Treating Water Using a Perforated Electrode Flow Through Cell

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Abstract

Perforated Electrode Flow Through cell (PEFT cell) is an undivided electro – chlorination cell designed by the University of Waikato. A new design was developed that consists of two sets of perforated electrodes assembled in a 3D printed casing. The aim of this research was to test the new PEFT cell for chlorine production, trial it for E-coli disinfection and iron and manganese removal by coupling it to a DMI-65 column. Maximum chlorine concentration was achieved at 0.1 mol/L NaCl concentration at a flow rate of 1.8 ml/s at 5 volts and 10 amps, and a current density of 44 mA/cm^2, resulting in a chlorine concentration of 510 mg/L. Chlorine production increased with increasing salt concentration but decreased with flow rate. Maximum chlorine production rate was at 0.14 mg/s.amp at 7.41 ml/s flow rate. Total inactivation of E-coli bacteria was achieved for all conditions tested. Iron and manganese removals of 92.5% and 90% respectively were achieved for synthetic bore water when the PEFT cell was coupled to a DMI-65 column.

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1 Introduction

1.1 Background

The Earth’s biosphere is enriched with water where it can be found as vapour, liquid or ice. All life forms on Earth depend on water, and ecosystems and livelihoods within a selected environment strongly depends on the available quantities and quality of the water (Young, 1994).

Human population growth projection for 2025 shows rapid growth mainly in developing countries. To maintain the population, demand for clean drinking water will increase globally (Young, 1994). With increasing population and complexity of life style, water use and management is important since ‘control of water is inevitably control of life and livelihood’. Water resource degradation, depletion and pollution led governments and natural resource protecting organizations to institute policies to encourage conservation of water resources and water quality (Strang, 2004).

3.5 million people are killed each year from untreated or poorly disinfected water (World Health Organization, 2001). Failure to supply safe water for human consumption is one of the greatest development failures in this century. It is been analyzed that if no action is taken, 135 million people will die by 2020 due to lack of water quality (Gleick, 2002). Main pathogens present in water are E-coli, camphylobacter, giardia, crytosporidium (Crockett, 2007). Recently in New Zealand the population of Havelock North was exposed to camphylobacter in their bore water supply which had been contaminated by pond water from a nearby sheep farm (Wilson, 2017).

Another problem in drinking supplies is heavy metals such as arsenic, manganese, iron, cadmium, boron, lead and mercury. Most of these contaminants can induce cancer and the other associated affects have been significant as well (Chowdhury *et al.*, 2016). In the Waikato region 33% of bore water contains high arsenic concentrations greater than the drinking water standard. Elevated levels of iron and nitrate are the most common ground water contaminants in the region. Most frequently iron and manganese co – exist in bore water (Waikato Regional Council, n.d).

Scientific research on water resource protection, water treatment, purification and water safety is becoming more important as scarcity of clean drinking water increases (Blatter & Ingram, 2001). Promising water purification and disinfection innovations include:

- Composite materials and nano particles developed for pathogen removal (Quang *et al.*, 2013; Tartanson *et al.*, 2014)
- Solar water disinfection (SODIS) (Hindiyeh & Ali, 2010).
- Photo- fenton method which using a mixture of ferrous ions and hydrogen peroxide, called Fenton's reagent, to oxidise organic water contamination (Ortega-Gómez *et al.*, 2012).
- Perforated Electrode Flow Through (PEFT) cell for chlorine production and disinfection (Nath & Langdon, 2013).

Compared to traditional disinfection methods such as chlorination, ozonation, and UV that have been used for decades, these novel techniques have a number of advantages (Ortega-Gómez *et al.*, 2012):

- Less or no storage facilities needed
- Less hazardous by-product generation
- No transport of chemicals or leakages
- Low cost

Therefore further developing these products will add in the evolution of water technology.

1.2 Research objectives

At the University of Waikato, the PEFT cell was developed that consisted of two perforated electrode plates spaced about 50 micrometers apart, contained within a chamber. An electric current between the plates electrolyzed a brine solution producing chlorine for disinfection. This system was only able to be operated in series. A new system was designed that allowed the system to be operated in parallel enabling greater throughput.

The aim of the research is to:

- Optimize the chlorine production of the new PEFT cell
- Assess optimum current for the maximum chlorine production
- Assess optimum operating voltage for the maximum chlorine production
- Assess optimum salt concentration of brine water (NaCl solution)
- Assess optimum flow rate of the brine water (NaCl solution)
- Assess disinfection properties on solutions containing E – coli
- Ability to remove iron and manganese dissolved in water by combining the PEFT cell with a DMI65 column will be assessed as the secondary objective.

1.3 Thesis outline

In Chapter Two a literature review is presented on water, water pollution, current treatments in water purification, evaluation of electro-chlorination in water disinfection and the use of PEFT as productive, low cost and in-situ chlorine generator. Furthermore, the chemical and physical behavior of the traditional treatments is presented.

Methodology and materials in this research are presented in Chapter 3.

In Chapter 4, results obtained from the study are presented and discussed.

Conclusions and recommendations for future work are laid out in Chapter 5.

2 Literature Review

2.1 Introduction

Purpose of this chapter is to guide the way enhancing performance of the PEFT cell and facilitate a background study to have a better understanding on the water, water contaminates, water quality standards, water treating methods and function of novel PEFT cell in water treatments. Study is relevant to New Zealand as to support the practical works carried out based on New Zealand water sources and standards.

2.2 Water

Pure water is colorless, odorless and tasteless and commonly found in liquid form that has number of unique properties. The chemical and physical nature of water makes it an un-replaceable essential for the existence of life (Shakhashiri, 2011).

Chemically water can be defined as a molecule formed by two hydrogen atoms and one oxygen atom. Group 6 ‘O’ atom has two unpaired electrons and group 1 ‘H’ atom has one unpaired electron; thus one ‘O’ atom shares it’s two unpaired electrons with two ‘H’ atoms each donating one unpaired electron to form a covalent bond (Evangelou, 1998). Unshared electrons in ‘O’ exert repulsive forces against each other and shared electrons exert less repulsive forces compared to unshared ones. This phenomenon makes oxygen skewed and the water molecule polar. The oxygen atom is slightly negatively charged and each hydrogen atom is slightly positively charged (Figure 2.1: Left). Polarity of the water molecule leads it to make weak hydrogen bonds with other polar molecules (Figure 2.1: Right) and it is the reason water is considered “the universal solvent”. Hydration is specific property water molecules demonstrate due to their polarity (Evangelou, 1998; Vaclavik, 2014).

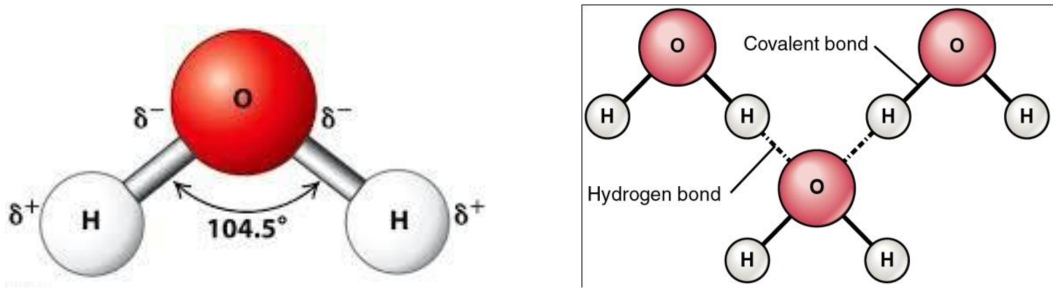


Figure 2.1 Left: Polar water molecule, Right: Hydrogen bonds between water molecules (commons, 2013; Lodish, 2008)

2.3 Water sources

Water divides into two categories: saline or sea water and fresh water. Saline contains 35,000 mg.l^{-1} of total dissolved solid, mainly due to sodium chloride and fresh water is less than 500 mg.l^{-1} of total dissolved solid. Saline and fresh water sources and their contribution to the global water availability are shown in Table 2.1.

Table 2-1 Water sources and their contribution to global water availability (Agnew, 2011)

Oceans	Saline	1.350,000,000 km^3	97.37%
Snow and ice	Fresh water	27,500,000 km^3	1.98%
Ground water	Fresh water	8,200,000 km^3	0.59%
Atmospheric	Fresh water	40,000 km^3	0.033%
Lake and rivers	Fresh water	207,000 km^3	0.015%
Soil moisture	Fresh water	70,000 km^3	0.005%

Water sources can also be categorized into surface waters and ground waters.

2.3.1 Surface waters

Surface waters refer to any source of water body that flowing or appear on the earth surface. Rivers, lakes and reservoirs are surface waters generated from different sources such as surface run off, direct rain fall into a water body or inter flow (Gray, 1999).

Most of the time heavy rain falls that cannot totally be absorbed by the vegetation and soil; create water steams such as rivers. These surface water run-offs are nurtured by the underground waters that penetrate through the soil as springs (Matthews, 1985).

Since ground waters also contribute in generating surface water, it indirectly affects the quality of the surface waters. A reasonable amount of dissolved solid comprised of soil, volcanic materials, bacteria, fungi and chemicals originate from ground water. Chemical discharges from industrial production accumulated in the atmosphere are brought back to surface water with rain fall (Gray, 1999).

Among various water sources, rivers themselves contain 0.0002% of water on Earth and 0.46% of the surface fresh water. River water conditions in New Zealand are identified as fairly good or very good compared to Europe, North America and Asia, but it has been declining over past 25 years by point-source pollution (wastewater discharge from industries and agriculture) and diffuse pollution from land use (Davies-Colley, 2013). New Zealand has a large number of lakes as well, but improper land use and submerged plant growth in these lakes has had negative impacts on water quality that restricts their use as a drinking water source (Verburg *et al.*, 2010).

Using river water for industrial, commercial and household water supply is common in New Zealand. The Waikato River is the longest river in New Zealand (425 km) which takes water from several other water bodies such as the Waipa River, Lake Taupo and Lake Karapiro (Kingston Reynolds *et al.*, 1975).

2.3.2 Ground waters

Groundwater is one important portion of water in the hydrological cycle. Water located in the Earth’s crust are simply identified as ground water, and originate from surface water bodies (Todd, 2004).

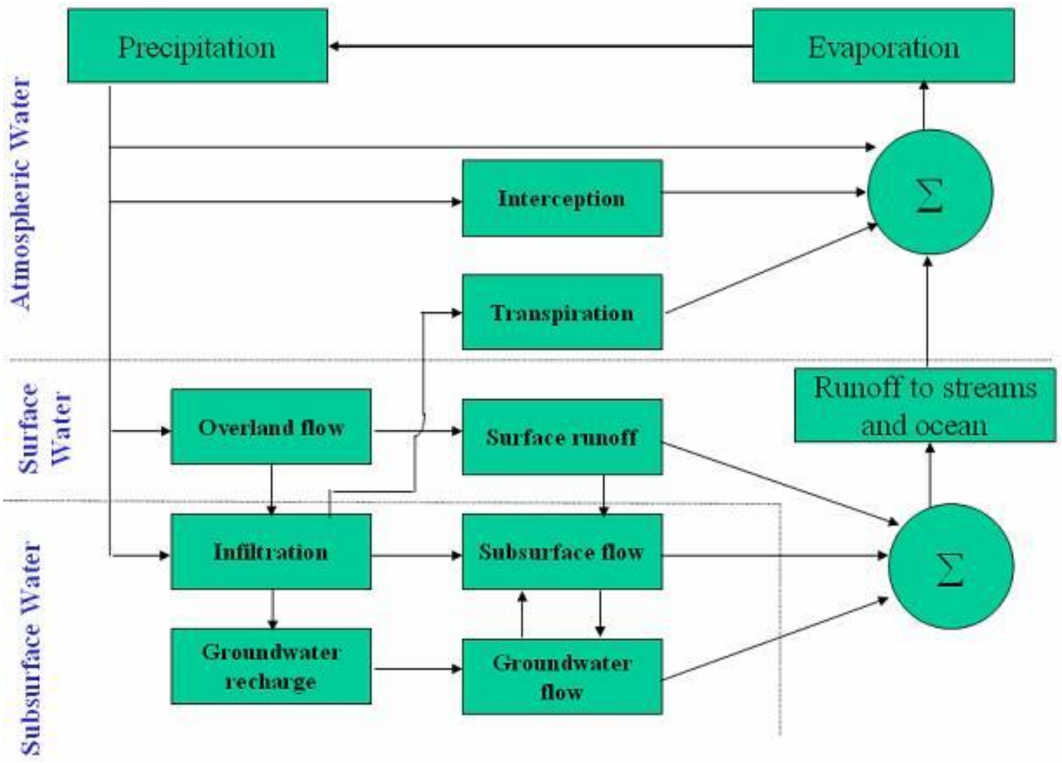


Figure 2.2 Global hydrological system (Todd, 2004)

Groundwater/sub-surface water is 98.97% of total fresh water and surface water and atmospheric water account for the remaining 0.87% and 0.16% respectively (Young, 2007). Groundwater reservoirs are interconnected by groundwater streams which are not rapid moving water streams such as surface waters. These groundwater storages are different according to their geological formation. The most frequently used underwater source, **aquifers**, are referred to as a saturated permeable reservoir with sufficient water quantities for springs and wells. These are water storages that have the ability to transmit water through the covering rock shells (unconfined storages). There are a few other confined beds that may or may not contain water. **Aquiclude** is saturated rock but with insufficient quantities of water for wells and no permeable cover. **Aquifuge** is a bed with impermeable layer of rocks without transmittable water in it. **Aquitard** is a water source that has poor permeable materials and impedes the groundwater movement (Todd, 2004). Visible surface water sources and aquifers are related to each other and share water in both directions. Mobile water seeps in between the surface and ground water systems depending on the area of contact (Margat, 2013). When water migrate either direction, it carries water soluble contaminants from one existing source to the other.

2.4 Water contaminants

The basic structure of environmental systems is disrupted by human activities and pollutants such as sewage, industrial byproducts, agricultural and radioactive materials. It is noted that natural processes also release harmful substances that can also cause serious impact on the environment. Water contamination is a crucial problem worldwide, but the water pollution in New Zealand is much less compared to Europe (which is highly industrialised) or Asia (which is highly populated) (Connell, 1993).

Chemical, physical or biological changes are caused by water pollution. Parameters such as suspended solids, turbidity, odour, nutrient levels, pH, heavy metals, non-metallic toxin levels, persistent organics and pesticides, and biological factors (BOD value, COD value) define the level of contamination (Palaniappan *et al.*, 2010). As groundwater and surface water sources are connected and exchange contaminants, the safety of the drinking water extracted by surface water or ground water source is affected by what has been discharged, e.g. micro-organisms, chemicals and even by disinfection by products (U.S. Environmental Protection Agency, 2013). According to a survey done in London, incidents of public health threatening water contaminations have been categorized and found the most frequent incidents are due to poor drinking water quality, chemical contamination, microbiological contamination and poor weather conditions (International Conference on Water Contamination, 2011).

High concentrations of water contaminants cause several problems to the quality of the water as well as to water treatment plant equipments and pipelines. Chloride from the mine water induces corrosion in pipelines and many other salts such as sulphates and carbonates result scaling or blockage (Scaling is chemical decomposition by crystallization or precipitation due to dissolved salt concentrations exceed saturation limit) (Stephenson, 1988).

Occurrence of health effecting contaminates in drinking water may be varied due to the source. Qualification and quantification analysis include observations in tap water, distribution systems, treated water in water treatment plants, source water, water sheds and aquifers, and historical and chemical production data (Contaminants, 1900).

Table 2-2 Drinking water Contaminants (Contaminants, 1900; Ministry of Health, 2007)

Inorganic contaminants (including heavy metals)	Organic contaminants	Biological contaminants
Barium Beryllium Cadmium Chromium Cyanide Fluoride Mercury Nitrite Selenium Calcium Chloride Ion Arsenic Silica (organic and inorganic) Lead Manganese	Benzene Benzoic acid Carbofuran Carbon tetrachloride Ascorbic acid Citric acid Ethanol Folic acid Glycerin Glycine	Viruses – Hepatitis A, flu virus, polio Bacteria – Campylobacter, Salmonella, Shigella , E-coli Protozoa – Cryptosporidium , Giardia Cyanobacteria– Cylindrospermopsin

Issues can be caused by some of the chemical substances contaminated in to water and their maximum levels are listed below (Chhatwal, 1996):

Arsenic (As) – since arsenic is present in tobacco and other food sources, the level of Arsenic in drinking water must not exceed 0.01ppm.

Cadmium (Cd) – electroplating activities and zinc galvanizing causes elevated levels of cadmium in water. Concentrations up to 0.01 ppm are acceptable.

Chloride (Cl^-) – higher levels of chloride make water taste salty. Maximum acceptable level of chloride is 250 ppm.

Chromium (Cr) – industrial pollution (plating/ tannery activities) add chromium ions with different valences. Hexavalent chromium (Cr^{+6}) is the most toxic form and it should not exceed 0.05 ppm.

Cyanide – the level of cyanide in water should be less than 0.01 ppm.

Iron (Fe) – iron in the water is common due to industrial operations as well as from the soil. It can cause health effects when consumed and damage to laundry and plumbing systems. The upper limit for iron is 0.3 ppm.

Lead – Serious health hazards are caused by lead replacing some of the metal ions in enzymes and deactivating them. The limit set for lead in water is 0.05 ppm.

Manganese – the upper limit is 0.05 ppm.

Other than the chemical contamination, one of the most concerning contamination of water is biological contamination (Oliveira *et al.*, 2013). Many studies on drinking water related diseases show pathogenic organisms such as viruses, bacteria, fungi, protozoa have been the cause. According to a research carried out in by EPA collaboration with Centers for Disease Control and Prevention (CDC) in the U.S., the most infectious pathogens were Giardia, Campylobacter, Cryptosporidium, Salmonella, zoonotic agents and E- coli bacteria. Public health issues including deaths and serious illnesses have been reported over the years. Outbreaks of these pathogens are associated with untreated or inadequately disinfected ground water, contamination of distribution systems where there are cross-connections, breaks and repairs, deficient storage tanks and unprotected reservoirs (Staff, 2005b). Statistical investigations by the EPA has identified even though most of the surface water goes through a disinfection process prior to the consumption, their quality often does not match the required standards. One other reason for the increasing number of pathogenic infections is most of the virus and bacteria show some resistance to physico-chemical disinfection treatments, because they have adapted to those treatments (Gleeson, 2002).

Water related microorganisms can be divided into water based and water borne pathogens. Water based pathogens need water to complete some of the stages of their lifecycle, but the waterborne pathogens spend their whole life in the water and are transmitted via the fecal-oral route. Identification of water borne pathogens is not easy. For the water monitoring procedures and other statistical evaluations quantitative data collection (bacterial counts etc.) is necessary. A widely used indicator organism is Escherichia-coli bacteria (Baker & Bovard, 1996). In the early stages of water microbiology, pathogen microbiologists made a list of criteria as an attempt to find an indicator pathogen. The main concern was the concentration or number of indicator microorganisms should be related to the extent of water contamination. Use of cholera vibrio as an indicator was had difficulties in isolating them in the water samples. In 1885, Escherich was able to identify a group of bacteria called coliforms as indicator bacteria which were easy to isolate. So, coliforms were quickly recognized as more accurate water quality indicator, and further evaluation of bacteriological techniques were able to detect even small numbers of coliform bacteria (Gleeson, 2002). Even now, the coliform index is still widely used to measure water quality. In this study, E-coli bacteria are used as the indicator to measure the disinfection power of the PEFT cell.

Coliforms are gram- negative, anaerobic, rod shaped bacteria where Escherichia-coli is the most common type of coliform bacteria found. E-coli bacteria containing samples grow in an agar medium made of lactose-peptone-eosin-methyl blue (EMB). After introducing a sample on to the medium it is incubated for 24-48 hours at about 37°C. E-coli bacteria grow as red colour colonies that can be counted using a microscope (Torres, 2010). Comparing E-coli counting with the E-coli standard index, conclusions on the water quality can be made.

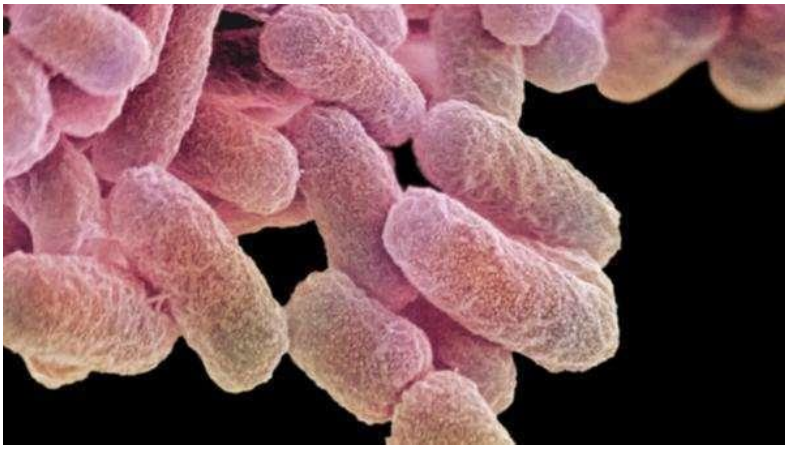


Figure 2.3 Scanning electron micrograph of Escherichia coli bacteria (Mundasad, 2011)

With the increasing industrialization and population, water contamination becomes more frequent and more complex. There is an emergence of research programs regarding expanding technology of water purification (Guidotti, 2009). The Department of Health and Human Services of United States has appointed environmental health policy committee which has a subcommittee on drinking water and health, and its role is to identify and take action where immediate attention is required. As observed by the committee more research is needed in areas of relationship between contaminants and adverse health effects, developing methodologies and models to understand the situation, developing laboratory techniques to measure the hazard and expanding the knowledge about waterborne health hazard in order to prevent them. The committee is assisting EPA (Environmental Protection Agency, US) in setting priorities for future drinking water contaminants and introducing new scheme to prioritize all contaminants based on their toxicity to human health/eco-systems, persistence, bioaccumulation and mass of the contaminant in the water streams/water sources. Furthermore, creating a future drinking water candidate list (CCL) has being considered over years with expertise knowledge that can predict potential contaminants and the way they behave in the water (National Research Council, 1999).

Ministry of Health, New Zealand, made a report on public health issues concerning drinking water. Department of Internal Affairs also collaborated in the project by reviewing where need funding and delivery of water and waste-water services was needed. According to the report public water supplies are in risk of contamination by chemical and biological substances because of inappropriate use of land, industry waste and farm waste disposal (Ministry of Health, 1994). While the Ministry of Health focuses on improving legislative and administrative support, the Department of Internal Affairs monitors and funds local authorities to overcome the issues.

2.5 Water standards

Water quality is influenced by number of key determinants such as geological location, climatic nature, hydrologic and geomorphic processes that associate the virgin water sources and human interaction (Baillie & Neary, 2015). Land uses for farming, forestry, mining and quarrying and waste disposal have a great impact on

New Zealand’s water (Reid *et al.*, 2012). World Health Organization (WHO) encourages every nation to follow better treatments and strategies to maintain the water standards to minimize or eliminate significant hazards during human consumption (Oliveira *et al.*, 2013). General water quality requirements for household water are shown in table 2.3.

Table 2-3 General quality requirements for household water (Health, 2013)

Household use	Quality requirement
Drinking	Biologically and chemically safe
Cooking and food preparation	Biologically and chemically safe
Bathing/showering	Biologically safe
Toilet flushing	Not discoloured or stain causing
Cloth washing	Not discoloured or stain causing

Both the water and waste water treatment processes follow water quality guidance in scientific and engineering approaches. After quantification analysis based on data collected and qualification analysis regarding chemical, microbiological, ecological and engineering aspect, standards are set to monitor the quality of water (Waite, 1984). The purpose of the setting drinking water parameters is to ensure the prevention of poisoning and long term health effects (Safe Drinking Water, 1976) .

In New Zealand, the main legislation for protecting water sources and drinking water standards include (New Zealand. Drinking-Water Regulatory & New Zealand. Ministry of, 1995):

Resource Management Act 1991

This gives regional councils responsibility to control the land use to protect the source water quality, control taking, using, damming and diversion of source water, and control discharges to the source water.

Water Supplies and Protection Regulations 1961

This covers protection of water distributed by the distribution system, i.e. every reservoir should have appropriate cover to protect stored water from contamination, and newly constructed reservoirs and distribution systems should be disinfected prior to the use.

Health Act 1956

This act was to ensure quality of the water supplied to the community, protect water courses, reduce the impact of discharges from treatment plants and protect individual house hold water quality.

Local Government Act 1974

This act supports the Health Act 1956 in the areas of water quality.

Under these legislations and acts there are a number of frameworks to establish drinking water quality. National Environmental Standards for raw drinking water sources prepared by Ministry for the Environment in 2004 propose a water quality grading system for the source waters. The Ministry of Health uses a ‘Multi-barrier approach’ in drinking water management to minimize the risk of chemical and microbiological contamination (Ministry for the Environment, 2004). A multi-barrier approach is a collection of several procedures, processes and tools that work together to reduce or eliminate contamination of drinking water from source to tap.

The grading system considers two factors, individual grade for identified contaminants and overall grade to check the suitability of raw water source. Individual grades for the contaminants are given based on catchment risk category and water quality category. (Ministry for the Environment, 2004)

Water quality regarding the contamination level for individual contaminants and the catchment is represented by a colour scale (Table 2.4, 2.5).

Table 2-4 Colour scale uses for the individual contaminant grading (Ministry for the Environment, 2004)

Grade	Suitability description	Interpretation
Green	Very good suitability	No treatment required
Yellow	Good suitability	Reliance on treatment to reduce low levels of contaminant to acceptable levels
Orange	Fair suitability	Reliance on treatment to reduce moderate levels of contaminant to acceptable levels
Red	Poor suitability	Reliance on treatment to reduce high levels of contaminant to acceptable levels
Black	Very poor suitability	Heavy reliance on treatment to reduce contaminant to acceptable levels

Table 2-5 Overall grade of source water and grade interpretation (Ministry for the Environment, 2004)

Grade	Level of Suitability	Interpretation
Green	Very good suitability	No treatment needs to make the water safe for drinking
Yellow	Good suitability	Reliance on treatment to remove low levels of microbes to make the water safe; or chemical or cyanobacteria present
Orange	Fair suitability	Reliance on treatment to remove moderate levels of microbes to make water safe
Red	Poor suitability	Reliance on treatment to remove high levels of microbes, chemicals or toxins to make water safe
Black	Very poor suitability	Heavy reliance on treatment to remove high levels of microbes to make water safe

Grading procedure of the drinking water is further broadened and updated by the Ministry of Health (Ministry of Health, 2001) to achieve international standards of water quality for supply (Table 2.6 and 2.7). Not only source water quality determines suitability of consumption, but also treatment procedure and distribution system. Therefore the Ministry of Health introduced a merit and demerit point grading system which was a hybrid protocol of existing grading systems at that time and the output of the Public Health Risk Management Plan (PHRMP).

Table 2-6 Keys use to grade source, treatment and distribution (Ministry of Health, 1995, 2001)

Grade	Description
A1	Complete satisfactory, negligible level of risk, demonstrably high quality
A	Complete satisfactory, very low level of risk
B	Satisfactory , low level of risk
C	Marginal, moderate level of risk, may be acceptable for small communities
D	Unsatisfactory, high level of risk
E	Complete unsatisfactory, very high level of risk

Table 2-7 Total points for the grading (Ministry of Health, 2001)

Grade	A1	A	B	C	D	E
Points	>90	80-89	70-79	50-69	40-49	< 40

Total points given for a source water/treated water or distributed water is sum of merit points and demerit points (Table 2.8 and 2.9).

Table 2-8 Award merit points for source/ treatment and distribustion criteria (Ministry of Health, 2001)

Compliance	Merit points for source/treatment	Merit points for distribution
E-coli compliance	49	60
P2 compliance	5	5
Protozoan compliance (only for source water/ treatment) Corrosion compliance (only for distribution)	15	5
Disinfection with residual	10	10
Aesthetic guideline value	5	10
ISO 14001/9002	16	10

P2 compliance – contaminated material getting in to water source

Demerit points are based on risk criteria such as not being able to draw enough water, water contamination, non-secure surface water or ground water, algicide, destratification, pre-oxidation, processes of coagulation, flocculation and clarification, aesthetics and fluoridation which are given deduction points ranging from 0 to 5 (Ministry of Health, 2001).

Drinking water standards for the New Zealand (DWSNZ) covers all areas of drinking water quality requirements that have been set for water delivery. DWSNZ specify the Maximum Acceptable Value (MAV) for each water contaminant (Table 2.9 and Table 2.10). MAV is concentration of a determinant in drinking water that is identified as no significant health risk to the consumer over the lifetime of consumption of that water (Ministry of Health, 2005).

Table 2-9 Maximum acceptable values for microbial determinants (Ministry of Health, 2008)

Micro-organism	Maximum Acceptable Value
Escherichia coli	Less than one in 100 ml sample
Viruses	No values set due to lack of reliable data
Pathogenic protozoa	Less than one infectious oocyst per 100 ml of sample

Table 2-10 Guideline values (GV) for aesthetic determinants (Ministry of Health, 2008)

Determinant	GV	Unit	Comment
Aluminum	0.1	mg/L	Above this depositions and discolouration could happen
Ammonia	1.5	mg/L	Odor threshold in alkaline conditions
Calcium			Hardness is checked
Chlorine	0.6- 1.0	mg/L	Taste and odor threshold
Chloride	250	mg/L	Taste and corrosion
Total hardness (Ca +Mg)	200	mg/L	Deposition, scum formation and corrosion
Iron	0.2	mg/L	Staining
Manganese	0.04	mg/L	Staining
Sodium	200	mg/L	Taste threshold
Sulphate	250	mg/L	Taste threshold
Zinc	1.5	mg/L	Taste threshold

2.6 Treating water

Water treatment is defined as the process of achieving the required water quality and standard by various treatment steps. Boiling water over fire, dipping heating rods into water and filtering water through sand and gravel filters have been in use since 4000 B.C. In 1804 the first municipal water treatment plant was installed in Paisley, Scotland. In 1829 slow sand filters being used to filter water. In 1835 operators started adding small amounts of chorine to disinfect water as recommended by Dr. Robley Dunlingsen. In 1856 Thomas Hawksley introduced a pressurized water system to prevent contamination. In 1881 laboratory tests identified chlorine was able to destroy bacteria. In 1892 Theobald Smith detected E-coli bacteria in water as a result of sewage contamination to water. In 1906 ozone was used for disinfection for the first time. In 1914 the fermentation tube method introduced by Theobald Smith came to practice in U.S Public Health Service to set biological standards of water and by the year 1941, 85% of the water supplied in USA had been chlorinated (Crittenden, 2012).

Factors affecting the selection of water treatment processes include (Staff, 2009):

- Source of water (ground water or surface water)
- Required treated water quality
- Capital and operating costs
- Plant installation
- By-products, residual disposal
- Applicability

All the water treatment processes contain a set of basic unit processes that each removes a targeted contaminant based on physical, chemical or biological theory. In other words, a treatment program is an integrated train of unit processes that remove or reduce undesirable constituents from the water reach the required drinking water standards (Schutte, 2006). Basic unit processes are listed in Table 2.11.

Table 2-11 Unit processes and applications (Schutte, 2006)

Unit process	Description and application
Screening	Screens are used at the intake gate or in the sump well ahead of pumps. Remove debris in the raw water
Aeration	Supply air in to the tanks. It oxidizes taste and odor-causing chemicals and oxidizes iron and manganese.
Mixing	Mechanical mixers use to mix the chemicals added in to the water
Coagulation	Add coagulants in to water to destabilize colloidal particles and promote making flocs
Flocculation	Facilitate aggregation of small floc to larger ones
Sedimentation	Allow sediment larger flocs or suspended particles in to the bottom of the sedimentation tank. And separates water layer
Sand filtration	Further removal of suspended particles or flocs in the water by passing water through multi-size sand/gravel filters
Activated carbon adsorption	Remove many small particles by adsorbing them in to the porous surface of activated carbon. It also removes many metals. It can be either powdered activated carbon (PAC) or granular activated carbon (GAC)
Ion exchange	Cation and anion resins are used to remove selected ions already have dissolved in the water. Resin beds are replaced when they reach maximum exchange level
Disinfection	Disinfection is important in drinking water treatments in order to kill all the disease causing organisms. Chlorination is the most popular disinfection method. But alternative disinfection methods such as ultraviolet radiation, ozone and chlorine dioxide are used either combined with chlorine or not

2.6.1 Screening

Screening (e.g. bar screens, fine screens, drum screens, and micro-screens) is a preliminary treatment step almost every water treatment process uses (water treatment and waste water treatment) to remove large sized solid contaminants (Hendricks, 2006).

2.6.2 Sedimentation

Suspended particles that cannot be separated by screening can be removed by allowing them to settle in sedimentation tanks. Settling velocity depends on particle size, shape, charge and specific gravity (Julien, 2010).

2.6.3 Coagulation

Particles which do not settle out can include humic materials such as tannins, lignins, phenolics, hydrocarbons, amino acids, trace metals, colloidal solids, bacteria, viruses, color causing particles or fine silts (Berger, 1987; Staff, 2009). These generally have a negative charge repelling each other and remain dispersed by Brownian motion (Prakash, 2014). These are treated by adding a coagulant such as alum, an iron salt or polymeric material that promotes charge neutralization and causes the particles to form small flocs (figure 2.4) (Howe, 2012; Racar *et al.*, 2017). Polymeric materials can be polyelectrolytes which have the ability to charge neutralize and make agglomerates or non-ionic polymers that bridge between colloidal particles to form larger agglomerates (figure 2.5) (Gregory, 2004).

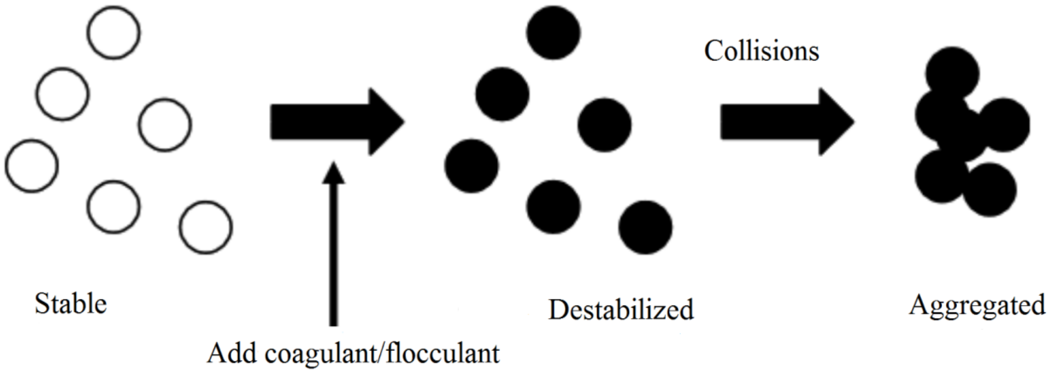


Figure 2.4 Coagulation and flocculation (Gregory, 2004)

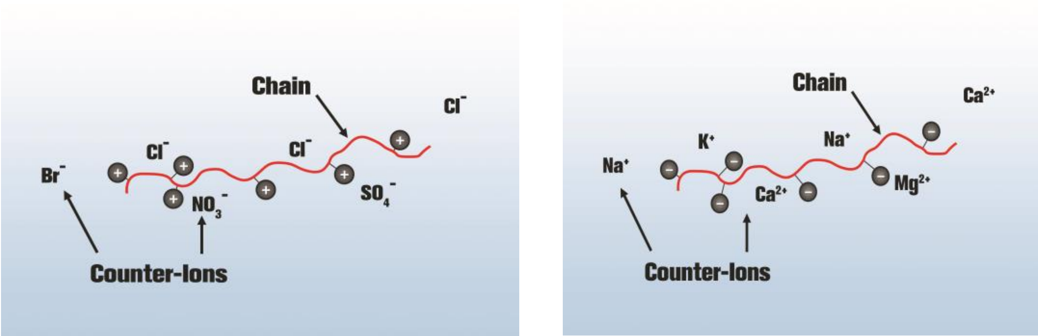


Figure 2.5 Cationic polyelectrolyte and Anionic polyelectrolyte

2.6.4 Filtration

Filtration is a physical-chemical process which involves passing water through a filter media to remove undesirable dissolved particles (Todaro, 2014). This can be rapid filtration, slow sand filtration, membrane filtration or a combination (Staff, 2010).

2.6.4.1 Rapid gravity filtration

Rapid gravity filters are packed bed of granular media of specific material that remove suspended substances by physicochemical mechanism (Han *et al.*, 2009). This has been the most widely used last step to remove suspended particulates in water treatment process by municipal water supply systems. Turbidity, suspended particles, water-born pathogen, and some trace metals (e.g. iron and manganese removal is possible during rapid gravity filtration (Upton *et al.*, 2017) (Tatari *et al.*, 2016).

2.6.4.2 Slow sand filtration

Slow sand filtration uses biological activity from planktons, diatomas, protozoa and bacteria on the filter surface (called a *schmutzdecke*) to remove pathogenic microorganisms and organic pollutants (Seeger *et al.*, 2016). Filter systems consists of a basin with relatively fine sand, underline outlet pipe and water inlet above the filter bed. The water outlet is surrounded by supportive gravel about 0.4 m – 0.6 m deep and on top of it is filter sand which typically is 0.8 m to 1.2 m in depth. Slow sand filters have very low filtration rates of between 0.1 to 0.3 m/hour (Logsdon, 2008). Quartz sand used in slow sand filters is usually negatively charged and has great bonding capability iron, manganese, aluminum and other metals (Huisman, 1974).

2.6.4.3 Membrane filtration

A membrane filtration process uses permeable membranes which permit water to flow through while resisting the passage of other suspended solids. Membrane filtration includes reverse osmosis (RO), nano-filtration (NF), micro-filtration (MF) and ultra-filtration (UF). MF and UF typically have pore sizes between 0.1 – 0.2 μm and 0.01 – 0.05 μm respectively while NF has pore sizes around 0.001μm. (Gupta, 2012). Reverse osmosis will allow water to pass while rejecting salts, while separation using UF and MF will reject protein sized molecules while allowing passage of salts and water (figure 2.6).

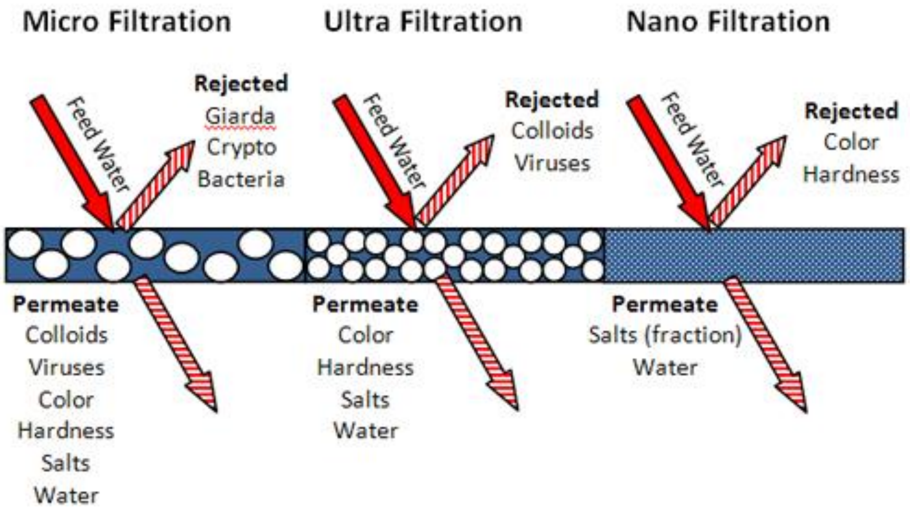


Figure 2.6 Filtration spectrum of MF, UF and NF (YAMIT Filtration and Water Treatement, n.d.)

2.6.5 Adsorption

Adsorption uses an absorbent which consists of a highly porous material such as activated carbon to absorb trace taste, odour, organic and metal compounds from water (Marsh, 2006)(Worch, 2012) through hydrophobic, electrostatic, and Van der waals interactions (Cheremisinoff, 2001). Physical adsorption can be increased by increasing porosity and chemical adsorption by increasing functional groups containing oxygen compounds such as acidic surface oxides, and carboxylic, phenolic and carbonyl groups (Cecen, 2011). Granular activated carbon is popular in water and drinking water treatment processes (Bahadori, 2013; Committee, 2011).

2.6.6 Ion exchange

Another form of adsorption is ion-exchange which uses a polymer resin to exchange similarly charged ions with ions in water (Slater, 1991). In practical cation and anion exchangers are placed in series for removal of salts (Paterson, 1970) and trace metals in water (Walton, 1990) such as manganese, zinc, barium, cadmium, chromium, lead, silver and mercury (Muraviev, 1999). One of the major drawbacks of ion exchange is it is not possible to exchange all the counter–ions due to several issues such as adsorption capacity and the need to regenerate the resin periodically to recover ion exchange capacity (Bolto, 1987).

2.6.7 Disinfection

Disinfection is destruction or deactivation of possible infectious species. Prevalent disinfection methods use in the drinking water purification/treatment process is chlorination, ultraviolet radiation and ozone (Kuo & Smith, 1996). More detailed review on individual disinfection modes will be delivered under ‘2.7 Disinfection’ section.

2.7 Disinfection

Poorly managed or poorly treated water utilities can result in microbiological waterborne diseases. Vulnerability depends on the potential of the water source to be microbiologically contaminated, treatment efficiency, treated water distribution system quality and general management (Joerin *et al.,* 2010; Nokes, 2004) Other than preventing contamination of source water with pathogens, using disinfection methods is the general strategy in water purification technology (Voeller, 2014).

A disinfectant is a chemical or physical agent that is capable of destroying diseases causing bacteria, fungi, viruses and protozoa but not be successful in inactivating bacterial spores. A bactericide, fungicide or virucide will destroy a particular bacteria, fungi or viruses respectively while a germicide destroys range of pathogenic organisms without focusing on particular species. Disinfection differs from sterilization which demolishes all organisms (Das, 2000).

2.7.1 Physical disinfection

Physical disinfection utilizes heat, radiation and filtration to deactivate microbial communities. Heat is the most widely used primary physical disinfection method which transfers thermal energy from one system to another due to temperature difference by conduction, convention or radiation. The mode of heat transfer can be wet or dry. Wet heat is considered as most effective form of heat as liquid or gaseous (steam) phase of water act as the disinfection agent. Dry heat is less effective under 140°C and usage is limited due to it. Radiation is emission of energy of unstable atoms as particles or electro-magnetic waves. Energy transmitted in the form of rays are, X-rays, ultra violet (UV) radiation and infra-red (IR) (McDonnell, 2007).

2.7.2 Chemical disinfection

Historically chemical disinfection was used as an additional operation parallel to physical disinfection until the early 19's; after which chemical disinfectants were more common (Buchanan, 2011). Most of the disinfection methods used nowadays in house hold and large scale water treatment plants are chemical disinfection methods. There are four widely used chemical disinfectants: free chlorine, hypochlorite, chloromines, chlorine dioxide and ozone (Twort, 2000). Chlorine has been the dominant and important water disinfection method used all over the world as it produces a residual that continuously delivers disinfection during distribution until consumption (Percival, 2013). These disinfectants destroy or damage the cell wall of microorganisms or get into the cell and inhibit enzyme activity of the microorganism. Factors effecting disinfection are contact time, concentration and type of disinfectant, intensity and nature of physical agent, temperature, number of microorganisms, type of microorganisms and water conditions (Das, 2000). Degree of removal or percentage removal of microorganism is used to define the disinfection yield. Chick's law describes the relationship of the rate of inactivation microorganism.

$$dN/dt = kCN \qquad \textbf{Equation 1}$$

Where N is the number of microorganisms, t is time, k is a rate constant which depends on the disinfectant, type of microorganisms and water quality, and C is concentration of the disinfectant (*Disinfection*, 2013).

2.7.3 Chlorination

Chlorine was discovered in 1774 by Swedish chemist Carl W. Scheele. Application of chlorine as a disinfectant started in 1908 for the Boonton water supply with filtration processes (McGuire, 2012). Chlorination has been used as the predominant disinfection method for 70 years in United States and it contributes 95% of disinfection of portable water. Chlorine is reactive against most of the pathogens (National Research Council, 1986) and widely used as because it is readily available as gas, liquid or powder, cheap, easy to apply, has high solubility in water, provides residual disinfection while distributing (Race, 2011; Tebbutt, 1997).

Chlorine dissolves in water forming mixture of hypochlorous and hydrochloric acids and the reaction is pH sensitive.

$$Cl_2 + H_2O \longrightarrow HOCl + HCl \qquad \text{Equation 2}$$

Chlorine dissolution mechanism shows following equilibrium,

$$Cl_2 + H_2O \longleftrightarrow HOCl + H^+ + Cl^- \qquad \text{Equation 3}$$

$$HOCl + H_2O \longleftrightarrow H^+ + OCl^- \qquad \text{Equation 4}$$

Hypochlorite ions (OCl^-) and hypochlorous acid (HOCl) together are termed as “free chlorine”. Hypochlorous acid is more affective in deactivating microorganisms than OCl^- ions. Therefore the pH condition should be controlled in favor of making more hypochlorous acids, i.e. pH 6 – 8. The concentration of HOCl is significantly reduced by organic matter and ammonia present in the water (Gomez-Lopez, 2012; Li & Zhang, 2012; Race, 2011).

Chlorine gas is greenish-yellow in color, reacts violently with many substances, and therefore is impossible to find pure chlorine gas in nature. Chlorine gas is manufactured by electrolysis methods from sodium chloride brine, and stored as a compressed liquid. The acids that form when it reacts with water are corrosive to metallic treatment plant equipment (Staff, 2005a).

Chlorine is also useful in metals removal from water supplies. Both free chlorine and combined chlorine react with ferrous and manganese ions to oxidize them.

$2Fe^{2+} + Cl_2 + 6H_2O \longrightarrow 2Fe(OH)_3 + 2Cl^- + 6H^+$ Equation 5

$Mn^{2+} + Cl_2 + 2H_2O \longrightarrow MnO_2 + 4H^+ + 2Cl^-$ Equation 6

Even ferrous bicarbonate ($FeHCO_3$) is oxidized to ferric hydroxide. Free elemental chlorine is more effective than the combined chlorine in oxidizing iron present in complex organic combinations.

Chlorine reaction with manganese ions gives manganese dioxide which is a solid but appears in colloidal form rather than particulate forms. Therefore the conventional filter media used to remove the colloidal form of manganese dioxide, is recommended to operate with excess chlorine in it to ensure oxidation of any adsorbed Mn deposits. Oxidation of manganese ions by free chlorine requires a longer contact time and the deposition of oxidized iron and manganese in plumbing systems are the major issues (White *et al.*, 2010).

Chlorination can also be achieved by adding chlorine compounds such as sodium hypochlorite, chloromines and chlorine dioxide (Park & Allaby, 2013). Chlorine dioxide (ClO_2) is stronger oxidant than chlorine and other chlorine compounds, is active over a wide pH range, but its use is limited in water treatment due to its complexity, risky nature of generation and high cost. Chlorine dioxide can also results in disinfection by-products (DBP) such as trihalomethane (THM) precursors (Solsona, 2003). Chloromines are a combination of chlorine and ammonia in water media to form monochloroamine at pH 8.3(Texas Commission on Environmental Quality, 2015):

$HOCl + NH_3 \longrightarrow NH_2Cl + H_2O$

Chloromination produces residual disinfection, acts as a biocide in the distribution system, does not create THM and formation of DBP is negligible. However, addition of ammonia contributes to nitrification in the waterways which can enhance pathogenic community growth and at the same time reduce residual chloromine amount (Staff, 2005a).

One major drawback of most of the chlorine disinfection methods is on-site generation requirement. It demands a large capital cost for storage tanks, chemical feed pumps, buildings to set up equipment, electrical and mechanical power. Structural modifications and maintenance over the time need additional money for physical apparatus and professional fee. It may require substitution mini plant in water treatment plant in case of breakdown or situations such as shut down for maintenance if the plant is covering large area of water supply. As process has to depend on the external chemical supplement, planning and monitoring deliveries and onsite chemical stocks is proposed. Chemical handling requires special training and supervision which is more labor intensive (Staff, 2014).

2.7.4 Ozonation

Ozone (O_3) is tri atomic structure of oxygen which forms according to the reaction of O_2 with another free radical oxygen. Central oxygen atom is attached to other two oxygen atoms in a particular angel of 116° 49´. All three oxygen atoms in ozone contain two unpaired electrons in valence cell. Since ozone molecule appears with two resonance structures it shows electrophilic and nucleophilic behaviors due to absence of one electron of each terminal oxygen at different stages (figure 2.7).

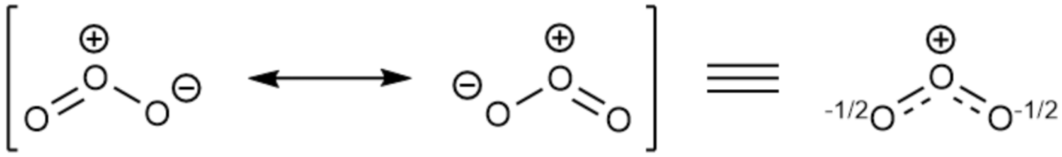


Figure 2.7 Resonance structures of ozone(Chemistry Stack Exchange Inc., 2015)

This structural nature of ozone makes it a vigorously reactive molecule. Formation of ozone (O_3) needs diatomic oxygen (O_2) to break down in to free radicals and those extremely reactive free radicals to react with other diatomic oxygen. Splitting of diatomic oxygen requires pronounced amount of energy usually acquires from UV radiation (188 nm wave length) (Donnell *et al.*, 2012).

O_2 + UV radiation $\longrightarrow$ $O^* + O^*$ Equation 7

$O_2 + O^* \longrightarrow O_3$ Equation 8

Alternative reaction mechanism for ozone production is NO_2 photolysis which also produces a free radical oxygen (Mathieson, 2010).

NO_2 + UV radiation $\longrightarrow$ $NO + O^*$ Equation 9

$O_2 + O^* \longrightarrow O_3$ Equation 10

Mechanism of ozonation explains the reason it to be more effective oxidant. Both direct and indirect chemical reactions occur in water simultaneously makes ozone way better than other oxidants; but reaction conditions such as pH of water, dissolved organic matter level and alkalinity impact on the reactivity. Indirect reaction initiates by OH^- free radicals in water which are very unstable and looking for electrons, to be stable.

$O_3 + OH^- \longrightarrow O_2^- + HO_2^-$ Equation 11

$HO_2^- \longrightarrow O_2^- + H^+$ Equation 12

All of these reactive species undergo radical reactions and form compounds after reacting with organic and inorganic substances in water. Ozone acts as an electro-philic agent with aromatic compounds and nucleo-philic agent with carbonyl compounds during direct reactions (Donnell *et al.*, 2012), and will also attack alkanes and cycloalkanes which is helpful in removing large organic compounds (Knipe, 2012). Ozone will attack cell membrane glycol-proteins, glycol-lipids and enzymes. After damaging cell membrane it will attack protein and DNA inside

(Donnell *et al.*, 2012). In addition, ozone is useful in oxidizing metals in water. Ozone will not produce DBPs, but it does not provide residual disinfection. It can also produce bromate (BrO_3^-) which is a carcinogenic substance from bromide (Br^-) containing water (Gottschalk *et al.*, 2010) which has limited use of ozone as a disinfectant (Loeb *et al.*, 2012).

Practical methods of ozone generation is allowing an electrical discharge to happen between high electrically charged conductors separated by an air gap. Techniques such as corona discharge, surface discharge, pulsed streamer discharge (PSD) and atmospheric pressure glow discharge use above principal to generate ozone. In water treatment plants corona discharge technique is popular as it has developed to large scale, commercial production (Alsheyab & Muñoz, 2007).

2.7.5 UV radiation

Solar radiation is electromagnetic (EM) waves emit from sun that ranges from X-rays to radio waves. These rays have both wave and particle properties; hence term 'photon' is refers to particle characteristic of radiation. Ultra Violet (UV) radiation (from 100 nm to 400 nm) is one important part in the EM spectrum (Figure 2.8) (Badescu, 2008) and can be categorized into four groups (Table 2.12).

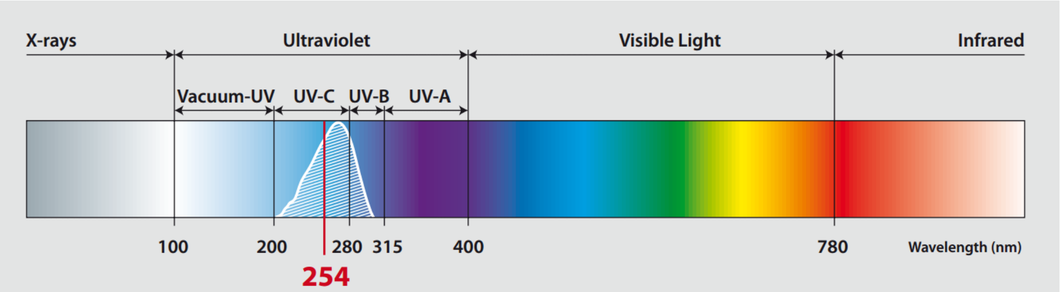


Figure 2.8 UV in Electromagnetic Spectrum (LIT UV elektro, n.d.)

Table 2-12 Distinct bands of UV (Akram, 2005)

Band	Wavelength
UV – A	315 – 400 nm
UV – B	280 – 315 nm
UV – C	100 – 280 nm
UV – Vacuum	100 – 200 nm

All the distinct wave lengths of UV have photochemical effect on pathogenic microorganisms, but UV– C is the most effective because it is absorbed by proteins, RNA and DNA (Kowalski, 2009), which will disrupt the single strand of RNA or double strands of DNA (Figure 2.9) resulting in inactivation of microorganisms. UV sensitivity of pathogenic microorganisms can be arranged as following sequence:

Bacteria = Protozoa > Viruses > Bacteria spores > Algae (Staff, 2008).

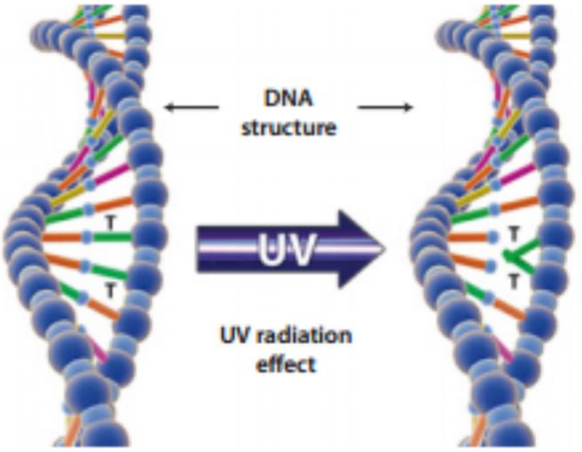


Figure 2.9 UV disrupts nucleotides in DNA (LIT UV elektro, n.d.)

Generally mercury lamps (low pressure or high pressure) are used for UV disinfection. Emission of UV decreases with fouling on the quartz covers of the lamps (Bitton, 2014) therefore regular cleaning and maintenance of the UV system is required (Solomon, 1998).

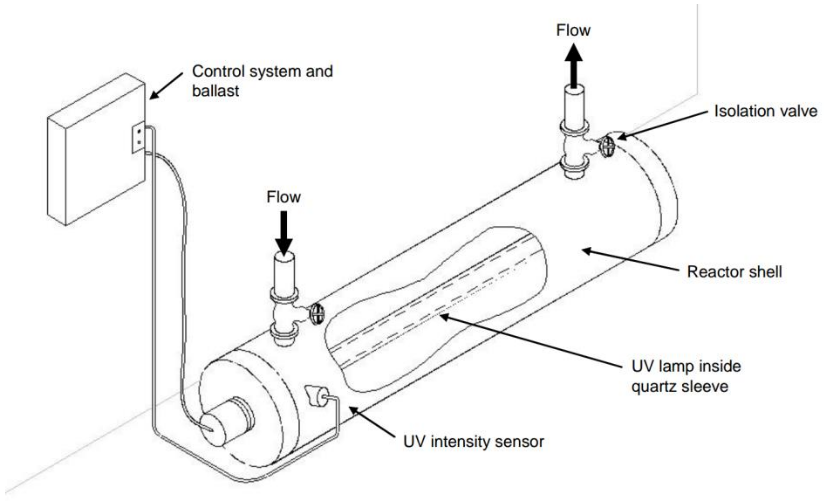


Figure 2.10 UV reactor installment (Ministry of Health, 2010)

In the presence of organic matter, UV light produces hydrogen peroxide which also contributes to disinfection (Matsuo, 2001). UV is paired with chlorine disinfection because chlorine provides residual disinfection and UV will deactivate microbes and spores unaffected by chlorine disinfection (Ray & Jain, 2014).

Table 2-13 Comparison of drinking water disinfectants (McGuire, 2016)

Disinfectant	Advantages	Disadvantages
Elemental chlorine (Cl_2) - the most commonly use form of chlorine	• low cost • the most energy efficient of all chlorine based disinfectants • unlimited shelf-life	• comes as pressurized gas- need special care of handling • additional regulation requirements (safety and health management standards)
Sodium Hypochlorite (NaOCl)	• a solution –less hazardous and easy to handle • less training requirements • less regulations requirements	• limited shelf-life- degrade • corrosive
Calcium	• More stable than NaOCl	• Precipitated

Hypochlorite $[Ca(OCl)_2]$	• Less training requirement	$[Ca(OCl)_2]$ can cause feeding problems • Higher cost compared to elemental chlorine • Explosive hazards • Can contain chlorate, chlorite while manufacturing
Chloromine (monochloromine) (NH_2Cl)	• More stable residual than free chlorine • Fewer dose requires – less odor and taste • Excellent secondary disinfectant • Protects distributed water	• Weaker disinfectant and oxidant • Longer contact times • May produce nitrosamine • May contribute in nitrification • Ammonia and chloromines toxic to fish- threats to aquatic life • Not good for kidneys
Chlorine dioxide (ClO_2)	• Reasonably effective against *cryptosporidium* • Fast inactivating *Gardia* • Active in wide pH range • Does not form chlorinated Dissolved by-products • Effective in taste and odor controlling • Oxidize manganese	• May form chlorite, chlorate • Highly volatile residual • Requires on-site generation • Requires additional training • Higher operation cost •
Ozone	• Strongest disinfectant available • Does not directly produce by-products • Effective against *cryptosporidium*	• Require higher technical knowledge • No residual disinfection • Forms by-products • Higher cost • Difficult to control & monitor
Ultra Violet radiation	• Effective against most viruses, protozoa and spores	• No residual disinfection • Higher doses require

	- No chemical generation or handling needed - Effective against *cryptosporidium* - Protolyzes nitrosamines	for some microorganisms - Difficult to monitor - Usually requires additional treatments/ pre-treatments

2.8 Contaminant removal

Dissolved impurities found in water are commonly ions (cations, anions), heavy metals, gases and disinfectants (Seneviratne, 2007).

Table 2-14 Common ions found in water (Seneviratne, 2007)

Cations	Anions
Calcium (Ca^{2+}) Magnesium (Mg^{2+}) Sodium (Na^{+}) Potassium (K^{+}) Iron (Fe^{2+}) Manganese (Mn^{2+})	Chloride (Cl^{-}) Sulphate (SO_4^{2-}) Nitrates (NO_3^{-})

Iron and manganese are frequently found cations. Iron concentration can be between 1 mg/L – 100 mg/L and manganese concentration up to 3 mg/L in source water. The aesthetic quality of the water is affected when the iron concentration is higher than 0.5 mg/L and manganese concentration is greater than 0.1 mg/L. There are two common oxidation states/valence states for iron: iron (II) and iron (III) and manganese has oxidation states of (II), (III), (IV), (VI) and (VII). Iron (VI), (V), and (VI) are less common due to low stability (Mackay, 2002; Sommerfield, 1999). Iron (III) oxide (Fe_2O_3) is insoluble in water (Housecroft, 2012). Permanganate (MnO_4^{-}) is another common form of manganese which soluble in water but when it is reduced to green manganate (MnO_4^{2-}) it is insoluble. The most thermodynamically stable state of Manganese is Mn^{2+} and it forms all the regularly found salts of manganese including nitrates, chlorides and sulphates (Rayner-Canham, 2014). Iron and manganese can be present in water in different forms; as bicarbonates, as chlorides, as nitrates or sulphates and even organically bounded complexes.

Commonly manganese and iron removal is addressed by oxidation using aeration, ozone or chlorination and filtration (Brandhuber, 2013; Geddes, 2014; Isaeva, 2011; Sen, 2005). Ferrous ions rapidly oxidize into ferric ions which are insoluble at pH higher than 3 (Table 2.11). Manganese is slower to oxidise than ferrous, but precipitates in similar manner at pH higher than 11. Oxidized ions form agglomerates usually 0.2 to 20 μm in size. Precipitated floc or agglomerates are removed by sedimentation or filtration (Odell, 2010).

Obstacles in removing Fe and Mn occur when organic carbon is over 2 mg/L, and ammonia or hydrogen sulphide is present. Possible removing methods available for organically bounded Fe^{2+} and Mn^{2+} are chlorination, aeration and using potassium permanganate ($KMnO_4$) under controlled conditions of pH, dosage and detention time (Sommerfield, 1999). Overdosing with potassium permanganate can result in permanganate carry over giving pink water (Kohl, 2006).

Table 2-15 Amount of oxidant require and reaction time for iron and manganese removal (Odell, 2010)

Oxidant	Manganese		Iron	
	mg/L of Mn	Reaction time	mg/L of Fe	Reaction time
Oxygen	0.29	80 min to day	0.14	<1 min – 1hr
Chlorine	1.28	15 min – 12hr	0.63	< 1 min – 1hr
Ozone	0.67	< 5 min	0.43	<2 min
Potassium permanganate	1.92	<7 min	0.94	< 5min
Chlorine dioxide	2.4	< 5 min	1.2	< 5 min

.

2.8.1.1 Filtration

Once iron and manganese have been oxidized and precipitated into insoluble salts, concentrations of up to 5 mg/L can be removed using filtration while greater concentrations can be removed using clarification and settling (Barloková & Ilavský, 2010). MF and UF manufacturers supply membranes that can remove particulate form of metals ions and are easy to clean and backwash (Civardi, 2015). Pretreatment with MF is recommended (Kunikane *et al.*, 1995). Chemically coagulated water flowing through MF or UF causes fouling and requires pre-treatment methods to avoid fouling, but still the issue is not totally solved (Bagga *et al.*, 2008).

Metal removal can also be achieved using bio-filtration granular beds which are colonized with iron oxidizing bacteria (IOB) such as *Gallionella* or manganese oxidizing bacteria (MnOB) such as *Pseudomonas manganoxidans* (Civardi, 2015; Pacini *et al.*, 2005). If the water to be treated contains both iron and manganese it requires two stages of biological filtration because the conditions of biological oxidation are different for iron to manganese (pH and redox potential) (Tekerlekopoulou *et al.*, 2013).

Ion exchange is less practical for metals removal if iron and manganese is present in high concentrations. Another disadvantage is that iron or manganese can oxidize during the exchange process and block the ion exchange pores due to fouling (National Environmental Services Center (NESC), 1998).

Manganese and iron removal using green sand (zeolite) has been practiced for nearly a decade. This involves adding an oxidant (generally potassium permanganate) to green sand to coat it with an oxide that adsorbs dissolved forms of iron and manganese in flowing water that have been oxidized by potassium permanganate. Granular size of green sand is very small (smaller than silica sand); therefore the increasing head loss is a limiting factor for heavy loadings of metals (Schneider, 2016; Staff, 2009).

Comparison of different ion and manganese removal methods is shown in table 2.15.

Table 2-16 Advantages and drawbacks of different iron and manganese removal methods (Odell, 2010)

Method use	Advantages	Drawbacks
Aeration followed filtration	• No chemical involvement • Easy	• High capital cost • Low filter loading rates for effective removal • Cannot remove Manganese or ion complexes with organic material
Chlorination followed by filtration	• Easy to use chlorine because often present in treatment plants as disinfectant	• May require pH adjustment for manganese removal • Low filter loading for effective removal • High capital cost
Ozone followed by filtration	• Ozone is strong oxidant , therefore need less reaction time	• May oxidize manganese to permanganate • Difficult to operate • High capital, operation and maintenance cost
Biological filtration	• Easy to operate • Low operating cost	• Take start-up time initially and shutdown time • May require two separate removal stages for iron and manganese • High capital cost
Ion exchange	• Easy to operate	• Only effective with reduced forms of iron and manganese • No pre-oxidation is preferable • Taste removal is less
Membrane filtration	• Easy to operate • High loading rates	• May cause fouling • Chemical preoxidation should control carefully • High operating and capital costs

Lime softening	- Can effectively precipitate Iron and Manganese	- High operating and operating costs - High amount of sludge
Oxide coated sand filtration	- Easy to operate	- Efficiency depend on the type of coating, thickness and oxidation state - Moderate capital cost
Potassium permanganate followed by filtration	- Strong oxidant - Less reaction times	- If over fed may be result in pink, purple colour water - Cause staining if spills

2.8.1.2 DMI – 65

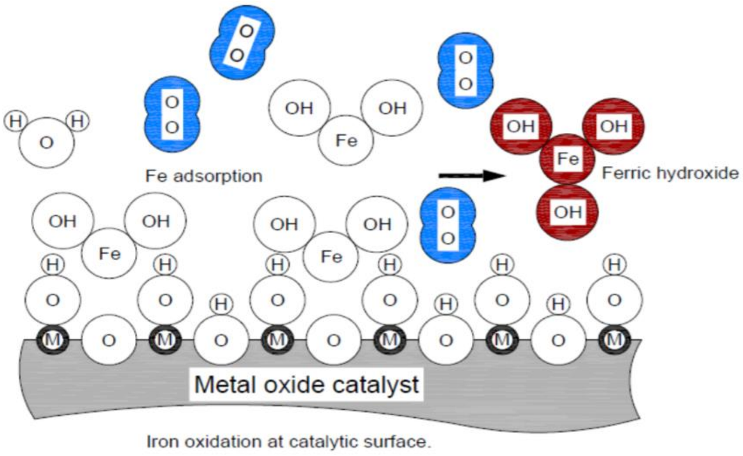
DMI-65 is a commercially available silica sand-based modified oxidation, filtration media that can be used to remove iron down to 0.005 ppm, manganese down to 0.001 ppm and arsenic in drinking water (ITOCHU Chemicals America Inc., n.d.). DMI-65 needs to be activated by an oxidant such as chlorine, and 0.1 – 0.3 ppm free chlorine concentration in the filter media should always be maintained. Usually the source of chlorine used as the activator is sodium hypochlorite (NaOCl) 12.5% since it is inexpensive, readily available and effective. Use of DMI 65 as a drinking water purification component has been certified in USA, Australia and England by corresponding water quality regulations (Quantum Filtration Medium Pty Ltd., n.d.).

Chemical, physical nature of DMI-65 and its operation conditions are listed in table 2.16.

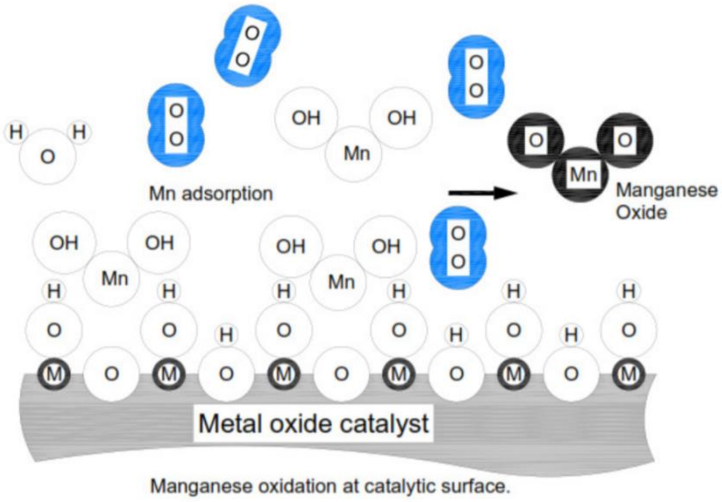
Table 2-17 Chemical composition, physical properties and operation conditions of DMI-65 (Quantum Filtration Medium Pty Ltd., 2010; Soon Ngai Engineering SDN BHD, n.d.)

Chemical composition	
Chemical components of DMI-65	Proportions
Quartz / Silicon Dioxide (SiO2)	> 90 %
Microcline (KAlSiO3O8)	< 9 %
Bixbyite (Mn2O3)	< 1 %
Calcite (CaCO3)	< 0.1 %
Physical properties	
Colour	Dark Black to Brown
Specific Gravity	1.46 g/cm^3
Effective Size	0.43mm
Porosity	45.8%
Solubility in water	Insoluble
Operation conditions	
Water pH range	5.8 – 8.6
Temperature	45°C (maximum)
Bed depth	600 mm (minimum)
Regeneration	Not required
Services Flow Rate	5 – 30 m^3 /m^2 per hr
Backwash Flow Rate	25 – 80 m^3 / m^2 per hr

DMI-65 oxidizes dissolved ferrous and manganese ions into insoluble ferric ions and manganese dioxide after they have been adsorbed on to the surface (Quantum Filtration Medium Pty Ltd., 2014) (figure 2.12). DMI–65 does not need strong oxidants, can be used at high flow rates, and no regeneration is required.



(a) Iron Oxidation at DMI-65 surface



(b) Manganese oxidation at DMI – 65 surface

Figure 2.11 Adsorption, Oxidation mechanism of iron and manganese by DMI-65

2.9 PEFT (Perforated Electrode Flow Through) cell

2.9.1 Electro-chlorination

In last few years electro-chemical technologies have been spread over variety of water treatment processes with the development of different electrode material and electro- chemical methods such as electro-chlorination, electro-dialysis and electro-coordination (Llanos *et al.*, 2014). Electro-chlorination is a relatively novel methodology used in water disinfection and purification processes. Oxidizing chloride ions in a salt solution to chlorine and production of hypochlorite by dissolving that chlorine in water is the principal behind the electro-chlorination. Applications in water and waste water treatments, swimming pools, ship ballast water and cooling water towers are becoming popular as it is cost effective and eliminate storing and handling of concentrated liquid chlorine or chlorine gas (Cha *et al.*, 2015). As previously discussed there are many disinfection methods currently use in water industry, out of those chemical chlorination is the majorly use pathogen removal method. Irregularity in chlorine dosage in water during the treatment causes taste and odor issues, DPB generation and negative impact on ecological environment. Most of these issues are avoided by electro-chlorination while providing effective disinfection against various microorganisms (Abderrahmane *et al.*, 2008). Indirect oxidation by electro-chlorination promotes oxidation of organic and inorganic pollutants the same as chemical chlorination does. Gas bubbles generated on the electrodes as byproducts of chlorine production carry oxidized suspended matter to the solution surface which can be easily separated as a foam (Khelifa *et al.*, 2013).

An ideal electrochemical cell contains separate cathode and anode chambers allowing selected ions in the salt solution to migrate from one to another. Sodium chloride (NaCl) and water mixture is introduced in to the anode chamber where oxidation of chloride ions happen and chlorine gas (Cl_2) is released. The positively charged sodium ions (Na^+) are attracted to the cathode end where water is reduced and hydrogen gas evolves. Excess hydroxide ions (OH^-) combine with sodium ions (Na^+) and form sodium hydroxide ($NaOH_{aq}$). There are three types of electro-chemical cells in practice; membrane cell, diaphragm cell and mercury cell (White *et al.*, 2010).

Chlorine generation system components such as electrodes, electrolyte, current and voltage supply are the significant factors deciding productivity of the system (Choi *et al.*, 2013). Current is supplied to cathode and anode to generate free chlorine from brine water (Ghernaout & Ghernaout, 2010). Large scale chlorination systems have adopted dimensionally stable anodes (DSA) such as ruthenium and iridium oxide-coated titanium because of their efficiency in chloride (Cl^-) oxidation. Platinum and doped diamond electrodes are used, but these electrodes are very expensive, contribute to higher capital cost. Some of the commercially available chlorine generators and their chlorine production are shown in table 2.17.

Table 2-18 Commercially available chlorine generators (Fujian Hada Intelligence Technology Co. Ltd., n.d.; MIOX Mixed Oxidant Solution (MOS), n.d.)

Chlorine generation system	Size /Application	Chlorine production	Current and voltage
Miniature integrated automatic sodium hypochlorite generator by Fujian Hada Intelligence Technology Co. Ltd.	small town water supply systems, small scale sewage treatment plants	20 g/hour to 150g/ hour at salt consumption of 3.5 kg salt/ kg FAC (Free Available Chlorine)	380VAC
MIOX Blackwater – mobile water treatment system		1000 mg/L at 1000 g/hour rate at salt consumption of 3.0 kg salt /kg FAC	250A 480VAC
OSEC B-Pack bipolar brine based hypochlorite generator	Municipal/ industrial chlorine generation drinking water disinfection	1250 – 28,333 g/hour	
OSEC low capacity bipolar hypochlorite generator	Municipal/ industrial drinking water disinfection	500 – 2000 g/hour	

Several studies have been carried out to investigate graphite or doped carbon based materials as electrodes (Saha & Gupta, 2017). Nath (Nath *et al.*, 2011) used 2.5 mm thick perforated graphite disk as anode material and stainless steel as cathode material in PEFT cell (figure 2.13). Graphite is robust, has good electrical properties, low cost, resistance to oxidation and safe to use in drinking water chlorination. The cathode and anode were separated by a thin insulating layer between them. New 3D printed PEFT cell consist graphite as both cathode and anode material. Graphite disks use in the modified PEFT cell is in 11.9cm diameter and 111.27 cm^2 area. Disks are assembled in a chamber where untreated water enters through the bottom, through the perforated electrodes, and chlorinated water exits through the top.

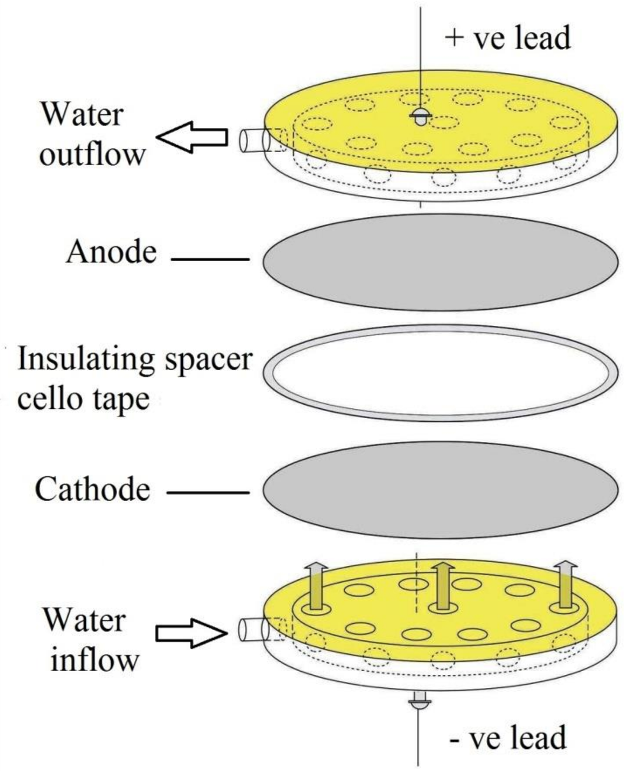


Figure 2.12 Schematic of existing PEFT cell

2.9.2 Voltage and Current

The free ions liberated at an electrode is directly proportional to the current passed through the salt solution (White *et al.*, 2010). Electrolysis of NaCl solution flowing through PEFT cell will generate chlorine at the anode (Mukherjee *et al.*, 2010).

$$Cl_2 + 2e \longrightarrow 2\,Cl^- \quad (E_{0anode} = +1.36\ V) \qquad \text{Equation 13}$$

$$2H_2O + 2e \longrightarrow H_2 + 2OH^- \quad (E_{0cathode} = -0.83\ V) \qquad \text{Equation 14}$$

The amount of chlorine produced is given by (Mukherjee *et al.*, 2010):

$$W = \frac{(I\ e\ t)}{F} \qquad \text{Equation 15}$$

W= amount of chlorine produced (g)
I = current passed through the cell (A)
t = time (s)
e = molecular weight of Cl (35.45 g/mol)
F = faraday constant (96500 C/mol)

The resistivity (ρ) of a material is defined as the ratio between the electric field (E) and current density (J) at that point (Halliday, 2001).

$$\rho = E/J \qquad \text{Equation 16}$$

Current density (J) can be defined as electric current (I) flowing through a cross sectional area (A) of a particular material.

$$J = I/A \qquad \text{Equation 17}$$

Electric field (E) is potential difference (V) between an object with L length or thickness.

$$E = V/L \qquad \text{Equation 18}$$

Substituting equation 17 by equation 18 and 19,

$$\rho = \frac{V/L}{I/A}$$

$$\rho = \frac{VA}{IL} \qquad \text{Equation 19}$$

Rearranging equation 20,

$$I = \frac{VA}{L\,\rho} \qquad \text{Equation 20}$$

Current (I) passing through the PEFT cell directly proportional to potential difference/Voltage (V) and cross sectional area of water volume inside the cell (A); inversely proportional to thickness/ high of water in the cell (L) and resistivity of water (ρ).

Conductivity (σ) of a material is defined as inversion of resistivity (ρ).

$\sigma = 1/\rho$ Equation 21

Water and NaCl solution are the conducting media in PEFT cell since resistivity of graphite is very high (~ 10^{16} Ωm). Water flowing through the PEFT cell always acquires shape of the 3-D printed chamber cavity, therefore the dimensions of cavity deicide A and L.

2.9.3 PEFT cell for disinfection and iron and manganese removal

Electro-chlorination is capable of disrupting microorganisms including viruses, bacteria and algae. A combination of an electro-chlorinating cell and granular activated carbon resulted in greater than 99.98% of E.coli cell removal (Hussain *et al.*, 2014). E.coli killing efficiency of 99.9% and even higher has been reported using electro-chlorinating cells with for contact times less than 10 seconds (Li *et al.*, 2004). The PEFT cell as a chlorine generator and disinfection was tested under NaCl concentrations of 0.1mol/L, 0.5 mol/L and 1 mol/L, achieving a total microbial inactivation of 6.6 log (Nath *et al.*, 2011).

Existing PEFT cell was successfully used for iron and manganese removal, achieving 99% instantaneous iron oxidation at 3 g/L of NaCl and electrolytic conditions of 5A, 6.1V, and a flow rate of 190 mL/min. Iron and manganese levels in treated water were 0.3 mg/L and 0.5 mg/L respectively, but not quite reaching the New Zealand drinking water standards of 0.2 mg/L and 0.04mg/L respectively (Nath *et al.*, 2011).

2.10 Conclusion

Structural deficiencies such as leakage, could only be operated in series and not able to achive New Zealand drinking water standards requirements in iron and manganese removal are the issues associating existing PEFT cell. Aim of the research is to modify PEFT cell and examine chlorine production, disinfection ability of modified PEFT cell and iron, manganese removable efficiency with coupling DMI65. New 3D printed PEFT cell with parallel cell component assembly will be tested.

3 Methodology

A new PEFT system was designed and fabricated by 3D printing that allowed the system to be operated in parallel enabling greater throughput. The aim of this research using the new system is to:

- Assess the effect of current and voltage for chlorine production
- Assess optimum salt concentration and flow rate of brine water (NaCl solution)
- Assess the disinfection properties on solutions containing E – coli
- Assess the ability to remove iron and manganese dissolved in water by combining the PEFT cell with a DMI65 column.

3.1 Materials

Materials used in this research included:

Sodium chloride, food grade (Science Stores, University of Waikato)
Sodium hypochlorite (Science Stores, University of Waikato)
Manganese sulphate, reagent grade (Sigma Aldrich)
Ferrous sulphate, reagent grade (Sigma Aldrich)
Palintest reagents for free chlorine, total chlorine, chloride, manganese and iron (Davey Watercare Products, New Zealand)
DMI-65 media (Taylor Purification, New Zealand)
E-coli containing water – University of Waikato lakes
Coliform blue test reagents and kit (Hach, New Zealand)
Distilled water (University of Waikato)

3.2 Equipment

PEFT cell and electrodes (University of Waikato)
Peristaltic pump (type and supplier)
12 mm diameter PVC tubing (University of Waikato)
12 mm brass hose fittings (Industrial Wholesale Supplies, Hamilton, New Zealand)
Power supply (10V, 30 amp)
Palintest photometer (Davey Watercare Products)
Glassware, measuring cylinders, buckets and stop watches (University of Waikato)

Outer appearance of new 3D printed PEFT cell and schematic of electrode arrangement and water flow is shown in figure 3.1 and figure 3.2 respectively.

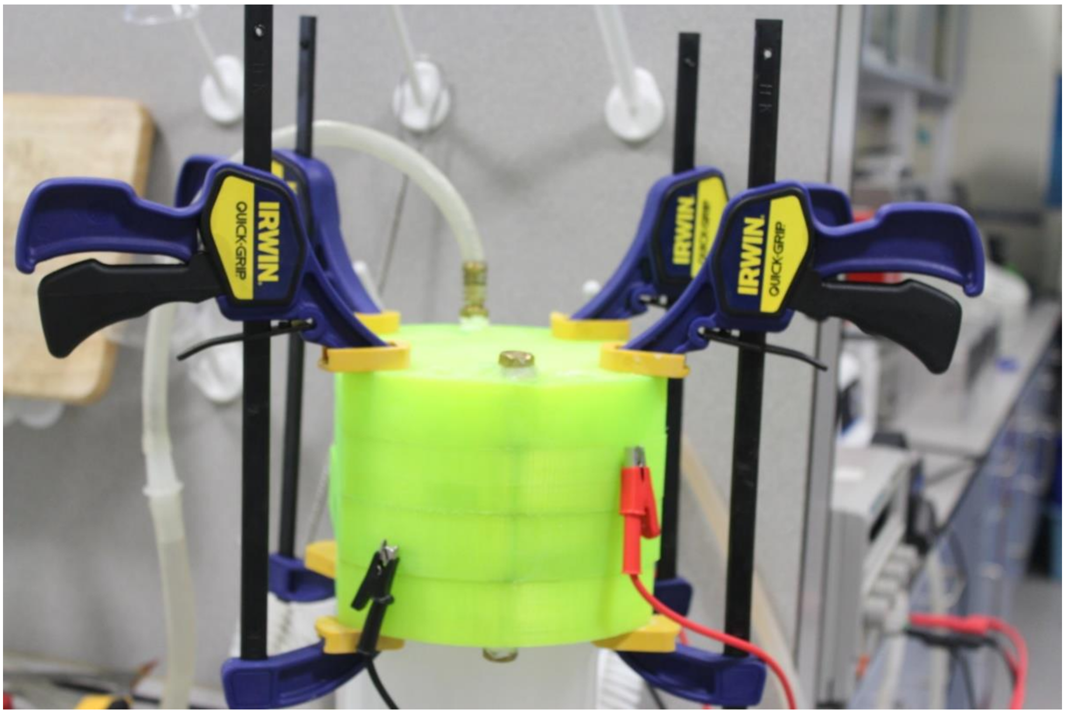


Figure 3.1 New 3D printed PEFT cell

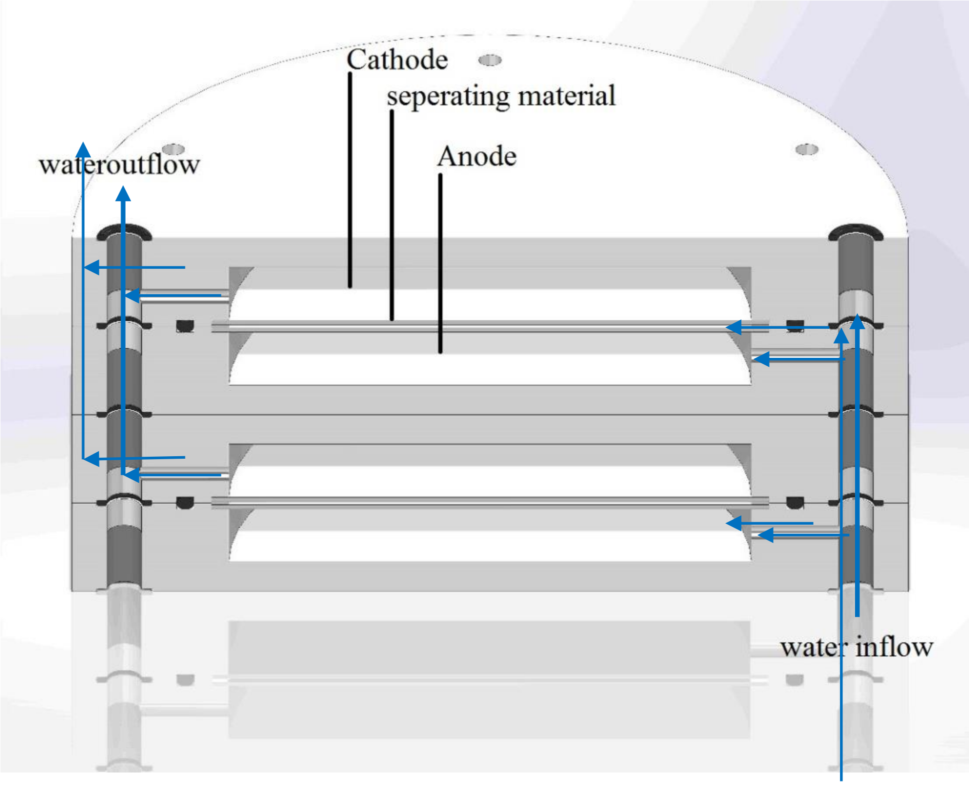


Figure 3.2 Schematic of new 3D printed PEFT cell

3.2.1 Palintest Photometer

The Palintest Photometer 7100 (Table 3.1) was used to measure total chlorine, free chlorine, iron and manganese concentrations in water

Table 3-1 Palintest photometer operating information

Optical source	Dual LED sources with optical filters
Optical detectors	Silicon photodiodes
Wave lengths	450nm, 500nm, 550nm, 570nm, 600nm, 650nm
Wave length selection *Photometer*	Automatic
Result units	g/l, mg/l, ppm, mmol/l, μmol/l, μg/l, ppb
Maximum reading	5 mg/l
Test cuvettes	12 – 20mm OD with automatic cuvette centering

3.2.1.1 Calibration

The Palintest Photometer 7100 was calibrated using sodium hypochlorite (NaClO) which decomposes into chloride ions which is palintest photometer measures as free chlorine. Sodium hypochlorite 12.5 W/V % was used as the stock solution to prepare the diluted samples for calibration.

3.2.1.2 Test for free chlorine

The DPD (diethyl-p-phenylene diamine) method was used in the Palintest Photometer to analyze free chlorine, which results in a pink colour. The Photometer was blanked using distilled water. A DPD1 tablet was crushed and dissolved in 10 ml of sample, the colour was allowed to form and measured in the Photometer (Palintest, n.d.-a).

3.2.1.3 Test for Iron

The ferrous form of iron is allowed to react with 1,10 – phenanthroline (Iron MR NO1 and Iron MR NO2 tablets which are crushed in 10 ml of solution) which forms an orange coloured complex. The colour intensity is proportional to ferrous ions present in the solution (Palintest, n.d.-b).

3.2.1.4 Test for Manganese

Manganese present in the sample is first oxidized into permanganate state by an oxidixing agent (Manganese NO1 tablet which is crushed in 10 ml of solution). Oxidized manganese is allowed to react with leucomalachite green (Manganese NO2 tablet which also added and crushed) over 20 minutes to form a turquoise coloured complex where total manganese concentration is proportional to colour intensity (Palintest, n.d.-c)

3.3 PEFT cell operation

Five different flow rates settings on the peristaltic pump were selected to pump water in to the PEFT cell. They were simply identified as 50, 100, 150, 200 and 250 as displayed on the water pumping machine. Actual flow rates were obtained by measuring the time taken fill a 1000ml measuring cylinder and flowrate calculated by:

$$\text{Flow rate} = \frac{\text{Water volume}}{\text{Time}} \qquad \text{Equation 22}$$

Resulting flowrates are given in Table 3.2.

Table 3-2 Flow rates

Pump reading	Water volume measured (ml)	Time measured (seconds)	Flow rate (ml/seconds)
50	1000	555	1.80
100	1000	253	3.95
150	1000	172	5.81
200	1000	135	7.41
250	1000	83	12.05

3.4 Optimum current, voltage and salt (NaCl) concentration for maximum chlorine production

Free chlorine generation was measured in the PEFT at the five different flowrates measured previously, at voltages of 2, 2.5, 3, 3.5, 4, 4.5 and 5 volts and three different NaCl concentrations. NaCl solutions were prepared at 0.01 mol/L (0.5844 g/L), 0.05 mol/L (2.922g/L) and 0.1 mol/L (5.844 g/L) concentrations. For each run, the PEFT cell was allowed 3 minutes to reach steady state after a variable was changed, then electric current was measured and sample collected for measuring free chlorine. A total of 105 measurements of chlorine generation were taken.

3.5 Assess disinfection properties by e – coli counting

Disinfection properties of the PEFT cell were using E-coli bacteria in University lake water. Salt was made up to the concentrations by dissolving NaCl in the lake water at 0.01 mol/L (0.5844 g/L), 0.05 mol/L (2.922g/L) and 0.1 mol/L (5.844 g/L) concentrations. The same procedure was followed as in the previous section, but samples for E-coli testing were collected in sterilized glassware.

3.5.1 Testing for e – coli

A suction apparatus shown in figure 3.3 was set up. It consisted of a conical flask attached to a vacuum line, rubber stopper, and sterilized plastic Buchner funnel placed on the stopper. Inside the Buchner funnel cup a sterilized Whatman glass microfiber GF/A 47 mm filter paper was placed flat and on top of it was placed a sterile Millipore HAWG047S6, 0.45μm, 47mm membrane. Each sample (including an untreated sample) was suction filtered through the membrane. After the filtration, the membrane was removed using sterile forceps and placed in a sterile PALL petri dish with a 50 mm diameter absorbent pad. E–coli growing media (m–ColiBlue 24) was added on top of the membrane, the petri dish covered and incubated for 48 hours at 32 °C. After 48 hours E–coli colonies grown on the membrane were counted. All equipment was either sterile packed as supplied, sterilized using an autoclave, or sterilized using 70% ethanol solution.

Figure 3.3 Suction apparatus

3.6 Coupling DMI-65 with the PEFT cell to remove iron and manganese

DMI-65 media was soaked in sodium hypochlorite 12.5% w/v for 3 days to activate it. This was then washed with water to remove excess chlorine. A DMI-65 column of about 6 cm height was constructed using a glass tube with a sintered glass base (Figure 3.4). Water was allowed to flush through the column until the free chlorine was below 0.03 mg/L. Then PEFT cell water outlet was then connected to DMI-65 column inlet.

A synthetic bore water containing 20 mg/ml iron (ferrous sulphate) and manganese (manganese sulphate) was prepared. NaCl was added to the synthetic bore water at concentrations of 0.5844g/L, 2.922g/L and 5.844g/L. Following the same procedure in section 3.4, solutions were passed through the PEFT cell and then through the DMI-65 column straightaway. Treated water from the DMI-65 column outlet was collected in beakers and residual iron and manganese concentrations were measured.

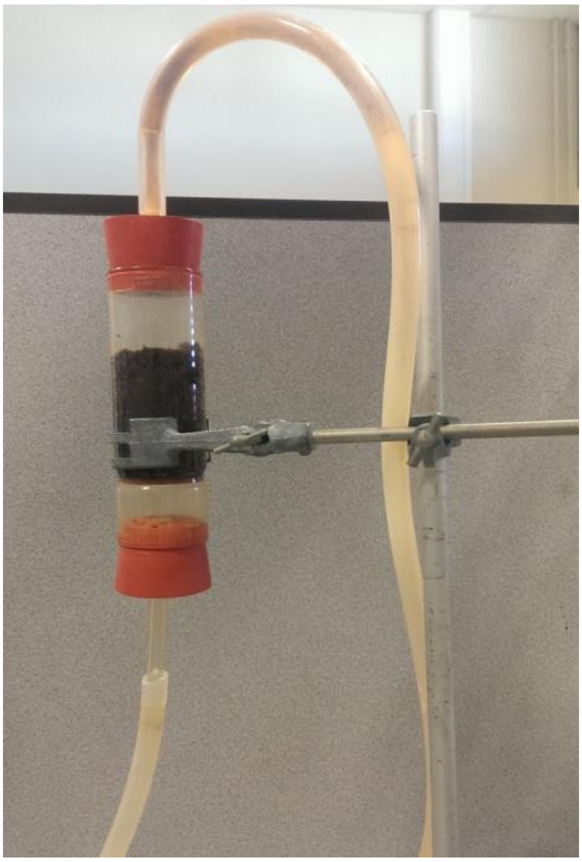


Figure 3.4 DMI-65 column

4 Results and Discussion

The aim of this research using the new PEFT system was to:

- Assess the effect of current and voltage for chlorine production
- Assess optimum salt concentration and flowrate of brine water (NaCl solution)
- Assess the disinfection properties on solutions containing E – coli
- Assess the ability to remove iron and manganese dissolved in water by combining the PEFT cell with a DMI65 column.

Results obtained from experiment will be presented in this chapter and discussed.

4.1.1 Optimum current, voltage and Salt (NaCl) concentration

Data collected for each NaCl concentrations (0.01 mol, 0.05 mol/L and 0.1 mol/L), different flow rates (1.80 ml/sec, 3.95 ml/sec, 5.81 ml/sec, 7.41 ml/sec and 12.05 ml/sec) and voltages of 2, 2.5, 3, 3.5, 4, 4.5 and 5V are presented in this section.

No current flow through the PEFT cell was observed for voltages less than 2 volts, due to the resistance of the solution between the electrodes (Figure 4.1, 4.2 and 4.3). PEFT cell current increased almost linearly in the range of 3.5 to 5 volts to 10-12 amps, and showed some slight variability with change in flow rate with higher flow rates showing slightly less current flow. Current density (amps divided by electrode area – 222.4 cm^2) was between 36.9 to 48 mA/cm^2 at 5 volts. Nath (Nath, 2011)achieved a current density of 80 mA/cm^2 at 5.5 volts and 100 mg/L NaCl concentration. Changing salt concentration did not appear to have a significant effect on current flow, which was unusual, but could be because the electrode gap was small enough (~50-100 μm) that there was not sufficient change in resistance for the effect to be observed.

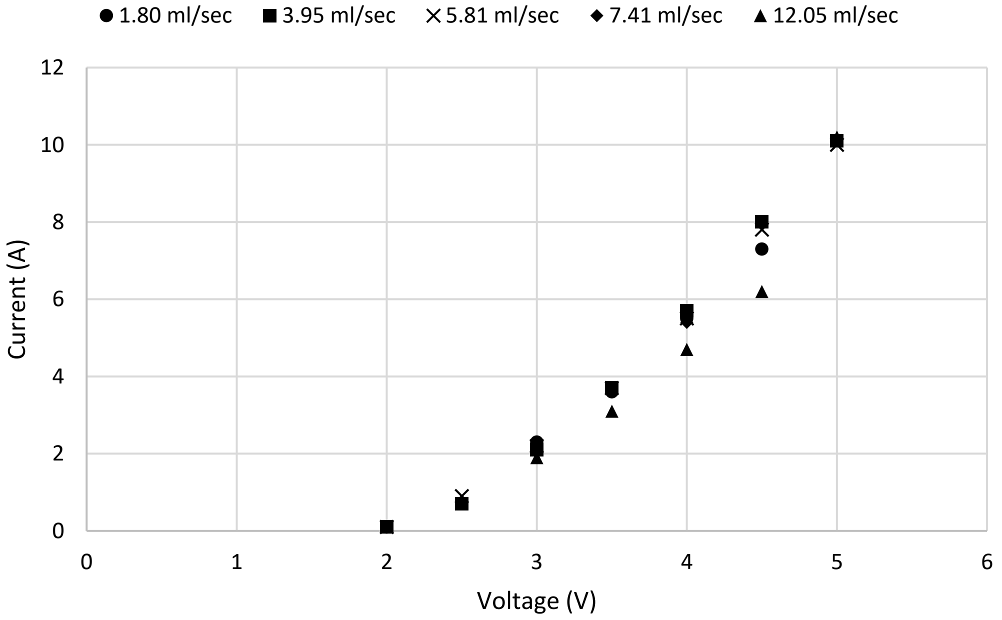


Figure 4.1 PEFT current vs voltage for 0.01 mol/L salt concentration

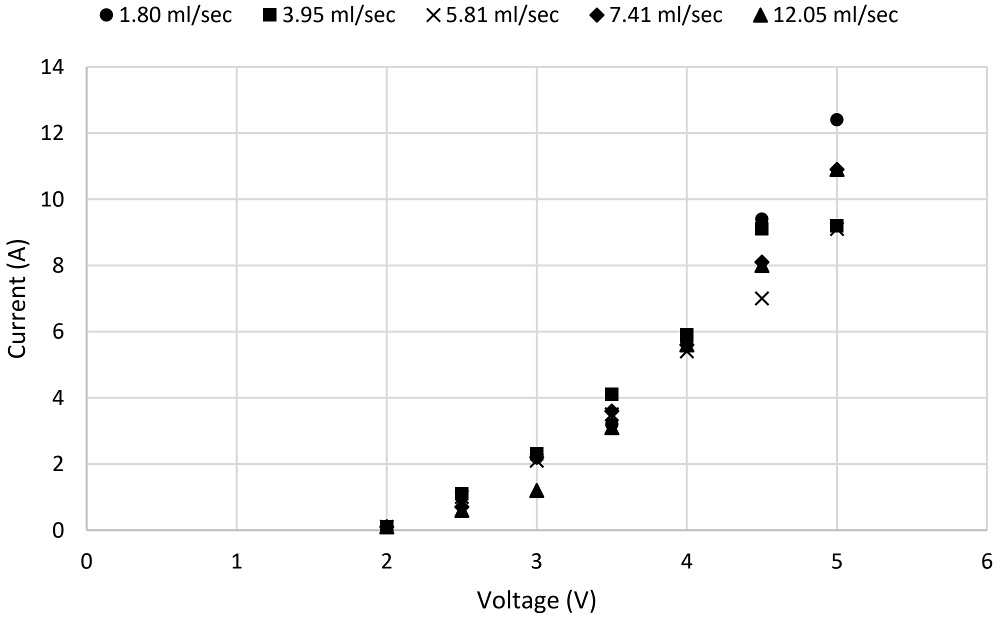


Figure 4.2 PEFT current vs voltage for 0.05 mol/L salt concentration

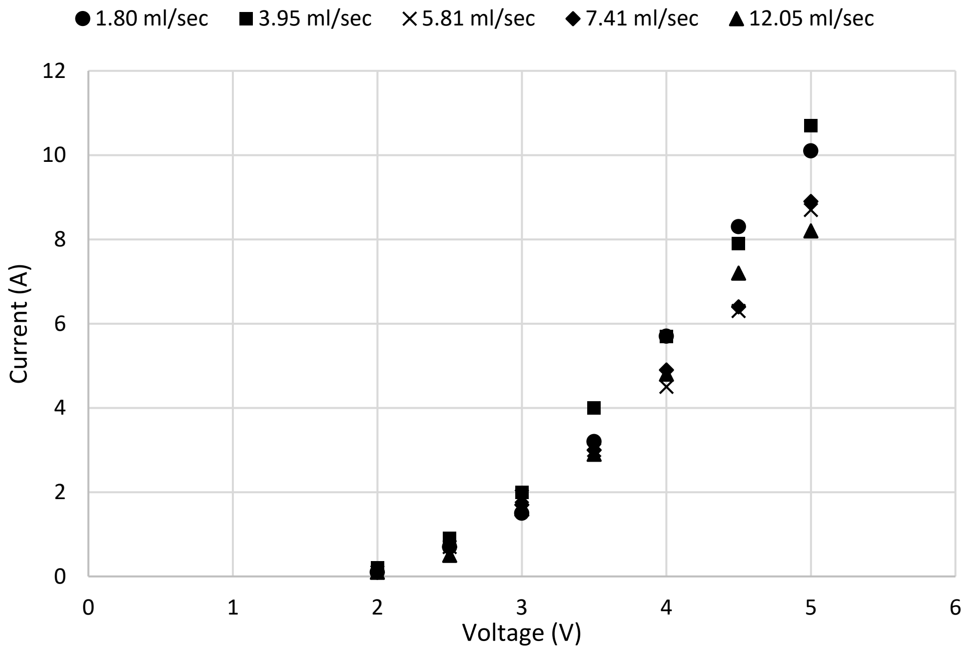


Figure 4.3 PEFT current vs voltage for 0.1 mol/L salt concentration

As current increased, free chlorine concentration increased, but as flowrate increased, free chlorine concentration decreased (figure 4.4, 4.5, 4.6). The increase in free chlorine concentration was not linear as the gradient of the increase decreased with increasing current, except for the highest starting salt concentration where the increase was linear. This suggested NaCl concentration was a limiting factor in chlorine production (Bishop, 2007). Increasing starting NaCl concentration increased free chlorine concentration. The lowest NaCl concentration of 0.01 mol/L (0.5844 g/L), at the lowest flow rate of 1.80 ml/sec and highest voltage and current (5V, 10A) produced 140 mg/L free chlorine. Increasing starting salt concentration to 0.05 mol/L (2.922g/L) increased chlorine concentration to 300 mg/L at 1.80 ml/sec flow rate.

The three different NaCl concentrations used in the experiments were 0.01 mol/L (0.5844g/L), 0.05 mol/L(2.922g/L) and 0.1 mol/L (5.844g/L). For the same flow rate, free chlorine production against current/voltage over three different NaCl concentrations were plotted to analyze the effect of NaCl concentration on free chlorine production. Generally with increasing NaCl concentration free chlorine production should be increasing. In figure 4.7, at 1.80 ml/sec flow rate indicates higher free chlorine production at higher NaCl concentration as expected. But at the higher flow rates NaCl concentration of 0.1 mol/L shows lower free chlorine production compared to 0.05 mol/L at some points (Figure 4.8, 4.9,4.10,4.11).

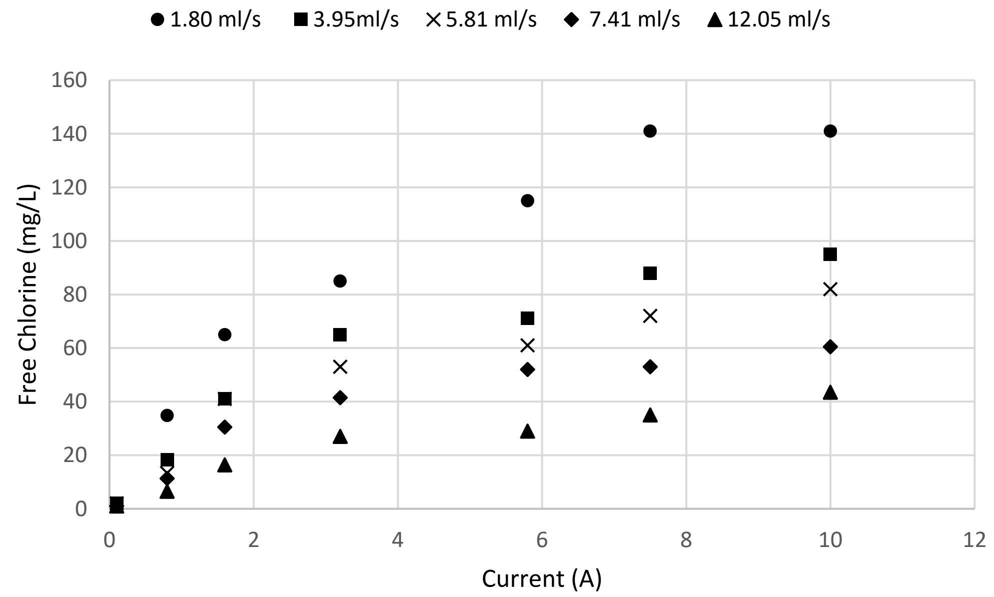


Figure 4.4 Comparison of free chlorine production at 0.01 mol/L (0.5844g/L) NaCl concentration under different flow rates

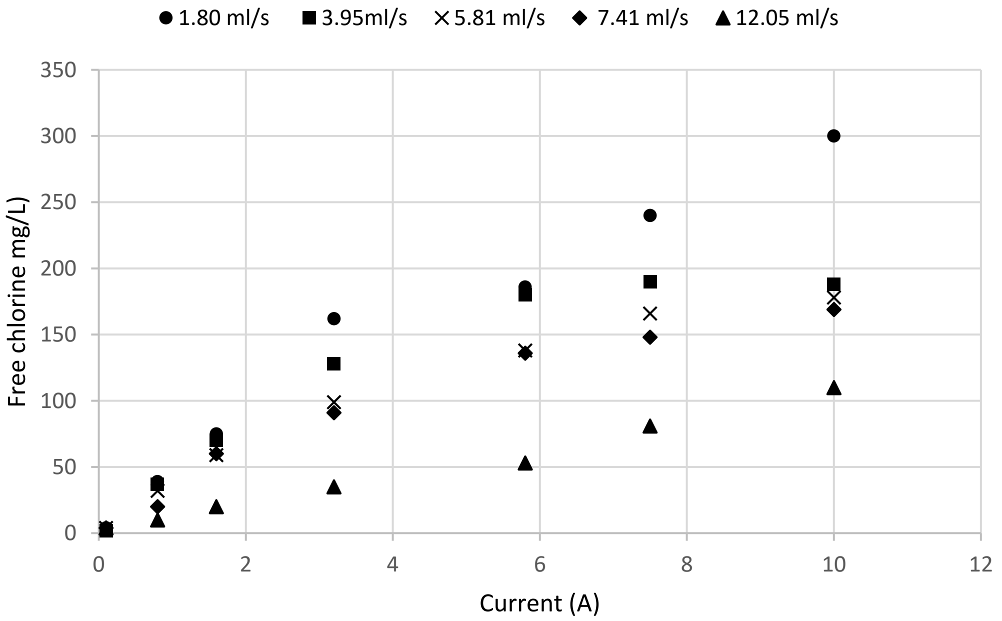


Figure 4.5 Comparison of free chlorine production at 0.05 mol/L (2.922g/L) NaCl concentration under different flow rates

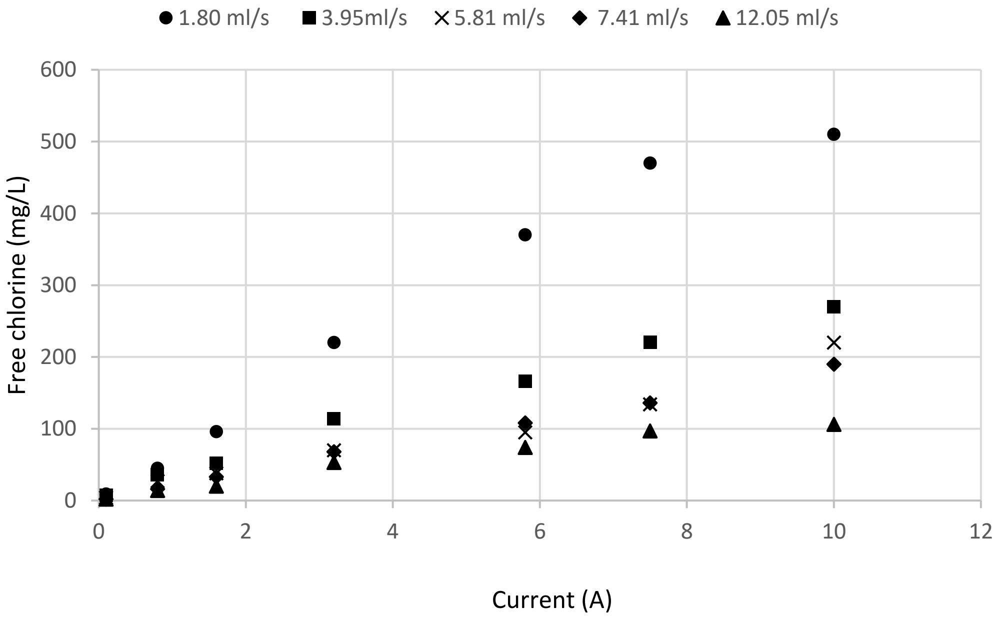


Figure 4.6 Comparison of free chlorine production at 0.1 mol/L (5.844g/L) NaCl concentration under different flow rates

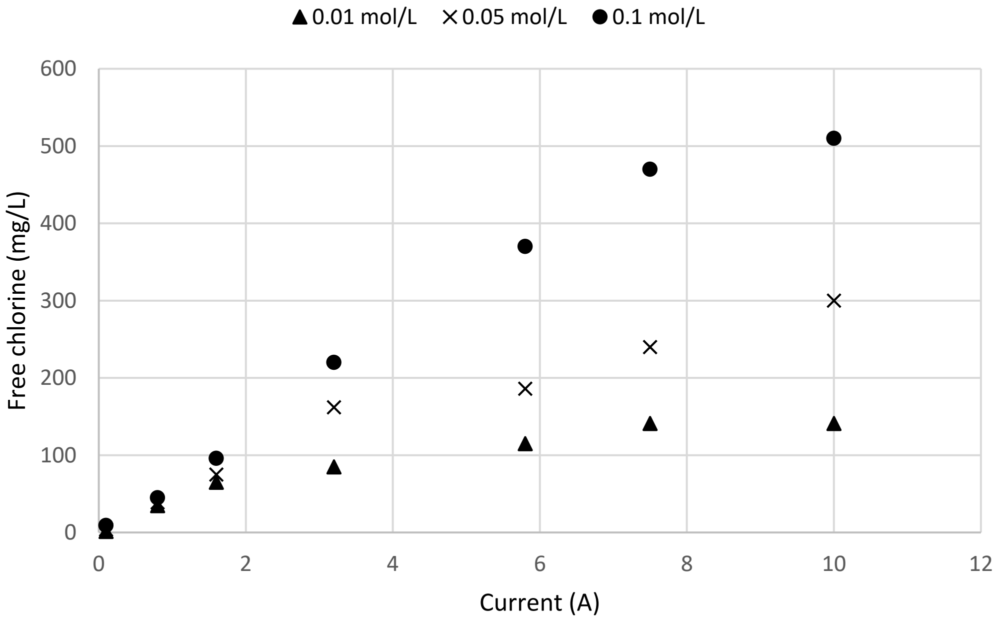


Figure 4.7 Comparison of free chlorine production with current at different NaCl concentrations at 1.80 ml/sec flow rate

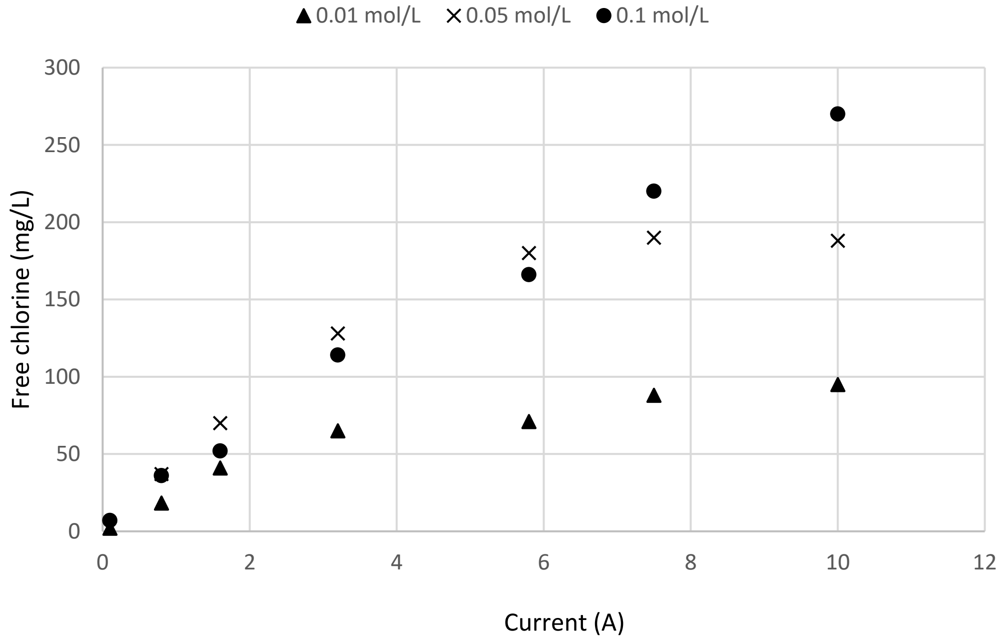


Figure 4.8 Comparison of free chlorine production with current at different NaCl concentrations at 3.95 ml/sec

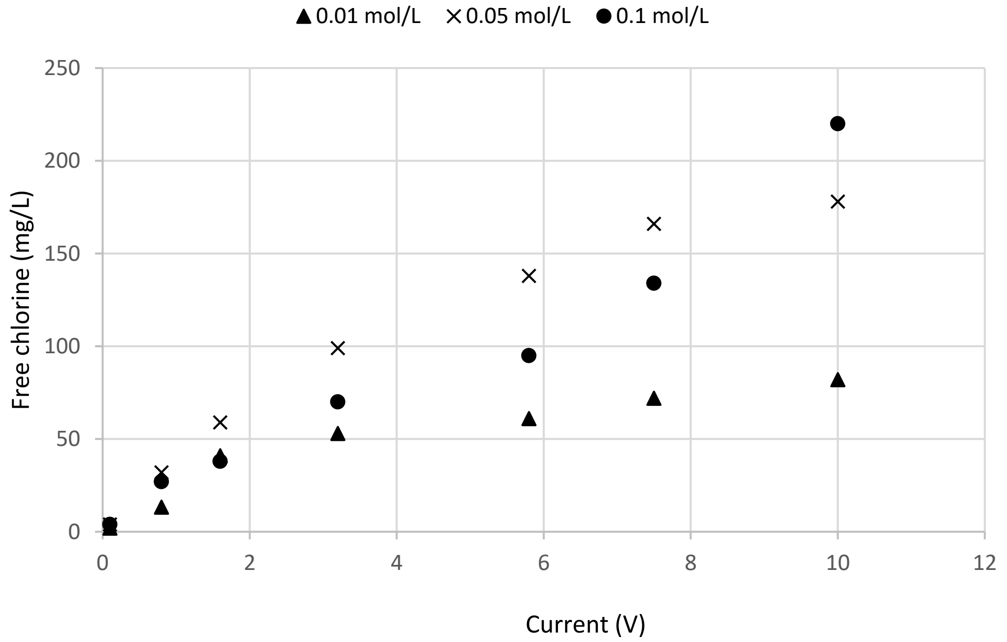


Figure 4.9 Comparison of free chlorine production with current at different NaCl concentrations at 5.81 ml/sec

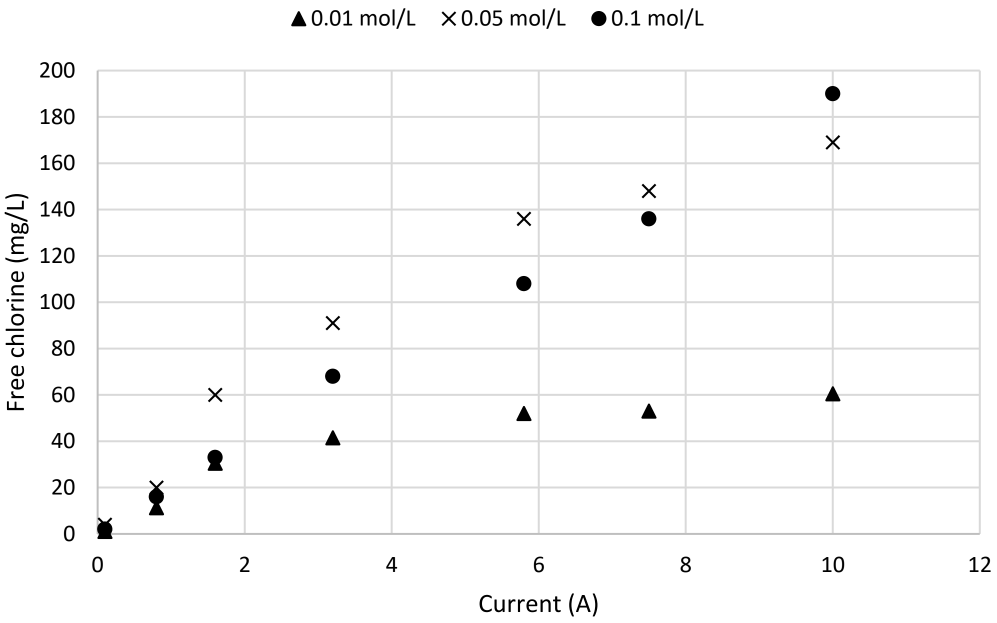


Figure 4.10 Comparison of free chlorine production with current at different NaCl concentrations at 7.41 ml/sec flow rate

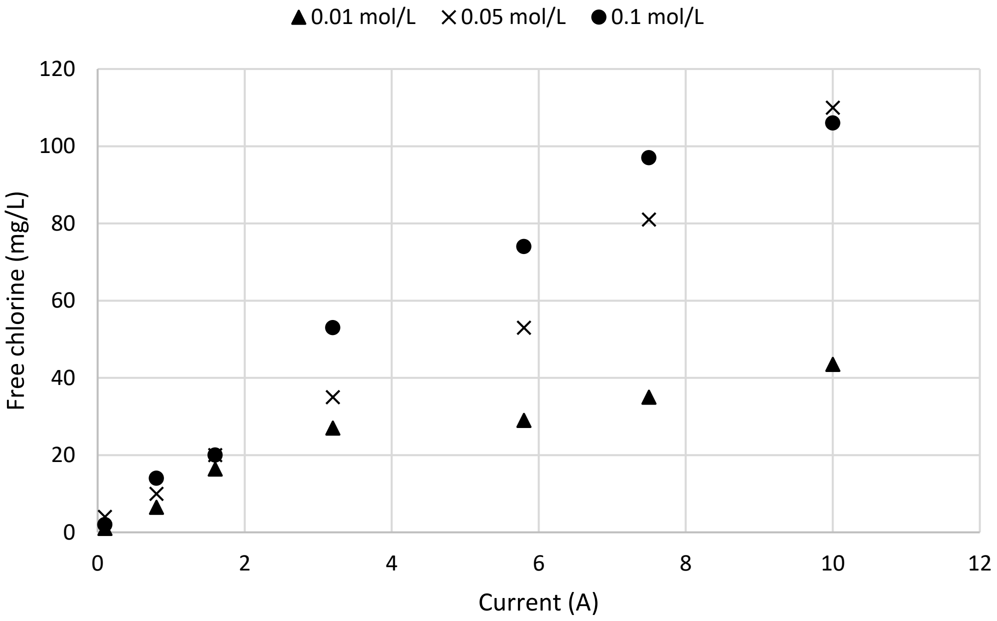


Figure 4.11 Comparison of free chlorine production with current at different NaCl concentrations at 12.05 ml/sec flow rate

Iron rust was observed coming out with the outflow water for some trials. The problem was identified for the 0.1 mol/L, 3.95 ml/sec flow rate trial. The PEFT cell was opened to find corrosion occurring on the conducting metal rings in contact with the PEFT cell electrodes and the screw holding the metal ring in place (Figure 4.12).

Figure 4.12 Corrosions inside the PEFT cell

Corrosion (rusting) is the redox reaction of iron (Fe) oxidizes in to Fe^{2+}, Fe^{+3} ions (Equation 24) in the presence of water and oxygen.

$$4\ Fe + 3O_2 + 6H_2O \longrightarrow 4\ Fe(OH)_3 \qquad \text{Equation 23}$$

In any redox reaction electrons are transferred from one molecule/atom to another. In corrosion Fe atoms release electrons to oxygen molecules. In the presence of any salts, the mechanism is faster due to salt ions increasing conductivity of the water (Chemistry Stack Exchange Inc., n.d.; Seri, 1994).

Electrodes were taken and placed in a beaker containing NaCl solution and power was supplied to the electrodes. Both set of electrodes were producing gas bubbles (H_2 and Cl_2 gases) which signaled there was no problem with current flowing through the cells, but the NaCl solution in the beaker turned a yellow colour after some time. This could be due to iron oxide, but the yellow colour suggested it could be ferric chloride due to a portion of chlorine produced reacting with iron to produce ferric ions (Fe^{3+}) to make ferric chloride ($FeCl_3$) which is yellow in colour (MEL Practicum, 2015) (figure 4.13). Therefore a fraction of chlorine produced is consumed by ferric ions and does not contribute to producing hypochlorite (thus free chlorine).

Figure 4.13 Yellowish color solution resulted in after current flowed through electrodes

Metal rings were replaced with small but thicker stainless steel plates (Figure 4.14). Electrodes were thoroughly washed but still corroded iron merged in to graphite surface of electrodes was seen.

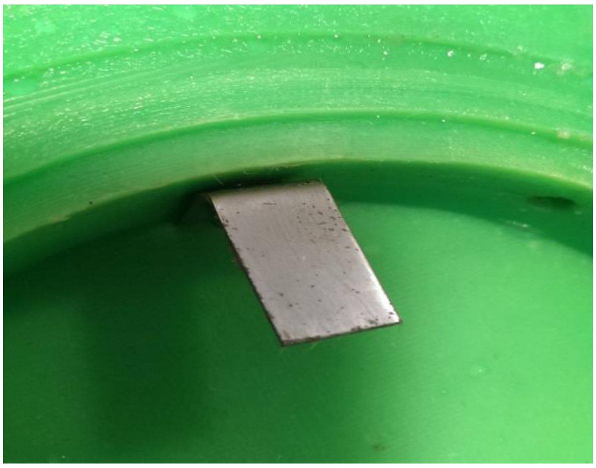


Figure 4.14 Replaced small metal plates

During the PEFT cell trials, NaCl concentration that flowed through the PEFT cell was 0.01 mol/L (0.5844g/L), 0.05 mol/L (2.922g/L) and finally 0.1 mol/L (5.844g/L). At the beginning of the trials the PEFT cell electrodes were unaffected by the salt concentration and chlorine generation. But at the higher salt concentrations (0.05mol/L and 0.1 mol/L) the conducting metal rings in contact with the electrodes were corroded and the surface of the PEFT cell electrodes were damaged with visible surface pitting. This impacted on chlorine production which was a reason why some of the trials using 0.1 mol/L NaCl concentration gave lower chlorine production compared to 0.05mol/L at some points.

Using the maximum chlorine production at 10 amps, chlorine production rate was calculated by multiplying chlorine concentration by flowrate to get mg/s and dividing by 10 amps to get mg/s.amp (Figure 4.15). At 0.1 mol/L NaCl concentration, chlorine production rate peaked at 0.14 mg/s.amp, and decreased with decreasing salt concentration. It was difficult to compare how this system performed compared to commercial systems due to the lack of information, specifically how much amps the commercial systems were drawing.

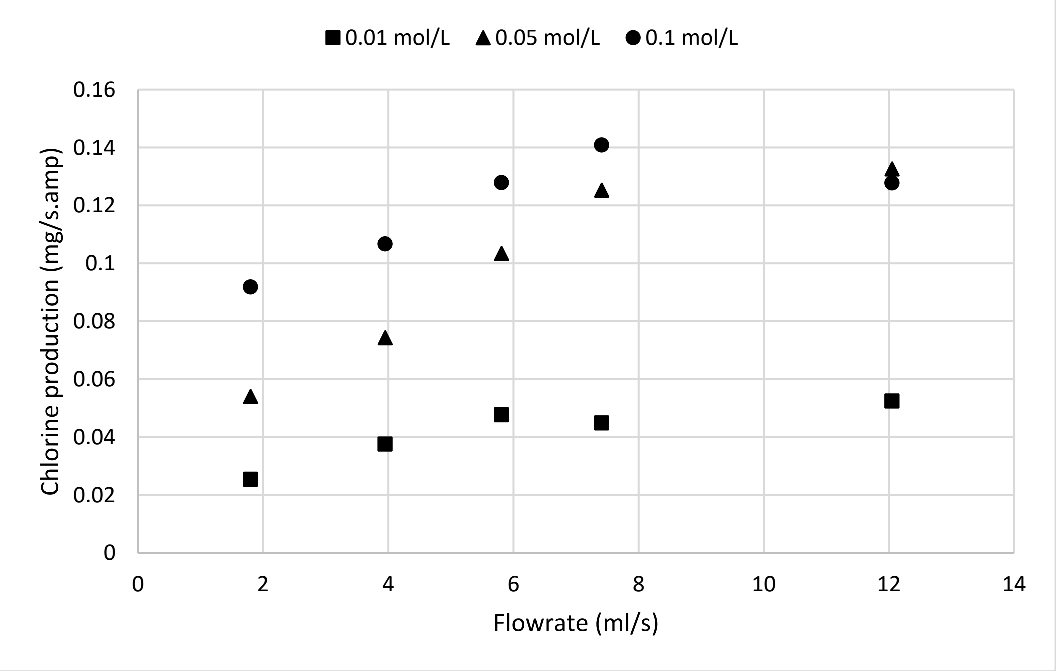


Figure 4.15 Chlorine production rate at the different NaCl concentrations and flowrates.

4.1.1.1 Short circuiting

One major obstruction faced in the experiments was short circuiting. Under normal conditions current flows through the system is at a certain voltage that does not damage the system, e.g. 10 amps at 5 volts. Excess current flow and low resistance is called short – circuiting (Mathur *et al.*, 2015), and resulted in overheating of the electrodes and cables, which also resulted in damaging the PEFT chamber (figure 4.16). The separating cello-tape material between the electrodes was too thin and allowed short circuiting in some instances. This was replaced with thicker material which increased the gap and reduced short circuiting.

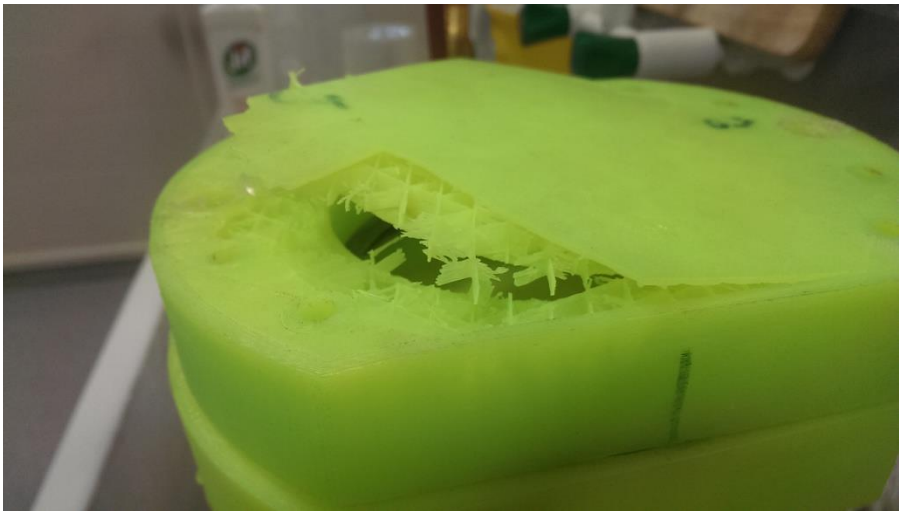


Figure 4.16 Damaged PEFT cell chamber due to short- circuiting

The other noticeable issue was waster leakage from the interspaces between assembled cell components. To minimize leakage silica gel was applied to the o-rings sealing between parts. Situation was able to control, but not guaranteed as a permanent solution. This was because the surfaces of the 3D printed parts were not smooth. Therefore future versions would need to be sanded smooth before attempting to seal the parts.

4.1.2 PEFT disinfection properties

Lake water containing E-coli was diluted to 10% and 50% using distilled water before testing for E-coli to determine a suitable dilution at which there would be sufficient colonies to easily count. The 50% dilution gave 338 E–coli colonies while the 10% dilution colony count was too low to use (Figure 4.17).

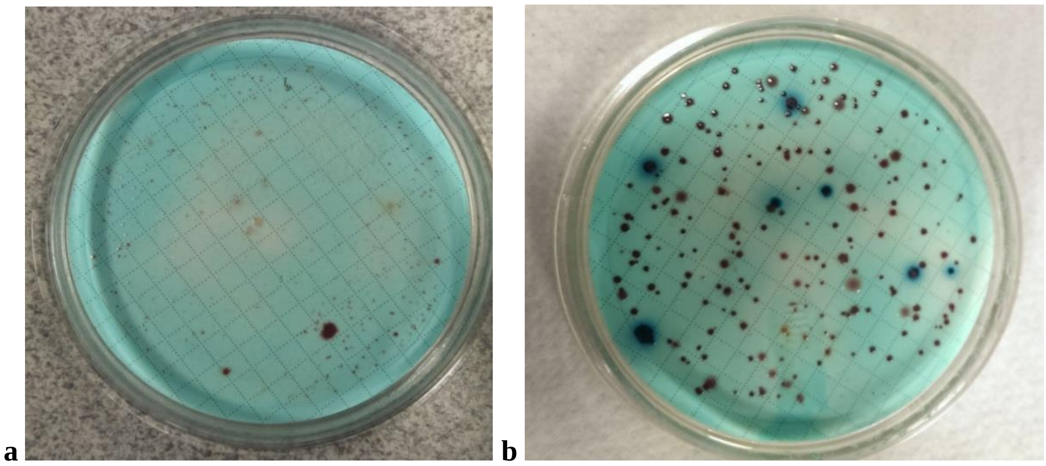


Figure 4.17 E-coli in untreated lake water samples a) 50% dilution b) 10% dilution

NaCl was added to the 50% diluted lake water to concentrations of 0.01 mol/L, 0.05 mol/L and 0.1 mol/L and passed through the PEFT cell. Even for the lowest NaCl concentration used, all the E–coli bacteria were killed. Not a single colony was found in any of the cultures (Figure 4.18).

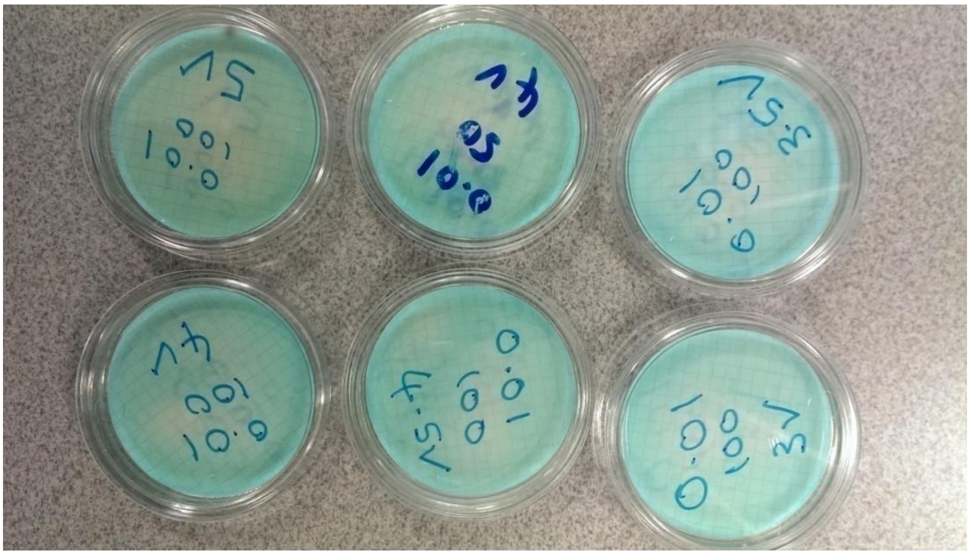
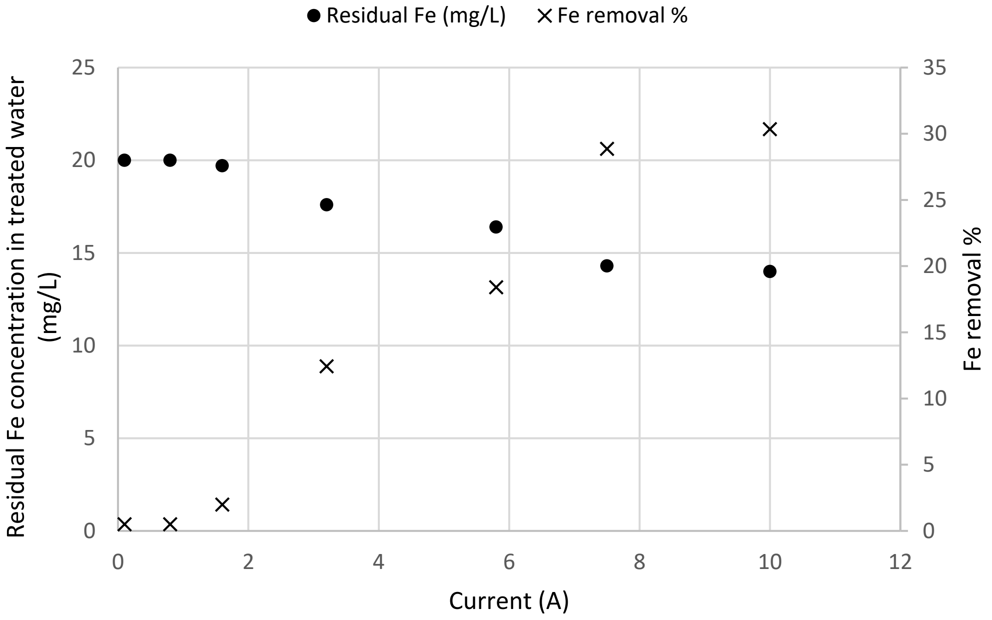


Figure 4.18 E-coli testing for treated lake water

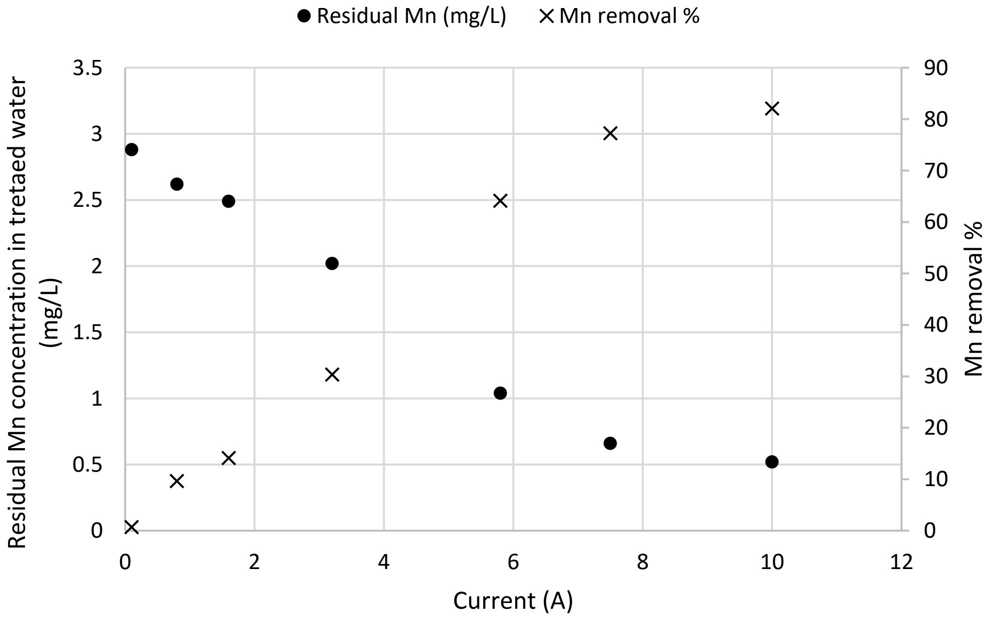
At 0.01 mol/L (0.5844g/L) NaCl and 12.05 ml/sec flow rate the observed free chlorine production was 1.05 mg/L, which was capable of delivering total microbial inactivation. Nath (Nath, 2011) achieved total microbial inactivation at 0.1g/L NaCl concentration, 3.16 ml/sec flow rate, and 80 mA/cm^2 current density using a PEFT cell made of stainless steel and graphite electrodes. While the current system was using six times the NaCl concentration it was also operating at four times the flowrate.

4.1.3 Iron and manganese removal capability in a coupled PEFT cell-DMI-65 column

Iron and manganese removal was investigated by passing iron and manganese containing water through the PEFT cell and DMI-65 column and measuring their residual in the treated water. Ferrous sulphate ($FeSO_4$) represented the iron in bore water while manganese sulphate ($MnSO_4$) represented manganese. Ferrous sulphate in the stock solution had tendency to precipitate after a few hours due to its oxidising. Therefore, only recently prepared stock solutions were used. Ferrous and manganese concentrations differed slightly between tests, 19–21.5 mg/L and 3.1–4.25 mg/L respectively. Initial ferrous and manganese concentrations were measured prior to every treatment. Iron and manganese removal percentages and residual amounts in treated water at different NaCl concentrations and different flow rates are shown in figure 4.19 to figure 4.23.

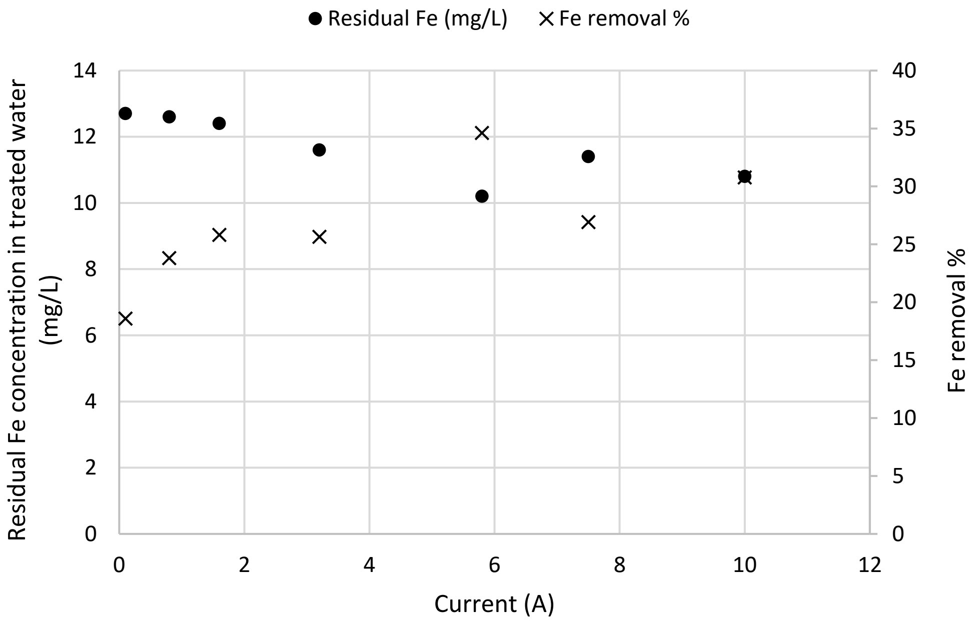


a)

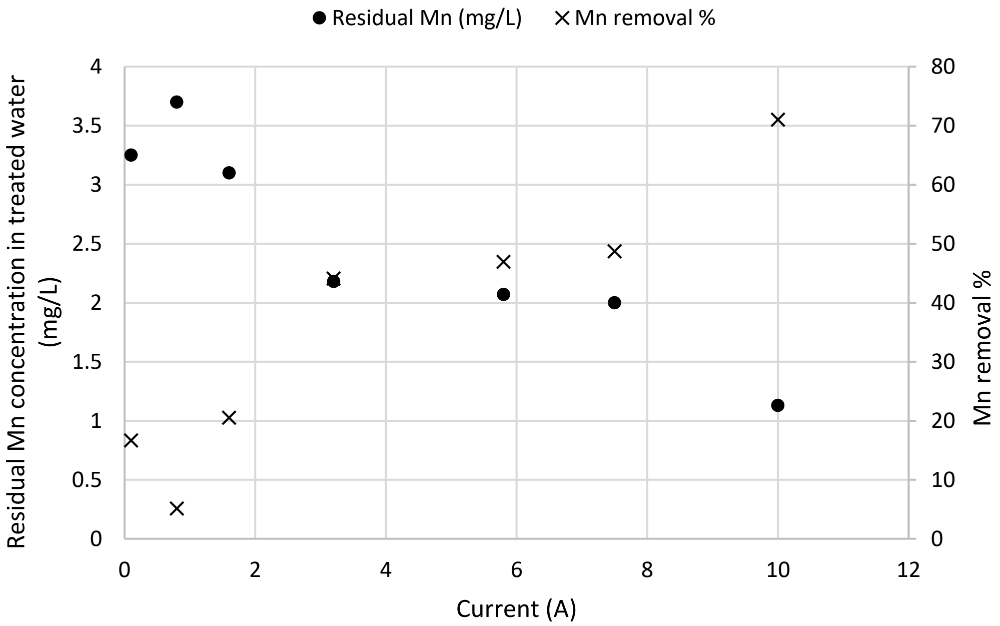


b)

Figure 4.19 a) Iron removal b) Manganese removal at 0.01mol/L (0.5844g/L) NaCl concentration, 1.80 ml/sec flow rate

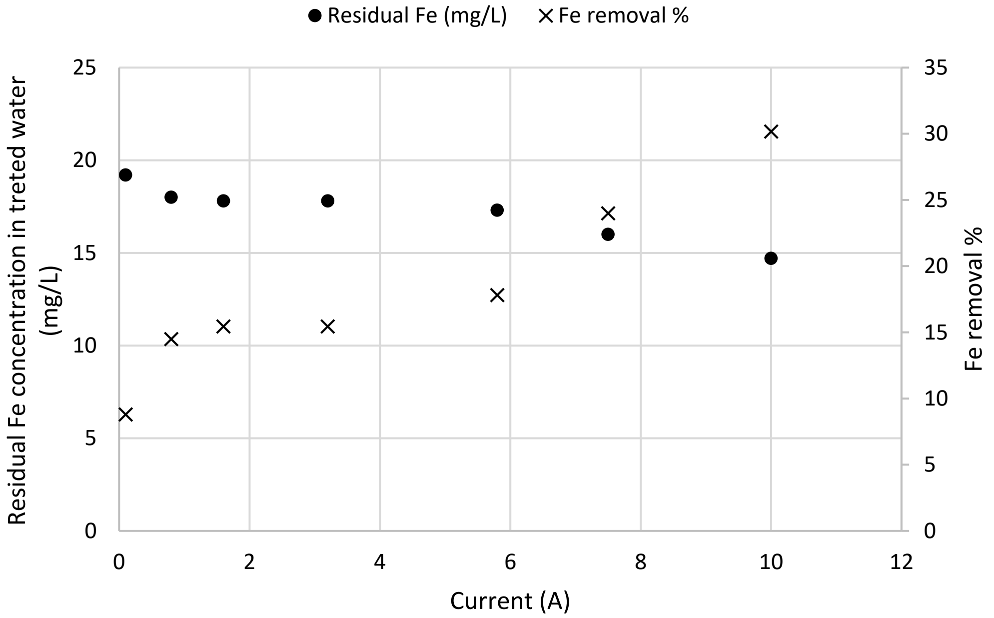


a)

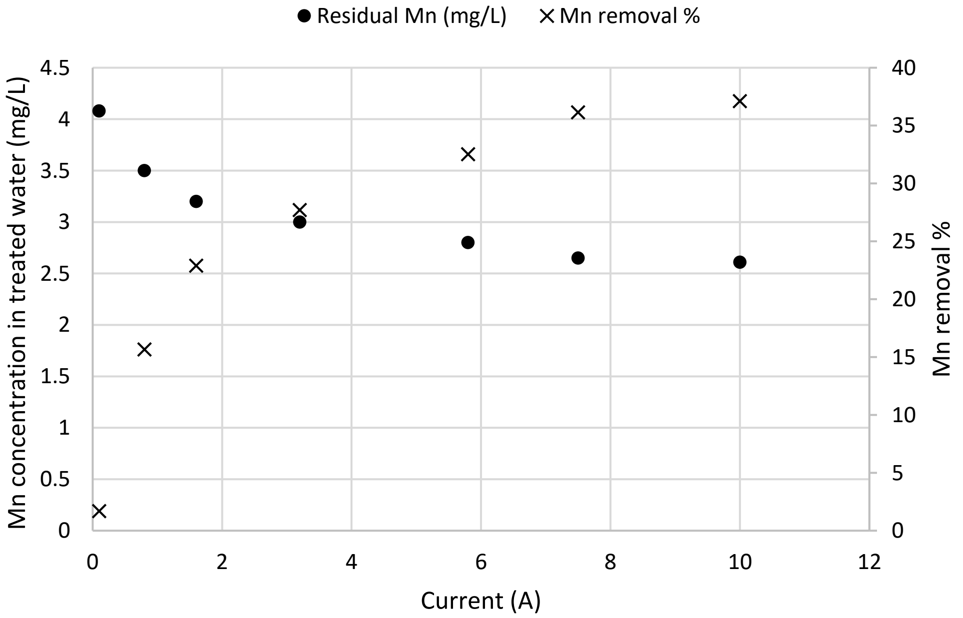


b)

Figure 4.20 a) Iron removal b) Manganese removal at 0.01 mol/L (0.5844g/L) NaCl concentration, 3.95 ml/sec flow rate

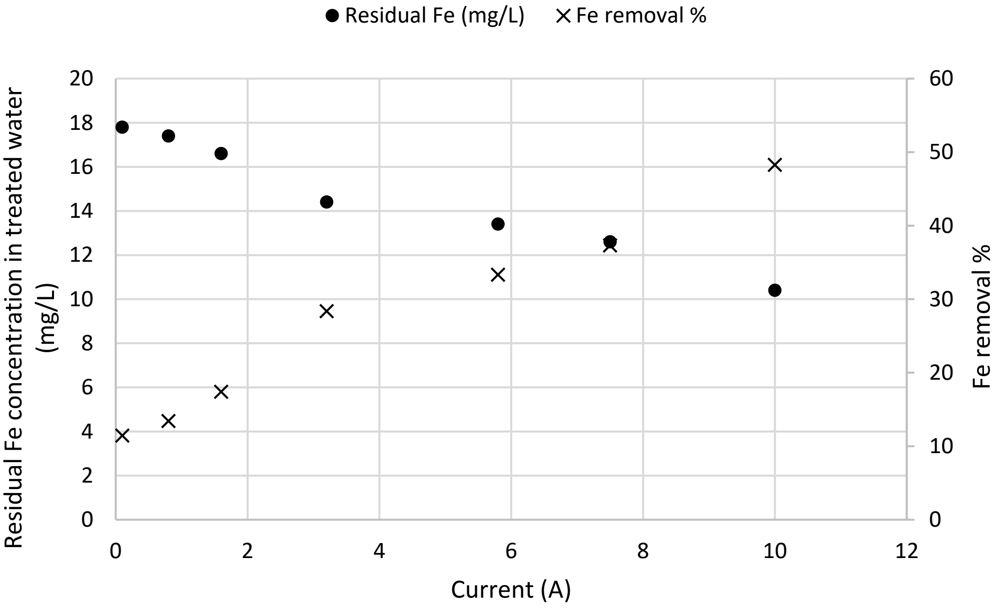


a)



b)

Figure 4.21 a) Iron removal b) Managanese removal at 0.01 mol/L (0.5844g/L) NaCl concentration, 5.81 ml/sec flow rate



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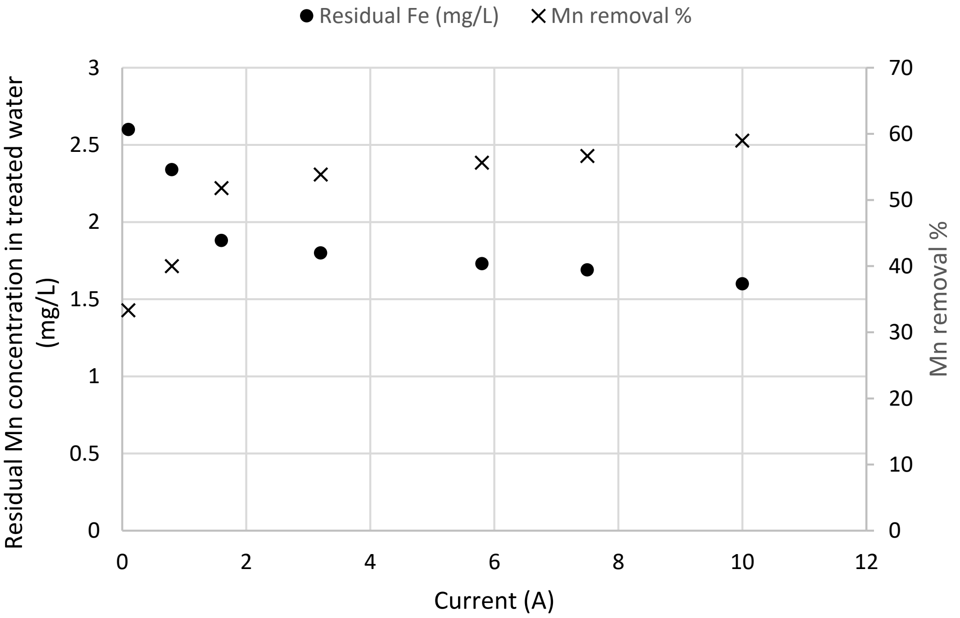
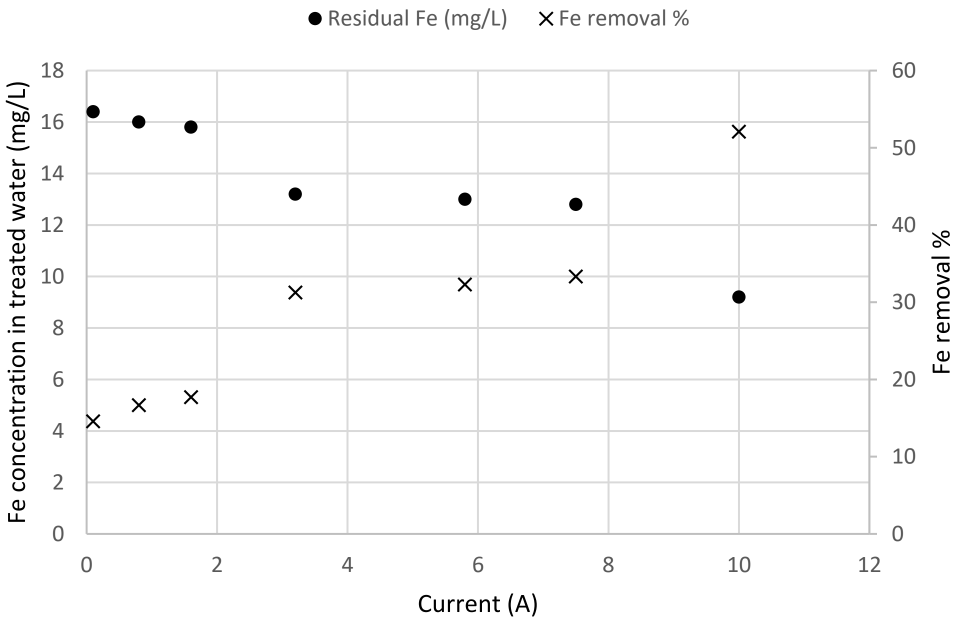
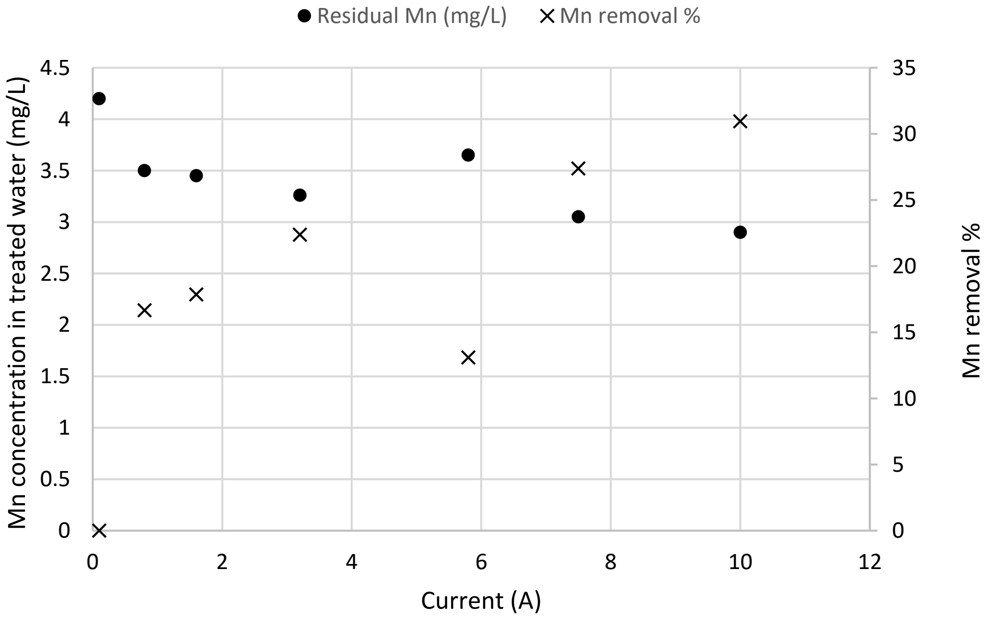


b)

Figure 4.22 a) Iron removal b) Manganese removal at 0.01 mol/L (0.5844g/L) NaCl concentration, 7.41 ml/sec flow rate



a)

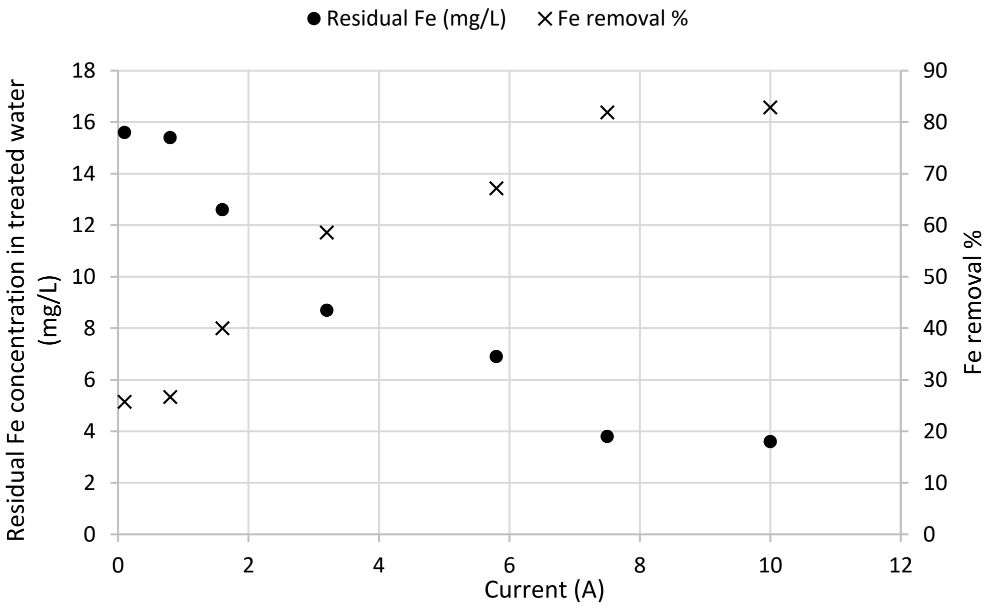


b)

Figure 4.23 a) Iron removal b) Manganese removal at 0.01 mol/L (0.5844g/L), 12.05 ml/sec flow rate

Trace metal removal by oxidation is very low at low NaCl concentrations. Ferrous and manganese oxidization and percentage removal increased as chlorine production for a given flow rate was increased with increasing current/voltage. Average Fe $^{2+}$ removal was 30% at 0.01 mol/L (0.5844g/L) NaCl concentration and Mn^{2+} removal varied between 82 – 30% . With increasing flow rates ion removal percentage was expected to decrease due to a decrease in chlorine concentration (section 4.1.1). But, at the higher flow rates such as 7.41 ml/sec and 12.05 ml/sec, ferrous ion removal percentages were 52% and 48% respectively and at the lower flow rates it was around 30% (Figure 4.22 and figure 4.23).

A fraction of ferrous sulphate which had oxidized was found to remain inside the PEFT cell cavity due to precipitation. With every pass of water for the different voltages tried, the remaining ferrous ions from the previous test contaminated treated water resulting in lower percentage removals. When the flow rate increased the ferrous ion precipitation inside the cavity decreased.



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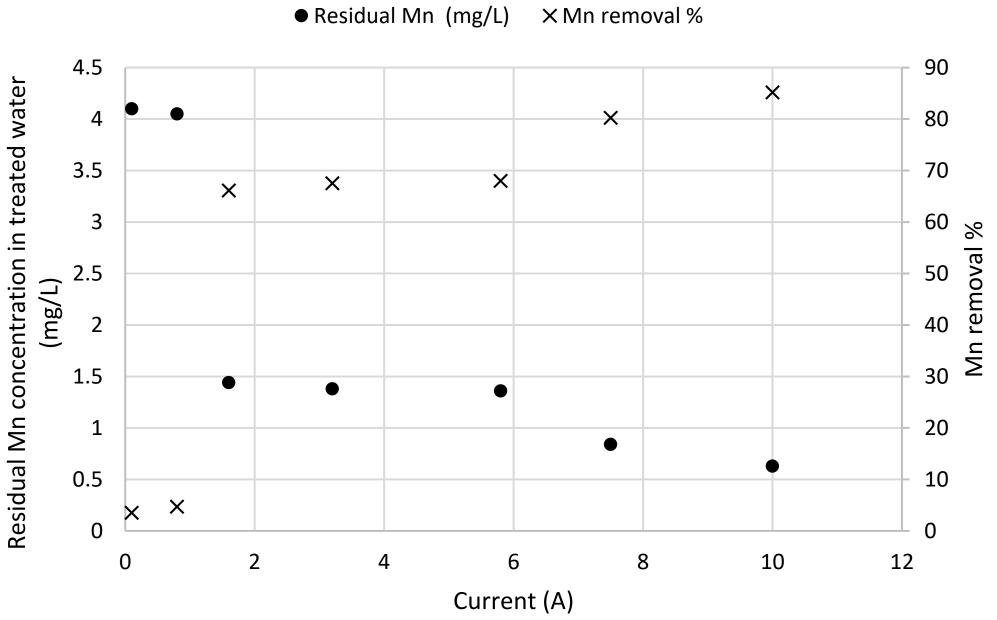
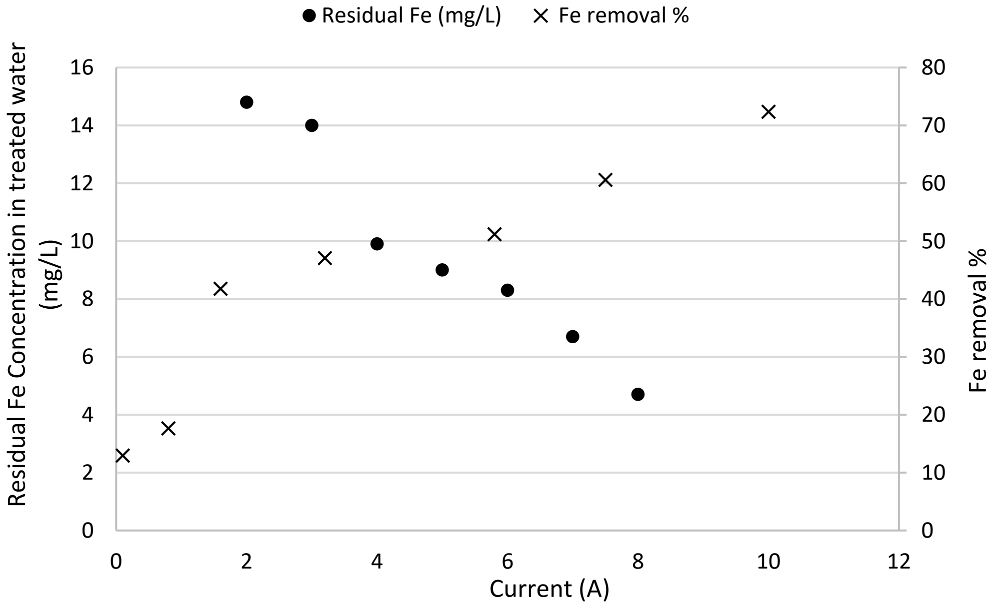


b)

Figure 4.24 a) Iron removal b) Manganese removal at 0.05mol/L (2.922g/L), 1.80 ml/sec flow rate



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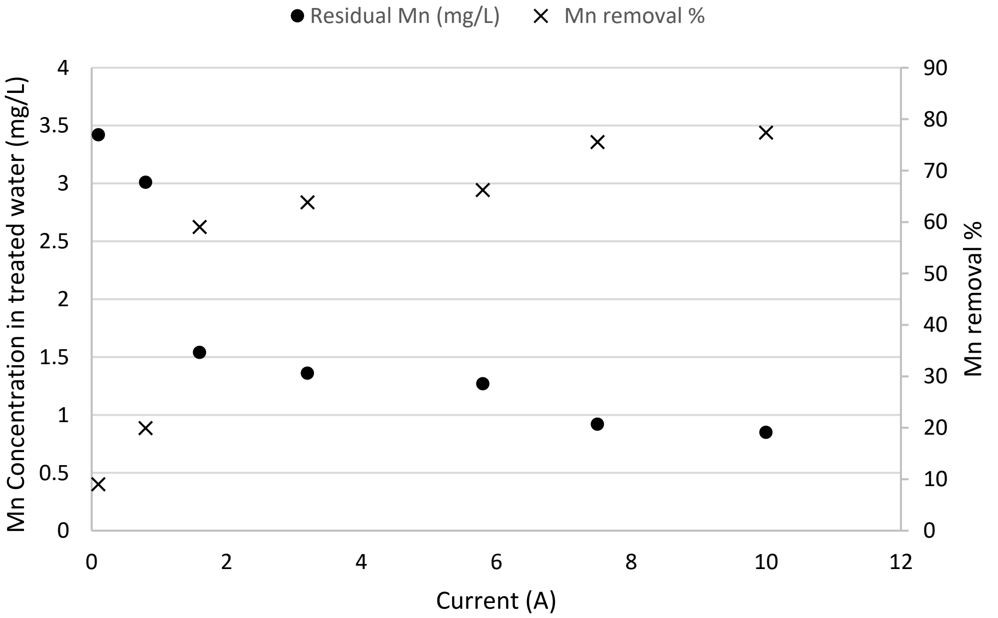
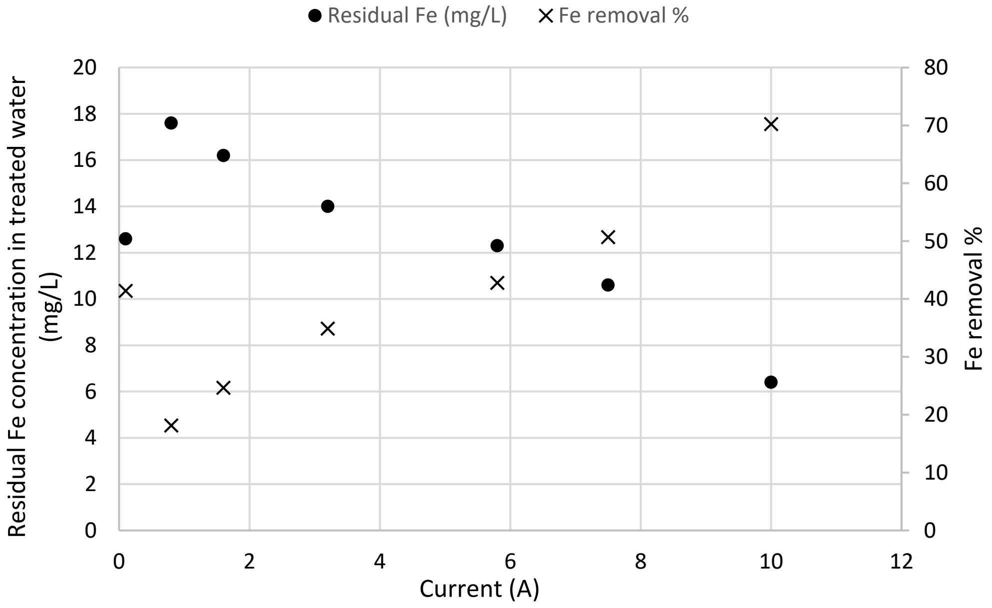
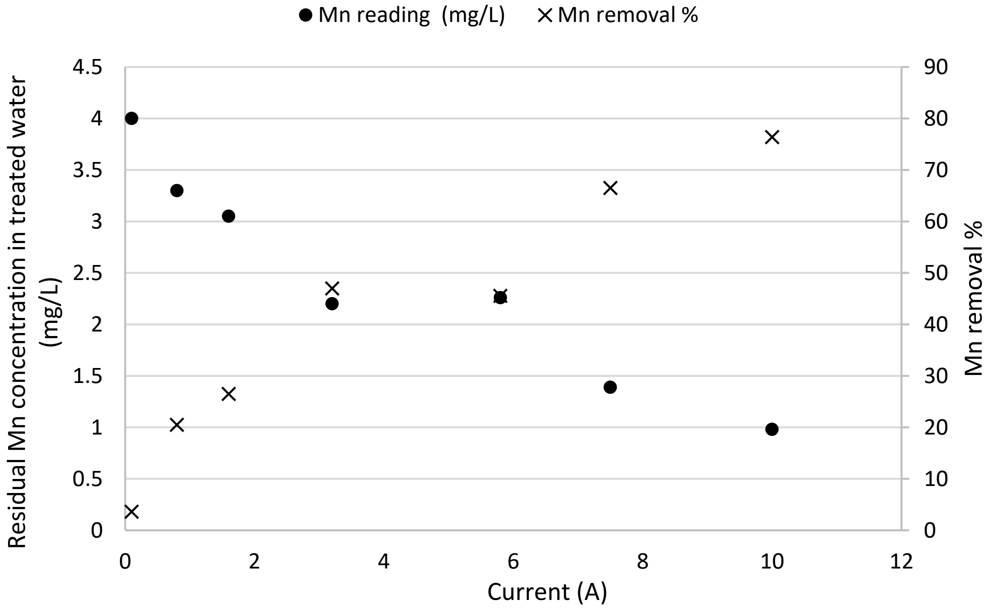


b)

Figure 4.25 a) Iron removal b) Manganese removal at 0.05 mol/L (2.922g/L), 3.95 ml/sec flow rate

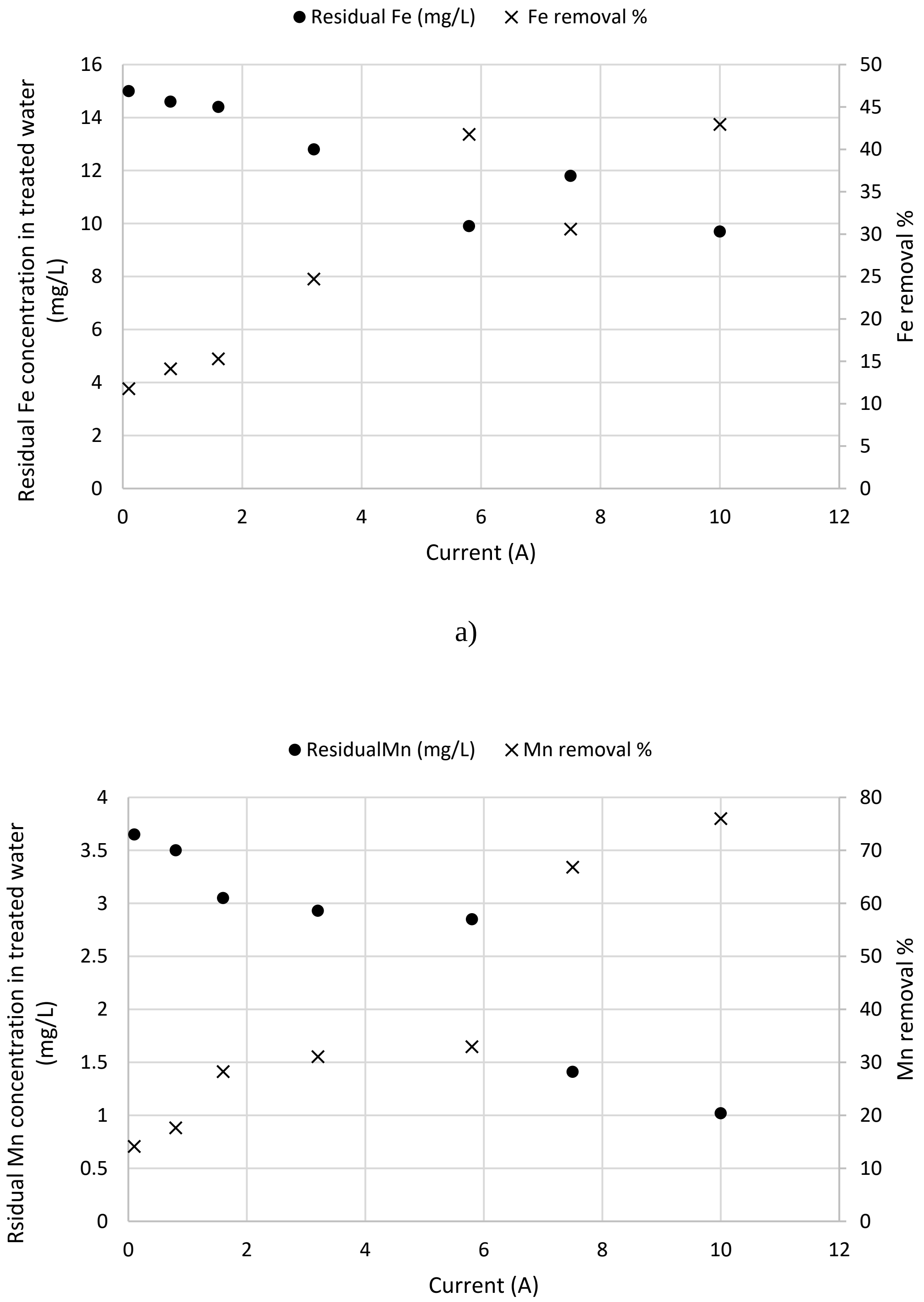


a)



b)

Figure 4.26 a) Iron removal b) Manganese removal at 0.5mol/L (2.922g/L) NaCl concentration, 5.81 ml/sec flow rate



a)

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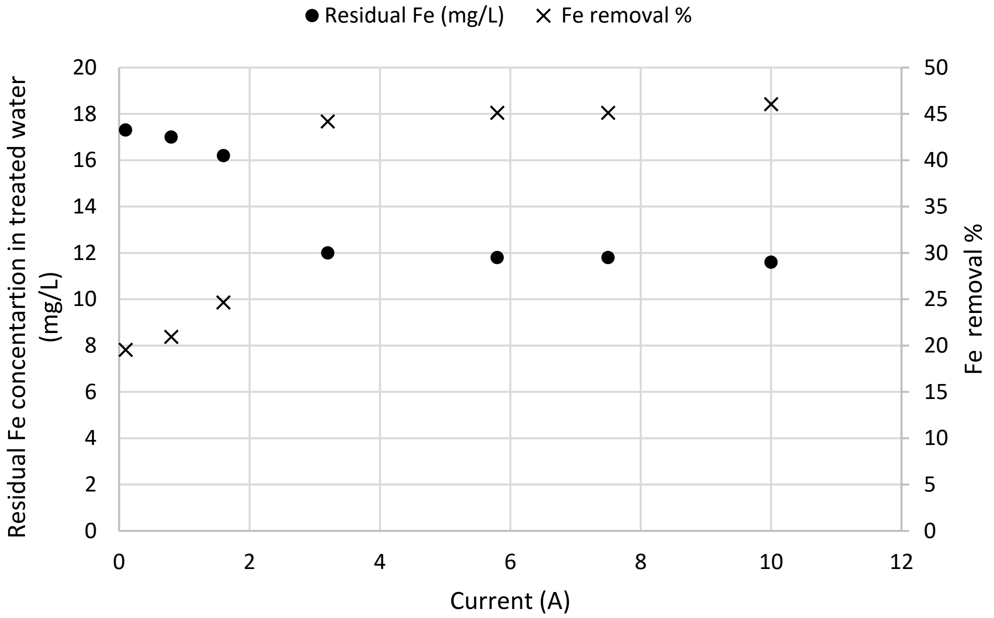
Figure 4.27 a) Iron removal b) Manganese removal at 0.05 mol/L (2.922g/L) NaCl concentration, 7.41 ml/sec flow rate



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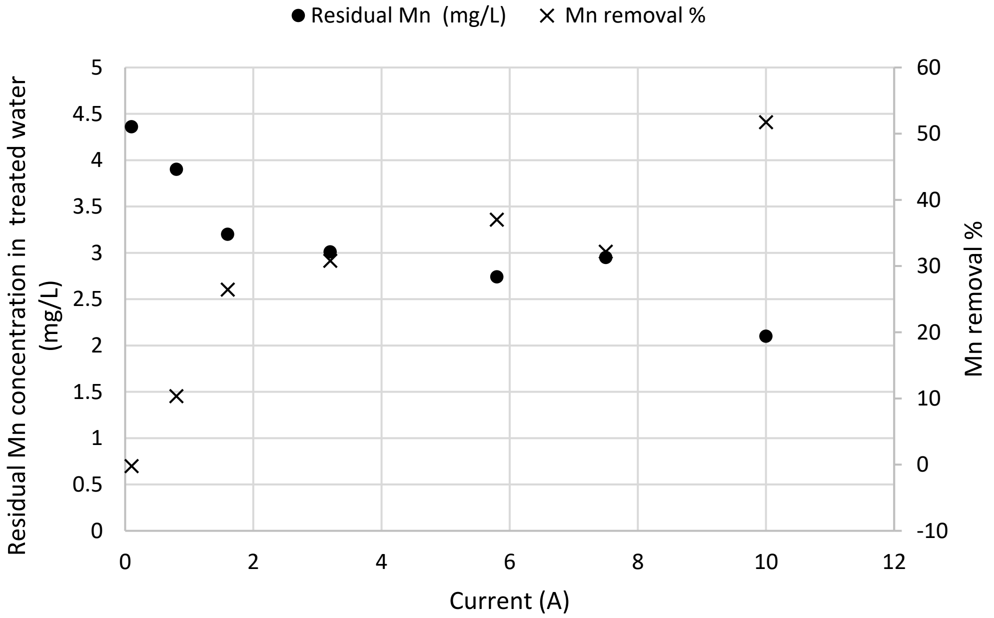


b)

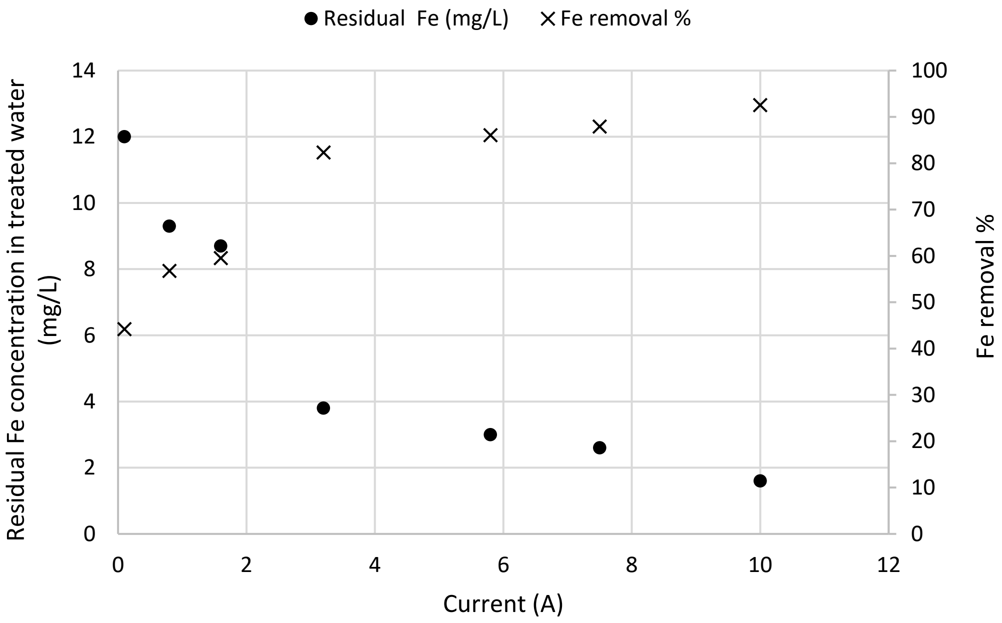
Figure 4.28 a) Iron removal b) Manganese removal at 0.05 mol/L (2.922g/L) NaCl concentration, 12.05 ml/sec flow rate

The second phase of iron and manganese removal was done with 0.05 mol/L (2.922g/L) NaCl concentration (figure 4.24 to figure 4.28). In this stage clean water was flushed through both the PEFT cell and DMI65 column after every flowrate test. It helped remove precipitated iron remaining inside the PEFT cell and clean the DMI-65 media. Therefore results obtained for 0.05 mol/L NaCl concentration are better compared to 0.01mol/L. Maximum chlorine production is at maximum current (10A) occupy at each flow rate. Table 4.1 shows maximum Fe and Mn ion removal for each flow rate at its maximum chlorine production (See section 4.1.1).

Table 4-1 Maximum chlorine production of different flow rates at 0.05 mol/L (2.922g/L) NaCl concentration and maximum metal removals

Flow rate (ml/sec)	Maximum chlorine production (mg/L)	Fe removal %	Mn removal %
1.80	300	82.85	85.17
3.95	188	72.35	77.39
5.81	178	70.23	76.38
7.41	169	42.94	76
12.05	110	46.04	51.72

Maximum ferrous ion removal percentage gained for 0.05 NaCl concentration is 82.85% which is at lowest flow rate of 1.80 ml/sec. Other than having a slightly increased Fe removal of 46% for 12.05 ml/sec flow rate all other data illustrate that as chlorine concentration decreased with increasing flowrate metal removal ability also dropped.



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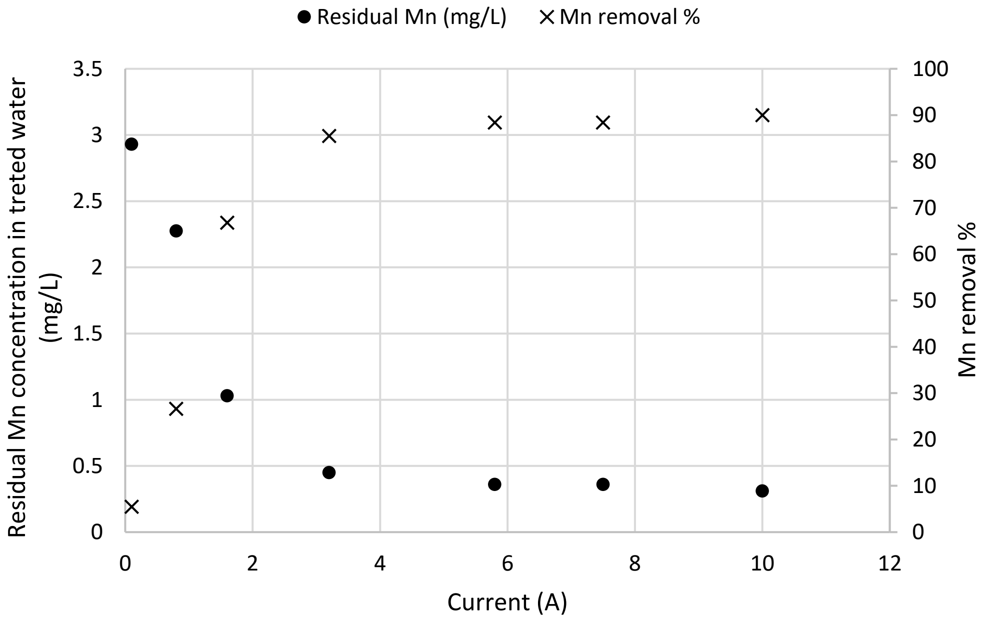
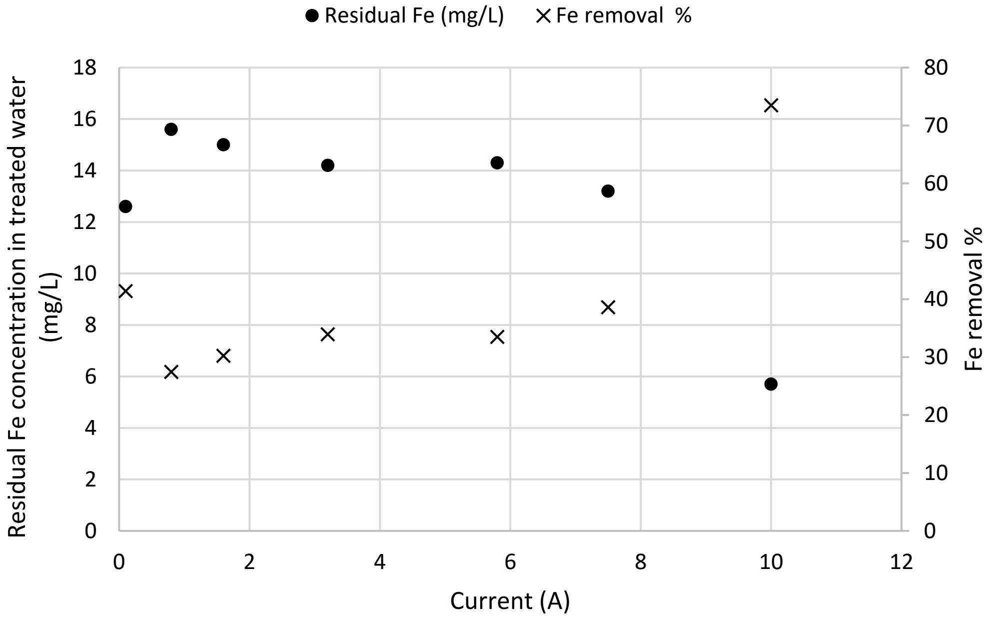


b)

Figure 4.29 a)Iron removal b) Manganese removal at 0.1 mol/L (5.844g/L) NaCl concentration, 1.80 ml/sec flow rate



a)

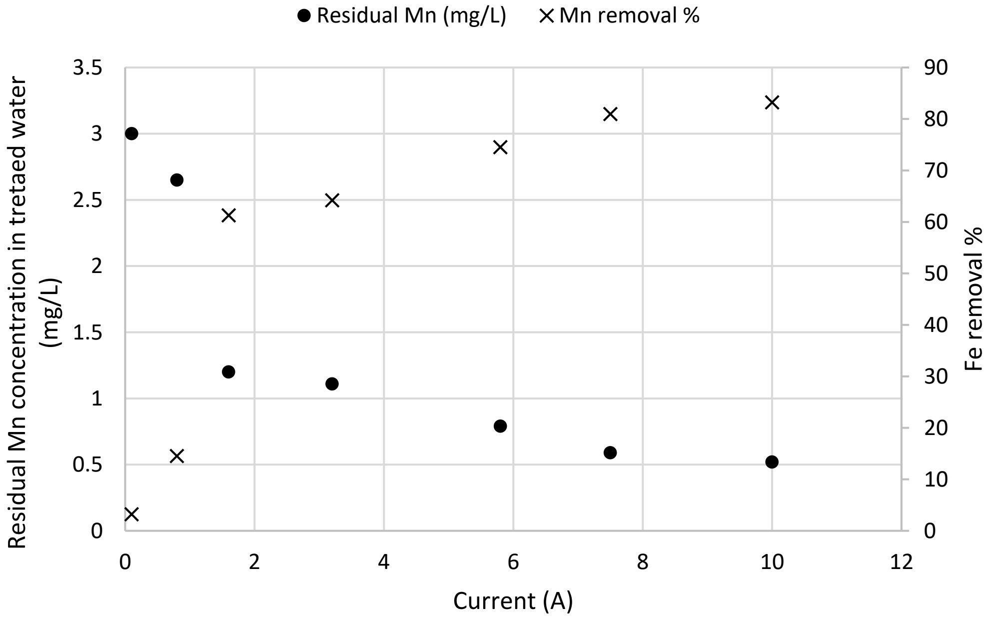


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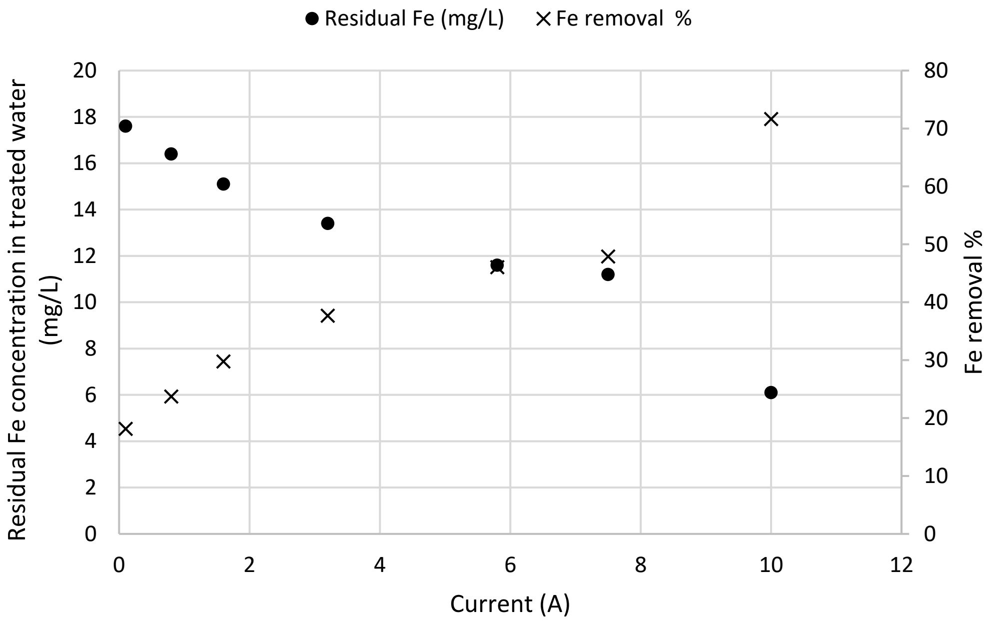
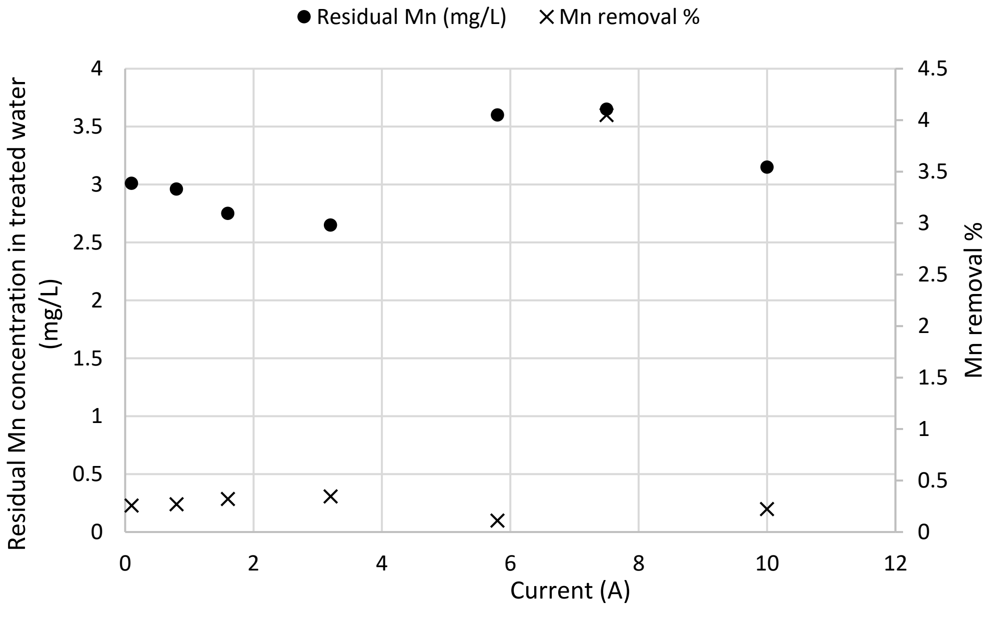
Figure 4.30 a) Iron removal b) Manganese removal at 0.1 mol/L (5.844g/L) NaCl concentration, 3.95 ml/sec flow rate

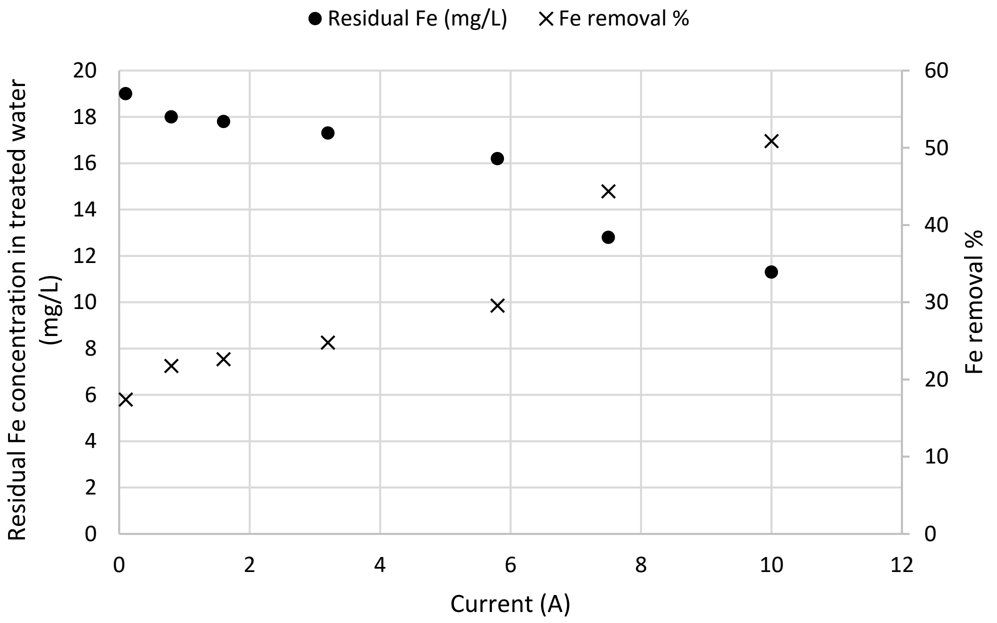


a)

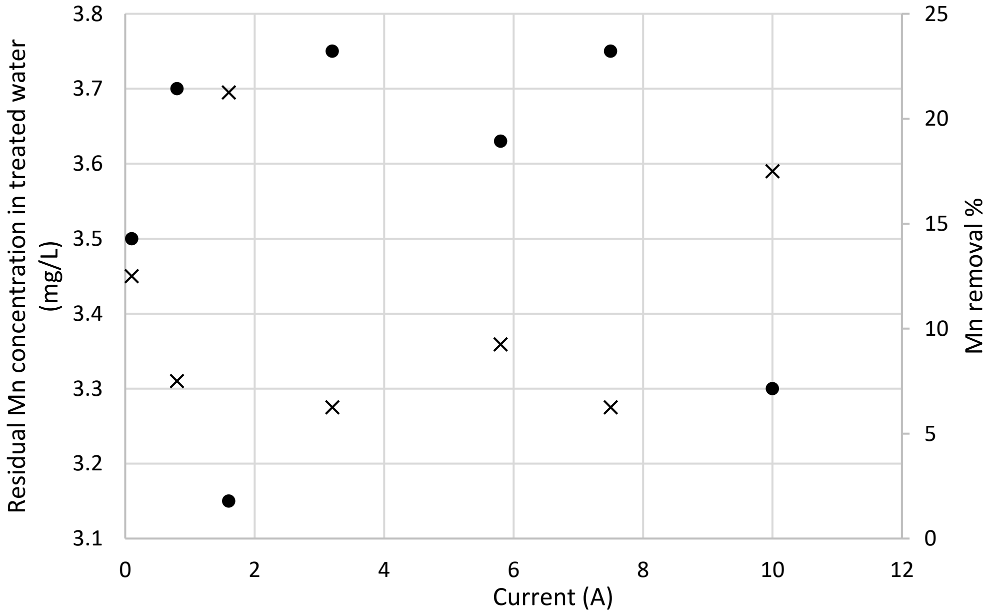


b)

Figure 4.31 a)Iron removal b) Manganese removal at 0.1mol/L (5.844g/L) NaCl concentration, 5.81 ml/sec flow rate

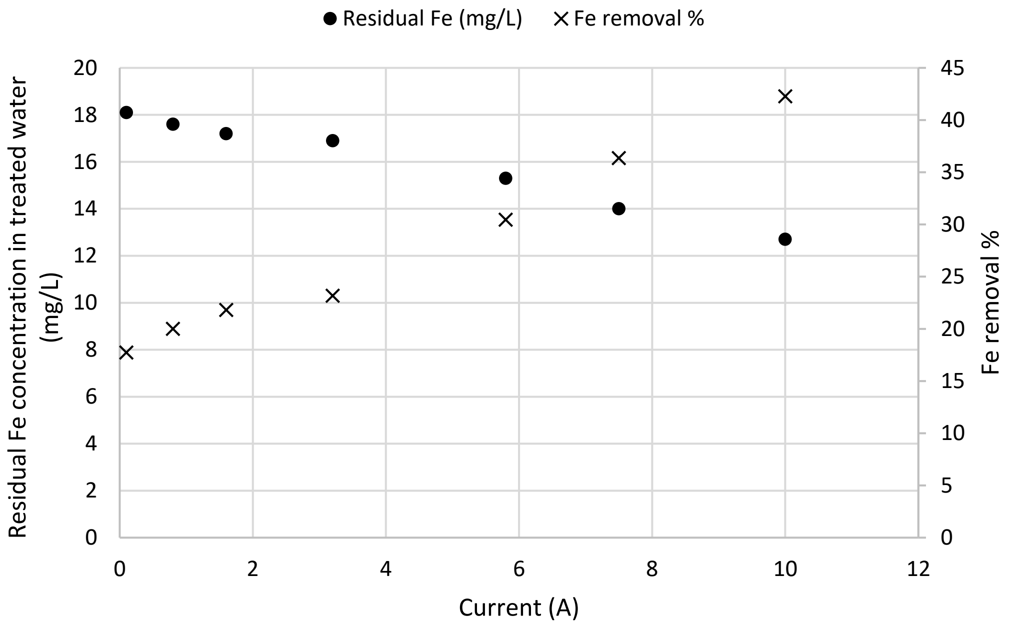


a)

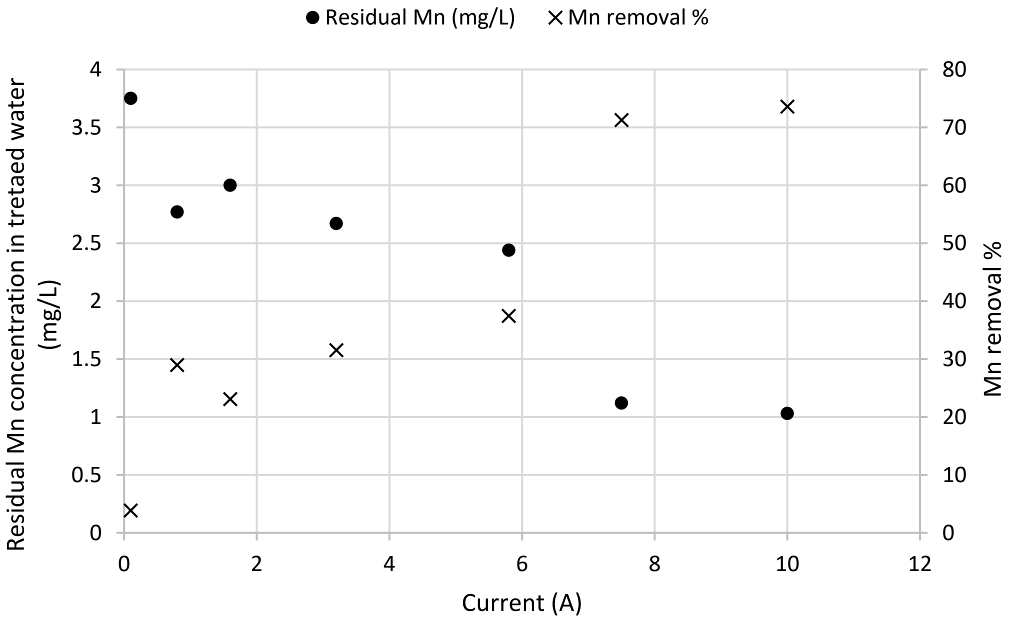


b)

Figure 4.32 a) Iron removal b) Manganese removal at 0.1 mol/L (5.844g/L) NaCl concentration, 7.41 ml/sec flow rate



a)



b)

Figure 4.33 a) Iron removal b) Manganese removal at 0.1 mol/L (5.844g/L) NaCl concentration, 12.05 ml/sec flow rate

Data obtained from all metals removal experiments (figure 4.29 to figure 4.33) for the highest chlorine production is listed in Table 4.24. Maximum Fe ion removal obtained for 0.1 mol/L NaCl concentration coupled with DMI-65 is 92.55% which is the highest removal gained. Highest ion removal is best at the highest chlorine production. This data set also demonstrates as flow rate goes up ferrous and manganese removal percentage goes down because of decline of chlorine production. But there are two odd results in the table 4.24 representing Mn removal percentage at 5.81 ml/sec and 7.41 ml/sec flow rates. Manganese removal can be identified as very low and unpredictable for those two flow rates as in figure 4.31 and figure 4.32. These values were measured twice and the same result was obtained, and could be due to manganese precipitate coming through the DMI-65 column.

Table 4-24 Maximum chlorine production of different flow rates at 0.1 mol/L (5.844 g/L) NaCl concentration and maximum ion removals

Flow rate (ml/sec)	Maximum chlorine production (mg/L)	Fe removal %	Mn removal %
1.80	510	92.55	90
3.95	270	73.48	83.22
5.81	220	71.62	0.22
7.41	190	50.86	17.5
12.05	106	42.27	73.58

5 Conclusions and Recommendations

5.1 Conclusions

5.1.1 Chlorine generation

- New PEFT cell using graphite electrodes as both anode and cathode material was proficient as a chlorine generator
- Maximum free chlorine generated at 0.01 mol/L (0.5844g/L) NaCl concentration is 141 mg/L, 0.05mol/L (2.922g/L) NaCl concentration is 300mg/L and 0.1 mol/L (5.844g/L) NaCl concentration is 510 mg/L.
- Chlorine production increases with increasing NaCl concentration.
- For a fixed NaCl concentration and fixed flow rate free chlorine generation increases with increasing current/voltage. That increment is linear for higher NaCl concentrations. But for lower NaCl concentrations linearity drop down at higher currents/voltages.
- The lowest flow rate utilized was 1.80 ml/sec which gave the maximum free chlorine production for every NaCl concentration.
- Free chlorine generation declined with increasing flow rates for a fixed NaCl concentration.
- If compared same flow rate at different NaCl concentrations, it will show same pattern in generating chlorine. But generated chlorine amount is higher at higher NaCl concentration for a certain current/voltage value.

5.1.2 Disinfection

- The PEFT cell was able to generate sufficient chlorine to disinfect E-coli containing water, even at the lowest free chlorine concentration of 1.05 mg/L (at 0.01 mol/L (0.5844g/L) NaCl concentration, 12.05 ml/sec flow rate, 0.1 A current and 2V voltage).

5.1.3 Iron and Manganese removal

- Chlorine produced by PEFT cell was successful in reducing the residual ferrous and manganese levels of water when coupled to a DMI-65 column.

- As free chlorine production increases residual ferrous and residual manganese concentrations decrease.
- Maximum ferrous ions and manganese ions removal reported at maximum free chlorine generation of 510 mg/L which is at 0.1 mol/L (5.844g/L) NaCl concentration, 1.80 ml/sec flow rate, 10A current coupled with DMI65 column. Ferrous removal was 92.55% and manganese removal was 90% for a synthetic bore water sample of 20 mg/L ferrous ions and 3 mg/L manganese ions.

5.1.4 PEFT cell modifications

One of the major drawbacks of all the electro-chemical processes is high cost associate due to expensive electrode materials (Llanos *et al.*, 2014). The PEFT cell utilized for this particular research consisted of two sets of graphite electrodes which are not costly. Using graphite as a cathode material and anode material in PEFT cell is possible.

Some precipitation of metals occurred inside the PEFT cell and desposited in the chambers, which resulted some times in carry over. Therefore the PEFT cell should be modified to increase mixing and reduce residence time.

5.2 Recommendations for future work

Short circuiting was a problem at high voltages, therefore a separating material between the electrodes with a high resistivity need to be investigated to prevent this.

More PEFT cell designs should be investigated to prevent metal ions precipitating inside the cell cavity. A horizontal assembly instead of vertical assembly might help as well as looking at reducing residence time inside the chamber and increasing mixing.

The metal rings and plates utilized in the existing PEFT cell have great potential to corrode when salt solutions are used. Examination of more corrosion resistant materials is suggested.

While the current system exhibited less leaks than the old system, the surfaces of the 3D printed parts could be made smoother to make sealing the system easier.

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