settling tank to determine if flocculation and coagulation continues within the settling chamber. In addition, four 100 mL samples were taken from the unit at various points of interest within the settling tank. The first was at the inlet of the settling tank. The second point of interest was the first of the front facing sample ports on the tank at the outlet of the first settling chamber. The third was the third front facing sample port situated at the entrance into the final settling

chamber. The final sample was taken from the outlet of the settling tank. The purpose of these 100 mL samples is to test total suspended solids concentrations throughout the settling unit. After sampling, a timer was set for 30 minutes, so that another sample period could be conducted. In total, three sample periods were conducted per experiment, so that results could be produced in triplicate.

Between experiments, cleaning and maintenance were conducted to prevent cross contamination and systematic errors such as drift. To accomplish this, electrodes were removed from the CMECR unit and first rinsed with deionized water to remove any excess wastewater. Following this, the electrodes were individually dried and sanded with medium grit sandpaper to expose aluminum beneath the oxidized layer. Following sanding the electrodes were rinsed once again to remove dust from the sanding process. The CMECR's PVC body was also rinsed using deionized water as well as the settling tank unit. All vinyl tubing was run through with deionized water for the same reason, to remove any excess synthetic wastewater in the system.

3.3.3 - Sample Analysis Methodology

Phosphorous

To analyze for total phosphorous, Hach Low Range (LR) PhosVer® 3 Method (Method 8048) was used (Hach, 2017). Samples taken from the two ports were first filtered using Whatman 2 filter papers (8 µm pore size) using glass vacuum filtration apparatus. The filtrate was then recollected in a separate sample vial for phosphorous testing. In some cases, it was necessary to dilute the sample prior to phosphorous testing. In these cases, a 1:10 dilution ratio was used with 5 mL of sample being added to 45 mL of deionized water in a 50 mL volumetric flask. Once the samples were prepared, the DR 3900 Lab Spectrophotometer was powered on and the LZV859

Light shield was inserted. On the display of spectrophotometer, program “535 P. React. PV TNT” was selected and loaded. Once the spectrophotometer was prepared, 5 mL of sample was added to the Reactive Phosphate Test’N’Tube (TNT) vial using a calibrated pipette. The vial was then mixed via inversion for 10 seconds and wiped clean of fingerprints using Kimtech® Wipes. The vial was then inserted into the 16 mm cell holder of the spectrophotometer and the device was zeroed. Next, the contents of the preprepared PhosVer® 3 Phosphate Powder Pillow reagent were added to the vial. The vial was then shaken vigorously for 20 seconds to allow the reagent to dissolve. At this point a timer was set for 2 minutes, so that the reaction could take place. Once the timer was complete, the vial was wiped again with Kimtech® Wipes then replaced into the spectrophotometer. Lastly, the program was run, and the results were recorded.

Ammonia

For ammonia analysis, the Hach Nitrogen-Ammonia AmVer™ (Salicylate) High Range (HR) Method was used (Hach, 2015). To begin, the DR 3900 Lab Spectrophotometer was powered on and the LZV859 Light Shield was inserted. The program “343 N, Ammonia HR TNT” was then selected and loaded. For some initial samples, a 1:2 dilution was necessary. This dilution was done by pipetting 25 mL of sample into a 50 mL volumetric flask and filling the remaining volume with deionized water. Once the samples were prepared, a blank was created for the spectrophotometer. To do this, 0.1 mL of deionized water was pipetted into an AmVer™ Diluent Reagent TNT vial. Once the blank was prepared, the sample vial was prepared by pipetting 0.1 mL of sample into a separate Diluent Reagent vial. In both vials, the blank and the sample, Ammonia Salicylate Reagent Powder Pillows were added. Subsequently, Ammonia Cyanurate Reagent Powder Pillows were added to each reagent vial. Each vial was then mixed vigorously via shaking and a timer was set for 20 minutes. After the timer expired, each vial was wiped with

Kimtech® Wipes to remove any fingerprints or moisture on the vial. The spectrophotometer was then zeroed using the blank vial and then the program was run on the sample vial to determine ammonia concentration.

Chemical Oxygen Demand (COD)

COD analysis was done using Hach's Chemical Oxygen Demand Reactor Digestion Method (Hach, 2019b). As the treated synthetic wastewater did not have significant solids content, it was unnecessary to blend the sample to homogenize the wastewater. It was also unnecessary to dilute the samples collected due to the wide COD range covered by the high range reagents. Prior to preparing the sample vials, the digester was set to preheat at 150 °C. The DR 3900 Lab Spectrophotometer was powered on and the LZV859 Light Shield was inserted. The program "435 COD HR" was then selected and loaded. Due to the dangerous compounds such as mercury present in the COD Digestion Reagent Vials, all work with the test kit was performed under a fume hood. To prepare the blank for the test, 2 mL of deionized water was pipetted into a COD Digestion Reagent Vial at a 45-degree angle to prevent splashing. In a separate vial, 2 mL sample was pipetted using the same technique. The sample and blank were then carefully inverted several times to fully mix the sample with the reagent. Once the COD digester was completely preheated, the blank and the sample vials were both slotted into the digester and the built-in timer was set to two hours. After two hours, the digester automatically stopped heating the vials and an additional 20 minutes were waited to allow the vials to slowly return to a temperature below 120 °C. The samples were then removed from the digester and inverted to re-mix settled materials. The samples were then allowed to cool to room temperature. At this point, the sample and blank were both wiped with Kimtech® Wipes to prepare for analysis. The blank

was first placed into the spectrophotometer and the “Zero” button was pressed. After zeroing, the sample vial was inserted, and the test program was run to determine the COD concentration.

Total Suspended Solids (TSS)

Gravimetric analysis is used to determine the total suspended solids in accordance with the Standards for the Examination of Water and Wastewater (AWWA, 1989). Prior to the test, Whatman size 2 (8 μm) filter papers were heated at 105 °C overnight to remove moisture in an aluminum dish. These filter papers were then placed in a desiccator for 20 minutes prior to being weighed for testing. The filters were weighed using a Denver Instruments APX-100 analytical balance. Once the filters were weighed, the volume of each collected wastewater sample was determined. This was done by pouring the samples into a 100 mL graduated cylinder. At this point, the glass vacuum filtration apparatus was prepared for testing. To do this, the vinyl tube connecting the filter flask to the vacuum pump was connected. The glass funnel attached to a rubber stopper was then inserted into the tip of the flask tightly. Atop the funnel, the dried and weight filter paper was flat on top of the funnel with forceps. A graduated funnel was then clamped on top of the glass funnel securing the filter paper in place. A small amount of deionized water was run through the filter to seat the filter paper atop the glass funnel. The vacuum pump was then switched on and the sample was poured into the graduated funnel and through the filter. Once filtration was complete, the vacuum pump was disconnected, and filter was removed and placed in an aluminum dish for drying. The dish was placed in a 105 °C oven over night to remove moisture once again. The filter was then placed in a desiccator for 20 minutes before being weighed on an analytical balance. The final TSS of the solution was then calculated using equation 4.8.

$$TSS = \frac{M_{filter+solids} - M_{filter}}{V_{Sample}} \quad (4.8)$$

3.4 - Results

3.4.1 - Phosphorus removal

In all cases, phosphorous removal was best achieved at higher current densities. Likewise, all experiments showed that the location of the port that was sampled from did not have a significant influence on the treatment results in the experiment. Phosphorous removal performance for the set of experiments using 15-minutes of detention time and the 96 mg/L wastewater formulation (Experiment No. 1 - 4) are shown in Figure 3.1. A maximum removal of 78% before settling and 79% after settling was achieved at a current density of 2.8 mA/cm². The lowest removal percentage recorded was 32% removal in the outlet of the settling tank at a current density of 0.7 mA/cm². The two factor ANOVA results examining the effect and interference between current density and port location on removal of phosphorus can be found in Appendix A1. It was found that with a confidence interval of 95%, the port location did not have a significant impact on the treatment results observed ($p = 0.084$, $F = 3.392$, $\eta^2 = 87.50$). However, in this experiment significant interference between port location and current density was observed ($p=0.013$, $F = 4.952$, $\eta^2 = 127.796$).

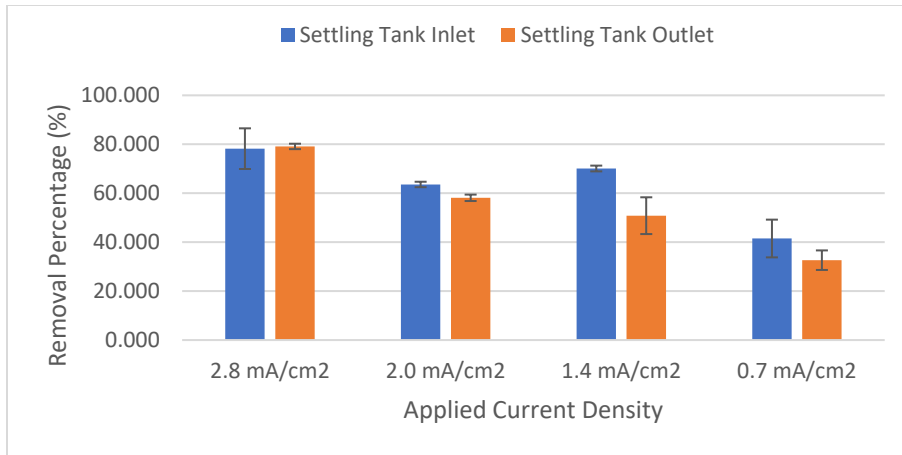


Figure 3.1: Phosphate Removal Percentage by Current Density (15 min HRT, 96 mg/L PO₄)

For experiments running at a 15-minute detention time and with the 20 mg/L synthetic wastewater, greater removal was observed across the board. These results can be observed in Figure 3.2. Removal of >95% of phosphate was observed with current densities greater than 2.0 mA/cm². With the smallest current density experimented with, 0.7 mA/cm², a mere 71% removal was observed. The two factor ANOVA results again indicated there was no significant difference between the settling tank inlet port sampling location and the settling tank outlet port ($p = 0.774$, $F = 0.085$, $\eta^2 = 0.247$)

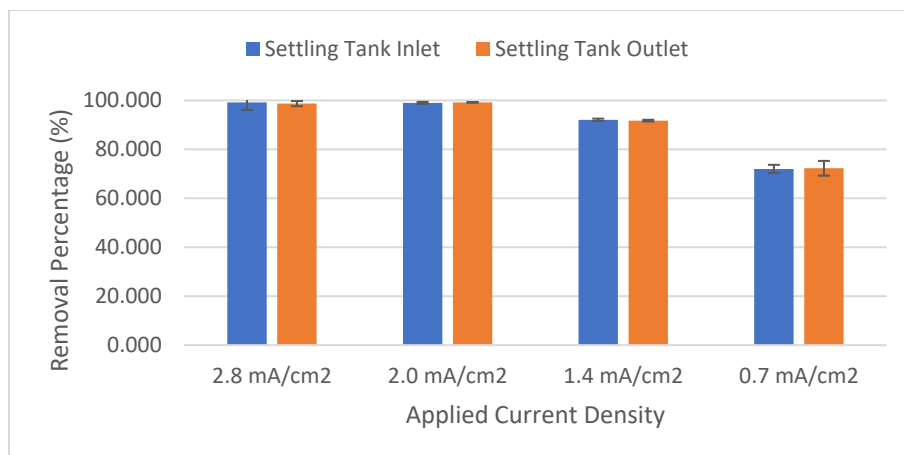


Figure 3.2: Phosphate Removal Percentage by Current Density (15 min HRT, 20 mg/L PO₄)

Higher retention time was also correlated with greater removal of phosphorous as shown in Figure 3.3. With a retention time of 30 minutes using the 96 mg/L formulation the greatest removal achieved was approximately 90% removal of phosphate. The lowest removal was just under 70% removal at 0.7 mA/cm². ANOVA results again indicate that the sampling port has no significant influence on removal of phosphate ($p = 0.218$, $F = 1.650$, $\eta^2 = 3.320$).

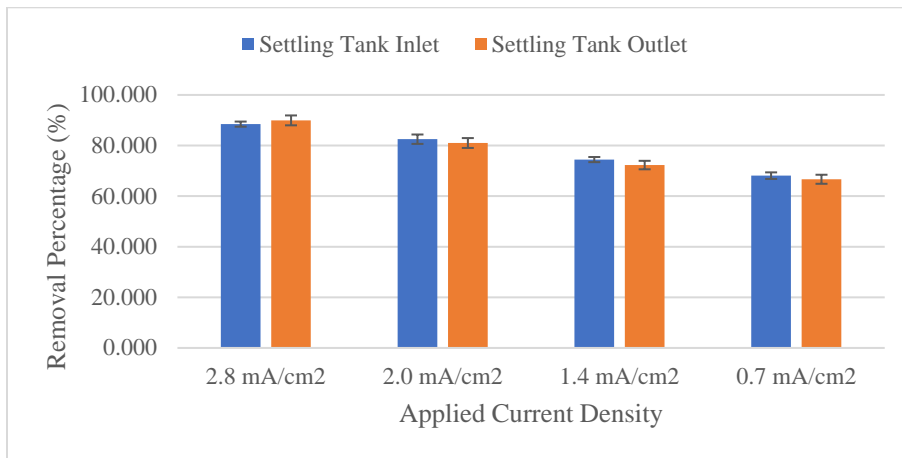


Figure 3.3: Phosphate Removal Percentage by Current Density (30 min HRT, 96 mg/L PO₄)

The final set of experiments was done with both a higher retention time and lower initial phosphate concentration (Figure 3.4). The result showed a dramatic increase in removal performance with none of the tested current densities falling below 90% removal of phosphate. The highest observed phosphate removal was 99% observed at both 2.8 mA/cm² and 2.0 mA/cm². The two factor ANOVA results for this set of experiments confirmed the sampling port used does not have a significant impact on the observed removal of phosphorous ($p = 0.969$, $F = 0.002$, $\eta^2 < 0.001$).

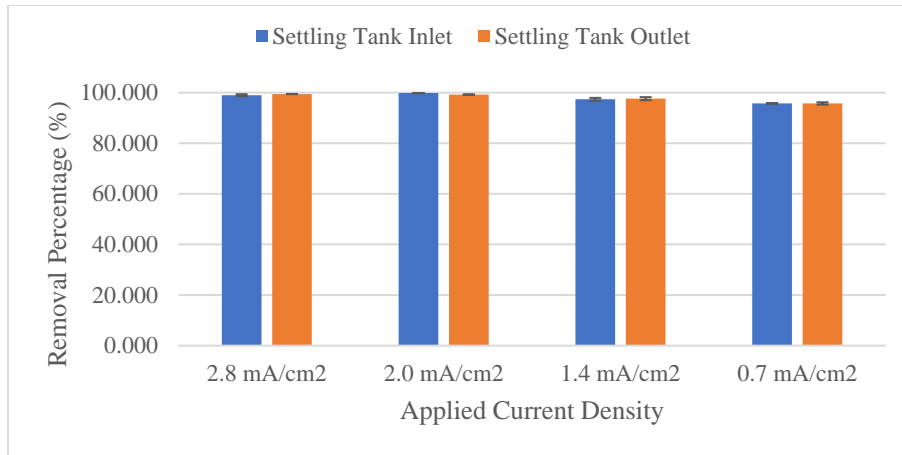


Figure 3.4: Phosphate Removal Percentage by Current Density (30 min HRT, 20 mg/L PO₄)

3.4.2 - Ammonia removal

Ammonia was not as readily coagulated as the phosphate species in the synthetic wastewater. Percentage removal for ammonia ranged from just 1% at low current densities to up to 20% under the ideal operating conditions. These conditions were found to be the 96 mg/L initial phosphorous concentration coagulated for 30 minutes within the electrolytic cell at 2.8 mA/cm². It is expected, however, that even greater detention times, initial phosphate concentrations and current densities would result in greater removal of ammonia. In the first ammonia test case, 15-minute retention with 96 mg/L initial phosphate concentration, the maximum observed reduction in ammonia was 8.8% at 2.0 mA/cm². There was however significant variance in the ammonia removal data likely due to the small scale of the removal percentages. The samples which average to the maximal 8.8% at 2.0 mA/cm² were found to have a standard deviation of almost 3%. There is greater confidence in the 8.3% reduction observed at 2.8 mA/cm² where the standard deviation between samples is just 1.3%. Due to the high variance between samples relative to the small differences in ammonia reduction between different applied current densities, the effect of current density on ammonia removal was found to be insignificant for this

set of experiments ($p = 0.163$, $F = 1.961$, $\eta^2 = 14.33$). Furthermore, the two-factor ANOVA determined that the sampling port used to collect the sample did not significantly influence ammonia reduction observed ($p = 0.213$, $F = 1.692$, $\eta^2 = 12.368$). The results for this set of experiments can be seen in Figure 3.5.

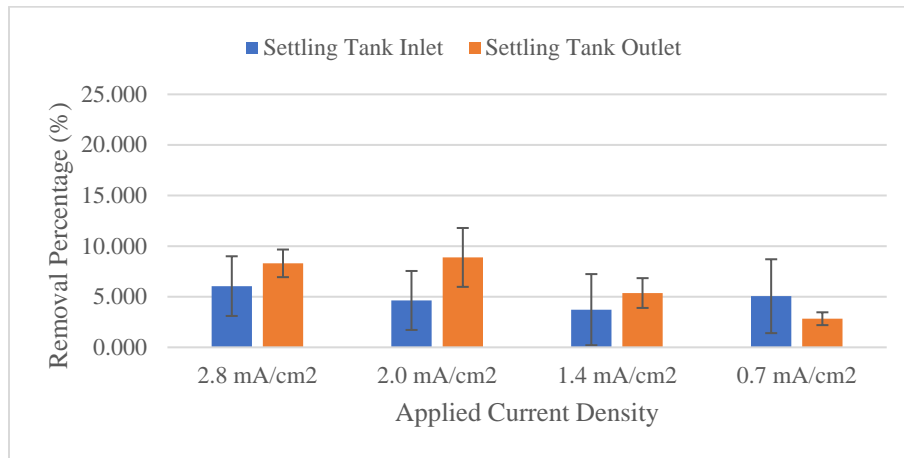


Figure 3.5: Ammonia Removal Percentage by Current Density (15 min HRT, 96 mg/L PO₄)

In subsequent experiments, current density was found to have a statistically significant impact on ammonia reduction through EC. This is due in part to smaller average sample variance observed in later experiments. In the case of the 15-min HRT experiments performed on the 20 mg/L PO₄ synthetic wastewater, the highest ammonia removal observed was 9.6% with a standard deviation between samples of just 0.31%. In this case, the current density was found to be significant at the 95% confidence interval but with a 99% confidence interval with a p-value of 0.012 ($F = 5.120$, $\eta^2 = 31.647$). Again, no significance was found in comparing which settling tank port the samples were taken from ($p = 0.629$, $F = 0.243$, $\eta^2 = 1.505$). The results for this set of experiments are shown in Figure 3.6.

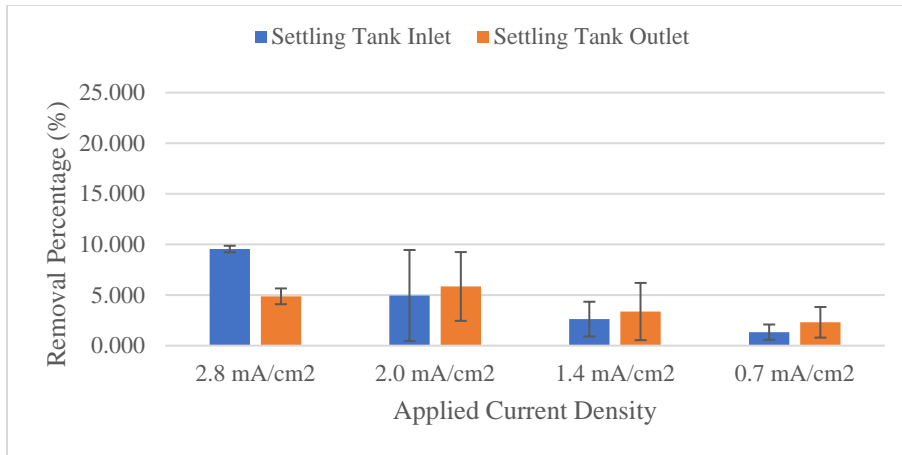


Figure 3.6: Ammonia Removal Percentage by Current Density (15 min HRT, 20 mg/L PO₄)

Of all experiments conducted, the greatest removal was found when using a current density of 2.8 mA/cm² for an HRT of 30 min on the 96 mg/L PO₄ synthetic wastewater. With these settings, the observed reduction in ammonia was found to be 19.4% with a standard deviation of 4% between samples analyzed. In other test cases at lower current densities, there is a sharp drop off in ammonia removal, dropping to 8.5% removal at 2.0 mA/cm² and then again to 2.5% at 1.4 mA/cm². Naturally, a significant relationship was observed between the applied current density and the treatment results ($p < 0.001$, $F = 28.464$, $\eta^2 = 377.188$). The complete results for this set of experiments can be found in Figure 3.7.

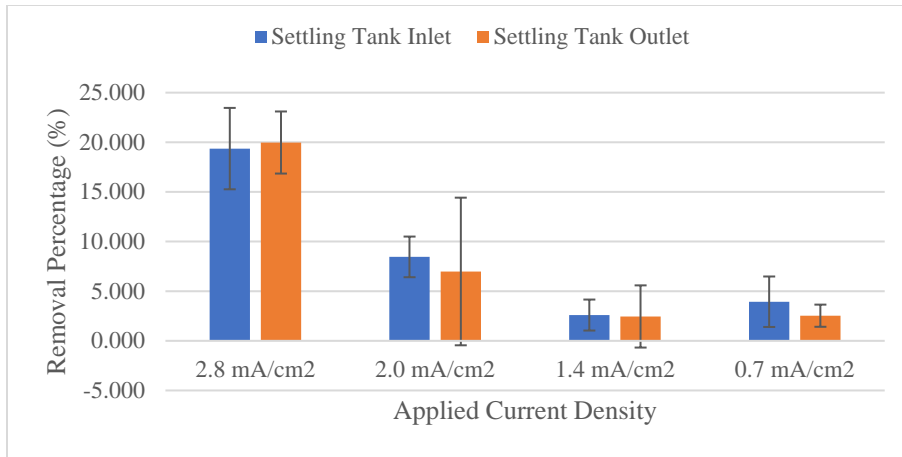


Figure 3.7: Ammonia Removal Percentage by Current Density (30 min HRT, 96 mg/L PO₄)

The final set of experiments was treating the 20 mg/L PO₄ formulation for a detention time of 30 min. In comparison to the previous set of tests, a significant drop off in performance was observed moving from the 96 mg/L formulation to the 20 mg/L formulation. No reduction greater than 6% was observed in this set of experiments. As such, the results observed applying a current density of 2.0 mA/cm² to the 96 mg/L PO₄ synthetic wastewater were greater than the results in applying 2.8 mA/cm² to the 20 mg/L formulation. The results for this set of experiments may be observed in Figure 3.8.

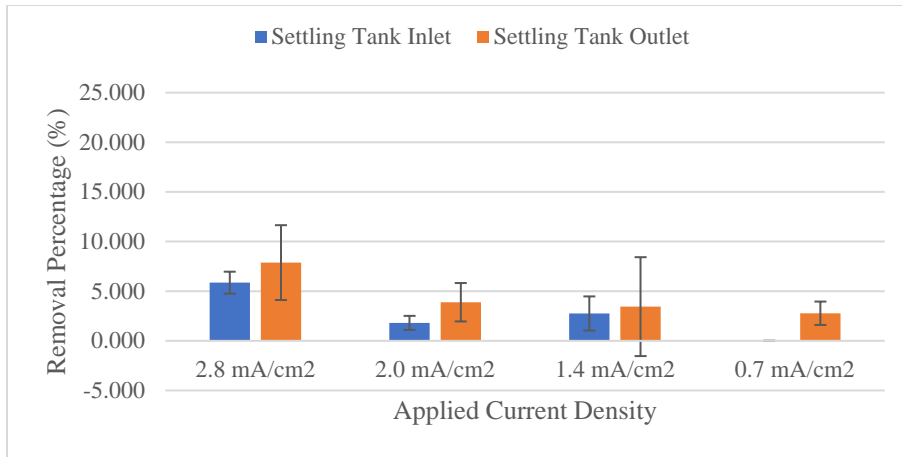


Figure 3.8: Ammonia Removal Percentage by Current Density (30 min HRT, 20 mg/L PO₄)

3.4.3 - Chemical Oxygen Demand Analysis

COD was not significantly removed in any of the test cases. The highest observed reduction in COD was a 4% reduction, however the standard deviation between the samples was 2.5%. In many of the tests, no removal was observable, due to the relatively high variance in the remaining tests, the reduction in COD observed is not reliable. As such, the result of these experiments indicates no significant removal of COD via EC. Charts for removal percentage by current density for COD can be found in Appendix A-2

3.4.4 - Total Suspended Solids Analysis

The total suspended solids concentrations observed were largely dependent on the initial phosphorous concentration of the synthetic wastewater as well as the applied current density. The highest observed TSS concentrations were just under 200 mg/L and were found from the settling tank inlet port when the 96 mg/L PO₄ synthetic wastewater was being treated at 2.8 A/cm². Samples taken further along in the settling process were found to have lower suspended solids per unit volume when working with 96 mg/L PO₄ synthetic wastewater. The largest drop

in TSS occurred between the first and second port. In experiments with the 20 mg/L synthetic wastewater, there was only a minor drop in TSS over the course of the settling tank. The TSS at the outlet port for the experiments conducted in this study ranged from 0 mg/L to 21.5 mg/L. This is below what is expected after secondary treatment in a septic tank system. Figures displaying TSS concentrations at each of the ports within the settling tank can be found in Appendix A-3.

3.5 - Discussion

3.5.1 - Phosphorous Removal

Significant phosphorous removal was achieved with synthetic wastewater. Current density was significantly correlated with observed phosphorous removal, with p-values below 0.001 in all experimental test cases. The dissolution rate of aluminum in the anode is directly proportional to current through the electrolytic cell. Since dissolved aluminum is the limiting reagent in the formation of aluminum hydroxides, current density directly impacts process effectiveness. Larger floc volume and surface area results in more contact and adsorption between phosphate species and the flocs. Previous work with the CMECR found that 96.4% and 99.8% orthophosphate removal could be achieved at current densities of 0.7 and 1.4 mA/cm², respectively (Hayden, 2020). In this experiment, 20 mg/L of orthophosphate and a sodium chloride electrolyte were the only constituents in the wastewater. In the present work, removal rates for phosphorous were lower for the 20 mg/L synthetic wastewater formulation operating at a current density of 0.7 and 1.4 mA/cm². It was found that 1.4 mA/cm² operating condition removed 92.1% of phosphate, whereas the 0.7 mA/cm² operating condition removed just 72.3%.

This discrepancy indicates that other constituents in the synthetic wastewater are reacting competitively with the mechanisms outlined in Equations 4.1 through 4.7.

3.5.2 - Ammonia Removal

Ammonia removal was observed in all experimental test cases. The range of ammonia removal was significantly lower than in the case of phosphorous with the best case being a removal of approximately 20% at a hydraulic detention time of 30 min and a current density of 2.8 mA/cm².

This removal rating agrees with other studies done on the removal of dissolved ammonia in particular. Aoudj et al. (2017) observed just a 15% drop from an initial concentration of 50 mg/L of ammonia to 42.51 mg/L over a period of 90 minutes at a current density of 1.5 mA/cm².

Another study found just a 14% removal efficiency in the removal of ammonia from leachate wastewater operating at a current density of 63.1 mA/cm² operating for 30 min (Ilhan et al., 2014). Feng et al. observed nearly 30% removal after 20 minutes of detention in a batch reactor at 1 mA/cm² (Feng et al., 2007). These results are indicative that ammonia has a relatively low affinity for dissolved aluminum hydroxide flocs. Research done on other nitrogen-based nutrients such as nitrates, nitrites and nitrogen dioxide have shown greater promise. Current density was only found to be a significant influence on ammonia removal in three of the four experimental test cases. The test case that did not observe a relationship between these two variables was 15-minute HRT and 96 mg/L PO₄ initial concentration tests with a p-value of 0.225. This was another finding the Aoudj et al. (2017) observed, that the removal of ammonia was not significantly correlated to current density. However, the range of current densities used in that research were relatively small ranging from 0.5 mA/cm² to 1.5 mA/cm² compared to this study. In both cases, it is anticipated that this result is due to the small removal percentage

relative to the sample variance of the experiment. Like with phosphate removal, there was no significant difference between ports meaning that there is no further treatment occurring in the settling chamber, which would result in higher removal efficiency. Higher initial phosphorous concentration improved the removal of ammonia by EC in both the 15-min and 30-min experiments. It is suspected that larger flocs formed in the presence of a greater amount of phosphate improved coagulation kinetics for ammonia. This also explains why higher retention times resulted in greater removal as it allows for more collisions between flocs and dissolved ammonia.

3.5.3 - COD Removal

No significant COD removal was observed in any experiment conducted. Existent research on COD removal via EC is largely conducted on more complex organic species in wastewater such as pharmaceuticals, industrial wastewater, and municipal wastewater (Moreno-Casillas et al., 2007; Tak et al., 2015). Glucose does not ionize when it dissolves, nor does it have a significant surface charge which is the likely cause of the current result. This would explain the minimal affinity for the glucose to sorb to the aluminum hydroxide flocs formed. Previous research using iron electrodes found also found negligible removal of both glucose and sucralose using an electrocoagulation process (Moreno-Casillas et al., 2007). Future experimentation should be done on samples of onsite domestic wastewater, which will have more complex organic character.

3.5.4 - TSS in Settling Unit

The settling tank was found to be effective at reducing TSS created in the electrocoagulation process. This was particularly true when there were significant suspended solids created as a

result of EC. This is due to the difference in the mass of the flocs, where larger flocs are more settleable than smaller flocs. This is true for both chemical and electrochemical coagulation as represented in Stokes Law (Tchobanoglous et al., 2014). For wastewater sources with smaller nutrient loading, it may be necessary to further flocculate flocs to improve settleability.

However, as observed in this study, there was no case where TSS exceeded expected effluent concentrations from a secondary treatment unit in a septic tank system. A prospective settling tank used in a full-scale unit would need to be designed based on the expected phosphate and TSS loading of the raw wastewater.

3.6 - Conclusions & Recommendations

The main objective of this study was to evaluate the suitability of the CMECR in treating nutrients and COD in synthetic wastewater. It was found that though competitive reactions lower removal efficiencies, CMECR can significantly (>95%) remove orthophosphates from representative synthetic wastewater. However, it was also found that it does not adequately remove glucose or ammonia on its own. A second objective of this study was to combine the CMECR unit with a settling tank unit to determine the settleability of created flocs and assess the treatment of nutrients that occurs in the settling tank. While it was found that there was no further coagulation of contaminants in the settling tank, significant removal of TSS was achieved particularly in the case of high phosphate loading. It is recommended that further studies be done with real septic tank effluent to accurately evaluate total nitrogen and COD removal. In addition, further testing should be done on the settleability of flocs created by EC at various levels of nutrient loading.

4 - Disinfectant Production using Electrolytic Cells for Application in Onsite Wastewater Systems

Abstract

Insufficient disinfection of onsite wastewater has created a need for an affordable and reliable onsite disinfection technology. This paper explores the use of onsite electrochemically generated hypochlorite for disinfection of septic tank effluent. The investigation was done through a series of bench scale experiments using a rectangular prism shaped graphite anode to develop an optimal design configuration for onsite wastewater applications. The parameters that were investigated were current density, cathode material, initial sodium chloride concentration and cathode to anode surface area. A simple empirical model was first developed to predict free chlorine production for a given detention time and current density. Following this, experiments were done to examine the differences in free chlorine yield under a range of different test conditions for each parameter. It was found that higher sodium chloride concentration increased free chlorine yield but decreased the sodium chloride-disinfectant conversion rate. Further, it was determined that using an aluminum cathode gave the best disinfectant

4.1 - Introduction

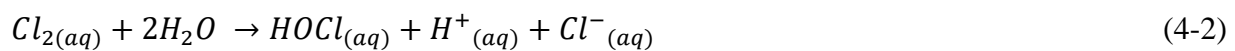
Disinfection of wastewater is required for water reuse and to prevent the spread of pathogens amongst humans and animals. Common pathogens appearing in wastewater are salmonellae, viruses, cholera, fecal coliform bacteria such as E. Coli., parasites and protozoan cysts (Cai et al. 2013). Standard decentralized wastewater treatment practices are known to be less effective in pathogen management compared to centralized systems (Park et al. 2016; Tilley et al., 2014). These differences are due to the pathogen removal mechanisms that are typical for these systems.

Centralized systems most typically employ chemical treatments such as hypochlorite contactors. In onsite septic systems, the most common decentralized systems in North America, disinfection primarily occurs in the soil drainage bed. Here, larger microorganisms are entrapped and naturally inactivated over time (Park et al. 2016). This is a long process, and it may take up to 100 days for fecal bacteria to be inactivated in soil (Fewtrell & Bartram, 2001). For bacterial species such as *E. Coli.*, a 1-log removal can be expected for a well-designed septic tank (Tilley et al., 2014). However, removal of pathogens is largely dependent on the type of soil used in the leaching field.

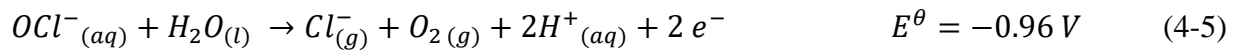
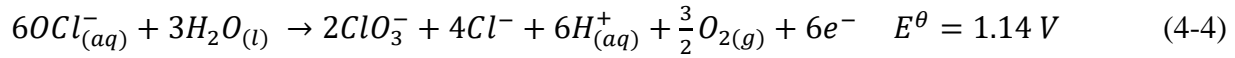
In many regions, local soils are inadequate for use as a biofilter. In such cases, additional treatment processes have been proposed to further disinfect septic tank effluent. One such option is using peat as a biofilter for septic tank effluent (Park et al., 2016; Agidi, 2013). These biofilters are capable of providing 2-log removal of fecal coliforms when used as a secondary treatment step (Agidi, 2013). Alone these biofilters are not capable of providing sufficient removal of pathogens for the purposes of water reuse or irrigation. In these cases, they are often paired with batch chlorinators prior to reuse (Agidi, 2013). These batch chlorinators use chlorine tablets which are fed and dissolved into the wastewater stream. However, this method has shown limited effectiveness in providing adequate dosing due to non-uniform dissolution of the tablets (Park et al. 2016). More complex methods of disinfection have also been used as to treat septic tank effluent. One such method is the use of ultraviolet (UV) light to deactivate pathogens in wastewater prior to the leaching bed (Liu et al., 2020). UV light has been proven to provide up to 4-log inactivation of pathogens including viruses and protozoan cysts (Liu et al., 2020). This method has a greater capital and operation cost due to the high intensity UV lamps that are required. These lamps also need to be replaced every few years if operated continuously. In

addition, the most common germicidal lamps contain mercury, which presents a safety risk to the user (Cotton et al., 2001). Research into providing safe, inexpensive, and effective onsite wastewater disinfection has led to the proposition of electrochemical disinfection technologies.

Electrochemical disinfection is the onsite production of free chlorine, usually in the form of hypochlorite, for use in water treatment (Groenen Serrano, 2018). Hypochlorite is a broad-spectrum disinfectant used in wastewater and drinking water treatment around the world. The main advantage of this system as opposed to other chlorine-based wastewater treatment solutions is that it only requires a source of chloride ions and electricity to operate, making it suitable for on-site treatment (Varigala et al., 2020; Kraft, 2008). Previous work has also shown that these systems can provide greater disinfection at the same hypochlorite concentration (Diao et al., 2004). It has been proposed that this observation is due to the presence of other advanced oxidation species from electrolysis such as hydrogen peroxide, hydroxide, and free radicals (Raut et al., 2019). In addition, electrochemical disinfection units can be easily combined with other electrochemical water treatment technologies. An example of this is the combination of electrochemical disinfection and coagulation units for more complete wastewater treatment (Lllanos et al., 2014; Cotillas et al., 2013). It is also safe and easy to both operate and automate dosing of hypochlorite. The hypochlorite used in disinfection is produced through electrooxidation of chloride ions present in the cell to dissolved chlorine. This dissolved chlorine then rapidly hydrolyzes to produce hypochlorite (Spasojević et al., 2015),



The reaction in Equation 4-1 occurs near the surface of the anode where oxidation is more likely to occur. Equation 4-2 is pH dependant, but at pH above 6.5 this hydrolysis reaction will occur rapidly within the anode diffusion layer, where it dissolves in Equation 4-3 (Spasojević et al., 2015). Concurrently, there are other electrochemical reactions which lower hypochlorite yield. At the anode, further oxidation of hypochlorite can occur creating chlorites, chlorates, and perchlorates (Kraft, 2008; Spasojević et al., 2015; Groenen Serrano, 2018). Simultaneously, reduction at the cathode results in the reversal of Equation 4-1,



These reactions along with electrolysis of water at both anode and cathode represent energy inefficiencies in the electrochemical system. The reaction in Equation 4-1 is typically charge-transfer controlled due to the abundance of chloride under normal operating conditions and high oxidation potential (Spasojević et al., 2015). Contrarily, Equations 4-4 and 4-5 are mass-transfer limited as they do not require as much activation energy. Commercial systems which generate hypochlorite using these redox reactions come in two different forms: divided and undivided cell formats. In the divided cell, a membrane separates the anode from the cathode which selectively allows chloride ions to permeate the membrane but is exclusive to hypochlorite (Kraft, A., 2008; Talekar et al., 2018). This prevents the reverse reaction, Equation 4-5, from reducing hypochlorite to chloride. In undivided cells, there is no membrane therefore the hypochlorite diffuses to the cathode surface and a reaction equilibrium must be reached.

There are several operational and design considerations when proposing a hypochlorite generation unit. The first of these is the electrode materials that will be used. The anode is of

great importance as the hypochlorite generation reaction occurs here. One of the most important considerations is the oxygen production overpotential of anode that is to be used (Qing et al., 2021; Shao et al., 2014). Oxygen production and hypochlorite production are competitive reactions with one another, greater oxygen overpotential results in faster oxidation and greater current efficiency (Raut et al., 2019; Shao et al., 2014). In addition, electrodes with high oxygen production overpotential have greater longevity as their surface does not oxidize as quickly as other electrodes. Of these, several electrodes that have electrocatalytic coating such as mixed metal oxide coatings or boron doped diamond have become popular among researchers (Shao et al., 2014; Raut et al., 2019; Martínez-Huitle & Brillas, 2008; Jeong et al., 2009). These materials have the highest oxygen over potential available on the market making them particularly useful for oxidation processes (Kötz et al., 1991). However, these materials are not without fault. Due to their oxidation capabilities, these electrodes will quickly oxidize hypochlorite into disinfection by-products (Bergmann, 2012). Disinfection by-products are of particular concern in environmental applications, where discharge can impact ecosystems and human health. Furthermore, these materials are expensive, and dimensionally stable anode (DSA) coatings are delicate when used in flow through electrolytic reactors (Kraft, 2008). Cheaper materials like graphite remain popular for this reason (Qing et al., 2021). While anode materials have been extensively studied cathode materials remain relatively unexplored. This is because cathodes are only responsible for reducing the already created hypochlorite, which is a relatively slow reaction compared to the formation of hypochlorite (Spasojević et al., 2015). Coatings, which diminish the reduction capability of cathodes have been investigated to further slow the reaction in Equation 4-5 (Lačnjevac et al., 2013). However, there is a gap in research in comparing different conventional cathode materials to one another.

Electrode geometry has been another large area of study for electrochemical disinfection units. Higher anodic surface area improves the rate of hypochlorite formation, whereas higher cathode surface area results in greater reduction of hypochlorite (Kuhn & Hamzah, 1980; Khelifa et al., 2004). To improve electrochemical disinfection systems, different forms of anode such as plate and mesh anodes have been employed to improve the surface area of the anode (Rodríguez et al., 2014). In optimizing these parameters, including the ratio of cathode to anode, it is typical to use flat plate electrodes which are prevalent in the literature (Khelifa et al., 2004).

This study evaluates the free chlorine generation of a rectangular rod graphite anode under several design configurations for the purposes of decentralized wastewater disinfection. The first objective is to develop a model for predicting approximate free chlorine generation at different current densities and retention times. The purpose of this model is to be a basis for estimating larger scale free chlorine generation in future research endeavors. This study will also evaluate the influence of cathode material on free chlorine generation. It is hypothesized that cathode materials with lower hydrogen overpotential would yield more free chlorine under the same operational parameters. Iron, aluminum, and titanium were investigated to determine the validity of this hypothesis and explore the relationship between hydrogen overpotential and free chlorine yield. The second design parameter is the anode to cathode surface area ratio of the electrolytic cell. It is suspected that a reduction in surface area of the cathode relative to the anode would result in a greater free chlorine yield at the expense of greater electrolytic cell resistance as shown in the literature. The objective of this research is to determine the effect of the geometry of the anode in a rod shape as opposed to the more prevalent plate shape found in the literature. From these experiments, an optimal design configuration was proposed. To further verify the

effectiveness of this design configuration, hypochlorite solution created via electrochemical disinfection was used to disinfect samples collected from the Speed River in Guelph, Ontario.

4.2 - Materials

The bench scale electrochemical hypochlorite generation unit consisted of a cylindrical reactor housing two electrodes fixed at 2.5 cm apart and submerged in the electrolyte solution. The reactor (Figure 4-1) housing the electrolyte solution and electrodes has a total volume of 400 mL. The anode used in the generator was a 2.5 cm wide, 1.25 cm thick 15 cm long conductive graphite bar. Three cathode materials were experimented with: aluminum, iron, and titanium. These materials were in rectangular plate form at 1 mm thick, 10 cm long and 6 cm wide. Only 250 mL of electrolyte solution was used in each test, only 5 cm of each electrode were submerged at maximum. Inside the electrolytic cell was a magnetic stir bar used to mix the contents of the beaker throughout experimentation. The stir plate used was a Fisherbrand™ Isotemp™ Hotplate Stirrer with a Fisherbrand™ Polygon Stir Bar. To power the electrochemical disinfection unit, a Global Specialties 1405 1-36VDC/0.25-3A 100W Power Supply Unit was used. The electrolyte solution used in the generator unit was comprised of only sodium chloride (>99.0% NaCl, CAS 7647-14-5) and deionized water. Analysis of samples for free chlorine concentration was done using the Hach DR 3900 Spectrophotometer and DPD test-n-tube (TNT) free chlorine test kits. Samples collected from the Speed River were kept in 1 L amber bottles. Coliform samples were analyzed using the Veolia Water Technology's Tecta B16 coliform analysis unit.

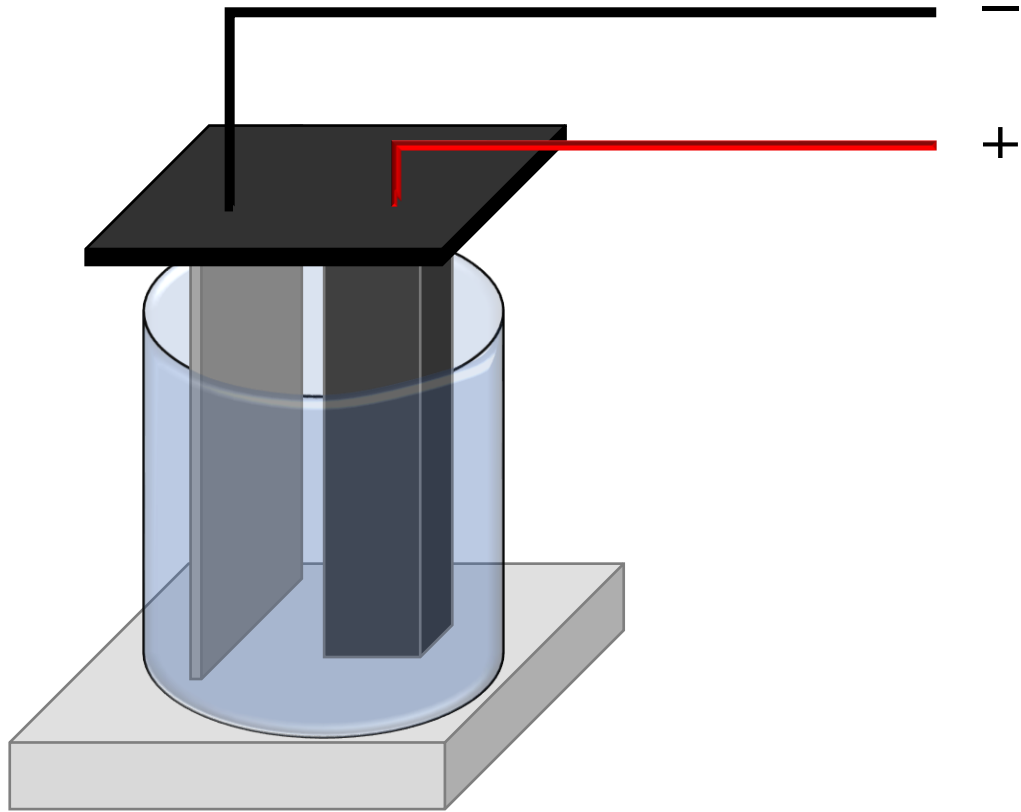


Figure 4.1: Electrolytic Cell Diagram

4.3 - Methods

4.3.1 - Experimental Plan

There are five major research objectives in the present work. The first is to develop a model for predicting free chlorine production using current density and detention time. A second objective is to determine the effect of initial concentration of sodium chloride on final free chlorine concentration at different current densities. The effect of the cathode material chosen at different

current densities is explored in the third research objective. The fourth objective is to investigate cathode to anode surface area ratio and how it is related to free chlorine yield. In the final research objective, the disinfection capability of the free chlorine generated by the unit was tested in disinfecting coliforms found in river water. All experiments were done in triplicate to minimize experimental error.

The first research objective was investigated by experimenting with 6 different retention times and 4 different current densities for a total of 24 test cases. The retention times that were experimented with were 5, 10, 15, 20, 25 and 45 minutes. The current densities used in mA/cm² were 25, 37, 49 and 62 (1, 1.5, 2, and 2.5 A of applied current). In these experiments, initial sodium chloride concentration was held constant at 60 g/L. The cathode material used was titanium for this set of experiments and electrodes were submerged to a depth of 5 cm within the electrolytic cell. At this depth, the surface area of anode exposed was 40.6 cm² and the surface area of the exposed cathode was 61.6 cm². The resultant cathode to anode surface area ratio was 1.5 cm²/cm² for this experimental set.

In the second set of experiments, the initial concentration of sodium chloride changed as well as current density. In total, there were 20 experiments in this set, five concentrations and three current densities. The concentrations experimented with 30, 60, 90, 150 and 300 g/L of sodium chloride. The current densities used were the same as those used in the first experimental set, 25, 37, and 49 mA/cm². The retention time for these experiments was maintained at 10 minutes for all experiments. Other experimental conditions were maintained the same as in the first experimental set.

In the cathode material experimental set, there were a total of 12 experiments, four current densities and three electrode materials. The three cathode materials experimented with were

aluminum, iron, and titanium. The same current densities from previous experiments were used in this set, 25, 37, 49 and 62 mA/cm². The retention time used in this set of experiments was 15 minutes. The anode to cathode surface area ratio used was the same as that in experimental sets one and two at 1.5 cm²/cm² and the initial sodium chloride concentration used was the same as that in experimental set one at 60 g/L.

The fourth set was again a set of 12 experiments using three different cathode to anode surface area ratios and four different current densities. The three cathode to anode surface area ratios tested were 0.5:1, 1:1, and 1.5:1, C:A. To get these ratios, the depth that the cathode was submerged to was changed while the anode depth remained constant. For a 1.5 ratio the cathode was submerged to a depth of 5 cm, for a 1 ratio it was submerged to 3.3 cm and for a 0.5 ratio it was submerged to a depth of 1.7 cm. A titanium cathode was used in these experiments, and the retention time for these experiments was 15 minutes. The initial sodium chloride concentration in the electrolytic cell was 60 g/L

The final set of experiments used free chlorine generated from the electrochemical disinfection reactor to disinfect 100 mL samples collected from the Speed River in Guelph. Four free chlorine doses were experimented within this set, 4 mg/L, 8 mg/L 12 mg/L and 16 mg/L. To create these doses, a stock free chlorine solution was created by running the free chlorine generator for 10 minutes at 25 mA/cm² using an initial concentration of 60 g/L of sodium chloride.

Table A.4 in the Appendix shows all experiments done in this study as well as the operating and design parameters for each experiment.

4.3.2 - Experimental Procedure

Preparation of the electrolytic solution was done first by weighing out the required mass of sodium chloride using on a Denver Instruments APX-100 analytical balance. The sodium chloride was then added to 250 mL volumetric flask. The flask was then filled with deionized water and was briefly mixed then inverted three times before being poured into the 400 mL electrolytic cell. The electrolytic cell was then placed on the Fisherbrand™ Isotemp™ stirrer and hotplate and the magnetic stir bar was placed in the cell. The electrodes were then inserted into the cell extending to the depth required to achieve the specified surface area requirement. The electrodes were then wired to the power supply unit which was set to the specified current for the experiment with the maximum voltage set to 36 VDC. At this point, stirrer was turned on and set to 1100 rpm then the power supply unit was turned on beginning the experiment. After the allotted time, the power supply unit was switched off and the stirrer was set to 0 rpm. The electrodes were then removed, and the stir bar was taken out of the electrolytic cell using a magnetic rode.

Samples for coliform analysis were collected from a weir in the Speed River located near the intersection of Wellington Street West and Edinburgh Road South in Guelph, Ontario Canada.

4.3.3 - Analysis Procedure

The analysis of the free chlorine generated in the electrolytic cell was done using Hach Method 10102 (Hach, 2019a). Samples were diluted by 100x in a 100 mL flask in deionized water. After dilution, the spectrophotometer was turned on and set to program 89 Chlorine F&T TNT. At this point, a blank was created by adding filling an empty 16 mm test-n-tube vial with deionized water. This blank was wiped with Kimtec Kimwipes™ and placed into the spectrophotometer and the “Zero” button was pressed. The sample vial was then prepared by filling a test-n-tube vial containing DPD Free Chlorine Reagent and inverting for 20 seconds. After thoroughly

mixed, the vial was placed in the spectrophotometer and the “Read” button was pressed. The sample was then disposed of under a fume hood into a DPD waste container.

Analysis of coliform count was done according to the Veolia Water Technology’s Tecta B16 operational instruction set in the user manual (Veolia, 2014). The concentration of free chlorine in a stock solution created from the electrochemical free chlorine generator was determined using the analysis method detailed above. At this point, the required volume of free chlorine stock solution needed to dose the 100 mL river water samples was determined. Dosing was done by adding free chlorine stock solution to the river water in a 100 mL volumetric flask. The samples were then poured into a beaker where 20 minutes of contact time was assigned. In addition, 100 mL of raw river water was poured into a beaker and left for 20 minutes to be used as blanks. After the elapsed contact time, samples and blanks were poured from the beakers into Tecta Complete Coliform Analysis (CCA) test cartridges. These cartridges were then placed in the Tecta B16 unit and left for 18 hours for the test to take place.

4.4 - Results

4.4.1 - Current Density and Detention time

Current density experiments were conducted at an initial sodium chloride concentration of 60 g/L, with a titanium cathode at a 1:1.5 anode to cathode ratio. As expected, current density determined the highest achievable free chlorine concentration that could be produced. The highest average concentration recorded was 984 mg/L produced at the highest retention time tested, 45 minutes, at an applied current of 2.5 amps (58 mA/cm²). At this retention time, the lowest concentration that was produced was 456 mg/L at 1 amp (24 mA/cm²). The lowest free chlorine yield occurred with a 5-minute retention at 1 amp (24 mA/cm²) resulting in 189 mg/L.

At the same retention time, 536 mg/L average yield was attained by applying 2.5 amps (58 mA/cm²). The complete results are shown in Figure 4-2.

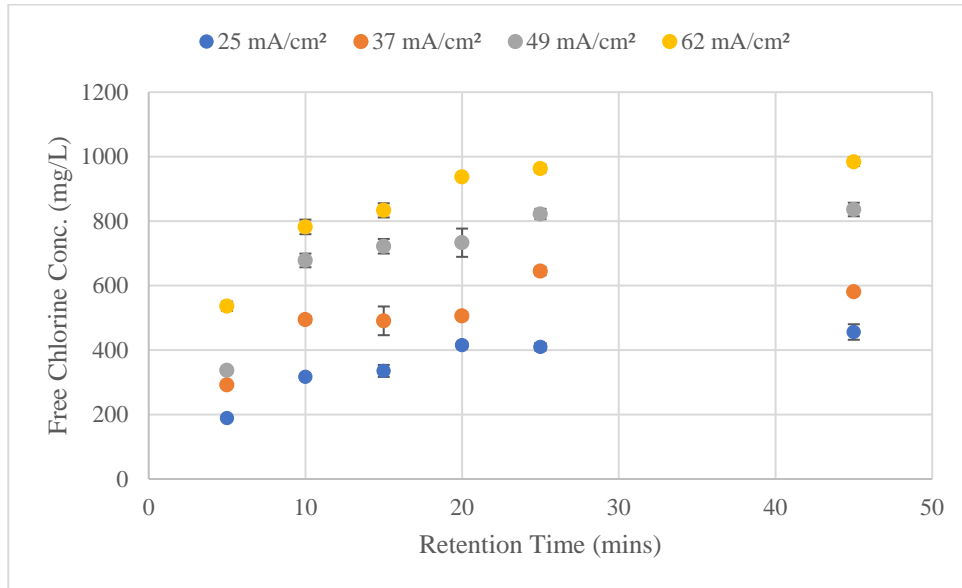


Figure 4.2: Effect of Current Density and Retention Time on Free Chlorine Yield

To verify the species of free chlorine present in the produced solution, the pH of the final solution was tracked at various current densities and retention times. In the process of producing free chlorine, the initial pH of the sodium chloride solution rose from 5.6 to 9.3 at an initial NaCl concentration of 60 g/L. However, the pH of the final solution was invariant regardless of the applied current density and the retention time. In all cases, over 95% of the free chlorine content of the solution was in the form of hypochlorite based on pH.

4.4.2 - Initial Concentration of Sodium Chloride

Initial sodium chloride concentration correlated with free chlorine yield at the conclusion of the experiment. The results for this experimental set are shown in Figure 4.3. The maximum

achieved free chlorine concentration in this set of experiments was 942 mg/L on average at an initial sodium chloride concentration of 300 g/L. This was the greatest initial sodium chloride concentration tested. At a current density of 25 mA/cm², the maximum achieved free chlorine concentration was 440 mg/L at 300 g/L initial sodium chloride concentration. The trend of the results was logarithmic, indicating that although initial chloride concentration improved final free chlorine concentration, higher initial sodium chloride concentrations had lower conversion rates. At 30 g/L initial sodium chloride concentration, lowest initial sodium chloride concentration experimented with, the final free chlorine concentration was 264 mg/L at 49 mA/cm² and 126 mA/cm² at 25 mA/cm². The influence of current density remained constant with a greater initial sodium chloride concentration. The difference in average yield between the test case of 25 mA/cm² and 49 mA/cm² was found to be 138 mg/L with an initial sodium chloride concentration of 30 g/L and 502 mg/L at 300 g/L.

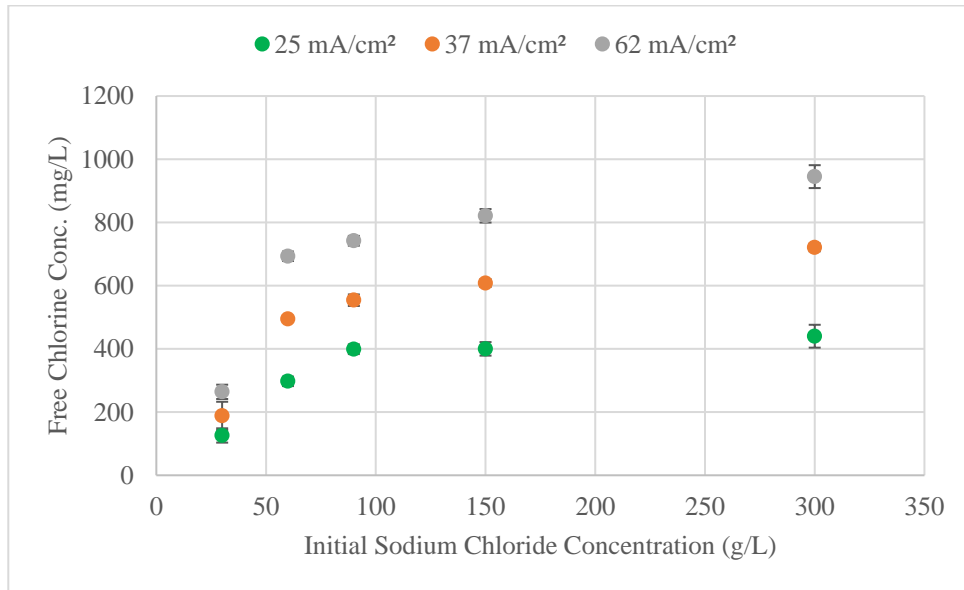


Figure 4.3: Effect of Current Density and Initial Sodium Chloride Concentration on Free Chlorine Yield

Adding more sodium chloride increases the amount of unreacted sodium chloride in the stock solution that will be used to dose the septic tank effluent. The concentration of unreacted sodium chloride was determined stoichiometrically using the free chlorine concentration. It was found that conversion rates for free chlorine were highest at 60 g/L of initial sodium chloride concentration. Beyond this point, lower conversion rates were observed,

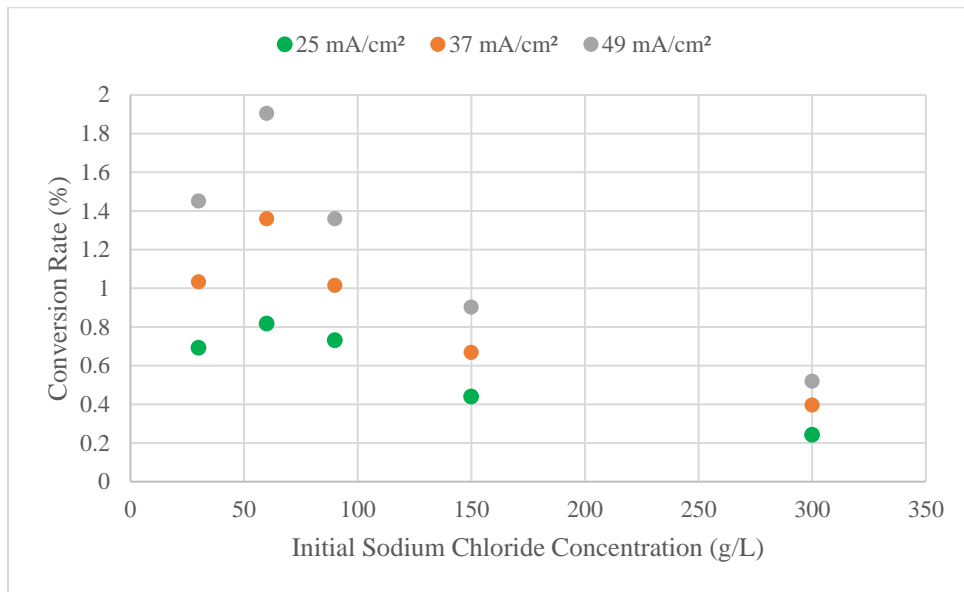


Figure 4.4: Effect of Current Density and Initial Sodium Chloride Concentration on Free Chlorine Conversion Rate

The greatest conversion rates were observed at the highest current density, 49 mA/cm², and the highest overall conversion rate was 1.9% found at 60 g/L of initial free chlorine. Low conversion rates in all test cases mean the residual sodium chloride concentration in the stock solution is within 2 grams of the initial sodium chloride concentration in all cases. The highest sodium chloride concentration was calculated to be 299.27 g/L of sodium chloride found at the lowest tested current density, 25 mA/cm², and the highest initial sodium chloride concentration, 300 g/L. Conversely, the lowest overall residual sodium chloride concentration was found at the

highest current density and the lowest initial sodium chloride concentration, 49 mA/cm² and 30 g/L respectively.

pH was also tracked at all initial sodium chloride concentrations to determine the most prevalent form of free chlorine. The results of this investigation are shown in Table 4.1. It was found that the pH of the final solution increases with the initial sodium chloride concentration. The lowest final pH was 8.6 where approximately 80% of free chlorine is in the form of hypochlorite with the remaining 20% being hypochlorous acid. At the highest initial concentration, approximately 100% of free chlorine is in the form of hypochlorite.

Table 4.1: Disinfectant Solution pH at Different Initial Sodium Chloride Concentrations

<i>Initial NaCl Concentration (mg/L)</i>	<i>Initial pH of Solution</i>	<i>Final pH of the Solution</i>
30	5.6	8.6
60	5.6	9.3
90	5.6	9.8
150	5.6	10.0
300	6.3	10.0

4.4.3 - Influence of Cathode Material

Three cathode materials were tested to determine how cathode material selection might improve free chlorine yield. The complete data for this experimental set are shown in Figure 4.5. It was found that the aluminum electrode was capable of producing the most free chlorine at any given current density. The maximum free chlorine concentration generated by the aluminum electrode was 1028 mg/L produced at a current density of 62 mA/cm². At this current density, the titanium

cathode experiments produced the lowest free chlorine yield at an average of 833 mg/L while the iron cathode produced an average of 912 mg/L. This represents a 24% increase in free chlorine yield between aluminum and titanium electrodes at this current density. At the lowest current density, 25 mA/cm², the use of an aluminum cathode resulted in a 20% increase in free chlorine yield in comparison to the titanium cathode experiments (335 mg/L to 402 mg/L). There was a much smaller observed difference between the iron and titanium cathodes used in the experiments. Due to the closeness of data from experiments collected in this experiment, a two-factor ANOVA was performed to determine if cathode material had a significant effect on free chlorine yield. The ANOVA results showed that there was a significant difference between different cathode materials.

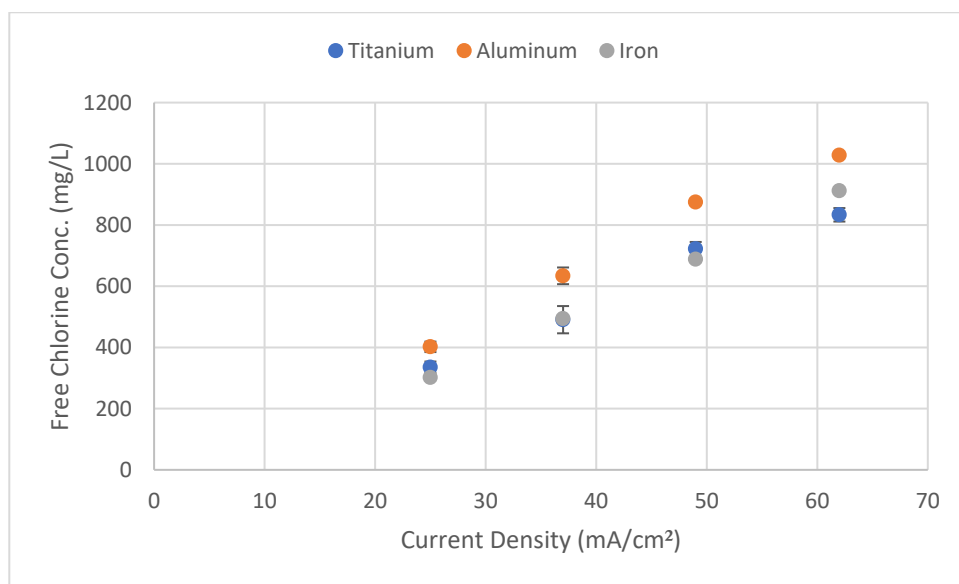


Figure 4.5: Effect of Current Density and Cathode Material on Free chlorine Yield

4.4.4 - Influence of Cathode to Anode Surface Area Ratio

Electrode surface area ratios were tested to investigate the impact that cathode surface has on free chlorine yield. The experimental results are shown in Figure 4.6. The results show clearly

that the greatest free chlorine yield is achieved in the lowest cathode to anode surface area ratio. The highest recorded average free chlorine concentration was 1272 mg/L that was achieved by applying 2.5 A (62 mA/cm^2) at a 0.5:1 cathode to anode surface area ratio. This was also the highest recorded free chlorine concentration found in any experiment conducted for this study. At 0.5:1 cathode to anode ratio, the free chlorine yield was on average 70% higher than experiments done with a 1.5:1 ratio and 33% higher than experiments done with a 1:1 anode to cathode ratio. In both the 1:1 and 1.5:1 ratio case, the advantage of using a smaller cathode was greater at lower current densities than at higher current densities.

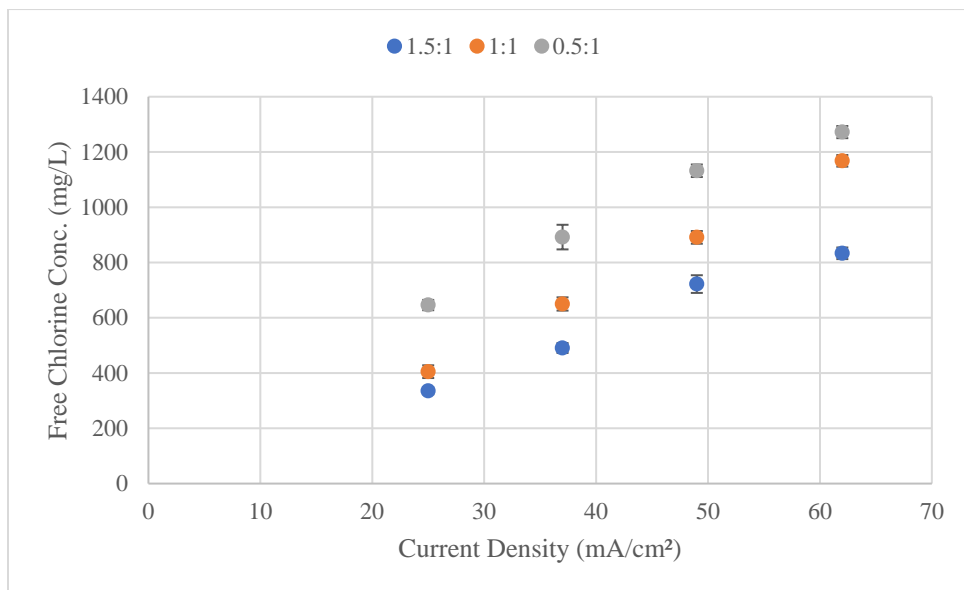


Figure 4.6: Effect of Current Density and Cathode to Anode (C: A) Ratio on Free chlorine Yield

Having a smaller cathode means there is less surface area for electrons to transfer to the electrolytic solution. This effect raises resistance in the electrolytic cell and lowers current efficiency. To gauge this effect, power consumption was tracked in each experiment by observing the current and voltage readings on the power supply unit. These observations are given in Figure 4.7 below,

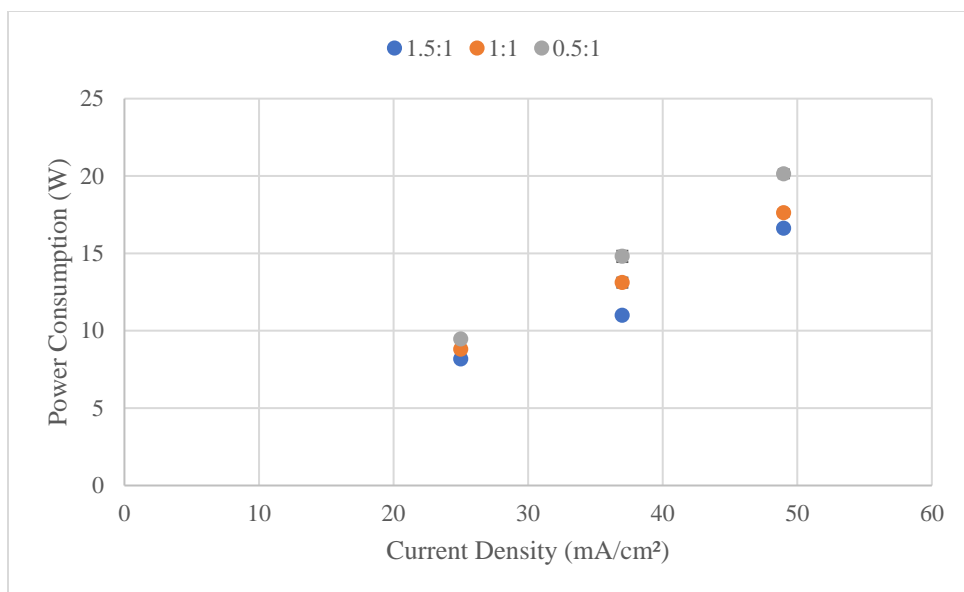


Figure 4.7: Effect of Current Density and Cathode to Anode (C: A) Ratio on Power Consumption

These power readings were normalized by free chlorine concentration to gauge the power consumption per unit free chlorine produced. The most energy efficient configuration was at 25 mA/m² with 0.5:1 where 93 mg/L of free chlorine per watt was achieved. Figure 4.8 shows the free chlorine production per watt of energy consumed at different current densities for each of the electrode surface area ratios.

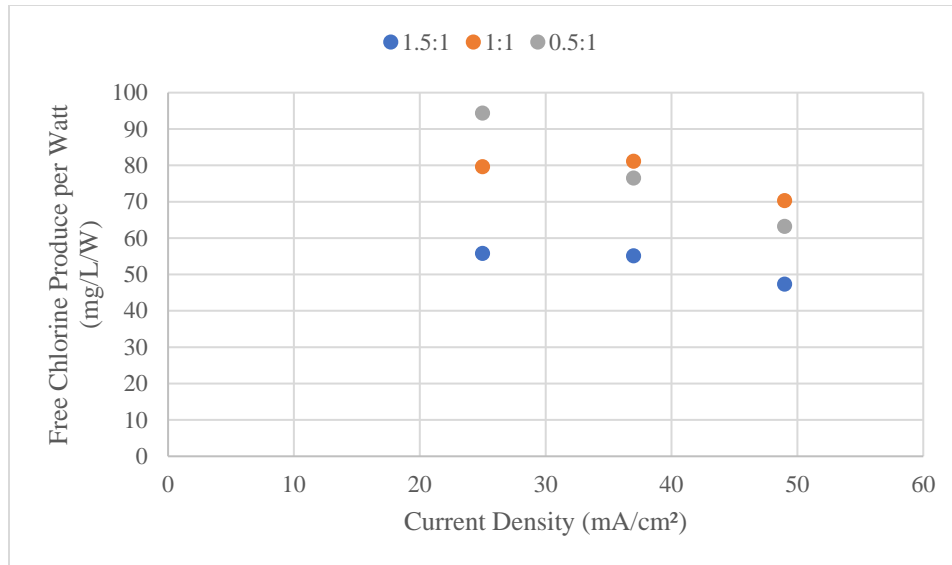


Figure 4.8: Free Chlorine Produced per Watt at different Current Densities and C: A Surface Area Ratios

4.4.5 - River Water Coliform Disinfection

Nearly, complete disinfection of river water was achieved through the application of electrochemical generated free chlorine. In Figure 4-5, the concentrations of coliform forming unit (CFU/100mL) are plotted against different free chlorine doses at a contact time (τ) of 20 min. The total coliform concentration for the Speed River water was found to be 161.5 CFU/100 mL in the untreated samples. Dosing 10 mg/L of free chlorine with a detention time of 20 min resulted in an average of 1-log (90%) disinfection of coliform units within the sample. An average of 98% reduction in coliform units was observed by dosing 16 mg/L of free chlorine with a detention time of 20 minutes, The coliform test results are plotted in Figure 4.9.

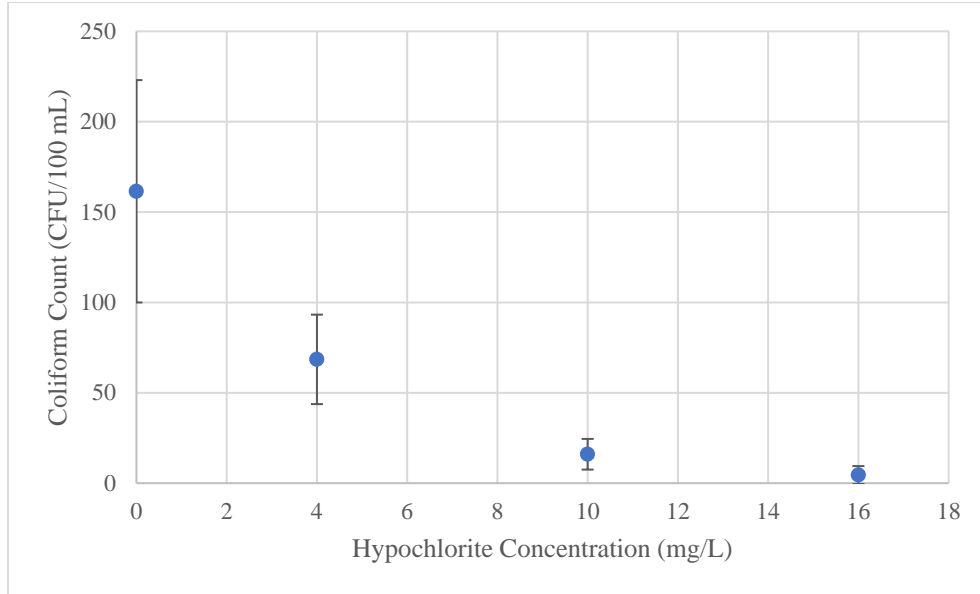


Figure 4.9: Coliform Count (CFU/100mL) After Disinfection at Different Free chlorine Doses ($\tau=20$ mins)

4.5 - Discussion

4.5.1 - Current Density and Detention time

Figure 4-1 shows a logarithmic relationship between detention time and free chlorine yield at all current densities. This is understood to be the approach towards the equilibrium concentration within the electrolytic cell. The form of this relationship is expressed in the following univariate model for each of the current density test cases,

$$C = a \cdot \ln(t) + b \quad (4-6)$$

where C is the concentration of free chlorine generated, t is the elapsed time of the experiment, and a and b are constants. To further investigate the relationships between free chlorine yield and retention time, a linear regression was performed. The base-10 logarithm was taken of each

retention time to account for the- logarithmic relationship between detention time and free chlorine yield. Graphically, the results of this regression are shown below in Figure 4.10.

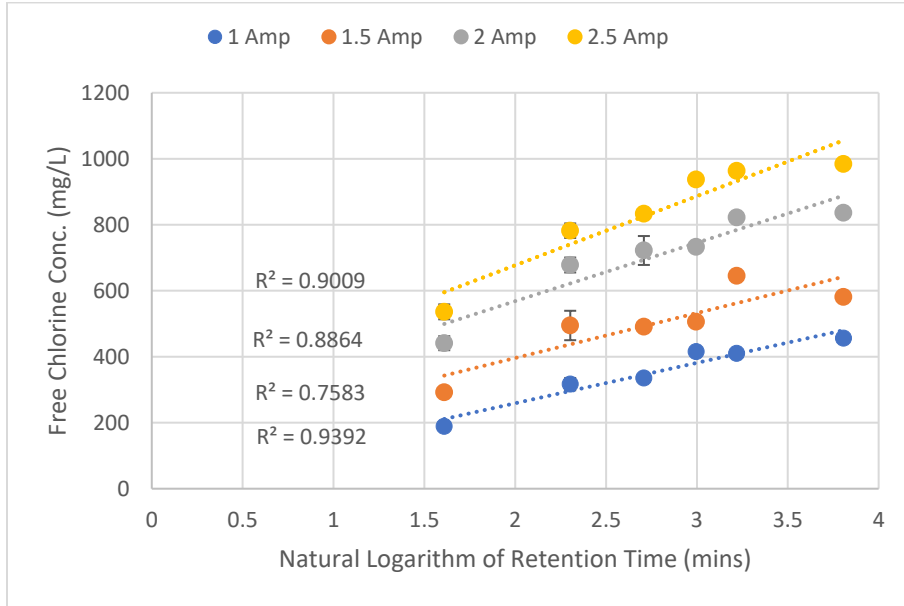


Figure 4.10: Linear Regression of Free chlorine vs Natural Log of Retention Time

The strong effect size of the regression model in each case confirms the logarithmic relationship between retention time and free chlorine concentration. The simple linear regression models at each of the current densities are given in the Table 4.2.

Table 4.2: Retention Model Inputs at Different Applied Current Densities

<i>Applied Current Density (mA/cm²)</i>	<i>Log Coefficient (a)</i>	<i>Intercept (b)</i>	<i>R²</i>
25	122.46	14.134	0.9392
37	136.33	123.44	0.7583
49	176.98	214.46	0.8864
62	209.49	258.19	0.9009

The increase in current density results in both an increase in the y-intercept of the log curve as well as the coefficient of the logarithmic term. This represents a greater steady-state free chlorine concentration at higher current densities as well as a less flat curve meaning slower time to steady state.

To further improve this model, current density was added as a second term. The current density variable was found to be linearly related to free chlorine concentration when isolated at a particular retention time, anode to cathode ratio and initial sodium chloride concentration. The multivariate model for free chlorine concentration with a known retention time and current density is therefore expressed as,

$$C = a \cdot \ln(t) + b(j) + c \quad (5-2)$$

where j represents the operational current density and c is constant. Using the data from the current density and retention time experiment set, a multiple linear regression analysis yielded the model,

$$C = 371.44 [\ln(t)] + 332.02(j) - 428.48 \quad (5-3)$$

The model was determined using the least squares approach and the JASP statistical software package. The R^2 value for this model was 0.941 and p-values for both variables were under 0.01 presenting strong evidence that the model is predictive and both variables are significant. Standard error for current density and retention time were 20.19 and 37.42 respectively.

The logarithmic relationship between free chlorine concentration and detention time is accounted for by the rate equalization of free chlorine electrosynthesis reactions and destruction reactions. This is because the free chlorine generation reactions and free chlorine reduction reactions taking place at the cathode are mass transfer limited (Spasojević et al., 2015). The rate at which these reactions take place is therefore proportional to mass transfer rate of chloride to the anode and free chlorine to the cathode. At longer retention times, the free chlorine and chloride concentrations reach equilibrium, therefore the free chlorine concentration can be modelled logarithmically with retention time. At smaller current densities, the assumption of a linear relationship between free chlorine production and current density holds true. In other works, it has been found that at longer detention times the free chlorine concentration begins to fall (Khelifa et al., 2004). This was particularly true when using mixed metal oxide coated anode materials, which is why this effect may not have been observed in this experiment.

Though this model appears adequate in predicting free chlorine yields for an electrochemical disinfection reactor with a rectangular rod anode, there are several limitations. Firstly, this model is only valid for the experimental conditions of this set of experiments. This includes the initial concentration of sodium chloride, electrode geometry, electrode surface area ratios, electrode spacing, operational temperature and pressure, electrode materials and reactor size and stir rate. These parameters all have significant influence on free chlorine production based on theoretical and empirical modelling efforts (Spasojević et al., 2015; Khelifa et al., 2004). This model

therefore has limited application in predicting free chlorine production capability to similar experimental set-ups and designs. For the purposes of estimation of free chlorine production in future larger scale applications of electrochemical disinfection in onsite wastewater, this model is adequate.

The pH was found to be basic at all retention times and current density test cases. The rise in pH observed is due to the formation of sodium hydroxide as a product of electrolysis and the dissolved sodium in the solution. The lack of observed increase in pH over different retention times and current densities indicates that the 60 g/L initial sodium chloride concentration limits the pH increase over the test conditions of this experimental set. The effect of pH and its variance with initial sodium chloride concentration is further discussed in section 4.5.2.

4.5.2 - Initial Concentration of Sodium Chloride

The objective for the second set of experiments was to investigate the impact of increasing initial sodium chloride concentration to further improve the system. As expected, increasing the sodium chloride concentration resulted in an improved sodium free chlorine yield. At a higher concentration of sodium chloride, more sodium chloride is diffused into the reactive zone close to the anode and the rate of reaction for free chlorine is proportionally quicker. This results in a proportionally larger free chlorine concentration at any given time. According to Le Châtelier's Principle, a higher initial sodium chloride concentration with the same initial free chlorine concentration results in a greater equilibrium concentration of free chlorine (Ebbing, 2009).

These natural observations can be observed based on the higher sodium chloride concentration at a given retention time observed in Figure 4.3. These effects were not observed to be linear, initial concentration of free chlorine was logarithmically related to the final free chlorine concentration. This is indicative of a second order reaction occurring in the forward direction.

It was also found that the conversion rate of sodium chloride to free chlorine was lower at initial concentrations of sodium chloride higher than 60 g/L. At all initial sodium chloride concentrations, the conversion rate was below 2%. Therefore, the unreacted sodium chloride concentration is significantly larger when using higher initial sodium chloride concentration. This concentration of sodium chloride is to be diluted in the wastewater stream when free chlorine is dosed, however the sodium chloride concentration is still an order of magnitude greater than the free chlorine concentration which may still be problematic. To investigate further, residual chloride concentration was calculated for a sample diluted to a 10 mg/L dose of free chlorine for all test cases. The lowest achieved chloride concentration was 515 mg/L at a current density of 49 mA/cm² at an initial sodium chloride concentration of 60 g/L. The results of this analysis are shown in Figure 4.11.

Currently, there are no regulatory limits on chloride concentration for onsite wastewater treatment applications (O. Reg. 312/12). There are however Canadian Water Quality Guidelines (CWQG) which outline environmental limits for the protection of aquatic life. In fresh surface water, the short-term exposure limit set in the CWQG is 640 mg/L whereas the long-term exposure limit is set to just 120 mg/L (Canadian Council of Ministers of the Environment, 2008). These limits are not a limitation in effluent concentration but rather environmental concentration of surface waters.

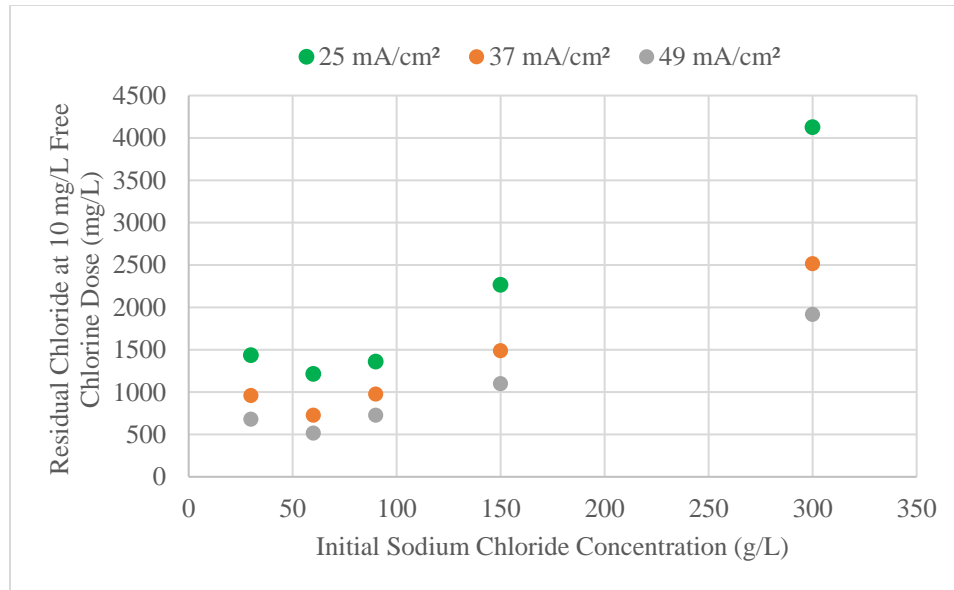


Figure 4.11: Residual Chloride Concentration when Dosing at 10 mg/L Free Chlorine

No guidelines were set for marine or groundwater chloride concentration (Canadian Council of Ministers of the Environment, 2008). However, chloride concentrations in aquifers that are used as a drinking water source must be given special attention. The upper bound for chloride concentration in drinking water is set at the point in which a salty taste becomes detectable, 250 mg/L (O. Reg. 169/03). The observed concentrations of unreacted chloride are significantly above both the drinking water concentration limit and the long-term guideline for the protection of aquatic life. Improving the conversion rate of chloride to free chlorine should be made a priority in future design iterations. Using an anode material with greater oxygen overpotential has been found to improve free chlorine yield at a given initial chloride concentration (Khelifa et al., 2004). As previously mentioned, the use of these electrodes has been found elevate concentrations of disinfection by-products like perchlorate (Bergmann M.E., 2012). This drawback is significant as disinfection by-products are dangerous at much lower concentrations than chloride. Long-term health effects have been observed at as little as 0.1 mg/L of perchlorate

in drinking water supplies (Clarkson et al., 2006). Other improvements to free chlorine yield may be made using the other parameters discussed in this study. The short-term guideline is met in a single test case, the 49 mA/cm² at 60 g/L initial chloride concentration test case.

The pH increase that was observed as a result of increasing sodium chloride concentration is significant to the effective production of a disinfection solution. This increase in pH is a result of the formation of dissolved sodium hydroxide in the electrolytic cell as a by-product of electrolysis and dissolution of sodium chloride (Ebbing et al., 2009). The sodium concentration limits the formation of sodium hydroxide; therefore, the pH of the solution is limited by the initial sodium chloride concentration. This is an important detail as the ideal pH range for the production of disinfectants is 5-6.5. In this range, the majority of free chlorine is in the form of hypochlorous acid which is a stronger disinfectant agent than hypochlorite (Tchobanoglous et al., 2014). The higher the initial sodium chloride concentration, the higher the pH will be and therefore the less effective the disinfectant will be per mg of free chlorine produced. It is therefore important to minimize sodium chloride concentration in order to avoid the transformation of hypochlorous acid to hypochlorite.

4.5.3 - Effect of Cathode Material

The cathode material governs the effectiveness of the reduction reactions which occur at the cathode. Materials which have a higher reduction overpotential are less likely to reduce particular species as the activation energy requirement for the reaction is greater (Heard & Lennox, 2020). Electrode materials and coatings are selected for both their energy effectiveness and selectivity in redox reactions. The present research was conducted due to the lack of data on the free chlorine reduction over potential and a lack of data comparing cathode energy efficiency for free chlorine synthesis. It is proposed that the reduction of water to hydrogen is a competitive

reaction with the reduction of free chlorine. Based on this, it was hypothesized that an electrode material with the greatest hydrogen evolution over potential would have the lowest free chlorine yield. Overpotential is not well understood theoretically and must be empirically determined. In water splitting applications, the hydrogen production overpotential for titanium, iron and aluminum are -0.61, -0.4 and -0.58 V respectively (Heard & Lennox, 2020). It was predicted that a lower hydrogen evolution overpotential would result in a greater share of the energy going toward the production of hydrogen instead of reducing free chlorine.

The results of this research indicate that aluminum electrodes are the best choice to achieve the highest free chlorine concentration at a particular current density. This finding disproves the hypothesis that hydrogen overpotential would be inversely correlated with free chlorine production efficacy. Due to the relative closeness of the hydrogen production overpotentials for the three electrode materials it is likely that other variables are more important in differentiating the free chlorine reduction rate. These other factors could be related to surface charge transfer barriers such as aluminum oxide on the surface of the electrodes which inhibit electron transfer (Lačnjevac et al., 2013). It could also be due to the interactions between sodium ions and the surface of aluminum compared to iron and titanium. Further research is recommended to determine the specific cause for the observed 20% increase in free chlorine yield.

The results of this study show aluminum can outperform iron in free chlorine generation in terms of free chlorine yield at a particular current density. Aluminum also has the advantage of having greater conductivity, lowering resistance in the electrolytic cell, and improving energy efficiency. In onsite wastewater treatment applications, the amount of free chlorine solution that needs to be generated is small compared to commercial applications. As such, the higher cost of aluminum is not as large a hinderance in this application.

4.5.4 - Effect of Cathode to Anode Surface Area Ratio

Reducing the surface area of the cathode used to generate free chlorine relative to the anode surface area was found to improve free chlorine yield. This finding was expected based on previous research into asymmetric electrode surface area in electrosynthesis of free chlorine (Khelifa et al., 2004; Kuhn & Hamzah, 1980). The underlying cause of this observed effect is the smaller reactive zone where free chlorine can be reduced to chlorine gas as per Equation 4-5. As this reaction is mass transfer limited under the operating conditions of this experiment, diffusion of free chlorine into this zone limits the rate of reaction.

The greater free chlorine yield, however, comes at a cost of greater resistance in the electrolytic cell. As there is less surface area for charge to be transferred from the electrolyte solution to the electrode, the resistance to current flow is greater. This means a greater potential difference must be applied across the electrolytic cell to achieve the same current, resulting in greater energy expenditure. To gauge the energy efficiency of reducing the cathode to anode surface area ratio, the average power consumption for the 1:1 and 0.5:1 cathode to anode surface area ratio were compared. It was found that at 62 mA/cm^2 , the highest current density tested, the 0.5:1 surface area ratio created an average of 63.2 mg/L of free chlorine per watt whereas the 1:1 ratio produced an average of 70 mg/L per watt. This amounts to a 10% improvement in energy efficiency observed for an 8% reduction in yield. However, at the lowest current density experimented with, 25 mA/cm^2 , the 0.5:1 cathode to anode ratio had a greater energy efficiency than the 1:1 ratio set-up. This can be explained by the very minor observed difference in resistance at lower current densities as compared to differences in resistance at higher current densities. The greater electrode surface area allows for greater current throughput, at lower current densities this extra throughput isn't as necessary. In addition, the 1.5:1 had the cathode to

anode ratio had the lowest power efficiency at all current densities. This is indicative that the relationship between cathode to anode ratio and free chlorine yield per watt consumed is not linear. More data is required to better analyze this relationship.

Overall, this improvement in yield is not of value in an onsite wastewater application for several reasons. Firstly, reducing the size of the cathode reduces the longevity of the electrolytic cell. Since there is a smaller cathode surface area, corrosion will occur more quickly, and the cathode would need to be replaced more often. These replacements are inconvenient in onsite wastewater applications as the homeowner is usually the person who needs to maintain the system. Further, the greater yield comes at the cost of greater operational costs in the form of energy. To offset these increased operation and maintenance costs, the conversion rate of sodium chloride would need to be significantly greater due to the low cost of sodium chloride. As the free chlorine will ultimately be diluted in the wastewater stream, an 8 – 20% difference in free chlorine yield would not significantly impact performance. It will however reduce the chloride concentration in the wastewater stream. As discussed in section 5.2, the observed conversion rates were low in these experiments resulting in excess which would result in excess chloride in the wastewater stream. Cathode to anode surface area may be one tool that can be used to further reduce residual chloride concentration.

4.5.5 - River Water Coliform Disinfection

Coliforms found in the Speed River were successfully disinfected using free chlorine generated from small scale electrochemical synthesis. The required dose to disinfect the river water was higher than expected at 16 mg/L, however, this is likely due to the character of the river water itself. Other debris and organics within the samples may have raised the free chlorine demand of the samples. In an actual septic unit, up to 50% of solids and 40% of biological oxygen demand

(BOD) will have already been removed prior to disinfection (Tilley et al., 2014). In addition, full removal of coliforms is unnecessary as the leaching bed provides some treatment of pathogens. These results do not on their own suggest the formation of other advanced oxidizers which result in improved disinfection. Future experiments on samples of onsite wastewater should be conducted, including analysis of pilot scale wastewater samples for coliform count. In addition, further testing should be done to ensure the elimination of viral pathogens and protozoa.

4.6 - Conclusions and Recommendations

Onsite electrochemical generation of free chlorine is a promising disinfection method for decentralized wastewater treatment. Currently, the majority of onsite electrochemical chlorination equipment is designed for commercial production of free chlorine or disinfection of industrial wastewater, not for use in a septic tank system. To elucidate the application of this technology to decentralized wastewater treatment, several research objectives were met. First, a model was developed for the production of free chlorine via electrochemical synthesis. This model will be used as an entry point to estimate free chlorine production in future work. Next, it was determined that initial sodium chloride concentration improves free chlorine yield but lowers the overall conversion rate of free chlorine. It is important to select the initial sodium chloride dose and optimize conversion the rate such that the final amount of unreacted sodium chloride is lower than the CWQG long-term guideline for chloride content. Thirdly it was observed that the best cathode material used for producing free chlorine was aluminum. Future designs should incorporate aluminum electrodes as a cathode to improve free chlorine yield. Fourthly, it was determined that cathode to anode surface area ratio only marginally improved free chlorine yield in comparison to the energy consumption cost. Lastly, it was determined that

the free chlorine generated via electrochemical synthesis may be used immediately to achieve 98% removal of coliform units in raw river water.

Several recommendations can be made to improve on this work. Firstly, the model described here should be validated under a variety of test conditions to assess how robust the model is at predicting free chlorine production. It is known that the model is limited as it only incorporates two variables to predict free chlorine production, but the extent of this limitation was not explored. Further, experimentation to determine the specific cause of the observed increase in yield when using aluminum electrodes should be conducted. It is also important that improvements be made to the chloride-free chlorine conversion rate to better protect surface and groundwater supplies from chloride pollution. Lastly, larger scale testing should be done on septic tank effluent to determine the treatability of onsite wastewater. This testing will also provide a point of comparison, so that other forms of disinfection may be directly compared to this method.

5 - Conclusions & Recommendations

5.1 - Conclusion

Septic tank systems are limited in their capability to remove of pathogens and dissolved nutrients from domestic wastewater. Excess nutrients in surface water sources, particularly phosphorous, cause rapid growth of algae which has both ecological and economic effects. Groundwater contamination of nutrients may result in contaminated drinking water supplies which could result in illness or death. Moreover, pathogenic contamination of groundwater and surface water has the potential to cause outbreaks of waterborne illness. Together, pathogens and nutrient contaminants cause ecological, economic, and public health problems. As septic systems are integral to wastewater treatment in rural areas of Ontario and around North America more broadly, improved nutrient and pathogen management systems must be developed.

Electrochemical technologies such as electrocoagulation and electrochemical disinfection provide an economical solution to these issues. In this thesis, both technologies were studied with a focus on their application to onsite wastewater treatment.

Electrocoagulation is a promising nutrient removal process for septic tank effluent. In previous research done by Hayden and Abbassi, it was found that a manifold electrocoagulation system was capable of significant removal of ortho and polyphosphate. Continuing with this work, the nutrient removal capability of Hayden's design was tested using a representative synthetic wastewater. It was found that the significant phosphate removal could still be achieved at similar current densities and retention times. It can be concluded from this that there was no significant interference from other dissolved compounds in the electrocoagulation process. A second finding was that only minor ammonia removal and negligible COD removal was observed using the

manifold reactor. This finding suggests that ammonia has only very mild affinity for aluminum hydroxide flocs created by the electrocoagulation process. As the sole source of chemical oxygen demand in the synthetic wastewater was glucose, it remains unclear whether the manifold reactor would remove a significant portion of COD in a more heterogeneous wastewater. The experiments also showed that settling is an effective method of removing the precipitated flocs, but that further nutrient removal does not occur in the settling tank.

Electrochemical disinfection of septic tank effluent appears to be a viable solution to pathogenic contamination of onsite wastewater. From the results of the study in Chapter 4, it can be concluded that high concentrations of free chlorine can be quickly and economically generated using electrochemical methods and chloride salt. Further, it was found that the optimal cathode material to be used in a septic tank electrochemical disinfection unit is aluminum. It remains unclear why aluminum cathodes were more effective, but this was empirically determined to be the case. It was also found that the reduction in cathode size relative to the anode resulted in mediocre yield improvements at the cost of higher electrolytic cell resistance. In a septic tank application where constant free chlorine generation is unnecessary, this consideration proved to be inconsequential. This work also produced a model for current density and detention time to predict free chlorine yield. Together with the aforementioned findings, this study creates a foundation for future work in septic tank effluent disinfection.

Together, these studies are indicative that electrochemical processes are efficient solutions to water quality problems of septic systems. These processes, when used together, have demonstrably been effective at phosphate and pathogen removal.

5.2 - Recommendations

Based on the above conclusions several recommendations can be made. The first set of recommendations pertains to the onsite wastewater electrocoagulation process. In this process, limitations were identified with removal of both nitrogen compounds and COD. In the synthetic wastewater used in these experiments, the sole nitrogen species was ammonia, and the sole source of chemical oxygen demand was glucose. In real wastewater, a variety of nitrogen species and more complex organics will be present. For this reason, it is recommended to investigate the effectiveness of the unit using real septic tank effluent. This would be especially useful in a pilot scale study with a septic tank put into the ground as environmental and water quality conditions change over time. It should also be investigated whether electrocoagulation removes nitrates and nitrites more easily than ammonia. It may be possible to pretreat wastewater by converting ammonia into nitrates via electrochemical oxidation to improve total nitrogen removal. This oxidation process may also eliminate organics that are resistant to electrocoagulation. A remaining obstacle to the implementation of this technology is the management of the aluminum hydroxide sludge which settles in the settling tank. Further experiments should be done to determine the rate at which sludge accumulates to better design an appropriately sized settling basin.

For the electrochemical disinfection technology, there is much work to be done before a viable product can be produced. Disinfection by-product quantification should be a priority when investigating the effectiveness of a septic tank units. As the effluent of the septic tank is directly drained into the environment, it is important that the perchlorate, chlorate, and chlorite production are limited. Furthermore, larger scale testing should be done with completely automated free chlorine concentration monitoring. This system will need to be automated as it is

being proposed for use in domestic applications, as such it is important that pilot scale testing is done to ensure that free chlorine can be reliably monitored in coloured and turbid septic tank effluent. Finally, it is recommended that combination systems of electrocoagulation and electrochemical disinfection be investigated for septic tank effluent purification. These processes may be able to use the same power supply units and wiring, which will save capital costs compared to deploying each unit separately. To accomplish this, different forms of electrochemical disinfection should be explored. The most suitable for use in an electrocoagulation/electrochemical disinfection combination unit is a flow through design where free chlorine is directly produced in the wastewater stream itself. It should be investigated if background chloride content in septic tank wastewater is sufficient to produce enough free chlorine for disinfection year-round.

6 - References

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7 - Appendix

A1 – ANOVA Tables for Chapter 3 Experiments

ANOVA – Phosphorus Removal % (96 mg/L PO₄ – 15 min HRT)

Cases	Sum of Squares	df	Mean Square	F	p
Sample Port	87.520	1	87.520	3.392	0.084
Current Density (mA/cm ²)	5935.047	3	1978.349	76.667	< .001
Sample Port * Current Density (mA/cm ²)	383.389	3	127.796	4.952	0.013
Residuals	412.874	16	25.805		

Note. Type III Sum of Squares

ANOVA – Phosphorus Removal % (20 mg/L PO₄ – 15 min HRT)

Cases	Sum of Squares	df	Mean Square	F	p
Sample Port	0.247	1	0.247	0.085	0.774
Current Density (mA/cm ²)	2793.507	3	931.169	320.935	< .001
Sample Port * Current Density (mA/cm ²)	0.769	3	0.256	0.088	0.965
Residuals	46.423	16	2.901		

Note. Type III Sum of Squares

ANOVA – Phosphorus Removal % (96 mg/L PO₄ – 30 min HRT)

Cases	Sum of Squares	df	Mean Square	F	p
Sample Port	3.320	1	3.320	1.650	0.218
Current Density (mA/cm ²)	1450.409	3	483.470	240.313	< .001
Sample Port * Current Density (mA/cm ²)	13.743	3	4.581	2.277	0.121
Residuals	30.177	15	2.012		

Note. Type III Sum of Squares

ANOVA – Phosphorus Removal % (20 mg/L PO₄ – 30 min HRT)

Cases	Sum of Squares	df	Mean Square	F	p
Sample Port	2.107e -4	1	2.107e -4	0.002	0.969
Current Density (mA/cm ²)	55.633	3	18.544	139.545	< .001
Sample Port * Current Density (mA/cm ²)	0.872	3	0.291	2.186	0.129
Residuals	2.126	16	0.133		

Note. Type III Sum of Squares

ANOVA - Ammonia Removal % (96 mg/L PO₄ – 15 min HRT)

Cases	Sum of Squares	df	Mean Square	F	p
Current Density (mA/cm ²)	43.010	3	14.337	1.961	0.163
Sample Port	12.368	1	12.368	1.692	0.213
Current Density (mA/cm ²) * Sample Port	32.877	3	10.959	1.499	0.255
Residuals	109.643	15	7.310		

Note. Type III Sum of Squares

ANOVA - Ammonia Removal % (20 mg/L PO₄ – 15 min HRT)

Cases	Sum of Squares	df	Mean Square	F	p
Sample Port	1.505	1	1.505	0.243	0.629
Current Density (mA/cm ²)	94.941	3	31.647	5.120	0.012
Current Density (mA/cm ²) * Sample Port	29.220	3	9.740	1.576	0.237
Residuals	92.713	15	6.181		

Note. Type III Sum of Squares

ANOVA - Ammonia Removal % (96 mg/L PO₄ – 30 min HRT)

Cases	Sum of Squares	df	Mean Square	F	p
Sample Port	2.175	1	2.175	0.164	0.691
Current Density (mA/cm ²)	1131.565	3	377.188	28.464	< .001
Sample Port * Current Density (mA/cm ²)	4.630	3	1.543	0.116	0.949
Residuals	212.023	16	13.251		

Note. Type III Sum of Squares

ANOVA - Ammonia Removal % (20 mg/L PO₄ – 30 min HRT)

Cases	Sum of Squares	df	Mean Square	F	p
Sample Port	21.362	1	21.362	2.847	0.111
Current Density (mA/cm ²)	97.986	3	32.662	4.352	0.020
Sample Port * Current Density (mA/cm ²)	3.365	3	1.122	0.149	0.929
Residuals	120.074	16	7.505		

Note. Type III Sum of Squares

A2 – COD Removal Charts for Chapter 3

Figure A2.1: Phosphate Removal Percentage by Current Density (15 min HRT, 96 mg/L PO₄)

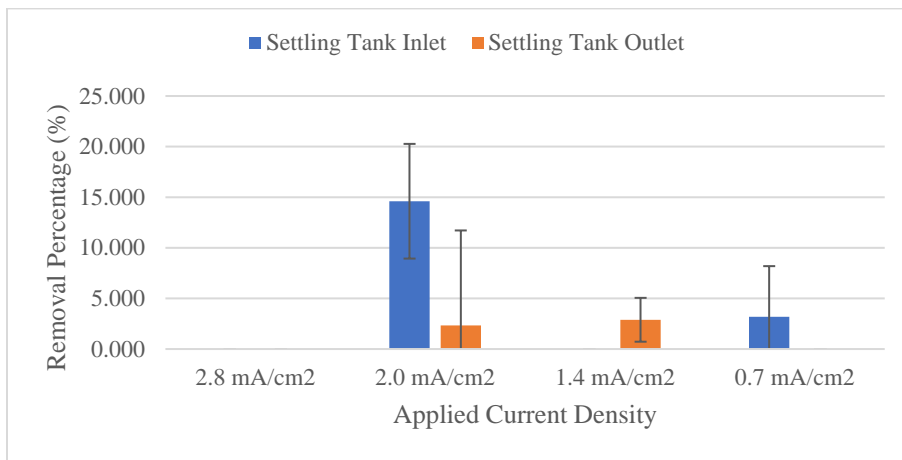


Figure A2.2: Phosphate Removal Percentage by Current Density (15 min HRT, 20 mg/L PO₄)

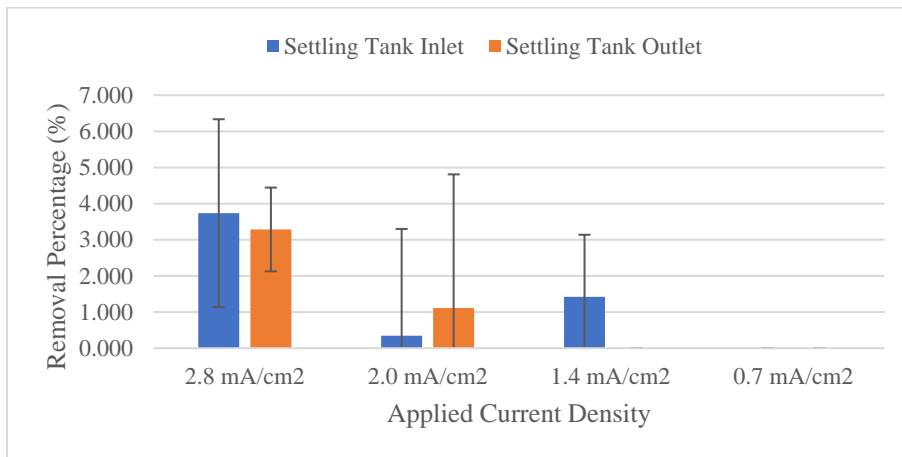


Figure A2.3: Phosphate Removal Percentage by Current Density (30 min HRT, 96 mg/L PO₄)

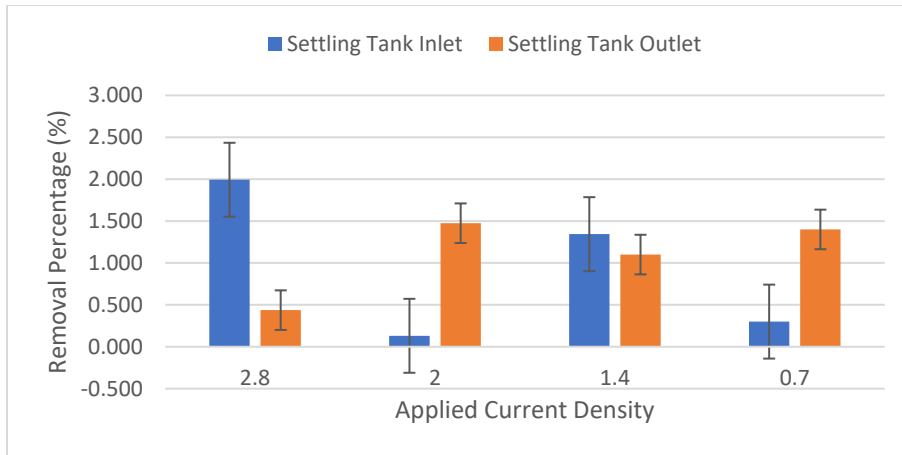
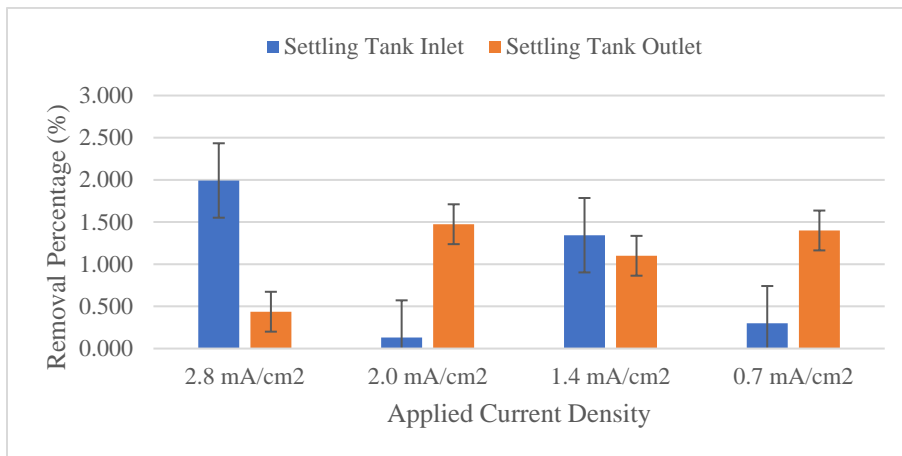


Figure A2.4: Phosphate Removal Percentage by Current Density (30 min HRT, 20 mg/L PO₄)



A3 – TSS Charts for Chapter 3

Note: Port 1 is at the inlet of the settling tank. Port 2 is located at the outlet of the first settling chamber. Port 3 is located at the outlet of third settling chamber. Port 4 is located at the outlet of the settling tank. See section 3.2.2 – Treatment Unit for more details.

Figure A3.1: TSS in Settling Tank at Various Current Densities (15 min HRT, 96 mg/L PO₄)

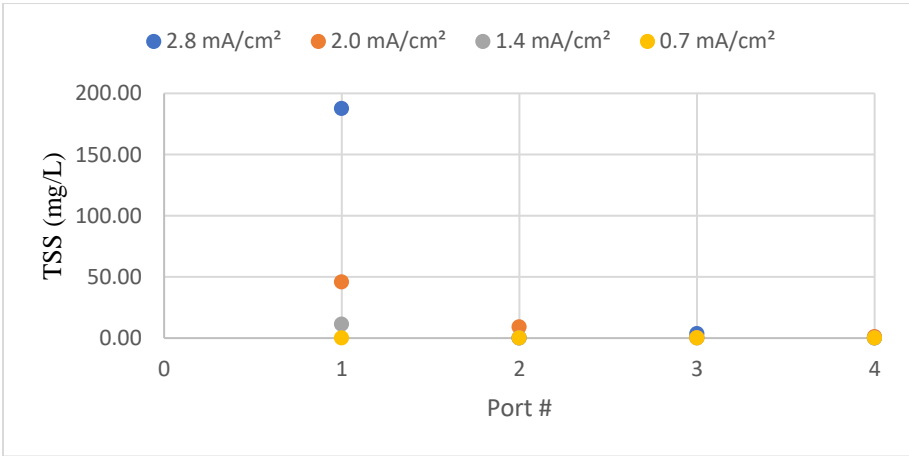


Figure A3.2: TSS in Settling Tank at Various Current Densities (15 min HRT, 20 mg/L PO₄)

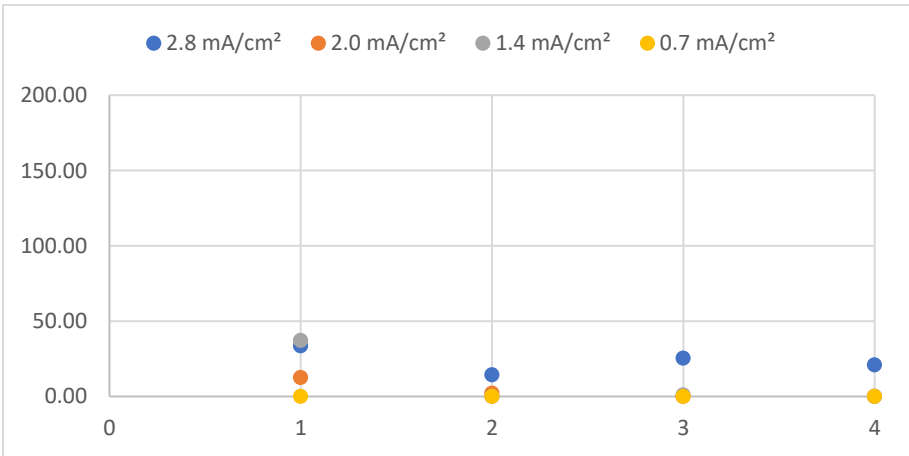


Figure A3.3: TSS in Settling Tank at Various Current Densities (30 min HRT, 96 mg/L PO₄)

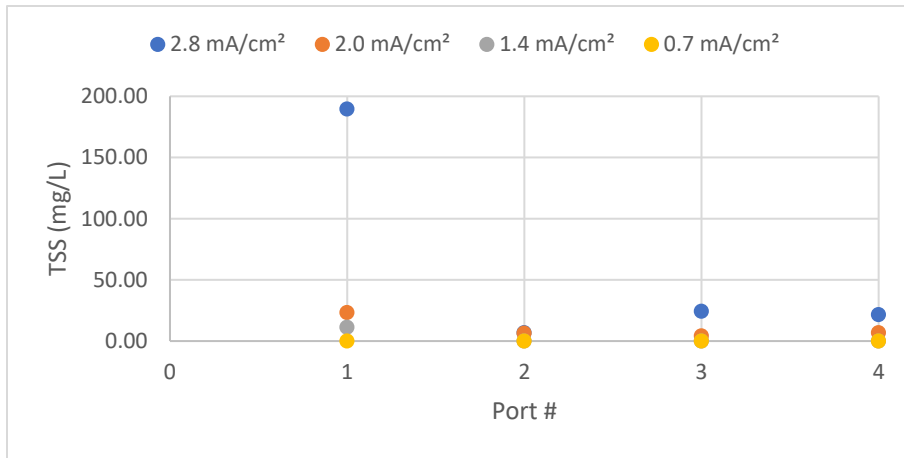
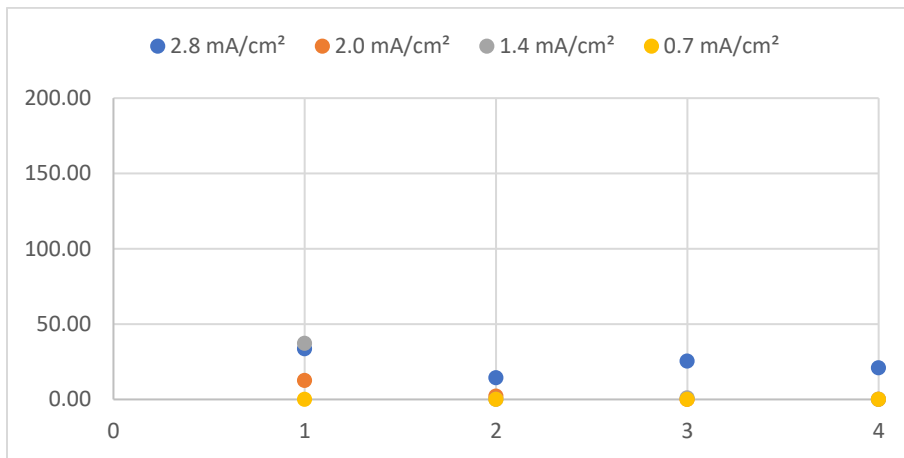


Figure A3.4: TSS in Settling Tank at Various Current Densities (30 min HRT, 20 mg/L PO₄)



A4 – List of Experiments for Chapter 4

Table A4: Table of Experiments in Research Objectives 1-4 (Each Performed in Triplicate)

Experiment #	Cathode Material	NaCl Concentration (g/L)	Current (A)	Retention Time (min)	C: A Ratio
Objective #1 - Retention Time and Current Density Model					
1	Titanium	60	1.5	5	1.5:1
2	Titanium	60	1.0	10	1.5:1
3	Titanium	60	1.0	15	1.5:1
4	Titanium	60	1.0	20	1.5:1
5	Titanium	60	1.0	25	1.5:1
6	Titanium	60	1.0	45	1.5:1
7	Titanium	60	1.5	5	1.5:1
8	Titanium	60	1.5	10	1.5:1
9	Titanium	60	1.5	15	1.5:1
10	Titanium	60	1.5	20	1.5:1
11	Titanium	60	1.5	25	1.5:1
12	Titanium	60	1.5	45	1.5:1
13	Titanium	60	2.0	5	1.5:1
14	Titanium	60	2.0	10	1.5:1
15	Titanium	60	2.0	15	1.5:1
16	Titanium	60	2.0	20	1.5:1
17	Titanium	60	2.0	25	1.5:1
18	Titanium	60	2.0	45	1.5:1
19	Titanium	60	2.5	5	1.5:1
20	Titanium	60	2.5	10	1.5:1
21	Titanium	60	2.5	15	1.5:1
22	Titanium	60	2.5	20	1.5:1
23	Titanium	60	2.5	25	1.5:1
24	Titanium	60	2.5	45	1.5:1
Objective #2 - Influence of Sodium Chloride Concentration on Hypochlorite Yield					
1	Titanium	30	1.0	10	1.5:1
2	Titanium	30	1.5	10	1.5:1
3	Titanium	30	2.0	10	1.5:1
4	Titanium	60	1.0	10	1.5:1
5	Titanium	60	1.5	10	1.5:1
6	Titanium	60	2.0	10	1.5:1
7	Titanium	90	1.0	10	1.5:1
8	Titanium	90	1.5	10	1.5:1
9	Titanium	90	2.0	10	1.5:1
10	Titanium	150	1.0	10	1.5:1

11	Titanium	150	1.5	10	1.5:1
12	Titanium	150	1.0	10	1.5:1
13	Titanium	300	1.5	10	1.5:1
14	Titanium	300	1.0	10	1.5:1
15	Titanium	300	1.5	10	1.5:1

Objective #3 - Influence of Cathode Material on Hypochlorite Yield

1	Titanium	60	1.0	15	1.5:1
2	Titanium	60	1.5	15	1.5:1
3	Titanium	60	2.0	15	1.5:1
4	Titanium	60	2.5	15	1.5:1
5	Aluminum	60	1.0	15	1.5:1
6	Aluminum	60	1.5	15	1.5:1
7	Aluminum	60	2.0	15	1.5:1
8	Aluminum	60	2.5	15	1.5:1
9	Iron	60	1.0	15	1.5:1
10	Iron	60	1.5	15	1.5:1
11	Iron	60	2.0	15	1.5:1
12	Iron	60	2.5	15	1.5:1

Objective #4 - Influence of Anode to Cathode Ratio on Hypochlorite Yield

1	Titanium	60	1.0	15	1.5:1
2	Titanium	60	1.5	15	1.5:1
3	Titanium	60	2.0	15	1.5:1
4	Titanium	60	2.5	15	1.5:1
5	Titanium	60	1.0	15	1:1
6	Titanium	60	1.5	15	1:1
7	Titanium	60	2.0	15	1:1
8	Titanium	60	2.5	15	1:1
9	Titanium	60	1.0	15	0.5:1
10	Titanium	60	1.5	15	0.5:1
11	Titanium	60	2.0	15	0.5:1
12	Titanium	60	2.5	15	0.5:1