Feasibility study of E.coli inactivation and development of portable water purifier using platinized titanium

Muhammad Shafique Hamid

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**FEASIBILITY STUDY OF *E.COLI* INACTIVATION AND
DEVELOPMENT OF PORTABLE WATER PURIFIER USING
PLATINIZED TITANIUM**

MUHAMMAD SHAFIQUE BIN HAMID

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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PLATINIZED TITANIUM**

MUHAMMAD SHAFIQUE BIN HAMID

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

A thesis submitted to the Nanyang Technological
University in partial fulfilment of the requirement for the
degree of Master of Science

2021

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Richard D. Webster

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Abstract

Water contaminated by pathogens poses the greatest threat to public health globally. Throughout the decades, there have been numerous technologies developed for the purification of water and electro-disinfection has emerged as a promising alternative treatment method. The efficacy of electro-disinfection has been extensively studied with investigations conducted on parameters such as electrode material and electrolyte. Non-portable water purifiers employing electro-disinfection have also been developed for commercial purposes. In this work, platinized titanium as electrodes were investigated for their capability to inactivate *E. coli* in different electrolyte media. Based on this investigation, the feasibility of developing a portable water purifier using platinized titanium was subsequently studied. Platinized titanium electrodes were found to be capable of inactivating *E. coli* in different electrolyte solutions with the inactivation trend of $\text{NaCl} > \text{Na}_2\text{SO}_4 > \text{NaNO}_3$ obtained. The cathode was individually investigated and found to have a greater *E. coli* inactivation capability than the anode. Using platinized titanium as the electrodes, the development of a portable water purifier prototype was found to be feasible where 32% of *E.coli* was inactivated by 6 hour achieving a $\log(\text{N}/\text{N}_0)$ of -5, although much higher inactivation from shorter times could be obtained using a bench top electrolytic system. Therefore, further optimizations on the prototype need to be performed to improve its disinfection capability.

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Chapter 1

Introduction

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1.1. The need for water purification

1.1.1. Importance of water

Water is an essential nutrient for all organisms on Earth.¹ It is an important building material that helps cells in the body grow, reproduce and survive.² Additionally, it serves various critical bodily functions such as acting as shock absorber for spinal cord and brain, flushing waste from the body through urine, assisting in digestion by forming saliva, lubricating joints, regulating body temperature, etc.² In order to survive, organisms such as humans must consume a certain quantity of water each day.²

1.1.2. Scarcity of safe drinking water

The availability and accessibility of safe drinking water is necessary for survivability and preserving good health.³ Although 70% of the Earth's surface consist of water bodies such as rivers, seas, streams, lakes and oceans, only 2.5% is suitable to be directly consumed and used by humans.^{3,4} With naturally available pure water being limited, water scarcity is an important issue that has grown in importance over the past several decades.⁵ Moreover, the quality of pure water in various waterbodies has been greatly degraded due to increasing global population, climate change and discharge of toxic waste from rapidly expanding human activities e.g. agriculture and industrial development.^{1,3-5}

The issue of pure water scarcity has been a challenge to most countries, especially the developing countries. It was reported by the World Health Organization (WHO) that an estimate of 663 million people around the world do not have access to safe drinking water.^{6,7} Out of this population number, 78% are from developing countries in regions such as South and East Asia, and Sub-Saharan Africa.^{1,5,6} Moreover, developing countries are experiencing rapid industrialization which give rise to the pollution of water bodies and hence, are the most affected from the issue of water scarcity.¹

Ahmad *et al.* reported that 50% of population who lack access to safe drinking water suffered from health problems.³ The shortage of safe drinking water has caused populations in developing and poor nations to rely on unhygienic water bodies e.g. rivers, ponds for their water supply.³ This has resulted in fatal diseases such as cholera, dysentery, tapeworms, polio, hepatitis and typhoid.³ Furthermore, statistics have shown that developing countries e.g. Niger

and Mozambique with no access to safe drinking water experience higher mortality rates, low birth success rate and shorter life expectancy as compared to developed countries.³ Each year, there are approximately 1.5 million deaths of children in developing countries reported where 30% are due to preventable water related diseases.^{3, 8} In fact, 80% of diseases in developing countries can be linked to bad sanitation conditions.^{5, 8}

Similarly, developed countries are not spared from health risks due to contaminated drinking water. It was reported that an estimate of 560,000 people suffered from serious waterborne diseases with 12,000 deaths each year in the United States of America.^{8, 9} Moreover, 50% of occupants in world's hospitals are suffering from water-related illnesses.^{5, 8}

1.1.3. Sources of water pollutants

The statistics demonstrated the severe impact of contaminated water on human health. Pollution of water bodies predominantly occurs from two sources; direct and indirect sources.⁵ Direct sources are mainly from residential and industrial areas such as factories, refineries and plants whereas indirect sources originate from agricultural activities e.g. entry of chemicals from pesticides and fertilizers use in crop fields into the groundwater.⁵ These sources contaminate the water bodies through the discharge of water pollutants.

There are several known water pollutants as listed below:¹⁰

- Herbicides and pesticides.¹⁰
- Heavy metals such as chromium, mercury, lead.¹¹
- Suspended solids and sediments.¹¹
- Radioactive pollutants.¹⁰
- Pathogens e.g. microorganisms, viruses, bacteria.¹¹

1.1.4. Microbial contamination of water

The most prevalent and common health risks related with drinking water are the infectious diseases caused by pathogenic microorganisms.^{1, 11, 12} Currently, the pollution of water by these pathogens pose the greatest threat to public health around the world.¹³ An estimate of 1.5 million children die yearly due to diarrheal diseases caused by poor sanitation and polluted drinking water.¹³ Moreover, according to the WHO, more than 50% (approximately 5 million people per year) of people who die of water-related diseases are attributed to microbial intestinal infections.¹³

Waterborne pathogenic microorganisms can be divided into viruses, bacteria and parasites (helminths and protozoa).^{7, 11} *Rotavirus*, *Hepatitis virus*, *Sapovirus*, *Astrovirus* and *Adenovirus* are some examples of waterborne viruses which can cause diarrhea, gastroenteritis and hepatitis.¹² The most common water-associated parasitic infections are caused by *Giardia* and *Cryptosporidium*.¹² They are responsible for the diarrheal diseases among children in developing countries.¹³ Other types of waterborne protozoa include *Entamoeba histolytica* and *Naegleria fowleri* causes dysentery and infection of the central nervous system (Primary Amebic Meningoencephalitis) respectively.¹²

Waterborne bacteria are comprised of species that can cause a wide range of deadly diseases.¹² Known fatal diseases such as typhoid fever and cholera are caused by bacterial species, *Vibrio cholera* and *Salmonella enterica* respectively.^{8, 13} Food and drinking water contaminated with *Helicobacter pylori* account for majority of chronic gastric ulcers and gastric cancers cases.^{8, 13} *Escherichia coli* (*E. coli*) is responsible for acute and bloody diarrhea, and gastroenteritis.^{7, 8, 11, 14} It was reported that *E. coli* constitutes the highest percentage of infant deaths by diarrheal disease.¹⁵ Moreover, a strain of *E. coli* known as O157 contains plasmid which can synthesize Shiga-toxin and causes fatalities.^{7, 8, 14} Its close resemblance, *Shigella spp* causes shigellosis or bacillary dysentery, a more serious form of gastroenteritis.^{8, 13, 14}

The severe threats to public health posed by contaminated water are evident. Therefore, paramount emphasis has to be placed on the purification of drinking water to ensure a healthy global population which in turn supports economic productivity.

1.2. Existing technologies for water purification

Currently, there have been numerous development in technologies to produce high-quality safe drinking water.³ Engineers and scientists are continually researching and establishing innovative technologies to purify water at affordable costs in an effort to mitigate the health risks posed by the shortage of clean water.³ Some common methods for water purification include chlorination, ultraviolet disinfection, filtration, heating and electrical current.¹¹ Although these methods are established and have been typically used, they possess their respective advantages and disadvantages as displayed in table 1.

Method	Advantages	Disadvantages
Chlorination 6, 13, 16, 17	<ul style="list-style-type: none">• Uses chlorine gas or chlorine compounds e.g. chloramines (RNHCl), chlorine dioxide (ClO₂), hypochlorite (OCl⁻), to effectively eliminate waterborne pathogens• Provides a disinfection reservoir which prevents recontamination for a certain period of time• Inexpensive• Chlorine compounds can be easily stored and transported	<ul style="list-style-type: none">• Not effective in killing some microorganisms resistant to the effects of chlorine e.g. <i>Cryptosporidium</i>, <i>Norwalk</i> virus and <i>Giardia</i>• High chlorine levels can result in bad odours and flavours• Safety concerns as the use of chlorine and its derivatives are highly toxic to humans and animals• Generation of carcinogenic and toxic disinfection by-products (DBPs) e.g. trihalomethanes (THMs) and haloacetic acids (HAAs)• Requires careful control and application• Hazards involved in handling large quantity of chlorine

Ultra-violet (UV) radiation ^{3, 18}	<ul style="list-style-type: none"> • Effective in inactivating a wide range of pathogenic microorganisms, even those that are resistant to chlorine • Does not require storage and handling of hazardous chemicals • Does not produce any by-products that might be harmful to humans 	<ul style="list-style-type: none"> • Low dosage allows some microorganisms to undergo photo-reactivation which reverses the mutation effects caused by UV irradiation • Presence of total suspended solids (TSS) and turbidity can render the method ineffective • High cost
Ozonation ³	<ul style="list-style-type: none"> • Possess stronger germicidal effect than chlorination • Eliminate organic and inorganic impurities such as iron, manganese and sulfur • Used to improve the taste and odour of drinking water 	<ul style="list-style-type: none"> • Requires specific instruments and trained personnel • Higher equipment and operational costs • Requires special mixing techniques which is energy consuming • Production of carcinogenic and mutagenic by-products e.g. ketones and brominated aldehydes
Sand filtration ¹³	<ul style="list-style-type: none"> • Inexpensive 	<ul style="list-style-type: none"> • Requires additional pretreatment processes e.g. coagulation, flocculation, sedimentation and post-filtration treatment
Membrane – based filtration ¹³	<ul style="list-style-type: none"> • Removes a wide range of contaminants such as microorganisms, nitrates, micro-pollutants, salinity, natural organic material, metals and hardness 	<ul style="list-style-type: none"> • Expensive and requires a large amount of energy. • Performance can be degraded overtime from damages, formation of scale, biofouling, clogging and leaching

		<ul style="list-style-type: none"> • Requires routine monitoring and replacement due to their limited lifetime • Membrane filters have to be customized to the types of contaminants to be filtered
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Table 1. Advantages and disadvantages of several water purification methods

1.3. Electro-disinfection for water purification

1.3.1. Background

There has been growing interest throughout the years in using electricity as an alternative method for drinking water purification.¹⁹ Common terms that have been used to describe this treatment method include ‘Electrochemical disinfection’, ‘Electrolytic disinfection’, ‘Anodic oxidation’ and ‘Electro-disinfection’.¹⁶ As early as the nineteenth century, the use of electricity or electrolysis to purify water has been reported and proposed in the United Kingdom.²⁰ Since then, there have been numerous efforts to establish electro-disinfection as a dependable water treatment but the method was not used long-term or accepted widely within the water purification industry.¹⁶

The increasing demand for high quality drinking water with a stricter environmental regulations have pushed industries to source out for alternative water treatment processes.¹⁶ Electro-disinfection has emerged as a promising alternative method in the past 20 years due to the advantages it brings over conventional treatment methods such as chlorination.¹⁶ The advantages and disadvantages of electro-disinfection are as follows:

Method	Advantages	Disadvantages
Electro-disinfection	<ul style="list-style-type: none"> • Possess the ability to kill a comprehensive range of pathogenic microorganisms such as bacteria, viruses, algae and Euglena due to its 	<ul style="list-style-type: none"> • Formation of toxic by-products such as perchlorate, bromate and chlorate.¹⁹ • High energy consumption.¹⁹

	<p>primary and residual disinfection capability.¹⁶</p> <ul style="list-style-type: none"> • Generates disinfectants on-site and does not require any transport, storage of hazardous disinfectants such as chlorine and hypochlorite.¹⁶ • Easy operation, low maintenance and higher efficiency than other disinfection methods.^{16, 17, 19} • Can be modified for automation and portable application, easily optimized for maximum disinfection capability and modified to meet the requirements of on-site application. Doses of the disinfectants generated on-site can be controlled.¹⁶ • Can be combined with other water purification methods to create stronger disinfection capability.¹⁹ • Can be employed on the site far from electrical supply due to the photovoltaic technology.^{16, 19} The method requires lower area of land for occupation. 	<ul style="list-style-type: none"> • High cost to minimize formation of toxic by-products.¹⁹
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Table 2. Advantages and disadvantages of Electro-disinfection

1.3.2. Principles of Electro-disinfection

The working principle of electro-disinfection involves inserting electrodes, minimally one anode and one cathode, into a bypass pipe or a container of water for disinfection.^{16, 17} Electrolysis of the water will occur as a direct current (DC) voltage is applied between the electrodes.¹⁶ Oxidation occurs at the anode where oxygen and hydrogen ions (H^+) are produced which acidify the water near the anode.¹⁶

At the cathode, hydroxide ions (OH^-) and hydrogen gas are generated which result in the water surrounding the cathode to become alkaline.¹⁶

1.3.3. Mechanisms of electro-disinfection

There have been numerous studies proposed on several mechanisms of electro-disinfection.¹⁶ Generally, the killing mechanisms of electro-disinfection can be categorized into two modes of action; direct and indirect action.²¹

Direct inactivation action

- Electric field can cause the irreversible puncturing and destabilization of microbial cell membranes resulting in the formation of permanent pores. Furthermore, the presence of such pores will cause the transport of important components out of the cells and disrupt chemical gradients.^{16, 17, 22}
- Exposure to electrical field or electrical current can cause direct electrochemical oxidation of significant components of microbial cells e.g. intracellular coenzyme A.^{16, 22} This can cause an immediate killing of microbial cells.
- Negatively charged cells e.g. *E. coli* can be adsorbed onto the surface of electrodes through electro-sorption and electrons are transferred directly from the electrodes to the cells resulting in microbial inactivation.¹⁶

Indirect inactivation action

- Electro-disinfection produces oxidants during water electrolysis such as free chlorine or reactive oxygen species (ROS) e.g. atomic oxygen, ozone, hydrogen peroxide and hydroxyl radicals ($\bullet\text{OH}$).²³ These oxidants can cause cell stress and death through their oxidation reaction with the vital constituents of microbial cells e.g. nucleic acids.^{16, 17, 22} They may also enter the cells through the pores formed by the permeabilization of cell membranes by electric field.²³ Moreover, they can damage the membrane proteins and affect their permeability and functions such as diffusion procedures of enzymes, transporting of K^+ ions and synthesis of cellular ATP.²⁴

1.3.4. Disinfecting agents

Disinfecting agents, mainly oxidants, are produced during the electrolysis of microbial solutions at the electrodes. In the presence of certain compounds or ions, various types of disinfecting agent are generated.¹⁶ For instance, chlorine species e.g. Cl_2 , HOCl , OCl^- , ClO_2 are produced electrochemically in the presence of chloride ions.¹⁶ If oxygen is present in the microbial solution, oxidants such as hydrogen peroxide (H_2O_2) and ozone (O_3) can be produced.^{16, 23} Moreover, recent studies have shown that electro-disinfection may produce energy-rich and short-lived products with strong microbial inactivation capability known as radicals.^{16, 25} It was also reported that electric current and disinfecting agents might act interdependently to inactivate microorganisms.^{16, 23}

1.3.4.1. Chlorine species

The use of electrochemically generated chlorine for microbial inactivation or electro-chlorination is one of the most widely employed electro-disinfection methods for the purification of water.²⁶ It passes direct current to a water system containing chloride such as seawater or drinking water to electrochemically produce disinfecting agents known as “free chlorine” which kills the pathogenic microorganisms.²⁷ Free chlorine, consists of hypochlorite and hypochlorous acid, are generated at the anode through a side reaction apart from the evolution of oxygen.¹⁶ This reaction starts with the electrochemical oxidation of chloride ions in the water system to chlorine:

Equation 3

Chlorine, then undergoes hydrolysis to form hypochlorous acid which will donate proton ions to produce hypochlorite anion in a pH-dependent equilibrium.^{16, 28}

Equation 4

Equation 5

Free chlorine are part of the chemical oxidants produced through electrolysis as they releases atomic oxygen which oxidizes cells causing stress and death.^{16, 28}

Equation 6

Equation 7

Electro-chlorination can be effectively employed for water system with high concentration of chloride ions such as seawater or very low chloride concentrations (less than 100ppm).¹⁶

1.3.4.2. Electrochemically produced oxygen

Oxygen, the main product at the anode side of water electrolysis has been reported to exhibit some microbial killing ability.^{16, 29} However, this oxidant is only effective for odour-producing anaerobic bacteria as it eliminates the vital anaerobic condition needed by these bacteria.¹⁶ Platinum coated electrodes have shown to be most suitable as anodes due to their strong ability in producing oxygen during electrolysis.^{16, 29}

1.3.4.3. Ozone

Ozone can also be produced electrochemically from water by using the appropriate conditions such as low temperature, high current density and anodes with high oxygen overvoltage.^{16, 29} However, the electrochemical generation of ozone poses several disadvantages e.g. unstable electrode materials, low current efficiency, and complicated electrolyte systems.^{16, 29}

Equation 8

1.3.4.4. Hydrogen Peroxide

During water electrolysis, majority of the oxidants are generated at the anode.¹⁶ One oxidant that can be produced at the cathode is hydrogen peroxide (H_2O_2) through the following reaction.^{16, 30}

Equation 9

The oxygen in the reaction can originate from two sources; (1) oxygen dissolved in water with a concentration of 10 ppm (equilibrium with air at 25 °C) or (2) oxygen generated from the anode.^{16, 30} H₂O₂ is less effective in killing microorganisms than ozone or free chlorine due to its lower oxidation potential which requires longer disinfection time and higher concentrations.¹⁶ On the other hand, the disinfection action by H₂O₂ does not produce harmful by-products or undesirable residues.^{16, 30}

1.3.4.5. Radicals

There have been numerous mechanisms proposed to elucidate the major microbial inactivation by electro-disinfection but recently, more attention has been focused on free radicals e.g. •OH and O₂^{•-}.^{16, 17, 31} It was suggested that in chloride-containing systems, free radicals play an important role in the killing of microorganisms in addition to the inactivation effects by electro-chlorination.^{16, 31} These radicals are described to possibly possess stronger oxidizing power and inactivation capabilities than free chlorine.^{16, 31} A new theory hypothesized that chloride ions may act as catalyst in the inactivation action by free radicals.^{16, 31} Excess chloride ions catalyze the chain reactions which increase the lifetime of •OH radicals by a factor of 10.^{16, 31} Free radicals with longer lifetime will be significantly more effective for microbial inactivation.^{16, 31}

In a chloride-free system, free radicals produced during water electrolysis were postulated to play a significant role in the bacterial inactivation. Studies performed by Cong *et al.* and Jeong *et al.* have demonstrated the existence and generation of such radicals electrochemically in chloride-free systems.^{32, 33} Kerwick *et al.* observed that in a chloride-free sodium sulfate solution, inactivation activity only occurs during water electrolysis and there was no residual effect in the absence of electrical current.³⁴ They suggested that the microbial inactivation might be due to short-lived oxidants generated from water electrolysis, sharing similar characteristics with free radicals.³⁴

An interesting mechanism reported by Chen known as electro-oxidation illustrated the role of •OH radicals in killing of microbial cells through direct and indirect oxidation.^{20, 28} Microbial cells can be oxidized and killed directly at the anode surface by the •OH radicals generated during electrolysis (equation 10).^{20, 28} These radicals can also react with one another to form

hydrogen peroxide (equation 11) or react with electrochemically produced oxygen to produce ozone (equation 12 and 13).^{20, 28} These disinfecting agents will then oxidize and inactivate the microbial cells in the solution.^{20, 28} Therefore, $\bullet\text{OH}$ radicals do play a role in the indirect oxidation of microbial cells through the formation of the mentioned disinfecting agents.

1.4. Electro-disinfection without generating chlorine

1.4.1. Background

Electrochemically generating chlorine to kill microbial cells is a widely used and common electro-disinfection method.^{26, 32} However, due to the production of chlorine species, it was suggested that electro-chlorination shares similar disadvantages with chlorination.^{16, 34} There are two main issues regarding electro-chlorination. The first issue involves the generation of harmful chlorinated by-products.¹⁹ Chlorine species generated such as hypochlorous acid, hypochlorite ions, Cl_2 and oxidized chlorine species (ClO_3^- , ClO_2^-) might react with other species in the water system to form more toxic and durable chlorinated products.^{19, 25, 27} Other harmful organic by-products notably halo-acetic acids and trihalomethanes are also found to be produced during electro-chlorination.^{19, 25} The second issue with electro-chlorination is the generation of inorganic DBPs such as perchlorate and chlorate which are mutagenic and carcinogenic.^{19, 21, 27} They are generated electrochemically through the reduction of organic DBPs.^{19, 35}

Therefore, to overcome the issues faced by electro-chlorination, current research is placing more attention towards investigating the capability of electro-disinfection methods without generating chlorine.^{22, 32, 33, 35, 36} However, there is still a lack of extensive studies performed in this area.

1.4.2. Effect of electrolytes on the inactivation of bacteria

Existing research investigated the use of chloride-free electrolytes to study the capability of electro-disinfection methods without the production of chlorine. Examples of electrolytes

studied include Na_2SO_4 , Na_2CO_3 , NaH_2PO_4 , Na_2CO_3 and NaHCO_3 . The mechanism of microbial inactivation in chloride-free electrolyte is based on the action by disinfecting agents apart from chlorine species which includes O_3 , O_2^- , $\bullet\text{OH}$ and H_2O_2 .³⁵ These disinfecting agents are effective in inactivating a wide range of pathogenic microorganisms.³⁵

There have been several studies performed on the effects of electrolytes on the inactivation of bacteria e.g. *E. coli*. It was reported that the types of anions present in the electrolyte may have significant effects on the effectiveness of the bacterial inactivation.²² Kourdali *et al.* conducted a study to investigate the nature of electrolyte on the disinfection of *E. coli* using a platinum anode and a stainless steel cathode.²² The group found that *E. coli* were greatly inactivated in NaCl and Na_2SO_4 as compared to Na_2CO_3 .²² They attributed the results to the presence of sulfate (SO_4^{2-}) or chloride (Cl^-) ions during electrolysis which increase the effectiveness and rate of *E. coli* inactivation.²² The presence of such ions produces strong disinfecting agents such as Cl_2 , HClO and ClO^- .²² Moreover, the presence of Cl^- ions assists in the production of disinfecting agents by increasing the dissolution of metal during electrolysis and obstructing the passivation layer formation on the electrode.²² As for Na_2SO_4 , it was reported that the peroxodisulfates ($\text{S}_2\text{O}_8^{2-}$) formed by the oxidation of SO_4^{2-} ions contribute significantly to the *E. coli* inactivation.^{22, 32}

The lower *E. coli* inactivation in carbonates (CO_3^{2-}) was attributed to two reasons; reaction of carbonates with $\bullet\text{OH}$ radicals and passivation of carbonates on the anode.²² Carbonates are effective scavengers of $\bullet\text{OH}$ radicals as they donate an electron to the radicals which inhibit the oxidative action of these radicals.²² Additionally, carbonates inhibit the inactivation of *E. coli* through the passivation at the anode which reduces the dissolution of the metal and hence, decreases the production of oxidants and catalysts.²²

Result obtained by Kourdali *et al.* were in agreement with the study performed by Long *et al.* In their study, a stainless steel cathode and a boron doped diamond (BDD) anode were used to investigate the inactivation rate of *E. coli* in NaCl , Na_2SO_4 and NaH_2PO_4 .³⁶ 99% of *E. coli* were inactivated in 0.8 hours and 1.2 hours for NaCl and Na_2SO_4 respectively.³⁶ Na_2HPO_4 solution had the slowest *E. coli* inactivation with 99% in 10 hours.³⁶ Similar results were also presented by Kerwick *et al.* which investigated *E. coli* inactivation in similar set of electrolytes using a platinum clad niobium anode and a steel cathode.³⁴ There was a high *E. coli* inactivation within 60 minutes in both NaCl and Na_2SO_4 with 7-log and 4-log inactivation respectively.³⁴

For NaH_2PO_4 , a 4-log inactivation was attained after 105 minutes.³⁴ The low *E. coli* inactivation in NaH_2PO_4 was attributed to two reasons; adsorption of phosphate ions on the electrode surface and reaction of phosphates with $\bullet\text{OH}$ radicals.³⁴ The adsorption of phosphate ions onto the surface of the electrode may block active sites and prevent the adsorption of water which affects the generation of disinfecting agents greatly.³⁴ Additionally, phosphates are effective scavengers of $\bullet\text{OH}$ radicals which disrupt the action of these radicals.^{16, 34}

Another study conducted by Li *et al.* utilized a stainless steel cathode and a BDD anode to investigate the inactivation of *E. coli* in 3 different electrolytes; Na_2SO_4 , NaNO_3 and NaH_2PO_4 .³⁵ *E. coli* inactivation was the highest in Na_2SO_4 with 5.62-log obtained in 1 hour. Only 0.88-log and 0.25-log was attained for NaNO_3 and NaH_2PO_4 respectively.³⁵ The result was attributed to the highest concentration of disinfecting agents produced in Na_2SO_4 as compared to the other two electrolytes, which signals efficient inactivation.³⁵ Similar to the study by Kourdali *et al.*, it was suggested that the production of $\text{S}_2\text{O}_8^{2-}$ ions plays a part in the greater inactivation capability in Na_2SO_4 which were not generated in other electrolytes.³⁵ Li *et al.* also demonstrated the inactivation of *E. coli* in 0.2 M sodium peroxodisulfate without electrolysis which supported the role of $\text{S}_2\text{O}_8^{2-}$ in the mechanism.³⁵ More importantly, this study clarified that the *E. coli* inactivation was primarily contributed by $\bullet\text{OH}$ radicals and its products.³⁵ The inactivation of *E. coli* in Na_2SO_4 was significantly decreased to 0.99-log in 1 hour with the addition of excess methanol, a $\bullet\text{OH}$ scavenger.³⁵ Therefore, $\bullet\text{OH}$ radicals play a significant role in the electro-disinfection in chloride-free electrolytes.

Studies performed by Cong *et al.* and Jeong *et al.* demonstrated the major role $\bullet\text{OH}$ radicals play in the inactivation of microorganisms in chloride-free electrolyte.^{32, 33} Cong *et al.* confirmed the generation of $\bullet\text{OH}$ radicals in the electro-disinfection of coliforms in Na_2SO_4 by electron spin resonance (ESR).³³ Furthermore, Jeong *et al.* reported a decrease in the % inactivation of *E. coli* from 90% to 40% in phosphate buffer solution with the addition of excess methanol during electrolysis.³² This clarified the role of $\bullet\text{OH}$ radicals in the electro-disinfection of microorganisms.³² Jeong *et al.* also suggested that the inactivation of *E. coli* involving $\bullet\text{OH}$ radicals proceeds in two stages.³² The first stage involves the electro-sorption and rapid inactivation of *E. coli* on the anode surface through direct electron transfer.³² $\bullet\text{OH}$ radicals will be generated at the second stage where they oxidize and further inactivate the *E. coli*.³²

Gusmão *et al.* studied the inactivation of *E. coli* in unbuffered (Na_2SO_4) and buffered (phosphate buffer) solution using a stainless steel cathode and titanium coated with TiO_2 and RuO_2 , as dimensionally-stable anodes.³⁷ It was reported that the *E. coli* inactivation in buffered solution (50% in 1 hour) was lower than in unbuffered solution (85%).³⁷ This observation was attributed to a weaker pH gradient or lower change in pH due to the effects of buffer.³⁷

These studies have demonstrated that electro-disinfection can be effectively carried out in chloride-free electrolytes without generating chlorine and harmful disinfection by-products.^{32, 33} However, the nature of the electrolyte is important in ensuring an effective inactivation. This green technology may be relatively efficient as it is based on the synergistic effect of strong oxidizing species (radicals, O_3 and H_2O_2) and electric field.^{22, 23, 35} Other powerful germicidal agents might also be produced if certain ions are present.^{21, 22} Furthermore, the presence of such species might be capable in inactivating bacteria that are difficult to be inactivated by chlorine species.³³ Hence, there is a potential use of chloride-free electrolytes for the disinfection of water.

1.5. Microbial inactivation by platinized titanium

The material of the electrode is an important parameter for the inactivation of microorganism using electro-disinfection.^{35, 38, 39} Several studies have been performed using different electrode materials including BDD, stainless steel, titanium coated with TiO_2 , RuO_2 or IrO_2 , and platinum. BDD has shown to be one of the promising materials for the inactivation of microorganisms due to the advantages it possess such as high oxygen over-potential, inertness, insusceptible to corrosion, high oxidation capacity and capability to produce large amounts of $\bullet\text{OH}$ radicals.^{16, 39, 40} However, it can be quite costly to prepare BDD for large-scale or commercial applications.^{19, 36, 40} Moreover, BDD electrodes are only conventionally employed for research purposes or limited to small-scale applications.^{19, 37} Although BDD has good capability in producing radicals, the generation of large amounts of such radicals might pose problems as they can react readily with other species present to produce many unknown and harmful by-products.^{29, 41}

Titanium-based electrodes have gained increasing attention for the past 25 years.⁴² One such electrode is titanium coated with platinum or platinized titanium, which integrates the anti-corrosion properties of titanium and improved electrochemical qualities of platinum.⁴²

Moreover, platinized titanium is more cost-effective than platinum, is commercially available, can be readily obtained, and can be easily integrated into products.⁴²⁻⁵⁰ There are already existing commercial products such as water ionizers which employ platinized titanium as the electrodes.^{51, 52} Furthermore, the less costly platinized titanium possesses a desirable advantage of platinum in that it produces a small amount of active chlorine and hence, does not generate harmful chlorine by-products such as chlorates and perchlorates.⁴¹ A study conducted by Jeong *et al.* and a review by Kraft *et al.* demonstrated that platinum has the lowest free chlorine production efficiency among the electrodes tested including BDD and titanium coated with IrO₂, RuO₂ or Pt-IrO₂.^{29, 39, 41} It was also pointed out that BDD may oxidize hypochlorite to perchlorate and chlorate due to its high oxygen over-potential.^{19, 29, 41} This presents another disadvantage for BDD to be employed for application purposes.^{19, 29, 41} Therefore, platinized titanium might be more suitable than other electrodes in controlling the generation of reactive species in various applications.³⁸

Up to the present time, there appear to have only been a few studies conducted on platinized titanium in relation to microbial inactivation with only 3 reports found. The first set of studies were conducted by Kraft *et al.* which compared the capability between platinized titanium and iridium oxide (IrO₂-Ta₂O₅) for electrochemical disinfection of water through their production of active chlorine or hypochlorite.⁵³ In the first study, the rate of active chlorine production for both materials were investigated using various conditions such as concentration of chloride ions, temperature and current density.⁵³ It was reported that iridium oxide has a significantly higher active chlorine production rate than platinized titanium in all conditions.⁵³ Despite the weaker chlorine production ability displayed by platinized titanium, the result is in fact favourable as it showed that large amounts of chlorine species will not be generated from the use of platinized titanium. Moreover, the study found that there was a negligible production of chlorine by-products in the diluted chloride solutions.⁵³ Since platinized titanium does not possess a strong capability in producing chlorine species, disinfection using the material will thus not produce harmful by-products.

Kraft *et al.* furthered their previous study by looking into the feasible application of electro-disinfection for drinking water. The group employed a flow-through reactor containing the electrodes where tap water was continuously pumped through and the concentration of active chlorine measured.⁵⁴ Similar results were obtained where iridium oxide has higher active chlorine production than platinized titanium in various conditions e.g. temperature, flow rate

and current density.⁵⁴ An interesting problem that was reported was the effect of calcareous deposits on the electrodes.⁵⁴ To remove the deposits, regular polarity reversal of the electrodes were employed and studied but such reversal might affect the performance of electrodes.⁵⁴ It was found that the regular polarity reversal has no effect on the active chlorine production rate of platinized titanium electrodes.⁵⁴ Furthermore, platinized titanium still retained its capability and be in use after 1 year despite it being subjected to frequent polarity reversal.⁵⁴ The same could not be said for iridium oxide where its active chlorine production capability decreased significantly after polarity reversal.⁵⁴ In addition, the working life span of iridium oxide electrodes was reduced to 3 months.⁵⁴ Therefore, this set of studies demonstrated the stability, durability and robustness of platinized titanium.

Only one study has been conducted which used platinized titanium to inactivate micro-organisms notably *E. coli* and *Legionella pneumophila* in small-scale laboratory experiments.⁴² The effects of several conditions such as electrical potential, duration, speed of mixing, volume of contaminated solution, area and spacing of electrodes on the microbial inactivation were investigated so as to optimize the electrode configuration to achieve the most effective disinfection.⁴² From the study, higher voltage, lower electrode spacing, larger electrode area, faster mixing and lower volume of contaminated solution resulted in the faster inactivation of micro-organisms.⁴² With the optimized conditions, a 5-log inactivation of *E. coli* and *Legionella pneumophila* were achieved for the configuration after 25 min and 45 min, respectively.⁴² This study by Cossali *et al.* provided the first insight on the capability and effectiveness of platinized titanium as electrodes for the disinfection of drinking water.

1.6. Commercial products employing platinized titanium

Currently, platinized titanium has been used as electrodes in existing commercial products notably portable and non-portable hydrogen-generating water ionizers.⁵⁵⁻⁵⁹ However, the function of platinized titanium electrodes in these products is for the generation of hydrogen gas during electrolysis and not for anti-microbial purposes.⁵⁵⁻⁵⁹ An example is the GOSOIT hydrogen and alkaline water generator bottle shown in figure 1.⁵¹ Furthermore, in non-portable water ionizers such as Novita Hydroplus® Premium Water Ionizer NP10000, there is a separate membrane filtration system containing layers of sediment, membrane filters, activated carbon and calcium installed to remove microorganisms and purify the water.⁵⁹

Figure 1. GOSOIT hydrogen and alkaline water generator bottle, an example of portable water ionizer

Most of the commercial portable water purifier products employ membrane filtration to remove pathogenic microorganisms and produce safe drinking water.⁶⁰ There are also other types of purifier which utilizes UV light for water purification. An example is the LARQ Bottle PureVis™, a self-cleaning water bottle which is proposed to purify water.⁶¹ Another example is the Viqua SteriPEN® ultra handheld UV water purifier.^{62, 63} This handheld product is claimed to disinfect a water system by the emission of UV light as it is immersed in a container of water.^{62, 63} Although these products are effective in removing microorganisms, they have their own set of disadvantages. Membrane filters require routine monitoring and replacement due to their limited lifetime or degraded performance from damages, fouling and clogging.¹³ This requirement might deem these products not cost-effective as they employ several layers of different types of filters to remove microorganisms effectively.

The main issue for UV light purifiers is the health dangers they pose to the users if such products are handled incorrectly.^{62, 64} To use such products effectively and safely, proper care is needed as the exposure to UV light can cause severe damage to the eyes and skin.^{62, 64} Therefore, education on proper handling and application has to be conducted before users purchase these products.^{62, 64} Moreover, the purifiers require regular and comprehensive calibration and monitoring as their effectiveness depend on numerous parameters e.g. light intensity, wavelength, distance and duration of exposure.^{62, 64} Therefore, these devices might also be costly due to the health risks and stringent requirements of UV-light handling.^{62, 64}

There are existing water purifier products that employ electro-disinfection methods to purify water. An example is ActivH2O non-portable water purifier which utilizes a patented hydraulic electrode cell containing 6 titanium electrodes to generate disinfecting agents and eliminate pathogenic microorganisms.⁶⁵ Another example is Potable Aqua® Pure™ Electrolytic Water Purifier, a portable device that employs brine solution and electrolysis to generate a disinfectant solution containing a mixture of oxidants.⁶⁶ The disinfectant solution is then poured into the solution to be purified. To the best of our knowledge, there are currently no portable water purifier products which disinfect water directly using electrolysis and utilize platinized titanium as the electrodes.

1.7. Research Gap

Several studies have reported the influence of electrode materials and electrolyte on the effectiveness of bacterial inactivation through electro-disinfection. The electrode materials that have been commonly studied include BDD, stainless steel, platinum and titanium coated with IrO₂, RuO₂ or Pt-IrO₂. Currently, there has only been a few research studies carried out on platinized titanium in relation to microbial inactivation. However, there are no studies present which investigated the effect of electrolytes on the inactivation of *E. coli* by platinized titanium electrodes.

Existing commercial products that employ platinized titanium as electrodes are limited to only portable and non-portable hydrogen-generating water ionizers. Most of the commercially available portable water purifier products utilize membrane filtration or UV as the main method to eliminate pathogenic microorganisms. Current electrolytic water purifier products are either non-portable or adopt an indirect purification of water by electrochemically generating solution of disinfecting agents before adding into the solution to be purified. Hence, there are no commercial products which employ electro-disinfection to directly purify water in a portable system.

1.8. Scope and Objectives

The general aim of this thesis is to study the feasibility of developing a portable water purifier system employing an electro-disinfection method. Two key objectives are established to support this study. The first objective is to conduct preliminary investigations on two important

features to be adopted into the portable water purifier system, which are the electrodes arrangement and electrode material. Typically, existing water ionizer products employ a two-electrode arrangement as it is less costly and simpler to be designed and manufactured. This study aims to establish a comparison between the two- and three-electrode arrangements and conduct a short study to improve the 2-electrode arrangement.

For the electrode materials, the study aims to investigate the electrochemical properties e.g. conductivity and stability of platinized titanium with other commercially available materials such as platinum and titanium. Since the aim of this thesis is to develop a portable water purifier system, cost is a paramount factor as the product cannot be too expensive or it will not be commercially attractive to consumers. Therefore, the materials of interest are those that are easily available and low cost. Other electrode materials which might have superior performance and commonly used in electrochemical disinfection studies such as BDD, IrO₂-coated titanium, RuO₂-coated titanium and Pt-IrO₂-coated titanium will not be studied due to their high cost and requirement of complex processes to create such electrodes.

In addition, this study aims to investigate the inactivation of *E. coli* by platinized titanium electrodes in different media and electrolyte solution with similar ionic strength due to a lack of research in this area. *E. coli* K-12 was chosen as an indicator bacteria as it can be easily grown under laboratory conditions and is a common bacterium parameter to test for water quality.^{15, 35, 67}

The second objective is to design and develop a prototype for the portable water purifier system using 3D printing. Although portable products that employ electrolysis process exist e.g. water ionizers, their main function is to electrolyze water to generate hydrogen gas. These products may not be adequate to purify water as they do not have a feature to ensure a maximum disinfection of microorganisms in the water. Electrodes are situated at the bottom of the ionizer where electrolysis takes place. There are possibilities that some of the microorganisms at the bottom or near the electrodes can be inactivated. However, microorganisms at the bulk solution are not in close proximity with the electrodes and thus, not disinfected. Such products do not have any feature to transport the remaining bulk microorganisms to the electrodes' surroundings to be inactivated. The same explanation can be said for oxidants. In such water ionizers, oxidants or disinfecting agents may be generated at the electrodes. Due to the lack of

a circulation feature, these disinfecting agents remain in the proximity of the electrodes or at the bottom of ionizers and cannot kill microorganisms at other areas of the bulk solution.

With this in mind, the main priority for the second objective is to design, develop and integrate a feature into the water purifier prototype which generates a good circulation of water in the system. This is to allow the maximum amount of microorganisms to be inactivated either by coming into contact with electrodes or by disinfecting oxidants which are well-distributed throughout the water body. Several parameters of the 3D-printed water purifier prototype such as potential required, pH, chlorine concentration and *E. coli* inactivation will also be studied.

For this thesis, tap water was chosen as the main electrolyte to be studied due to several reasons. Firstly, tap water contains ions which allows electrolysis to occur without the application of a relatively high voltage. Secondly, although tap water contains some concentration of ions, it does not contain a high level of chloride ions. The range of chloride ions present in tap water reported by the Public Utilities Board (PUB) of Singapore is between 5 to 45ppm.⁶⁸ Hence, tap water can be categorized as a low chloride concentration solution which will not produce a high level of harmful chlorine or its by-products during electrolysis. Finally, tap water was studied extensively in these studies because it is the most common water source and reports of poor quality of tap water exist in various locations, even in developed countries such as the United States of America.⁹ The portable water purifier was envisioned to be used to readily purify tap water in situations such as homes or during travel where there are instances of poor quality water or where there is uncertainty as to whether the bottled water is safe to drink.

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Chapter 2

Experimental methods

- 2.1. *Chemical & Reagents*
- 2.2 *Materials*
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References

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2.1. Chemicals & Reagents

Unless otherwise specified, all reagents and chemicals used in the project were purchased and used as received. Tap water samples were obtained from NTU SPMS analytical laboratory 04-43 and 04-44. Hydrochloric acid, sodium hydroxide, sodium sulfate, and sodium chloride were procured from Sigma-Aldrich. Sodium nitrate was purchased from Thermo Fisher Scientific. Buffer, reference standard, pH 4, 7 and 10 for the calibration of pH meter was purchased from Sigma-Aldrich. Water samples from a cold water dispenser were obtained from NTU SPMS coffee/seminar room 04-04. Sodium chloride, potassium dihydrogen phosphate and N,N-diethyl-1,4-phenylenediamine sulfate were procured from Sigma-Aldrich. Potassium permanganate and disodium EDTA were purchased from Thermo Fisher Scientific. Hydrogen peroxide and anhydrous disodium hydrogen phosphate was purchased from Alfa Aesar. Sulfuric acid was purchased from Honeywell Research Chemicals. For *E. coli* inactivation experiments, Nutrient Agar and Tryptic Soy Broth were procured from Sigma-Aldrich. All solutions were prepared with ultrapure water which was purified by ELGA Purelab option-Q.

2.2. Materials

Different materials were studied as the electrodes. Platinum gauze (0.198 mm diameter wire) and Titanium gauze (0.13 mm diameter wire) were purchased from Alfa Aesar. Two types of aluminium were studied as the anode, which were Diamond Heavy Duty aluminium foil and aluminium sheet that were purchased from Art Friend. The stainless steel plate was procured commercially from goodhome.sg. Nafion membranes, carbon felt and platinized titanium screens were purchased from the Fuel Cell Store. A commercial toy boat propeller and low current DC motor were procured from SGBotic Pte Ltd. Electrical wires were purchased from Sun Light Electronics Pte Ltd. The design 2 propeller was fabricated using the aluminium sheet purchased from Art Friend.

2.3. Cyclic voltammetry instrumentation

Cyclic voltammetry (CV) measurements were performed with a computer-controlled Eco-Chemie Autolab PGSTAT302N potentiostat using a three-electrode system. The working electrode was a 2.0 cm by 2.0 cm platinum gauze, used in conjunction with a Pt-wire counter electrode (Metrohm) and an Ag wire miniature pseudo-reference electrode (eDAQ Pty Ltd). The working electrode was cleaned by polishing on a Buehler Ultra-polishing cloth with

alumina oxide slurry, washing with ultra-pure water, drying before introducing into the cell at the start of the experiment. All cyclic voltammograms were recorded at 295 K inside a Faraday cage.

2.4. Cyclic voltammetry procedure

CV experiments were performed in tap water, inside of a glass cell that was dried in an oven at 373 K for 30 min. All voltammograms were obtained at a fixed scan rate of 0.1 V s^{-1} and in a fixed potential window of *ca.* between -2 to 2 V to ensure a consistent timeframe for all cycles.

2.5. Electrolysis instrumentation and procedure

Electrolysis measurements were conducted with a computer-controlled Eco-Chemie Autolab PGSTAT302N potentiostat using either a three-electrode or two-electrode arrangement. Electrolysis experiments were carried out either at constant potential or at constant current at 295 (± 2) K. Electrolysis were performed either in a two-compartment electrolysis cell divided by a sintered glass frit with a porosity no. 5 or a glass cell with only one compartment depending on the nature of the experiments.

2.6. Comparison study between 2-electrode and 3-electrode arrangement

For 3-electrode arrangement, the working electrode a 2.0 cm by 2.0 cm platinum gauze, used in conjunction with a Pt-plate counter electrode and an Ag wire miniature pseudo-reference electrode (eDAQ Pty Ltd). For the two-electrode arrangement, the working electrode and counter electrode used were the same as for 3-electrode systems but without the reference electrode (the reference and auxiliary leads from the potentiostat were connected to the counter electrode). The electrodes were washed with ultra-pure water and dried before introducing into the cell at the start of the experiment. Electrolysis experiments for this study were performed at constant potential for 280 s in a two-compartment electrolysis cell divided by a sintered glass frit with a porosity no. 5. The volumes of tap water in both electrode compartments were approximately 20 mL each.

2.7. Improvement of conductivity for 2-electrode arrangement

In this study, the working electrode (anode) used was a 2.0 cm by 2.0 cm platinum gauze, used in conjunction with a Pt-plate counter electrode (cathode). The electrodes were washed with ultra-pure water and dried before introducing into the cell at the start of the experiment. Electrolysis experiments for this study were performed at constant potential for 280 s inside of a glass cell that was dried in an oven at 373 K for 30 min. The volume of tap water in the glass cell was approximately 25ml.

2.8. pH studies of electrodes after electrolysis

For this study, the working electrode (cathode) used was a 2.0 cm by 2.0 cm platinum gauze, used in conjunction with a Pt-plate counter electrode (anode). The electrodes were washed with ultra-pure water and dried before introducing into the cell at the start of the experiment. Electrolysis experiments for this study were performed at a constant potential for 300 s in a two-compartment electrolysis cell divided by a sintered glass frit with a porosity no. 5. The volumes of tap water in both electrode compartments were approximately 20 mL each. pH of the tap water before and after electrolysis were measured with a calibrated and portable pH meter (Metrohm 826 pH mobile). Prior to every measurement, KCl was added to the solutions to ensure an ionic strength of 0.05 M.

2.9. Conductivity study of different materials as anode and cathode

In the conductivity study, the 2-electrode arrangement was employed. Different materials with identical sizes (2.0 cm by 2.0 cm) were used for the cathode and anode. The electrodes were washed with ultra-pure water and dried before introducing into the cell at the start of the experiment. Electrolysis experiments for this study were performed at a constant potential of -4 V for 300 s inside a glass cell that was dried in an oven at 373 K for 30min. The volume of tap water in the glass cell was approximately 25 mL.

2.10. Stability study of different materials under long duration of electrolysis

In the stability study, the 2-electrode arrangement was employed. Different materials with identical sizes (2.0 cm by 2.0 cm) were used for the cathode and anode. The electrodes were washed with ultra-pure water and dried before introducing into the cell at the start of the experiment. Electrolysis experiments for this study were performed at constant current of -5 mA for 3 h inside a glass cell that was dried in an oven at 373 K for 30 min. The volume of tap water in the glass cell was approximately 25 mL. In the conductivity and stability studies of different materials, the 2-electrode arrangement was employed. Different materials with identical sizes (2.0 cm by 2.0 cm) were used for the cathode and anode. The electrodes were washed with ultra-pure water and dried before introducing into the cell at the start of the experiment.

2.11. 3D-printing instrumentation

Components of the 3 prototype designs, compartments for the study of propeller effects and water purifier final prototype were designed using Autodesk Fusion 360. They were then printed with 1.75mm PolyLactic Acid (PLA) using the software, Simplify3D and Dreamer FlashForge 3D printer.

2.12. Electrochemical potential studies of the 3 prototype designs

Electrolysis was conducted for the chronopotentiometry studies for the 3 designs of the water purifier prototype at constant currents for 200-300 s. Different materials were used for the cathode and anode where the sizes depended on the designs of the prototype. The electrodes were washed with ultra-pure water and dried before introducing them into the prototype at the start of the experiment. The volume of tap water in the prototypes was approximately 50-100 mL.

2.13. Nafion pre-treatment

2.13.1. Pre-treatment with ultra-pure water at 80°C for 4h

Nafion membrane was soaked in an ultra-pure water bath from room temperature to 80 °C for 4 h. The Nafion membrane was then rinsed in ultra-pure water at room temperature twice. Nafion was then stored in ultra-pure water overnight.¹

2.13.1. Pre-treatment with H₂O₂, ultra-pure water and H₂SO₄

The Nafion membrane was soaked in 3% H₂O₂ at 80 °C for 1 h. The Nafion membrane was rinsed with ultra-pure water and then soaked in ultra-pure water at 80 °C for 2 h and in 0.5 M H₂SO₄ at 80 °C. The membrane was then rinsed with 80 °C ultra-pure water and stored in ultra-pure water.

2.13.1. Pre-treatment with with H₂SO₄ at 80°C

The Nafion membrane was soaked in 1 M H₂SO₄ from room temperature to 80 °C for 4 h, rinsed with ultra-pure water at room temperature twice and then stored in ultra-pure water overnight.¹

2.14. pH studies of water purifier prototype design 3

For this study, the electrodes used were platinized titanium mesh (2.0 cm by 2.0 cm). The electrodes were washed with ultra-pure water and dried before being introduced into the prototype at the start of the experiment. Electrolysis experiments were then performed at constant current for 300 s in the prototype. The volume of tap water in the prototype was approximately 100 mL. The pH of the tap water before and after electrolysis was measured with a calibrated and portable pH meter (Metrohm 826 pH mobile). Prior to every measurement, KCl was added to the solutions to ensure an ionic strength of 0.05 M.

2.15. Preparation of *E. coli* suspension

E. coli K-12 was provided by Nanyang Environment and Water Research Institute (NEWRI). For the preparation of pre-culture, a single colony was inoculated in 5 mL of sterile tryptic soy broth and grown at 35 °C for 24 h with 130 revolutions per minute (rpm) agitation.² The pre-culture was then inoculated in 100 mL fresh tryptic soy broth and grown at 35 °C for 24 h with

130 rpm agitation.² Prior to each experiment, 20 mL of the *E. coli* culture was centrifuged at 10000 rpm for 10 min and supernatant liquid removed.² The *E. coli* pellets were washed with the sterile electrolyte and centrifuged at 10000 rpm for 10 min.² The supernatant liquid was also removed and *E. coli* pellets were suspended with the sterile electrolyte to form 10^8 colony forming units per milliliter (CFU/mL) for use in the experiments.

2.16. *E. coli* inactivation experiments

Electrolysis at constant potential of -10 V was performed for the *E. coli* inactivation experiments in a 30 mL beaker equipped with two platinized titanium electrodes with identical sizes (2.0 cm by 2.0 cm). Before the start of experiments, platinized titanium electrodes were washed with ultra-pure water, dried and measured for their resistance. The separation between the electrodes in the system was kept constant at 5 mm. All apparatus and consumables such as micro-pipettes were autoclaved at 120 °C for 15 min before use. The 25 mL electrolytic system was continuously mixed by a magnetic stirrer bar throughout the experiment. Samples were withdrawn before and after electrolysis to determine the pH. At regular timed intervals, samples were extracted during the experimental runs for the determination of optical density and concentration of survival *E. coli* cells.

2.17. *E. coli* inactivation study of anode and cathode

Electrolysis at a constant potential of -10 V was performed for the *E. coli* inactivation experiments in a two-compartment electrolysis cell divided by a sintered glass frit with a porosity no. 5. Each compartment contained a platinized titanium electrode with identical sizes (2.0 cm by 2.0 cm). Before the start of experiments, platinized titanium electrodes were washed with ultra-pure water, dried and measured for their resistance. All apparatus and consumables such as micro-pipettes were autoclaved at 120 °C for 15 min before use. Each compartment contained 35 mL of prepared *E. coli* suspension. Samples were withdrawn before and after electrolysis to determine the pH. At regular timed intervals, samples were extracted during the experimental runs for the determination of the optical density. Samples were also taken out at 15 min to determine the concentration of viable *E. coli* cells.

2.18. Study of the effects of pH on *E. coli* inactivation

pH of 15mL *E. coli* suspensions were adjusted using NaOH and HCl to the desired pH range. After the adjustment of pH, the suspensions were left to stand for several time intervals (10min, 3h and 24h) where samples were taken for the determination of optical density.

2.19. *E. coli* inactivation of water purifier prototype (final design)

Electrolysis at constant potential of -10 V was performed for the *E. coli* inactivation experiments in the water purifier prototype final design equipped with two platinized titanium electrodes with identical sizes (2.0 cm by 2.0 cm). Before the start of experiments, platinized titanium electrodes were washed with ultra-pure water, dried and measured for their resistance. All apparatus and consumables such as micro-pipettes were autoclaved at 120 °C for 15 mins. before use.

The 100 mL electrolytic system was continuously stirred by a magnetic stirrer bar throughout the experiment. Samples were withdrawn before and after electrolysis to determine the pH. At regular timed intervals, samples were extracted during the experimental runs for the determination of optical density and concentration of survival *E. coli* cells.

2.20. Analytical techniques

2.20.1. Viable *E. coli* cells by plating

The concentrations of viable *E. coli* cells were determined by plating and counting colonies.³ Samples that were withdrawn were diluted and plated on Nutrient agar media and incubated at 37 °C for 24 h.³ The viable cells of *E. coli* were recorded as $\log(N/N_0)$ where N_0 is the number of colonies counted at 0 h and N is the number of colonies counted of the withdrawn samples at different time intervals.³ The number of colonies was reported on the results by the colony-forming unit (CFU).³

2.20.2. OD₆₀₀ determination

Optical density of the *E. coli*-containing samples were determined by measuring the absorbance at 600 nm (OD₆₀₀).³ The instrument used was a monochromator multi-plate reader Tecan Infinite M200. OD₆₀₀ is commonly used to measure the density of bacterial suspension which is proportional to the number of bacterial cells where 600 nm is the most suitable wavelength

to measure opacity.³ For the studies in this thesis, OD₆₀₀ allows us to estimate the degradation in the opacity of the sample suspension which in turns reflects the reduction in the number of *E. coli* cells.

2.20.3. Measurement of chlorine

Measurement of active chlorine in samples were performed as parts per million (ppm) using the N,N-diethyl-*p*-phenylenediamine (DPD) colorimetric method.⁴ Potassium permanganate was used in place of Cl₂ standards where 0.0891 g/L potassium permanganate solution is equivalent to 100 ppm Cl₂.⁴ From the potassium permanganate stock solution of 100 ppm Cl₂, a 1 ppm Cl₂ working solution was created and used to make the standards with 0.03, 0.05, 0.07, 0.1, 0.2, 0.3 and 0.4 ppm Cl₂. A calibration graph of absorbance against Cl₂ concentration was plotted. Two essential reagents, buffer and DPD were prepared for the determination of chlorine.⁴ The buffer solution was prepared by mixing anhydrous disodium hydrogen phosphate, potassium dihydrogen phosphate and disodium EDTA in ultrapure water. The buffer solution was measured with a Metrohm pH meter to ensure that the pH was in the range of 6.2 – 6.5. The DPD reagent was prepared by mixing N,N-diethyl-1,4-phenylenediamine sulfate, sulfuric acid and disodium EDTA in ultrapure water.⁴

Before each measurement with a LAMBDA 750 UV/Vis/NIR spectrophotometer, the sample was mixed with buffer and DPD reagent in a ratio of 20:1:1 for 3 minutes.⁴ DPD is oxidized by the presence of chlorine which forms a magenta product.⁵ The concentration of magenta product was measured by the spectrophotometer at 515 nm.⁵

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Chapter 3

Preliminary studies for water purifier prototype and *E. coli* inactivation by platinized titanium

- 3.1. *Chapter Overview*
- 3.2. *Preliminary studies of electrolysis of tap water*
 - 3.2.1. *Cyclic Voltammetry of tap water*
 - 3.2.2. *Comparison between 2-electrode vs 3-electrode arrangement for tap water electrolysis*
 - 3.2.3. *Improvement of IR-drop for 2-electrode arrangement*
- 3.3. *pH studies of anode and cathode compartments after electrolysis*
- 3.4. *Electrode material studies for electrolysis*
 - 3.4.1. *Conductivity of different materials as anode and cathode based on current density*
 - 3.4.2. *Stability of materials under long duration of electrolysis*
 - 3.4.2.1. *General Overview*
 - 3.4.2.2. *Formation of titanium dioxide on titanium anode*
 - 3.4.2.3. *Changes in the appearance of aluminium and steel*
 - 3.4.2.4. *Conductivity and stability of carbon felt*
 - 3.4.2.5. *Conductivity and stability of platinum as cathode and anode*

3.4.3. *Conductivity and stability of platinized titanium under long electrolysis duration*

3.5. *Inactivation of E. coli by platinized titanium electrodes*

3.5.1. *General Overview*

3.5.2. *E. coli inactivation by platinized titanium electrodes in different electrolyte media*

3.5.3. *E. coli inactivation by platinized titanium electrodes in different electrolytes with similar ionic strength*

3.5.4. *E. coli inactivation by platinized titanium electrodes in different electrolytes with excess methanol*

3.5.5. *E. coli inactivation by anode and cathode*

3.5.6. *Effects of pH on bacterial disinfection*

3.6. *Conclusion*

References

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3.1. Chapter Overview

An essential component of an electrochemical-based water purifier system is the electrode.¹ Inactivation of pathogenic microorganisms is achieved by the electrode either directly, by direct contact or oxidation on the surface of electrode, or indirectly, by generation of disinfecting agents e.g. oxidants, radicals.^{2, 3} Therefore, the system and material of the electrodes must be suitable to ensure maximum disinfection of microorganisms in the water to be purified.

In this chapter, preliminary basic studies to understand the electrolysis of tap water were performed, including using cyclic voltammetry, conductivity and pH measurement. Cyclic voltammetry of tap water was carried out to observe the potentials at which water electrolysis occurs. From the potential obtained, a comparison study between two- and three- electrode systems and an improvement study for the two-electrode system were performed. We also investigated on the change of pH at the respective electrodes (anode and cathode) after electrolysis of tap water.

In the second part of the chapter, we investigated on a range of commercially available and low-cost materials that are suitable as electrodes for our portable electrochemical water purifier prototype. The materials studied included platinum, titanium, aluminium, carbon felt, steel and platinized titanium. Two properties of the materials were investigated in this study which were conductivity and stability during long electrolysis periods. For this range of materials, platinized titanium was found to be the most useful material due to its advantageous properties (high stability, wide potential window, cost-effectiveness) that have been used in various existing commercial products, e.g. water ionizers.

For the last part of the chapter, we focused on studying the *E.coli* inactivation by platinized titanium electrodes in different media and electrolyte solutions. Media that were studied were tap water, high and low chloride concentrated solutions and phosphate buffered saline (PBS) solutions. This study provided a preliminary understanding of the efficiency of *E.coli* inactivation by platinized titanium. For the investigation of the electrolyte effect, electrolytes that were of interest include sodium chloride, sodium sulfate and sodium nitrate. These electrolytes were prepared with similar ionic strength to ensure similar conductivity. Results obtained from this study provided the first insight on the effect of electrolytes on the *E. coli* inactivation by electrified platinized titanium. We furthered this study and investigated the

effects of electrolyte on the inactivation of *E.coli* at the anode and cathode electrodes separately.

3.2. Preliminary studies of electrolysis of tap water

3.2.1. Cyclic Voltammetry of tap water

The first preliminary study of tap water performed was cyclic voltammetry to observe the potentials at which electrolysis occurs. Cyclic voltammetry of tap water was performed in two directions; from negative to positive potential and from positive to negative potential. From figure 1, there are no significant differences between the voltammograms in the two directions. The only difference observed is the higher current generated at -2 V for the direction from -2 V to 2 V (all potentials are given relatively to the Ag/AgCl reference electrode). Due to the low conductivity of tap water, cyclic voltammetry was repeated in tap water spiked with 0.1 M Na_2SO_4 . As expected, the current generated is significantly greater in tap water spiked with 0.1 M Na_2SO_4 due to larger concentration of ions present. Similar observations were obtained for the voltammograms in figure 2 for Na_2SO_4 as with tap water.

Figure 1. CV of tap water. Red line indicates the direction from positive to negative potential. Blue line indicates the direction from negative to positive potential.

Figure 2. CV voltammogram of tap water with 0.1 M Na₂SO₄. Red line indicates the direction from positive to negative potential. Blue line indicates the direction from negative to positive potential.

A common trend in all voltammograms is the gradual increase in current from potentials of 1.1 V and -1.0 V onwards. Cyclic voltammetry is based on the reactions at the working electrode and therefore, at these potentials, oxidation and reduction of tap water take place based on equations 1 and 2 below. Potentials observed where there is an increase in current are near to the standard potentials for oxidation and reduction of water at 1.23 V and -0.83 V respectively. The shape of voltammograms obtained in this study are also in agreement with voltammograms of tap water conducted by other studies where there are continual increases in current at the extreme ends of the voltammograms.⁴ This indicates that an increase in potential or over-potential will further increase the current generated which produces greater amount of oxygen and hydrogen. Therefore, for a 3-electrode system, the minimum potential required for the electrolysis of tap water is 1.1 V or -1.0 V vs. Ag/AgCl (3 M KCl). Therefore, it was thought to apply an over-potential for our system to produce a higher concentration of disinfecting agents so as to ensure maximum bacterial inactivation.

3.2.2. Comparison between 2-electrode vs 3-electrode arrangement for tap water electrolysis

Electrolysis using a 3-electrode and 2-electrode arrangement in tap water were compared by comparing the currents at different applied potentials. From figure 3 and 4, a similar trend is observed for both 2-electrode and 3-electrode arrangements where an increase in potential will generate greater current based on Ohm's law equation given below. Interestingly, for the 3-electrode arrangement, the currents generated after 300 s at 1.35 V and 1.5 V were similar with a sharp increase when the potential was increased from 1.5 V to 1.8 V.

Figure 3. Graph of current against time for 3-electrode arrangement for different potentials

Figure 4. Graph of current against time for 2-electrode arrangement for different potentials

$$\text{Current (A)} = \frac{\text{Potential (V)}}{\text{Resistance (\Omega)}} \quad \text{Equation 3. Ohm's law}$$

As expected, the 3-electrode arrangement allows the generation of significantly higher currents than 2-electrode arrangement at similar potentials, as shown in figure 5. The current generated at 1.8 V in a 3-electrode arrangement is approximately 40 times greater than in the 2-electrode arrangement. This is because the a 3-electrode arrangement has significantly lower IR-drop than the 2-electrode arrangement. In a 2-electrode arrangement, there is a lack of compensation for the potential drop across the tap water due to resistance posed by the solution.^{5, 6} On the other hand, the use of a third electrode (reference electrode) with stable potential in a 3-electrode arrangement provides compensation for the voltage drop across the solution.^{5, 6} Moreover, the voltage drop between the reference and working electrode is small due to two reasons. Firstly, there is negligible current passing through the reference electrode.⁷ Secondly, the distance between the reference and working electrode is kept as minimal as possible.⁷

Figure 5. Comparison of current between 3-electrodes and 2-electrodes arrangements at 1.8 V.

Although the IR-drop in the 3-electrode arrangement is better, it was decided to adopt the 2-electrode arrangement in our water purifier prototype. With the end product in mind, a 3-electrode arrangement requires more resources and complex processes to manufacture the circuit board that will program the functions for the 3 electrodes. This will definitely incur higher cost in the manufacturing process and programming such circuit boards are beyond our expertise. On the other hand, a 2-electrode arrangement require the circuit board to only provide voltage to the 2 electrodes which requires simpler program, lesser resources and lower

cost. These 2-electrode voltage regulator circuit boards are already present in various products e.g. water ionizers, water purifiers and can be obtained commercially.^{8,9}

Therefore, there is a need to mitigate the potential drop present in the 2-electrode arrangement and there are two possible ways that this can be carried out. The first way is to decrease the resistance in the solution through the introduction of electrolyte into the tap water, which increases the conductivity.⁷ Although, we envisioned our water purifier product to electrolyze water sources without the need to add electrolyte, it was understood that it would be useful to study the inactivation of biological species (such as *E. coli*) with the presence of electrolyte. This is because the conductivity of tap water is low due to the presence of small amount of ions and the addition of electrolyte will improve the conductivity which was proposed to enhance the inactivation of microorganisms due to higher current passing through the electrodes and generation of more disinfecting agents.¹⁰ An investigation was performed on the effects of different electrolytes on *E.coli* inactivation during electrolysis experiments and are presented in section 5 of this chapter.

The second way to decrease the resistance is to minimize the distance separating the anode and cathode.⁷ For a 3-electrode arrangement, this resistance is kept minimal by minimizing the distance between the reference and working electrode.⁷ Therefore, a similar concept can be applied to a 2-electrode arrangement by minimizing the distance between anode and cathode, and it should be possible to improve the conductivity of the system. The result of this study will be discussed in the next section.

3.2.3. Improvement of IR-drop for 2-electrode arrangement

Improvement of the IR-drop for the 2-electrode system is achieved by reducing the distance between the cathode and anode.⁷ The comparison between 2-electrode and 3-electrode arrangements described previously (section 3.2.2), used a two-compartment electrolysis cell separated by a sintered glass frit. In this two-compartment cell, the distance between the anode and cathode was approximately 50 mm (with a glass frit positioned between the two electrodes). To lower the separation between the two electrodes, we utilized a glass cell with an approximately 10 mm separation between the cathode and anode. Experiments performed at a constant current of -1 mA or 1 mA presented in figures 6 and 7, respectively, clearly shows the significantly lower potential required by having the smaller separation between the 2

electrodes. This indicates that reducing the separation between the cathode and anode significantly lowers the IR-drop of the 2-electrode arrangement.

Figure 6. Chronopotentiometry graphs (Potential against Time) of small and large electrodes separation at -1mA

Figure 7. Chronopotentiometry graphs (Potential against Time) of small and large electrodes separation at 1mA

A similar concept has been applied in existing water ionizer products where the cathode and anode are separated by a thin layer of a proton exchange membrane or solid polymer electrolyte.¹¹⁻¹³ Hence, there is a minimum distance between the electrodes as they are kept as close to each other as possible. However, it was elected not to have a membrane separating the anode and cathode in our water purifier prototype as there is a need for good circulation of water through the cathode to ensure a maximum disinfection of pathogenic microorganisms.

Nevertheless, from the observation gained from the preliminary study on electrode spacing, it is clear that the distance between the electrodes in our water purifier system should be kept minimal to minimize the IR-drop. This allows more faradaic current to pass through the system, permitting greater intensity of electrolysis, generating more oxidants and hence, greater killing effect on the bacteria.

3.3. pH studies of anode and cathode compartments after electrolysis

The purpose of this study is to observe the changes of pH at the individual electrodes after electrolysis. In this study, a two-compartment electrolysis cell separated by a sintered glass frit was used with each electrode occupying its individual compartment. After electrolysis, the solution at each compartment was extracted to measure its pH. Based on the half-cell reactions equations shown in equations 1 and 2, H^+ and OH^- ions will be produced at anode and cathode, respectively, during electrolysis. The generation of these ions will result in a change in the pH at the vicinity of the electrodes. The measurement of pH was carried out before electrolysis and after electrolysis at several applied potentials. Table 1 shows that there is a change in pH at each electrode after electrolysis with the pH of the cathode compartment moving towards alkalinity and anode compartment moving towards acidity. The observation is in agreement with theoretical half-cell reactions due to the production of H^+ and OH^- ions. The results in Table 1 illustrate that as the applied potential between the electrodes increases, there is an accompanying increase in the pH change at the different electrodes. This is because the increasing voltage results in greater electrolysis with higher current passing through the system, generating more H^+ and OH^- ions.

Samples	pH	
Tap water (start of experiment)	7.44	
Tap Water + Potential (V)	Cathode	Anode
-2	7.42	7.40
-4	7.51	7.34
-6	7.47	7.29
-8	7.66	7.14

Table 1. Table of samples and pH readings

3.4. Electrode material studies for electrolysis

3.4.1. Conductivity of different materials as anode and cathode based on current density

A preliminary study was conducted to compare the conductivity of titanium, a material of interest against platinum, a commonly used metal and electro-catalyst for the electrolysis of water.¹⁴ Platinum has been reported to exhibit one of the best electro-catalytic performance in accelerating the electrolysis of water to form hydrogen and oxygen.¹⁵ This is due to the favourable properties of platinum such as high electrical conductivity, high electrochemical, mechanical and mechanical stability, and active surface with optimal adsorption by hydrogen allowing high current density.¹⁶ Although the “benchmark” platinum is commonly used, it is hindered by its low abundance naturally and high costs.¹⁴⁻¹⁷ Therefore, we are interested in searching for an alternative material to platinum. Titanium as an electrode material is of a great interest due to the properties it possesses. It is less costly than platinum, has strong corrosion resistance ability, can be produced on a mass scale easily, available in higher abundance than platinum, has good stability and high mechanical strength.^{18, 19} It has also been used to prepare stable electro-catalyst such as dimensionally stable anode (DSA) electrodes.¹⁸

Figure 8 demonstrates an expected observation, which is that the use of platinum as both cathode and anode generates the highest current due to high conductivity and low overpotential for the hydrogen evolution reaction (HER). In this experiment, the working electrode is the cathode and a potential of -4 V was to this electrode. The use of a platinum plate as the cathode generates the highest current density among the materials. The area of platinum plate was 2 cm², which is smaller than the area of the platinum mesh of 4 cm². A smaller working electrode results in a smaller ohmic drop across the solution and thus allowing more current to pass through the system.⁷ This accounts for the higher current generated by the platinum plate than platinum mesh.

Generally, the use of platinum as an electrode surface resulted in greater currents than the use of titanium, although the difference was not great, as shown in figure 8. Therefore, more studies can be conducted on the feasibility of using titanium as electrodes in our water purifier system due to the properties it possesses. One way of taking advantage of titanium’s properties is through coating titanium with a more conductive material. Hence, platinum-coated titanium is interesting as a suitable material for electrodes.

Figure 8. Comparison of current density between different electrode materials (platinum mesh, platinum plate, titanium mesh)

3.4.2. Stability of materials under long duration of electrolysis

3.4.2.1. General Overview

In this study, we conducted an investigation on a range of commercially available and low-cost materials that can be used as electrodes for our water purifier prototype. Platinum, a commonly used metal for the electrolysis of water is hindered by its high-cost and low abundance. Therefore, there is a need to search for alternative materials as electrodes. Since our general theme is to study the feasibility of a portable water purifier system, cost is a paramount factor as the product cannot be too expensive or it will not be commercially attractive to consumers. Therefore, the materials we focus on are those that are easily available and low cost.

Two properties of the materials were investigated in this study which are conductivity and stability during long electrolysis periods. The stability of the electrode materials was studied by physical observation of the material surface or formation of precipitates in the solution after electrolysis. Figures 9 and 10 illustrate how the potential of the anode materials coupled with either a titanium or platinum cathode varied at a constant applied current of -5 mA. Titanium is of a great interest to be used as a cathode due to the properties it possess such as high mechanical strength, insusceptible to corrosion, inertness and decent conductivity.²⁰

Figure 9. Graphs of Potential vs Time for different anode materials with a platinum cathode at -5 mA

Figure 10. Graphs of Potential vs Time for different anode materials with titanium cathode at -5 mA

3.4.2.2. Formation of titanium dioxide on titanium anode

When comparing figures 9 (that uses a Pt cathode) and 10 (which uses a Ti cathode), it can be observed that the potential at the cathodes varies depending on what material is used for the anode (in order to maintain a current of -5 mA). The effect is particularly pronounced when titanium is used as the anode, where the potential applied to the platinum or titanium cathodes (to reach the desired current of -5 mA) rapidly increases to the maximum set output of -10 mV. A closer look at the graphs shown in figure 11 shows that the potential increases drastically within 200 s, which is likely due to a decrease in activity of the titanium anode forcing the

potential to increase between the two electrodes to maintain the desired current. This phenomenon can be accounted by the formation of titanium dioxide (TiO_2).²¹ When titanium is used as an anode in an electrolyte, oxygen (O_2) is produced at the surface of anode.²¹ O_2 produced reacts with the titanium to form titanium dioxide which significantly increases the resistance of the electrode due to its electrically insulating nature.²² Therefore, with increasing durations, higher potentials are required to maintain the constant current of -5 mA.²² The higher potential will result in formation of more titanium dioxide which forms a thicker film on the anode. Therefore, the potential will keep increasing with time due to the increasing thickness of titanium dioxide with results in higher resistance.²² We also observed that there is a change in the colour of the titanium mesh. As shown in figure 12, the colour of titanium mesh changes from silver to blue, which is also evidence of titanium dioxide formation. The presence of TiO_2 causes interference between light and the oxide or variations of refractive and reflective index producing colours on the titanium surface.^{21, 22} As reported by Napoli et al, different voltages will vary the thickness of titanium dioxide film, which will produce different colours of anodized titanium.²¹ The appearance of the blue colour is produced at the lower voltage range which is in agreement with the observation in this study.²¹

Figure 11. Graphs of Potential vs Time for titanium anode with titanium and platinum cathode at -5 mA

Figure 12. Appearance of colour on titanium mesh before electrolysis (right) and after electrolysis (left)

3.4.2.3. Changes in the appearance of aluminium and steel

From the data in figures 9 and 10, aluminium allowed the lowest potential difference between the working and counter electrode among the materials studied as anode. It is followed by stainless steel, an alloy consisting of iron and certain percentage of carbon. This result is in agreement with the trend of conductivity values obtained theoretically; Aluminium > Stainless Steel > Platinum > Titanium > Carbon.²³ However, the main drawback of these materials is the changes in their appearance and formation of precipitates when oxidized at the anode.

It can be observed from figure 13 that there is a change in the appearance of the aluminium surface after 3 hours of electrolysis. The appearance of aluminium changes from a shiny and clean surface to the presence of white coloured precipitates on the surface.

A closer analysis of the potential vs time plots for aluminium (green lines in figures 9 and 10) reveals the presence of sharp potential drops at several time durations. Another observation that can be made is the gradual increase in potential from 0 s to 3 h which might be due to higher resistance contributed by the formation of white coloured precipitates on the aluminium surface. Moreover, the increase in potential is much steeper when the aluminium anode is coupled with a platinum cathode as compared to a titanium cathode. Appearance of white coloured precipitate can also be observed for stainless steel (Figure 14).

Figure 13. Appearance of aluminium before (left) and after 3h electrolysis (right)

Figure 14. Appearance of stainless steel before (left) and after 3h electrolysis (right)

Although aluminium and stainless steel have desirable conductivity properties, their susceptibility to changes in appearance and formation of precipitates under applied positive potentials makes them unsuitable for our water purifier system. Such materials, if used as anode in our system, might be easily damaged and thus, reducing the shelf life of our anode. Users might have to replace the electrodes frequently which makes our product unattractive. Moreover, we observed the appearance of precipitates in the tap water after 3 hours of electrolysis. From figure 15, a gelatinous white precipitate and a reddish brown precipitate (rust) are observed for aluminium and stainless steel, respectively. The formation of such precipitates is not desirable as it will deter users from using the product and frequent consumption of the precipitates will pose health risk to the users.

Figure 15. Presence of white gelatinous precipitate in water for aluminium anode (left) and reddish-brown precipitate for stainless steel (right)

3.4.2.4. Conductivity and stability of carbon felt

Carbon felt when used as an anode does not exhibit any formation of precipitates or changes in appearance. There is no significant difference in the appearance of the carbon felt as shown

in figure 16. However, the drawback of using carbon felt is its poorer conductivity as observed in figures 9 and 10. Apart from the titanium anode, carbon felt requires higher potentials to generate -5 mA for both cathode materials. Among the materials, it has one of the lowest conductivities which is expected based on theoretical conductivity values. Carbon felt's poor conductivity is not desirable to be used as electrodes as it will not permit a large amount of current to pass through the system, hindering the electrolysis process. As a result, this will hinder the generation of larger amount of disinfecting oxidants which affect the effectiveness of the water purifier to inactivate pathogenic microorganisms. A further disadvantage of carbon felt is that it is less mechanically robust than the metallic electrodes, which can result in small pieces of carbon being released into the solutions during electrolysis.

Figure 16. Appearance of carbon felt before (left) and after 3h electrolysis (right)

3.4.2.5. Conductivity and stability of platinum as cathode and anode

For the range of anode materials studied, platinum cathodes generally display better conductivity than titanium cathodes. This is expected due to higher theoretical conductivity value of platinum as compared to titanium.²³ Moreover, as an anode, platinum possesses the desirable qualities not observed in other materials such as stability, corrosion resistance and generally good conductivity. There was no significant difference in the appearance of platinum and formation of precipitates after 3h electrolysis.

However, as mentioned previously in the general overview section, there is still a need to search for an alternative material to be used as electrodes for our water purifier system due to the high cost and limited supply of platinum. The use of titanium was of interest, but it is hindered by its poorer conductivity in its oxidized form and unsuitability to be used as an anode due to the formation of titanium dioxide. A way of taking advantage of titanium's properties is through coating titanium with a more chemically stable material such as platinum in the form of

platinized titanium.²⁴ Platinized titanium integrates the anti-corrosion properties of platinum with the reasonable conductivity and light weight of titanium metal.²⁴ It is inexpensive, commercially available, can be obtained easily and can be easily integrated into products as it is already been used in existing commercial products.^{11, 12, 25-31} Kraft et al have reported the desirable durability and stability of platinized titanium in their study where platinized titanium are still usable after a year.³² Moreover, electrolysis at platinized titanium has also been reported to effectively kill *E. coli* and *Legionella pneumophila* in tap water.³² Hence, due to the advantages it brings, platinum-coated titanium becomes a great interest to us to be studied as an electrode material for our water purifier prototype.

3.4.3. Conductivity and stability of platinized titanium under long electrolysis duration

In this study, the conductivity and stability of platinized titanium was investigated under a 3 hours electrolysis of tap water. As illustrated in figure 17 below, platinized titanium as a cathode has higher conductivity than titanium and platinum in the duration of 0 to 7000 s, shown by how the potential needed to maintain a current of -5 mA was the lower. From 7000s onwards, platinized titanium has similar conductivity with platinum. This demonstrates that platinized titanium as that cathode has good conductivity which is comparable with platinum. The use of platinized titanium as both electrodes further improves the conductivity of the system greatly as illustrated in figure 17. In addition, there was no significant difference in the appearance of platinized titanium and formation of precipitates after 3 hours electrolysis.

This study demonstrated the two important properties possessed by platinized titanium which are high conductivity and stability. It has conductivity which is higher than titanium and comparable with platinum. Moreover, platinized titanium will not introduce harmful precipitates into the water system as shown in figure 18.³³ Due to the advantages it brings, platinized titanium was chosen as the material to be studied for *E. coli* inactivation and used in the final prototype of the water purifier system.

Figure 17. Comparison between platinized titanium as cathode and anode with other materials (-5mA)

Figure 18. Appearance of platinized titanium before (A) and after 3h electrolysis (B) and absence of precipitates in the water after electrolysis of platinized titanium (C)

3.5. Inactivation of *E. coli* by platinized titanium electrodes

3.5.1. General Overview

Based on the results of previous studies and the advantages it brings, platinized titanium was chosen as a suitable alternative material to platinum. Moreover, there are few studies conducted on bacterial inactivation on electrolyzed platinized titanium and no reports on the effect of different electrolytes on the inactivation. Therefore, this study might provide us with the first insight into the inactivation of *E. coli* by electrolyzed platinized titanium in different electrolyte

media. In this study, platinized titanium is used as both electrodes and all *E. coli* inactivation experiments were performed at constant potential of -10 V. To characterize the *E. coli* inactivation, two measurements were performed; (i) the OD₆₀₀ which measures the density of bacterial suspension and, (ii) counting of viable *E. coli* cells expressed as $\log(N/N_0)$.³⁴ The pH of the *E. coli* solutions was also measured before and after electrolysis.

Figure 19. Schematic diagram of *E. coli* inactivation experiments

3.5.2. *E. coli* inactivation by platinized titanium electrodes in different electrolyte media

E. coli inactivation by platinized titanium was firstly investigated in different media; high concentrated chloride solution (8181.6 ppm NaCl), low concentration chloride solutions (250 ppm NaCl and tap water) and buffer solution (Phosphate Buffer Saline (PBS)). Figure 20 illustrates the % *E. coli* inactivation with time in different media using the OD₆₀₀ measurement. As expected, *E. coli* inactivation in 8181.6 ppm NaCl has the highest rate of bacterial inactivation where 100% inactivation was achieved in 3 hours. This is followed by 250 ppm NaCl solution with lower concentration of chloride, which achieved 90% inactivation by in hours. Tap water and PBS achieved 68% and 50% *E. coli* inactivation by in hours, respectively.

Figure 20. % *E. coli* inactivation in different medium at -10V using OD₆₀₀ measurement

Figure 21 shows the change in appearance of the *E. coli* suspensions in the various media (tap water and chloride solutions) at different time intervals. It can be observed in all of the media that the opacity of suspensions decreases with time which signify a decrease in the concentration of *E. coli* present. This is primarily due to inactivation by electrolysis. In agreement with our OD₆₀₀ results, suspension in 8181.6ppm NaCl becomes the most clear and transparent by 3 h as 100% of the *E. coli* has been inactivated. Nevertheless, these results show that there are some degree of *E. coli* inactivation occurring even in low concentrated chloride solution such as tap water.

0h	1h	3h	6h
8181.6 ppm NaCl			
250 ppm NaCl

Figure 21. Photographs of *E. coli* culture subjected to electrolysis at -10 V in different media. First row is 8181.6 ppm NaCl. Second row is 250 ppm NaCl. Last row is tap water.

Counting of *E. coli* on an agar plate was also conducted to determine the number of viable cells at several durations (0, 1, 3 and 6 hour) of electrolysis. However, we only managed to perform *E. coli* counting for tap water, 8181.6 ppm NaCl and 250 ppm NaCl. The graphs of $\log(N/N_0)$ with time are presented in figure 22. The trend obtained is 8181.6 ppm NaCl > 250 ppm NaCl > tap water with 8181.6 ppm NaCl having the greatest *E. coli* inactivation capability. The trend obtained is in agreement with the trend obtained using OD_{600} measurements. It can be observed in figure 22 that $\log(N/N_0)$ for 8181.6 ppm NaCl is until 1h. This is because there were no viable cells observed on the agar plate at the 3 hour duration.

From the results, the trend of *E. coli* inactivation capability obtained is 8181.6 ppm NaCl > 250 ppm NaCl > tap water > PBS. The higher inactivation capability in chloride medium is due to the presence of chloride which generates strong oxidants in the form of chlorine species such as HClO, ClO^- and Cl_2 .^{2, 3} These oxidants are known to have strong germicidal capabilities.^{2, 3} Moreover, it was hypothesized that chloride ions can act as catalysts in the inactivation action by highly germicidal free radicals most notably $\bullet\text{OH}$ radicals.³ These chloride ions assist in increasing lifetime of $\bullet\text{OH}$ radicals, allowing these radicals to inactivate bacteria more effectively.³ The presence of larger concentrations of chloride in the solutions will generate more chlorine species during electrolysis which will increase the inactivation

efficacy of *E.coli*.^{1, 3} This explains the higher *E.coli* inactivation in 8181.6 ppm NaCl as compared to 250 ppm NaCl.

Figure 22. Log(N/N₀) for E coli inactivation in different medium at -10V

In addition, the presence of higher concentration of ions in the chloride solutions will allow more current to pass through the system due to higher conductivity.⁷ Higher current not only allows the generation of more oxidants, it creates a stronger electric field.³⁴ Electric field has been known to be harmful to bacterial cells as they cause irreversible permeability of cell membranes, damage important cell components and kill cells by oxidizing intracellular coenzyme A.³⁴ A stronger electric field will cause greater damages to the bacterial cells resulting in more *E.coli* to be killed.

Nonetheless, there is a certain degree of *E. coli* inactivation occurring in tap water as well. There might be production of chlorine species as tap water is reported to contain approximately 5 – 45 ppm of chloride ions.³⁵ However, the concentration of chloride ions in tap water is small and will not produce a large amount of chlorine species to inactivate *E. coli*. Hence, the *E. coli* inactivation in water might not be primarily be due to the disinfecting action of chlorine.^{1-3, 10} There might be other factors that contribute to the inactivation of *E. coli* such as the effects of the electric field and generation of other disinfecting agents.^{1-3, 10} It was reported that in water with low or zero chloride concentration, the inactivation of bacteria is attributed by the action of other disinfecting agents other than chlorine species such as ozone, O₂, H₂O₂ and radicals

(•OH).^{1-3, 10} More studies are conducted in the next section where we investigate the *E. coli* inactivation in solutions with no chloride concentration.

The pH measurement of the *E. coli* suspensions was also conducted before electrolysis and at 6 hours duration (or 3 hours for 8181.6 ppm NaCl). The pH readings of different media are shown in table 2. The pH for tap water and NaCl solutions increases or become more alkaline after electrolysis. For these experiments, the two electrodes are placed in the same compartment. The reaction at the anode produces H^+ and the reaction at the cathode produces OH^- (equations 1 and 2, respectively). However, because there is also chloride present that can be oxidized at the anode, it results in less acid being produced compared to base, which accounts for the overall increase in pH. We postulate that a change in pH towards the alkaline range, might contribute to the inactivation of *E. coli*.³⁶ Gusmão *et al* suggested that in a chloride-free solution, the presence of pH gradient near the electrodes can be one of the factor contributing to the killing of bacteria.³⁶ To study the effect of pH, we conducted an investigation on *E.coli* inactivation in different pH range without electrolysis which is presented in a later section,

Sample	Duration	
	0h	6h
Tap water	7.05	10.00
PBS	7.03	6.77
8181.6ppm NaCl	7.01	12.24 (@ 3h)
250 ppm NaCl	7.26	10.54

Table 2. pH readings of *E. coli* suspensions in different media at 0h and 6h electrolysis (3h for 0.14 M NaCl)

Another interesting observation from the pH measurement is the slight pH decrease for *E. coli* inactivation in PBS, a buffer solution. This might be due to the effect of the buffer reducing any drastic change in the pH of the system. Interestingly, PBS has the lowest % *E. coli* inactivation after 7 hours although it contains a greater concentration of ions (137 mM NaCl, 2.7 mM KCl, 8 mM Na_2HPO_4 and 2 mM KH_2PO_4) than tap water and NaCl solutions. A similar observation was reported by Gusmão *et al.* where the decrease in cell viability is lower in buffered solution as compared to unbuffered solution.³⁶ The observation was explained by a weaker pH gradient and bacterial inactivation was only due to direct transfer of charge or by the generation of •OH radicals at anode surface.³⁶ In other words, the inactivation of bacteria is reduced by a lower change in pH when electrolysis is carried out in a buffered solution. This

suggests that pH or pH gradient generated during electrolysis of water might contribute to the inactivation of bacteria.

3.5.3. *E. coli* inactivation by platinized titanium electrodes in different electrolytes with similar ionic strength

In the previous section, we discovered that there is some degree of *E. coli* inactivation in solution with low concentration of chloride e.g. tap water. The inactivation in these solutions might be due to other factors apart from chlorine species.^{1-3, 10, 34} In this section, we investigated the inactivation of *E. coli* in chloride-free electrolyte solutions including Na₂SO₄ and NaNO₃, and the bacterial inactivation capability of a combined electrolyte solution containing 3 different electrolytes; NaCl, Na₂SO₄ and NaNO₃. In a chloride-free electrolyte, no chlorine species will be formed and therefore, any *E. coli* inactivation cannot be attributed to the chlorine species.^{1-3, 10, 34} The ionic strength of the electrolyte solutions are kept the same so as to ensure the same conductivity in the system. The concentration of 250 ppm was chosen for NaCl as this is the maximum concentration of chloride ions permitted in drinking water which will not affect its taste and smell.^{37, 38}

The trend of *E. coli* inactivation capability obtained from figure 23 is as follows: NaCl > Na₂SO₄ > NaNO₃, although after 7 hours there was relatively little difference between the electrolytes. The trend we obtained is in agreement with previous studies which utilized boron diamond-doped anode and stainless steel cathodes to study *E. coli* inactivation in different electrolyte solutions.^{10, 34} The trend is expected as the presence of chloride in NaCl solution during electrolysis will generate chlorine species, commonly known and established disinfecting agents.^{1-3, 10, 34} Similar trend is also obtained during the counting of viable cells as shown in figure 24. Interestingly, the difference in the *E. coli* inactivation between NaCl and the other electrolyte solutions most notably Na₂SO₄ is not significant. This implies that there are other factors contributing to the *E. coli* inactivation in solutions with zero chloride concentration and that chlorine species may not be the only strong disinfecting agent. There might be the generation of other disinfecting agents which have similar inactivation capability with chlorine species.^{1, 3, 10, 34}

Figure 23. % *E. coli* inactivation in different electrolyte with similar ionic strength

Figure 24. Log(N/N₀) for different electrolyte solution at -10V

Figure 25 illustrates the change in appearance of the *E. coli* suspensions in the various electrolyte solution with similar ionic strength at different time intervals. It can also be observed that the opacity of suspensions decreases with time in all of the electrolyte solution which signify a decrease in the concentration of *E. coli* present. There is little difference in the appearance of the electrolyte solutions at 6h. Therefore, there are good degree of *E. coli* inactivation occurring even in non-chloride electrolyte solutions.

Figure 24. Photographs of *E. coli* culture subjected to electrolysis at -10 V in different electrolyte solution. First row is 250ppm NaCl. Second row is 203ppm Na₂SO₄. Third row is 363ppm NaNO₃. Last row is combined electrolyte solution of 84ppm NaCl + 68ppm Na₂SO₄ + 121ppm NaNO₃.

Although NaNO₃ and Na₂SO₄ have lower *E. coli* inactivation than NaCl, the difference is not very significant although these solutions do not contain any chloride ions. There are other

factors attributing to the inactivation of *E. coli* in chloride-free solution such as effects of the electric field and generation of other powerful disinfecting agents most notably, ozone, O₂, H₂O₂, O₂⁻ and radicals (•OH).^{1-3, 10, 34} The production of such disinfecting agents is possible due to the presence of oxygen either in the water, atmosphere or through the oxidation of water at the anode.^{1-3, 10, 34} Moreover, analysis of the trend will also show that *E. coli* inactivation in Na₂SO₄ is greater than in NaNO₃. Electrolysis in Na₂SO₄ will produce a strong oxidant, peroxodisulfate (S₂O₈²⁻) which is not generated in NaNO₃ solution.¹⁰ It is reported that formation of S₂O₈²⁻ is the main reaction during the electrolysis process.¹⁰ It possesses powerful oxidizing ability which displays strong germicidal properties.¹⁰ Equation 9 displays the oxidation reaction of SO₄²⁻ to form S₂O₈²⁻.¹⁰ Li *et al* also reported that inactivation of *E. coli* was observed in 0.2 M sodium peroxodisulfate despite the absence of an electrolysis process which confirm the germicidal properties of S₂O₈²⁻.¹⁰

Equation 9

An observation of the % *E. coli* inactivation at 5 minutes duration of figure 23 shows that NaNO₃ has the greatest % *E. coli* inactivation followed by NaCl and Na₂SO₄. A possible reason for this observation is due to greater concentration of NaNO₃ (363 ppm) resulting in a higher current produced in the early stages of electrolysis. A higher current enables the system to kill more *E. coli* initially due to more oxidants formed and stronger electric field.^{2, 3, 34} As time progresses, the % *E. coli* inactivation in NaCl and Na₂SO₄ surpasses that of NaNO₃. This might be due to the formation of stronger disinfecting agents produced in the other two electrolyte solutions notably, chlorine species and S₂O₈²⁻ in NaCl and Na₂SO₄ respectively.^{1, 10, 32, 34}

We also investigated the effects of a combined electrolyte solution containing the 3 electrolytes (NaCl, Na₂SO₄ and NaNO₃) as compared to a single electrolyte solution. Generally, it can be observed that the combined electrolyte solution has a lower % *E. coli* inactivation at all time intervals as compared to the other three single electrolyte solutions from figures 23 and 24. Conductivity is not the main issue here as the ionic strength of the combined electrolyte solution and the individual electrolyte solution are the same. A possible reason for the lower *E. coli* in combined electrolyte might be due to the competition between the ions for adsorption onto the surface of the electrode which greatly affects the concentration of disinfecting agents produced.¹ Since NO₃⁻ ions do not produce any active oxidant species when electrolyzed, the adsorption of these ions on the surface of the electrodes might block active adsorption sites.¹

This prevents H_2O and other ions such as SO_4^{2-} , Cl^- and OH^- from adsorbing onto the electrode surface and producing disinfecting agents.¹ A decrease in the concentration of disinfecting agents produced will reduce the *E. coli* inactivation ability of the system. Although having different electrolytes in the same solution affect the *E. coli* inactivation, it is an interesting concept to be studied to determine the favorable combination of electrolytes in terms of type and concentration of electrolytes.

pH measurement of the *E. coli* suspensions were also conducted before electrolysis and at 6 h duration. The pH readings of different electrolytes are shown in table 3. Similar to the pH readings of different media in the previous section, the pH for the electrolyte solutions increases or become more alkaline after electrolysis. We postulate that a change in pH towards the alkaline range, might contribute to the inactivation of *E. coli*.³⁶

Sample	Duration	
	0h	6h
250ppm NaCl	6.82	10.85
203ppm Na_2SO_4	6.90	9.41
364ppm NaNO_3	6.87	9.77
83.4ppm NaCl + 121.3ppm NaNO_3 + 67.6ppm Na_2SO_4	7	10.23

Table 3. pH readings of *E. coli* suspensions in different electrolyte solutions at 0h and 6h electrolysis

The main observation for this study is that although NaCl has a higher % *E. coli* inactivation than Na_2SO_4 and NaNO_3 , the difference is not significant. This implies that there are other factors contributing to the *E. coli* inactivation in solutions with zero chloride concentration e.g. electric field and other disinfecting agents with similar inactivation capability as chlorine species.^{1-3, 10, 34} The significance of this result is to show the potential application and possibility of employing non-chloride electrolytes for the purification of water using platinized titanium. Not only can pathogenic microorganisms be effectively disinfected in these electrolytes which is comparable with chloride solutions, harmful disinfection by-products, notably chlorine species e.g. Cl_2 , hypochlorite, hypochlorous acid, chlorate and perchlorate will not be generated.

3.5.4. *E. coli* inactivation by platinized titanium electrodes in different electrolytes with excess methanol

We furthered our study on the *E. coli* inactivation by platinized titanium in different electrolytes (NaCl, Na₂SO₄ and NaNO₃) with the introduction of excess methanol (30 mM). The purpose of methanol is as a scavenger for any •OH radicals produced at the surface of the electrode.¹⁰ Therefore, this study was to investigate the role of •OH radicals on *E. coli* inactivation.¹⁰ As shown from the OD₆₀₀ and log(N/N₀) results in figures 26, 27, 28 and 29, it is evident that there is a decrease in the *E. coli* inactivation across the three electrolytes with the presence of methanol. This suggests the role that •OH radical and its consecutive products play in electrochemical disinfection of both chloride-containing and chloride-free solutions.

Figure 26. % *E. coli* inactivation in different electrolyte with methanol

Figure 27. $\text{Log}(N/N_0)$ for NaCl solution with and without methanol at -10V

Figure 28. $\text{Log}(N/N_0)$ for Na_2SO_4 solution with and without methanol at -10V

Figure 29. Log(N/N₀) for NaNO₃ solution with and without methanol at -10V

It is also apparent that the decline in the *E. coli* inactivation is smaller in NaCl as compared to NaNO₃ and Na₂SO₄. This implies that •OH radicals play a less significant role in the inactivation of *E. coli* in chloride solutions due to generation of other strong oxidants e.g. chlorine species. The greater decrease in the *E. coli* inactivation in Na₂SO₄ is in agreement with another study conducted which clarified the role played by •OH radicals in the electrochemical disinfection in chloride-free solutions.¹⁰ Nonetheless, the *E. coli* inactivation in chloride-free solutions is not completely halted which indicates that other factors e.g. electric field and disinfecting agents apart from •OH radicals were also responsible for the inactivation.^{1-3, 10, 34}

3.5.5. *E. coli* inactivation by anode and cathode

We attempted to study the % *E. coli* inactivation at each electrode (anode and cathode) separately in the three electrolyte solutions that were previously investigated, i.e. NaCl, Na₂SO₄ and NaNO₃ with both electrodes in the same compartment. Another purpose of these experiments is to have a clearer understanding of the disinfection abilities of each electrode. The general results of the study are presented in figure 30. From the results, no relationships or trends can be deduced between % *E. coli* inactivation and time duration for both electrodes. This might be due to the fact that a short time duration is studied and hence, the degree of *E. coli* inactivation within the short interval might not be evident. Moreover, there is no consistent trend observed among the 3 electrolytes for both electrodes as there are different observations at different time intervals.

Figure 30. % *E. coli* inactivation by anode and cathode in different electrolyte solution at -10V

Therefore, we decided to focus our analysis of trends observed for 15 minutes duration. From the OD₆₀₀ result in figure 31, it can be evidently observed that the cathode has a greater % *E. coli* inactivation than anode for all of the 3 electrolyte solutions. This is also in agreement with the result of viable cell count or $\log(N/N_0)$ shown in figure 32. These results suggest that cathode has a stronger *E. coli* inactivation ability than anode at a short time duration.

Figure 31. % *E. coli* inactivation by anode and cathode in different electrolyte solution at -10 V (15 min)

Figure 32. Log(N/N₀) for anode and cathode in different electrolyte solution at -10 V (15 min)

Another observation for % *E. coli* inactivation using OD₆₀₀ and log (N/N₀) in figure 33 shows that NaNO₃ has the greatest *E. coli* inactivation among the 3 electrolytes for both electrodes at 15 min. This is similar to the trend obtained in the previous study (section 2) where NaNO₃ has the highest % *E. coli* inactivation at 5 min duration. As explained previously, a possible reason for this trend might be due to greater concentration of NaNO₃ (363ppm) resulting in a higher current produced in the initial duration allowing the formation of more oxidants and stronger electric field for direct killing of *E. coli*.³⁴

Figure 33. Log(N/N₀) for anode and cathode in different electrolyte solution at -10 V (15 min)

The general observation obtained from this study is a higher *E. coli* inactivation by cathode than anode, even in NaCl solution. This is intriguing as there are supposedly more germicidal

oxidants e.g. chlorine species, radicals, O₂, O₃, peroxodisulfates are generated at the anode which should lead to a stronger disinfection.^{1-3, 32, 34} The only oxidants generated at the cathode are radicals and H₂O₂.³ This might suggest that there is a significant factor attributing to the better inactivation capability by the cathode at the initial short duration of electrolysis. One postulation we had previously was that a change in pH towards the alkaline range, might contribute to the inactivation of *E. coli*.^{36, 39-41} As expected, the pH of anode and cathode after electrolysis is in the acidic and alkaline range respectively as shown in table 4. The results obtained in this study support our postulation and suggest that *E. coli* can be inactivated in alkaline pH better than acidic pH. To further support this postulation, we conducted an investigation on *E. coli* inactivation in different pH range without electrolysis in the next section of this chapter.

pH readings			
Sample	Electrode	Duration (min)	
		0	20
NaCl	Anode	6.45	2.28
	Cathode	6.51	11.69
Na ₂ SO ₄	Anode	6.86	2.53
	Cathode	6.95	11.30
NaNO ₃	Anode	6.80	2.52
	Cathode	6.46	10.89

Table 4. pH readings of *E. coli* suspensions for each electrode in different electrolyte solutions at 0 min and 20 min electrolysis

3.5.6. Effects of pH on bacterial disinfection

A suggestion made in the previous section was that *E. coli* can be inactivated in alkaline pH better than acidic pH. To further support this postulation, we studied the effect of pH on the inactivation of *E. coli* without electrolysis. Based on figure 32, it is evident that there is a greater *E. coli* inactivation in alkaline than acidic condition. The pH measured for anode and cathode in the previous study was in the range of 2.5-2.8 and 10.50-11.50 respectively. This study demonstrates that the *E. coli* inactivation in the pH range of 10.0 – 11.0 is greater than the pH range of 2.5-2.8 as shown in figure 34. The result implies that alkaline pH plays a role in the inactivation of *E. coli*.

Figure 34. % *E. coli* inactivation for various pH range (10 min exposure)

Another observation that can be made from the figure 34 is that a further increase in pH in the alkaline range (12-13) and decrease in pH in the acidic range (1-2) results in a higher % *E. coli* inactivation. Additionally, $\log(N/N_0)$ results shown in figure 35 also indicates that there is a greater % *E. coli* inactivation at higher pH ranges. The result obtained is similar to other studies conducted.³⁹⁻⁴¹ Moreover, a longer duration in alkaline pH will increase the % *E. coli* inactivation as evident in figure 36. On the other hand, a longer duration in acidic pH will cause a slight increase in the *E. coli* inactivation.

The results obtained in this study are in agreement with other studies which reported a rapid decline in the *E. coli* population at high pH levels or alkaline environment.³⁹⁻⁴¹ High pH has been shown to inactivate gram-negative bacteria such as *E. coli* by disrupting the cytoplasmic membrane resulting in the leakage of important cellular contents.⁴⁰ Gram-negative bacteria are more susceptible to alkaline pH due to their thin peptidoglycan layer which is less capable of preventing the bursting of cytoplasmic membrane weakened by high pH.⁴⁰ High pH weakens the membrane by solubilizing the membrane proteins exposing the hydrophobic sites of neighbouring lipids to the external environment.⁴⁰

One common observation from our *E. coli* inactivation studies is the increase in pH, to more alkaline, in most of the solutions after electrolysis. We postulate that a change in pH towards the alkaline range, might contribute to the inactivation of *E. coli*.^{36, 39-41} This study illustrates that there is a good degree of *E. coli* inactivation in alkaline environments, higher than acidic environments. Therefore, apart from electric field and generation of disinfecting agents,

alkaline pH created by electrolysis plays a role in the electrochemical inactivation of *E. coli* by platinized titanium.

Figure 35. Log(N/N₀) of various pH at 2 hours exposure

Figure 36. % *E. coli* inactivation of extreme acidic and basic pH for different duration

3.6. Conclusion

In conclusion, based on studies on electrode materials and configuration, it was decided to employ a 2-electrode system and platinized titanium in the water purifier prototype. The efficiency of the 2-electrode system is improved by keeping the separation between the cathode and anode as minimal as possible. Apart from being cost-effective, platinized titanium was chosen because it has higher conductivity than the other materials studied. Moreover, there is no significant difference in its appearance and absence of precipitates after electrolysis.

For the last part of the chapter, it has been shown that platinized titanium can effectively inactivate *E. coli* in different media such as chloride solutions, PBS and tap water. Moreover, we have acquired the first insight on the effect of electrolytes on the *E. coli* inactivation by platinized titanium. The *E. coli* inactivation trend of $\text{NaCl} > \text{Na}_2\text{SO}_4 > \text{NaNO}_3$ obtained is in agreement with previous studies. Although NaCl has a higher *E. coli* inactivation than Na_2SO_4 and NaNO_3 , the difference is not significant, implying the *E. coli* inactivation in solutions with zero chloride concentration is attributed by other factors. Additionally, we have clarified the role of $\bullet\text{OH}$ radicals in electrochemical disinfection of chloride-free solutions. The significance of this result is to show the potential application and possibility of employing non-chloride electrolyte for the purification of water using platinized titanium.

Moreover, we observed that for all of our *E. coli* inactivation studies, the pH of the solutions increases to more alkaline levels after electrolysis. Therefore, we postulate that a change in pH towards the alkaline range, is highly likely to contribute to the inactivation of *E. coli*.^{36, 39-41} This was further supported by the individual electrode study where it was found that the *E. coli* inactivation is greater in the cathode compartment than anode compartment. As expected theoretically, the pH of the solution containing the cathode increases to alkaline levels. The study that was conducted on the effect of pH on the inactivation of *E. coli* clarified the role of alkaline pH which shows that there is a good degree of *E. coli* inactivation in alkaline environments, higher than acidic environments. Therefore, apart from electric field and generation of disinfecting agents, alkaline pH created by electrolysis plays a significant role in the electrochemical inactivation of *E. coli* by platinized titanium.

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Chapter 4

Development of water purifier prototype using 3D-printing and studies to test its performance

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References

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4.1. General Overview

The main focus of this chapter is to design and develop a prototype for the portable water purifier system using 3D printing. It was aimed to integrate a feature into the water purifier prototype which generates a good circulation of water in the system. As mentioned in chapter 1, section 5, the purpose of the feature is to allow and ensure maximum amounts of microorganisms to be inactivated either by coming into contact with electrodes or by the disinfecting oxidants that are well-distributed throughout the water body. Three designs for the mixing feature were developed. Two essential studies; conductivity and circulation mechanisms were performed for each design to determine whether they are able to execute the function of the intended feature and suitable to be integrated into the water purifier prototype.

Based on the results of the preliminary studies, it was planned for the water purifier prototype to use the cathode as the main electrode for the inactivation of bacteria. This is based on the results of the study of electrolyte effects on individual electrodes, where it was discovered that for all the electrolytes, the cathode had a greater *E. coli* inactivation than the anode. In addition, chlorine will not be generated at the cathode during the electrolysis of water. A concern that is present in the electrolytic system is the generation of harmful substances such as chlorine species. Water ionizer products utilize a solid polymer electrolyte membrane to separate the anode and cathode. In such systems, the membrane is permeable to small ions e.g. H^+ and prevent gas or larger ions from passing through and enter the water system.¹⁻³ Gases such as chlorine and ozone are then vented out through a small outlet at the bottom of the water ionizer as shown in figure 1. By having the cathode as the main electrode for the inactivation of bacteria, it provides the opportunity to integrate Nafion (a cation exchange membrane) into the water purifier prototype by acting as a barrier at the anode to prevent any chlorine generated from entering the electrolyzed water system. Therefore, the feasibility of integrating Nafion into the water purifier prototype was investigated.

Once the major required electrochemical features had been finalized, experiments proceeded to design, and 3D print the portable water purifier prototype. Some modifications were made to incorporate a bottle-like container into the prototype to allow the storage of water. Several parameters of the printed water purifier prototype such as pH, conductivity in different types of water, generated chlorine concentration and *E. coli* inactivation were studied and optimized

Figure 1. Outlets at the bottom of GOSOIT hydrogen and alkaline water generator bottle to vent out gases

4.2. Prototype design 1

4.2.1. Mechanism for design 1

As discussed previously, it was aimed to integrate a feature into the water purifier prototype which allows a good circulation of water in the system. The purpose of the feature is to ensure maximum amounts of microorganisms to be inactivated either by coming into contact with electrodes or by the disinfecting oxidants that are distributed throughout the water body.⁴⁻⁸ Therefore, this feature is designed to enable water to be pushed towards the cathode, allowing a continual stream of water to continually come in contact with the cathode.

One way of accomplishing this is via a propeller with a design mimicking that of a fan blade or boat propeller.^{9, 10} The propeller can be connected to a motor and powered by batteries which will cause the propeller to rotate. The rotation of the propeller will push the water body upwards to the cathode. As the water is pushed upwards, new batches of water will enter the compartment of the propeller. The mechanism of this design was inspired by the working actions of fan blade and boat propeller which pushes air or water to the front as shown in figure 2. A schematic diagram of design 1 is presented in figure 3.

Figure 2. Working actions of fan blade (left) and boat propeller (right) pushing air or water to the front

As shown in figure 3, the cathode can be placed above the propeller in the direction of the water movement. On the other hand, the anode will be placed surrounding the cathode. The general circulation of water induced is that it will enter through the propeller compartment at the bottom and be pushed up to the cathode where it will leave the compartment and enter the bulk of the solution. The propeller and prototype design 1 were created by 3D-printing as presented in figures 4 and 5.

Figure 3. Schematic diagram of design 1. Arrows denote the movement of water.

Figure 4. 3D-printed propellers

Figure 5. 3D-printed design 1 water purifier prototype

4.2.2. Conductivity studies of design 1

Basic conductivity studies were performed for Design 1 using platinum and titanium cathodes, and an aluminium anode. Aluminium was chosen as the anode as it can be shaped to form a hollow cylinder surrounding the cathode. At constant currents of -2 mA and -10 mA, the potential required were measured for 300 s with and without the action of the propeller. As shown in figure 6, it was found that electrolysis can be performed in the design 1 prototype for both with and without propeller action as bubbles can be observed forming from the cathode.

Figure 6. Bubbles formed at the cathode in design 1 prototype at -2 mA (left) and -10 mA (right) indicating the occurrence of electrolysis

As expected, the potential required for the system with the platinum cathode was lower than the titanium cathode, indicating a lower overpotential required for electrolysis. Moreover, a higher current requires a higher potential. The observation of interest in this study is the comparison of the potential required to achieve the desired current between the system with and without the action of propeller. From the figures below, it can be observed that the systems with the action of propeller require higher potential to generate the current set. An exception would be for the system with platinum cathode at current of -2 mA but figure 7 shows that at duration of 200 s onwards, the current required from with the propeller action is projected to be higher. As for current of -10 mA, it is evident that potential required is higher with the action of propeller for both cathode materials. The results indicate that the action of the propeller raises the required potential of prototype design 1 which is not desirable.

Figure 7. Graph of Potential vs Time for Platinum cathode and Aluminium anode without propeller and with propeller at -2 mA

Figure 8. Graph of Potential vs Time for Platinum cathode and Aluminium anode without propeller and with propeller at -10 mA

Figure 9. Graph of Potential vs Time for Titanium cathode and Aluminium anode without propeller and with propeller at -2 mA

Figure 10. Graph of Potential vs Time for Titanium cathode and Aluminium anode without propeller and with propeller at -10 mA

4.2.3. Issues with prototype design 1

The study of the circulation mechanism of the propeller for design 1 will be discussed in this section. The increase in required potential in the presence of the propeller was surprising, since stirring the solution should have had the effect of decreasing the concentration polarization (which should have resulted in the lowering of the required potential). The action of the propeller does ensure mixing of the water in the prototype, but it does not push the water to the cathode in the way that was intended. Instead, it created a vortex-like mixing with a void in the middle. This results in some area of the cathode not covered in water as illustrated in figure 11. The effect caused by the propeller action has two consequences. Firstly, it affects the electrical potential greatly as time passes as concentration polarization increases due to some area of the cathode not covered with water. Since water is not in contact with some parts of the cathode, there are insufficient reactants reaching the electrode surface which will increase the electrical potential required. Secondly, lesser contact between water and cathode means that the propeller's effect does not allow maximum amount of bacteria to come into contact with the cathode. Additionally, lower amount of disinfecting agents can be generated. As a result, lower concentration of bacteria can be inactivated which is undesirable.

Moreover, since the action of the propeller does not push the water to the cathode, new batch of water is not allowed to enter the compartment at the bottom. Hence, there is no continuous circulation of water in the propeller; water pushed up to the cathode, leaving the propeller's compartment allowing a new batch of water to enter the compartment. There is mixing of water

as water is swirled by the propeller but the bulk of the water does not come into contact with the cathode. Therefore, the propeller for design 1 is unable to execute the function of the intended feature.

Figure 11. Vortex-like mixing by design 1 propeller which cause some area of cathode not to be in contact with water

4.2.4. Study on the vortex-like mixing by design 1 propeller

A short study to gain a better understanding on the action of the propeller was performed. For this study, two types of propeller were used; 3D-printed and commercially purchased. A 3D-printed compartment similar to the compartment in the water purifier prototype was attached the propeller at the bottom. Figure 12 shows that both types of propeller created similar vortex-like mixing effects with a void in the middle with no water. In fact, it was observed that water is pushed upwards but in little amounts and only at the edge of the compartment. The observation obtained in this study might explain the issue that was faced for prototype 1. The design for this type of propeller and its compartment mixes solutions through a vortex-like effect instead of pushing water upwards directly.

Figure 12. Vortex-like mixing by 3D-printed (left) and commercial (right) propeller in its printed compartment and not submerged in water

For the previous experiment, the propeller and its compartment were not submerged in water and hence, it might not mimic the actual action of propeller in the proposed water purifier. Therefore, the study was furthered by submerging the propeller in water in 2 situations; with and without the compartment. Under water, it can clearly observed that water is being pushed upwards but in the vortex-like movement with the void in the middle as shown in figure 13. The movement of water observed is similar to the action of blender where the circular motion of the blades creates a vortex.¹¹ The vortex creates a vacuum which pulls the water and food towards the middle.¹¹ The liquefied food then follows the blender's blade in a whirling fashion which forms a shallow well near its center.¹¹ The lack of space and whirling motion pushes the water and liquefied food out the sides and upwards. The circulation of food and water continues.¹¹

Figure 13. Vortex-like mixing by commercial propeller with (left) and without (right) it's printed compartment and submerged in water

Based on this observation, studies continued to determine whether water is pushed out the sides at the bottom of the propeller. For this study, a hole was created at the bottom of the propeller's

compartment as illustrated in figure 14. It was observed that water is being pushed out from the hole instead of entering the propeller's compartment which is similar to the action of a blender. Therefore, this study helped to reach the conclusion that the design 1 of the propeller was not suitable to be integrated into the water purifier prototype as it does not create the circulation of water that was intended.

Figure 14. Hole created at the bottom of the propeller compartment. Water is observed being pushed out through the hole.

4.3. Prototype design 2

4.3.1. Mechanism for design 2

Despite the issues that were faced for design 1, an interesting observation was made where water is being pushed out to the sides by the propeller and water entering through the middle. Therefore, a propeller was created that pushed water directly into the cathode causing water to enter through the sides. Instead of using fan blade-like propeller, a simple propeller shown in figure 15 was designed and created, which mimics a home-made water pump mechanism.^{12, 13} For this propeller to work effectively, a special compartment for the propeller was designed and printed as presented in figure 15. As the propeller turns, the water leaves the compartment through the only exit available which is the hole at the top containing the cathode. As water is being pushed upwards and out of the compartment, a void of space is created in the propeller compartment forcing a new batch of water to enter the compartment through the sides. This propeller design creates the desired circulation of water and ensures that water is continuously being pushed and comes into contact with the cathode. Hence, the maximum amount of bacteria

can be inactivated either by direct contact with the cathode or the continuously generated and well-distributed oxidants. The schematic diagram of design 2 propeller and its compartment is presented in figure 16.

Figure 15. Design 2 propeller attached to motor (left) and special compartment for propeller (right)

Figure 16. Schematic diagram of design 2. Arrows denote the movement of water.

Figure 17. Schematic diagram of design 2 propeller and its compartment. Arrows denote the movement of water.

4.3.2. Circulation study for design 2 propeller

A short experiment was performed to investigate if the design 2 propeller was able to create the circulation of water intended. As shown in figure 18, water was observed being pushed upwards through the hole at the top. Similar movement of water was also observed when a titanium mesh was placed at the top covering the hole. Moreover, a new batch of water continually entering the hole at the sides as shown in figure 19 was observed. This movement of water was continuously maintained when the motor is turned on. This indicates that the design 2 propeller is able to create the desired circulation of water and continuously supplying water towards the cathode to inactivate bacteria and generate disinfecting agents. It is able to execute the function of the intended feature.

Figure 18. Water is pushed upwards through the hole by the propeller without (left) and with titanium mesh (right)

Figure 19. New batch of water observed entering the design 2 propeller compartment

4.3.3. Electrochemical potential study for design 2 prototype

Due to the success of the design 2 propeller in creating the desired circulation of water, a 3D-printed water purifier prototype was constructed with the integration of the propeller. Figure 20 shows the prototype for the design 2 water purifier prototype. In this design, it was elected to decrease further the separation between the cathode and anode such that the anode surrounding the cathode is placed directly on top as illustrated in figure 16. Electrolysis of tap water at constant current of -2 mA was performed for the design 2 prototype and bubbles were observed forming on the electrodes. This indicated that electrolysis could successfully be performed in the design 2 water purifier prototype.

Figure 20. 3D-printed water purifier prototype design 2

Electrolysis at constant current of -2 mA was performed with and without the action of the propeller and the results are shown in figure 21. The potential required to generate -2 mA was similar in both situations meaning that the concentration polarization was similar with and without the propeller action.

Figure 21. Potential vs. time of design 2 water purifier prototype with and without the action of propeller

4.3.4. Electrochemical potential study for design 2 prototype with different cathode materials

In chapter 2 of this thesis, it was decided to use platinized titanium as electrodes in the water purifier prototype. Hence, further polarization studies were conducted on the design 2 prototype with an aluminium anode and different cathode materials to investigate the feasibility of using platinized titanium and comparing its performance with other materials such as titanium and the ‘benchmark’ platinum. As per previous studies, the polarization study was performed with and without the action of the propeller. As observed from figures 22 and 23, the trend for lowest potential at a fixed current was as follows; platinized titanium < platinum < titanium, where platinized titanium needs the lowest potential for both situations. Interestingly, for platinized titanium, the potential with the action of propeller is lower than without the action of propeller as presented in figure 24. This favourable result was not observed for the other cathode materials for platinum and titanium cathode, shown in figures 25 and 26 respectively. Hence, it is promising and desirable to use platinized titanium as cathode in the water purifier prototype.

Figure 22. Potential vs. time of design 2 water purifier prototype using aluminium anode and different cathode materials without the action of propeller

Figure 23. Potential vs. time of design 2 water purifier prototype using aluminium anode and different cathode materials with the action of propeller

Figure 24. Potential vs. time of design 2 water purifier prototype using aluminium anode and platinized titanium cathode with and without the action of propeller

Figure 25. Potential vs. time of design 2 water purifier prototype using aluminium anode and platinum cathode with and without the action of propeller

Figure 26. Potential vs. time of design 2 water purifier prototype using aluminium anode and titanium cathode with and without the action of propeller

4.3.5. Electrochemical potential study for design 2 prototype with different cathode materials using platinized titanium anode

A study in chapter 2 of this thesis showed that despite its desirable conductivity properties, aluminium is not suitable to be used as an anode in the water purifier system due its susceptibility to pitting corrosion which reduces its shelf life and forming undesirable corrosion products. Therefore, there is a need to search for alternative materials for the anode that have a reasonable conductivity and resistance to corrosion. Another previous study also demonstrated that utilizing platinized titanium for both electrodes (anode and cathode) yielded the lowest required potential among corrosion-resistant materials such as platinum and titanium. Hence, the purpose of this study is to investigate the operating potential of the design 2 prototype using platinized titanium as the anode and with cathode materials studied in the previous section.

General comparison between the two anodes, aluminium and platinized titanium shows that aluminium requires a lower electrochemical potential than platinized titanium to generate a current of -2 mA. This is in agreement theoretically as aluminium has higher theoretical conductivity value than both titanium and platinum. The required potential trends obtained for the aluminium anode were also observed for platinized titanium anode, which is platinized titanium < platinum < titanium as shown in figures 27 and 28. In addition, figure 29 shows that the concentration polarization of the prototype is improved with the action of propeller

compared to without the propeller for platinized titanium as both electrodes. Hence, the operating potential of design 2 prototype is improved by the action of the propeller which is desirable. Therefore, that platinized titanium can be used for both electrodes in the water purifier prototype as it has a low operating potential along with the desirable properties it possess.

Figure 27. Potential vs. time of design 2 water purifier prototype using platinized titanium anode with different cathode materials without the action of propeller

Figure 28. Potential vs. time of design 2 water purifier prototype using platinized titanium anode with different cathode materials with the action of propeller

Figure 29. Potential vs. time of design 2 water purifier prototype using platinized titanium anode and cathode with and without the action of propeller

Figure 30. Potential vs. time of design 2 water purifier prototype using platinized titanium anode and platinum cathode with and without the action of propeller

Figure 31. Potential vs. time of design 2 water purifier prototype using platinized titanium anode and titanium cathode with and without the action of propeller

4.3.6. Electrochemical potential study for design 2 prototype with Nafion membrane separating the electrodes

One concern of the water purifier system is the generation of harmful and undesirable substances notably, chlorine. One of the ideas elected for the water purifier prototype is to integrate a barrier surrounding the anode to prevent the chlorine generated from the oxidation of chloride from entering the water in the cathode compartment. Nafion was chosen as it permeable to water and small ions but does allow certain compounds e.g. chlorine to pass through.¹⁴⁻¹⁶ Therefore, water is still able to pass through Nafion and be in contact with the anode so that electrolysis can occur.

A study was performed to investigate the effect of Nafion on the conductivity of the prototype cell because its integration will increase the resistance of the system. Nafion was pre-treated using 3 different methods shown in table 1 to activate its function. The 3 methods are: (i) pre-treatment using ultra-pure water at 80°C for 4h, (ii) combination of hydrogen peroxide, pre-treatment using ultra-pure water and sulfuric acid, and (iii) pre-treatment using sulfuric acid at 80°C for 4h. The 3 pre-treatment methods were then investigated to determine which method will have the best impact on maintaining the conductivity of the prototype. Electrochemical potential measurements under fixed current were performed in several cycles with the action of propeller to allow water some time to permeate through the Nafion and be in contact with anode.

Figure 32. Schematic diagram of design 2 with Nafion acting as a barrier to anode

Nafion pre-treatment		
Ultra-pure water at 80°C for 4h	H ₂ O ₂ /ultra-pure water/H ₂ SO ₄	H ₂ SO ₄ at 80C for 4h
<ol style="list-style-type: none"> 1. Soak Nafion membrane in ultra-pure water bath from room temperature to 80°C for 4h 2. Rinse Nafion in ultra-pure water at room temperature twice 3. Store Nafion in ultra-pure water overnight 	<ol style="list-style-type: none"> 1. Soak Nafion in 80°C 3% H₂O₂ for 1hr 2. Rinse in ultra-pure water 3. Soak Nafion in 80°C ultra-pure water for 2hr 4. Soak Nafion in 80°C 0.5M H₂SO₄ 5. Rinse Nafion in 80°C ultra-pure water 6. Store in ultra-pure water 	<ol style="list-style-type: none"> 1. Soak Nafion membrane in 1M H₂SO₄ from room temperature to 80°C for 4h 2. Rinse Nafion in ultra-pure water at room temperature twice 3. Store Nafion in ultra-pure water overnight

Table 1. Table of 3 pre-treatment methods of Nafion and their procedures

It is evident from figures 33 - 35 below that the integration of Nafion significantly reduces the conductivity of the system, such that much higher potentials are needed in order to maintain the current of -2 mA. For two of the pre-treatment methods; ultra-pure water and combination of H₂O₂/ultra-pure water/H₂SO₄, the potential required to generate -2 mA is more than -10 V (exceeds potentiostat output) even after 5 cycles of electrolysis. Out of the three methods, pre-treatment using H₂SO₄ at 80°C yields the lowest potential which means that it has the best impact on the conductivity of the prototype. As shown in figure 33, the first 8 cycles of electrolysis require potentials lower than -10 V. The potential required becomes greater than -10 V for the 9th and 10th cycles which indicates a decrease in conductivity through the membrane with time.

Although this pre-treatment method has the best impact on the conductivity of design 2 prototype, it still reduces the conductivity of the system significantly. The potential required for design 2 prototype with Nafion of ~ -9.3 V is approximately double the potential required without Nafion (~ -4 V). The impact of Nafion on the conductivity of the prototype is not desirable and it might not be suitable to be used for the water purifier system.

Figure 33. Potential vs. time of design 2 water purifier prototype with Nafion pre-treated with H_2SO_4 at 80°C for 4h

Figure 34. Potential vs. time of design 2 water purifier prototype with Nafion pre-treated with ultra-pure water at 80°C for 4h

Figure 35. Potential vs. time of design 2 water purifier prototype with Nafion pre-treated with H_2O_2 + ultra-pure water + H_2SO_4

4.3.7. Issues with design 2

Although the design 2 propeller is successful in creating the desired circulation of water, there are still some issues observed with the design 2 prototype. Firstly, the propeller and its compartment might pose complications for the user and the fabrication process. The design and fabrication of the propeller compartment and prototype has to ensure that there are no possibilities for leakage of water which might enter and damage the internal parts of the motor. Entry of water into the motor might also reduce its working life span. As for the users, regular cleaning of the water purifier is an essential procedure so as to remove any dirt and unwanted particles which might be left behind after prolonged use. Regular cleaning also prevents the formation of algae or organic matter. The presence of such particles or organic matter might pose hazards to the health of users. From figure 36, it can be seen that there is a need to disassemble the motor, wires, propeller and propeller compartment to ensure a thorough cleaning for design 2 prototype. After cleaning, users have to assemble back the motor, propeller and its compartment properly to ensure no leakage of water. The water purifier might not operate normally if the internal parts are not assembled correctly. Therefore, design 2 prototype requires tedious dismantling and re-assembling of the internal parts of the water purifier for

cleaning. The inconvenience during the cleaning process might make the water purifier not user-friendly and unattractive as a commercial product.

Figure 36. Photographs of design 2 prototype which shows that there is a need to disassemble the motor, propeller and propeller compartment to ensure a thorough cleaning

Secondly, the anode is shaped into a hollow cylinder shown in figure 37 which might pose difficulties to fabricate, manufacture and assemble. Moreover, if a user purchases a new anode, it would be complicated for the user to reassemble. The user has to assemble the anode correctly to ensure that the proper working operation of the water purifier. There are possibilities of creating a designated compartment containing the anode which can be purchased commercially. This allows the user to assemble the anode compartment into the water purifier easily. However, the creation of such compartment may pose some issues in terms of added cost for the users and the need to connect the anode to the circuit board which can be complicated and tedious for the users.

Figure 37. Hollow cylindrical shape of anode and its compartment

Lastly, it was anticipated that the working life span of the motor might not be long as the propeller is working against the pressure of water and gravity. This might make the water

purifier to be unattractive for consumers as they have to change the purifier components or purchase a new purifier regularly.

4.4. Prototype design 3

4.4.1. Overview for design 3

The success of design 2 propeller provided valuable insights in overcoming certain issues, such as the material used for the electrodes and the use of a flowing system. Nevertheless, the flow system used where water was pushed upwards towards the cathode was not ideal, and tests were performed by pushing water to the sides, creating a void and forcing water to enter the compartment through the middle to come into contact with the cathode. The mechanism is similar to the propeller in design 1 but a compartment for the propeller was specifically designed to ensure that water is continuously pushed out to the sides. The design of the propeller's compartment is similar to the compartment in design 2. The schematic diagram of the propeller, compartment and its mechanism is illustrated in figure 38. The propeller compartment created by 3D-printing is shown in figure 39.

Figure 38. Schematic diagram of design 3. Arrows denote movement of water

Design 3 was proposed to use either a propeller attached to a motor at the bottom of the cell, or a stirrer bar which stirs by the action of strong magnet beneath it. Such technologies have already existed in current commercial products in the form of a self-stirring mug¹⁷ and hotplate stirrer¹⁸ which utilizes strong neodymium magnets to cause the movement of the stirrer bar. Therefore, the incorporate such technologies into the water purifier prototype was investigated. In this arrangement, the electrodes were placed parallel to each other. This is to ensure that the separation distance is similar throughout the area of the electrodes, unlike in design 2 where the anode and cathode are not parallel with each other. The feasibility of integrating a Nafion membrane into the system to see if it had a lower impact on the conductivity than the previous design was also investigated.

Figure 39. 3D-printed propeller compartment for design 3

4.4.2. Possible advantages for design 3

There are five possible advantages that might be present in this design. Firstly, the propeller or stirrer bar pushes water towards the sides instead of pushing water upwards. Therefore, the action of the propeller is not against gravity or pressure of the water. In fact, gravity and water pressure contribute in pushing water into the stirrer bar compartment through the middle to fill the void created by the action of the stirrer bar. Hence, the working life span of the motor might be improved. Secondly, the concept of hotplate stirrer was integrated into the purifier by utilizing strong magnets and a stirrer bar, it will minimize any possible the leakage of water as there is a solid barrier between the water system and the motor. Since there is no leakage of water, the internal parts of the motor will be protected from water and hence, have a lower possibility of being damaged.

Thirdly, the use of stirrer bar will ease the cleaning process by users. This is because the compartment and stirrer bar can be easily removed for washing and assembled back. Additionally, with a magnetic stirrer bar arrangement, there is no need for users to remove the propeller from the motor, an important component of the purifier which requires careful assembly. Fourthly, the fabrication of the anode compartment is much simpler than in design 2 as the anode is flat and not shaped to form a hollow cylinder. Moreover, other components of design 2 can be easily fabricated due to its simple design.

Lastly, the important parts of the water purifier such as stirrer bar, motor and electrodes can be easily replaced. If there is a need for the electrodes to be replaced, the simplicity of the design allows the replacement electrodes and its compartment to be fabricated easily which might incur a lower cost than design 2. In addition, users should be able to assemble the replacement parts to the water purifier easily.

4.4.3. Circulation study of design 3

A short study was conducted to determine if design 3 is able to create the desired circulation of water as postulated; pushing water out of the sides and a continual stream of water entering the compartment from the top. A red dye was introduced at the top of design 3 stirrer bar compartment and it can be clearly observed from figure 40 that water enter the compartment from the top. It is also evident that the red dye was pushed out through the sides by the stirrer bar. Moreover, the entire solution appeared to be mixed thoroughly within 5 seconds. Therefore, this study indicated that the design 3 mechanism was able to create the desired circulation of water by continuously pulling water towards the cathode to inactivate bacteria and generate disinfecting agents. It is able to execute the function of the intended feature.

Figure 40. Pictorial result of dye experiment. Red dye was introduced at surface of water which was observed to be drawn into the stirrer bar compartment at the top and pushed out to the sides.

4.4.4. Electrochemical potential studies of design 3

Due to its desirable properties and feasibility to be integrated into the design 2 water purifier prototype, platinized titanium mesh was used as both electrodes in the design 3 prototype. Electrochemical potential studies at fixed applied currents for the prototype were then performed. Figure 41 illustrates that there is no significant difference in the potential required to generate -2 mA at the cathode with and without the action of stirrer bar. The potential difference of the prototype with the action of stirrer bar was lower for the initial 100s. From 100s to 200s, the potential difference under constant current of the prototype with the action of stirrer bar slightly increases but the difference between the two arrangements (stirring/not stirring) is not significant. This result indicates the action of stirrer bar in design 3 does not significantly increase the cell voltage of the prototype. Hence, the stirrer bar mechanism and platinized titanium as electrodes could be potentially employed in the water purifier prototype.

Figure 41. Conductivity study of design 3 water purifier prototype using platinized titanium mesh electrodes with and without the action of stirrer bar

4.4.5. Electrochemical potential studies of design 3 with Nafion

Despite the poor results obtained for design 2, there was still interest in investigating the feasibility of integrating Nafion into the water purifier prototype. For design 2, it was observed that the integration of Nafion significantly reduces the conductivity of the system which is not desirable. Since the separation distance between the cathode and anode is similar throughout the areas of the electrodes in design 3, it was postulated that the conductivity of the prototype would not be significantly affected with the use of Nafion. The Nafion pre-treatment using H_2SO_4 at 80°C for 4h was selected as it has the lowest impact on the conductivity for design 2. The Nafion was placed between the cathode and anode, lying directly on the anode (figure 42).

Nafion pre-treatment	
H_2SO_4 at 80°C for 4h	
1.	Soak Nafion membrane in 1M H_2SO_4 from room temperature to 80°C for 4h
2.	Rinse Nafion in ultra-pure water at room temperature twice
3.	Store Nafion in ultra-pure water overnight

Table 2. Table of pre-treatment method used to activate Nafion for design 3 prototype and its procedure

Figure 42. Schematic diagram of design 3 with Nafion on top of anode.

Figure 43 illustrates the result for the electrochemical potential study at constant current for design 3 using a Nafion membrane between the cathode and anode. It is evident that the potential required for design 3 prototype with Nafion is higher than -10 V. This indicates that the Nafion membrane reduces the conductivity of design 3 prototype significantly although the better pre-treatment method was used. Therefore, Nafion membranes are likely not suitable to be integrated into the water purifier prototype due to the resistance it added to the system.

Figure 43. Potential vs. time study of design 3 water purifier prototype using Nafion with the action of stirrer bar

4.4.6. Electrochemical potential studies of design 3 with activated carbon cloth

It was reported that activated carbon can absorb certain substances such as chlorine.^{19, 20} Therefore, the feasibility of integrating activated carbon cloth into the system was investigated by placing the activated carbon above the anode to prevent any generated chlorine from entering the cathode compartment.

From figure 44, it can be observed that placing the activated carbon cloth above the anode reduces the conductivity slightly as the potential required is slightly higher than without the activated carbon cloth. The potential required for the prototype without the activated carbon cloth is approximately ~ 3.9 V whereas the potential required with the activated carbon cloth is ~ 4.6 V. This is expected as activated carbon cloth has lower conductivity than platinized titanium which adds resistance to the system, as well as blocking the flow of ions between the cathode and anode to maintain charge neutrality. Nonetheless, it is still much more conductive as compared to Nafion membranes. Moreover, there is no difference in the conductivity between the system without and with the action of stirrer bar as shown in figure 44.

Figure 44. Potential vs. time study of design 3 water purifier prototype using activated carbon cloth without and with the action of stirrer bar

Since the activated carbon cloth is placed above the anode, it is directly below the stirrer bar. One main issue of employing the activated carbon cloth is that its structural integrity was severely damaged by the action of stirrer bar after 5 minutes of electrolysis. Damage to the activated carbon cloth might reduce its capability of absorbing chlorine and creating holes in the cloth allowing generated chlorine to enter the water system. Although the conductivity of the system is not significantly affected, it might not be suitable to integrate activated carbon cloth into the water purifier prototype due to structural weaknesses.

4.5. Water purifier final prototype

4.5.1. General Overview

Based on design 3, a final prototype of the water purifier was 3D-printed as shown in figure 45. A thread mechanism to fix and incorporate an external bottle-like container into the prototype was also designed (figure 46). Through the thread mechanism, the external bottle-like container can be screwed and attached to the base of the prototype as shown in figure 46. This container allows the prototype to store approximately 500ml of water. Some parameters such as electrochemical potential under constant current, pH, conductivity in different types of water, chlorine studies and bacterial inactivation studies were performed on the water purifier prototype.

Figure 45. 3D-printed final prototype of the water purifier

Figure 46. 3D-printed thread mechanism to attach the external bottle-like container into the prototype base

4.5.2. Electrochemical potential study of water purifier prototype

Figure 47 illustrates the result of an electrochemical potential under constant current study performed for the water purifier prototype. It can be observed that the potential required for the water purifier prototype is similar to design 3 prototype, which indicates similar potential values. Moreover, the potential required to generate -2 mA is lower for the prototype with the action of stirrer bar than without the stirrer bar. Hence, the action of stirrer bar improves the polarization of the prototype which is desirable.

Figure 47. Potential vs. time study of water purifier prototype without and with the action of stirrer bar

An electrochemical potential study was also performed for different applied currents with the results shown in figure 48 and table 3. The study was only performed with the action of a stirrer bar. As expected theoretically based on Ohm's law, the generation of higher current requires higher potential. Although -5 mA is 2.5 times greater than -2 mA, the potential required was only 1.8 times greater. The same can be said for -10 mA where the potential required is only 1.7 times greater than -5 mA. The significance of this result is that higher potentials can be applied to the water purifier prototype to generate higher currents so as to ensure maximum inactivation of bacteria.

Figure 48. Potential vs. time study of water purifier prototype at different currents with the action of stirrer bar

Tap water + -10mA, 300s	-11.9 V
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Table 3. Potential required for water purifier prototype at -10 mA with the action of stirrer bar

4.5.3. pH measurement of water purifier prototype after electrolysis

The pH of the water in the purifier prototype was measured after electrolysis at constant current of -5 mA and -10 mA for 5 minutes. As shown in table 4, it can be observed that there is a decrease in pH after 5 minutes of electrolysis. Moreover, electrolysis at a higher current results in a greater change in pH. Nevertheless, although the pH is moving towards the acidic region with the application of higher current, the change in pH is not significant.

Sample + 0.05 M KCl	pH
Tap water	7.11
Tap water + -5 mA, 5 min	6.83
Tap water + -10 mA, 5 min	6.75

Table 4. pH in water purifier prototype after electrolysis at -10 mA with the action of stirrer bar

4.5.4. Electrochemical potential study of water purifier prototype for various types of water

The measurement of potential under constant current for the water purifier prototype was performed for 3 different types of water; tap water, water from a cold water dispenser and bottled mineral water. From figures 49 and 50, it is observed that the potential required for tap water and water from the dispenser are generally similar. On the other hand, the potential required to generate -2 mA for mineral water exceeded -10 V (table 5), which means that the conductivity is significantly lower in mineral water as compared to the other two types of water. This is likely due to the absence or significantly lower concentrations of ions in the mineral water.

Figure 49. Potential vs. time study of water purifier prototype for water from dispenser without and with the action of stirrer bar

Figure 50. Potential vs. time study of water purifier prototype for tap water without and with the action of stirrer bar

Sample	Without stirrer bar action	With stirrer bar action
Iced Mountain Mineral Water	Voltage Overload	Voltage Overload

Table 5. Potential required for water purifier prototype for mineral water with and without the action of stirrer bar

4.5.5. Study of free chlorine after electrolysis

Previous experiments indicated that it was not feasible to integrate Nafion membranes into the water purifier prototype as it increases the resistance of the system significantly. Moreover, the action of the stirrer bar will severely damage the activated carbon cloth, creating holes and allowing generated chlorine to escape into the water system. However, since many types of

water contains low levels of chloride that can undergo electrochemical oxidation to chlorine, it was thought necessary to determine how much chlorine is typically produced in chloride containing solutions. This would provide information as whether it is essential to have the anode and cathode in separate compartments (such as separated with a Nafion membrane) so that any generated chlorine is isolated, or whether the electrodes could be placed in the same compartment if chlorine generation was not significant.

The measurement of chlorine was performed using a N, N-diethyl-p-phenylenediamine (DPD) colorimetric method and UV-vis spectroscopy. The background principle of the DPD colorimetric method is that the generated chlorine will oxidize the DPD amine into two products, a semi-quinoid cationic Würster dye and an imine compound.²¹ At near neutral pH, Würster dye is the main product as it is relatively stable which forms the magenta colour during the DPD colorimetric method.²¹ At higher concentration of oxidants, the formation of the colourless and unstable imine compound is favoured.²¹ The concentration of Würster dye is measured photometrically at a wavelength of 515nm.²¹

Figure 51. Reaction between DPD and chlorine²¹

Due to the hazards and instability of using chlorine, potassium permanganate (KMnO_4) was used as a substitute standard as it is more stable, safe to use and will also oxidize DPD to form the Würster dye.^{22, 23} It is also prevalent practice to use KMnO_4 as a substitute standard.^{22, 23} As seen in figure 52, a calibration graph using several KMnO_4 standards was successfully generated, which gives a R^2 value of 0.9985. Hence, the calibration graph is suitable to be used for determining the concentration of chlorine in the water purifier prototype.

Figure 52. Calibration graph using potassium permanganate standards

Measurement of chlorine was conducted for 3 samples using the water purifier prototype; tap water, tap water with -5 mA current and 1000 ppm NaCl solution with -5 mA current. 1000ppm NaCl solution was investigated to determine the concentration of chlorine produced by the water purifier prototype in a solution with a high concentration of chloride. Figure 53 shows that the chlorine generated in tap water, tap water with -5 mA current and 1000 ppm NaCl solution with -5 mA current are 35, 59 and 62 ppb, respectively. The concentration of chlorine produced in a solution with electrolysis is only marginally higher than in a solution without electrolysis (tap water only). This indicates that electrolysis will result in production of chlorine as tap water contains approximately 5 – 45 mg/L of chloride.²⁴

Figure 53. Concentration of chlorine in 3 samples; tap water, electrolyzed tap water at -5mA and electrolyzed 1000ppm NaCl solution at -5mA

As expected, electrolysis of 1000ppm NaCl solution generates the highest concentration of chlorine. An interesting observation is that although the solution contains a relatively high concentration of chloride, the chlorine formed is in ppb level which is substantially below the maximum permitted level set by WHO (5ppm).²⁴ Theoretically, at 5 mA, the concentration of chlorine formed should be approximately 2.20 ppm based on the calculations below, if all the electrolysis current was due to formation of chlorine. However, it is clear that the electrolysis is not generating significant amounts of chlorine, possibly due to the oxidation of water at the platinized titanium electrode being kinetically favored over the oxidation of chlorine.

$$\text{Current} = \frac{Q}{t}$$

$$\frac{5}{1000} A = \frac{Q}{(3 \times 60)s}$$

$$Q = 0.9C$$

$$\text{No. of moles of } e^- = \frac{0.9 C}{96500}$$

$$\text{No. of moles of } e^- = 9.326 \times 10^{-6} \text{ mol}$$

$$2 \text{ moles of } e^- = 9.326 \times 10^{-6} \text{ mol}$$

$$1 \text{ mole of } e^- = 4.663 \times 10^{-6} \text{ mol}$$

$$4.663 \times 10^{-6} \text{ mol} \times 70.906 \frac{g}{mol} = 3.307 \times 10^{-4} g$$

$$3.307 \times 10^{-4} g \times 1000 \frac{mg}{g} = 0.331 mg$$

$$0.331 mg \div \left(\frac{150ml}{1000ml} \right) L = 2.20 ppm$$

Therefore, this study shows that there is not a need for the integration of a Nafion membrane or an activated carbon absorbent as the chlorine generated is well below the permitted level.

4.5.6. *E. coli* inactivation study of water purifier prototype

The inactivation of *E. coli* by the water purifier prototype was studied. Figure 54 illustrates that the % *E. coli* inactivation using OD₆₀₀ measurement at 6 h is approximately 32% average for two replicate measurements. Although there is a large difference at 3 h for one measurement, there is a small difference in the % *E. coli* inactivation at 6 h between the two repetitions. Log(N/N₀) at 3 h and 6 h are -4 and -5 respectively as shown in figure 55.

Figure 54 % *E. coli* inactivation of tap water by water purifier prototype using OD600 measurement

Figure 55. Log(N/N₀) of tap water by water purifier prototype by plate counting

Although there is a certain degree of *E. coli* inactivation by the water purifier prototype, the length of time required is too long to be useful as a commercial device. As compared to the

basic studies conducted in chapter 2 of this thesis, the % *E. coli* inactivation obtained by the water purifier prototype is also much lower. A possible reason for this might be due to the exposure of the electrodes to the bulk of the water. Since the anode is placed directly below the stirrer bar, the action of the stirrer bar might prevent more water from reaching and coming into contact with the anode to form disinfecting agents to inactivate *E. coli*. This is a different experimental arrangement from the *E. coli* inactivation experiments in chapter 2 of this thesis where the maximum amount of water can come in contact with both electrodes, allowing more bacteria to be killed by the action of both electrodes either through direct contact with electric field or the formation of disinfecting agents.

Another reason is that the stirrer bar mechanism might not be sufficiently effective to ensure a maximum distribution of disinfecting agents and maximum contact between the electrodes and the *E. coli*. After a certain duration, it was observed that there are numerous bubbles forming on the cathode which might impede the entry of water into the stirrer bar compartment. The presence of the bubbles might cause the water being stirred similar to the action of hotplate stirrer instead of the desired circulation of water. As a result, this might prevents more water and *E. coli* from reaching and coming in contact with the electrodes. Hence, the stirrer bar mechanism might not be effective in maintaining the desired circulation of water for a long period of time. Therefore, there might be a need to relook at a better mechanism to kill bacteria more effectively. More details will be presented in chapter 4 under Future Studies.

4.6. Conclusion

In conclusion, design 3 was chosen for the water purifier prototype as the stirrer bar mechanism is able to create the desired circulation of water. Moreover, electrochemical potential at constant current studies showed that the action of the stirrer bar had no significant impact on the conductivity and improved the concentration polarization of the design 3 prototype using platinized titanium. There were issues present for the other two designs. For design 1, the action of the propeller increased the concentration polarization of the prototype as it is unable to create the desired circulation of water. On the other hand, complications in dismantling and assembling of the important internal parts hinder design 2 from being chosen for the water purifier prototype.

It was also concluded that Nafion membranes to separate the anode and cathode might not be suitable to be integrated into the water purifier prototype as they significantly increase the

resistance of the system. The use of alternative materials in the form of activated carbon cloth have little impact on the conductivity. However, activated carbon cloth is easily damaged by the action of the stirrer bar creating holes and leaving small particulates suspended in the water.

Lastly, the attempt to design and create a prototype of the water purifier using 3D-printing was successful which is able to contain approximately 500 mL of water. Some parameter studies were also carried out for the prototype. Electrochemical potential measurements at constant current showed that electrolysis can be performed in the prototype with the action of the stirrer bar improving its concentration polarization. pH values of the tap water electrolyzed in the prototype showed a shift towards the acidic region but the change in pH was not significant. Moreover, the concentration of chlorine generated in the water purifier prototype was in the ppb levels which is significantly below the permitted level set by the WHO. Therefore, there is not be a need for the integration of Nafion membranes or other barriers to prevent generated chlorine from entering the water system.

Finally, the water purifier prototype was able to inactivate 32% of *E. coli* in 6 h achieving a $\log(N/N_0)$ of -5. Although there is a certain degree of *E. coli* inactivation by the prototype, it has lower inactivation capabilities as compared to the preliminary studies. This might be due to two possible reasons. The first reason is the small exposure of the electrodes to the bulk of the water. The second reason might be due to the ineffectiveness of the stirrer bar mechanism to maintain the desired circulation of water to ensure maximum distribution of disinfecting agents and maximum contact between the electrodes and the *E. coli*.

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Chapter 5

Summary

5.1. Summary

5.2. Future Work

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5.1. Summary

The most prevalent and common health risks related with drinking water are the infectious diseases caused by pathogenic microorganisms. Throughout the years, many efforts have been focused in developing technologies to produce high-quality safe drinking water at affordable costs to mitigate health risks posed by shortage of clean water. Electro-disinfection has emerged as a promising method in recent years due to the advantages it brings, including: (i) being environmentally-friendly, (ii) low cost, (iii) no requirement for the transport and storage of toxic chemicals, (iv) can be modified for automatic and portable applications, (v) easy operation, and (vi) able to kill a wide range of pathogenic microorganisms.

There have been numerous studies conducted on the inactivation of bacteria by electro-disinfection using a wide range of electrodes including boron-doped diamond, stainless steel, platinum, and titanium coated with $\text{TiO}_2/\text{RuO}_2$. Moreover, electro-disinfection technology has been developed into existing water purifier products which generate disinfecting agents to purify water. Platinized titanium, an electrode already employed in current products notably hydrogen-generating water ionizers, possesses desirable qualities such as low cost, high conductivity, anti-corrosion, commercially available and readily obtained. However, the material has not been comprehensively studied for its inactivation capability of bacteria. Moreover, it has been reported that electrolytes have influence on the effectiveness of bacterial inactivation through electro-disinfection, although there are no studies conducted that use platinized titanium. In addition, there are no portable products presently which utilize electro-disinfection to directly purify water, although such products that employ electrolysis processes to generate hydrogen (“hydrogen water”) or oxygen (“oxygenated water”) are commercially available.

The general theme of this thesis to study the feasibility of developing a portable water purifier system employing electro-disinfection methods with two main objectives. The first objective was to conduct preliminary investigations on the materials to be used as electrodes in the water purifier system. Once the suitable material had been decided, the inactivation of *E. coli* by the material as electrodes in different media and electrolyte solutions were studied. The second objective was to design and develop a prototype for the portable water purifier system including a feature that generates a good circulation of water, which is absent from the existing devices

that generate hydrogen or oxygen. Several parameters of the 3D printed water purifier prototype such as pH, chlorine concentration and *E. coli* inactivation were also studied.

In chapter 2, an investigation on the electrode material and its *E. coli* inactivation capabilities were performed, where platinized titanium was found to be the most promising and suitable material. It was also demonstrated that platinized titanium can effectively inactivate *E. coli* in different media such as chloride solutions, PBS and tap water. Moreover, the first insights on the effect of electrolytes on the *E. coli* inactivation by platinized titanium have been demonstrated in this thesis. Additionally, the role of $\bullet\text{OH}$ radicals in electrochemical disinfection of chloride-free solutions has been clarified. The pH of the solutions measured before and after electrolysis were measured and showed an increase to more alkaline levels after electrolysis. It was postulated that a change in pH towards the alkaline range, might contribute to the inactivation of *E. coli*. The study conducted on the effect of pH on *E. coli* inactivation without electrolysis clarified the role of alkaline pH.

Chapter 3 examined the feasibility of developing a portable water purifier prototype employing electro-disinfection methods and using 3D printing. Three designs were created and explored where design 3 was chosen as the final design for the water purifier prototype. It was also concluded that Nafion membranes and an alternative, activated carbon cloth, might not be suitable to be integrated into the water purifier prototype as they significantly reduce the conductivity of the system. A prototype of the water purifier was successfully designed and created using 3D-printing. The printed water purifier was found to be able to inactivate 32% of *E. coli* by 6 hours achieving a $\log(N/N_0)$ of -5.

5.2. Future Work

Although, this thesis has demonstrated the first insights on the effect of electrolytes on the *E. coli* inactivation by electrolysed platinized titanium, more studies can be performed to develop a comprehensive understanding on their effect. For the *E. coli* inactivation study of different electrolytes in chapter 2, the trend obtained is $\text{NaNO}_3 > \text{NaCl} > \text{Na}_2\text{SO}_4$ at 5 min duration. A possible reason for this observation might be due to a greater concentration of NaNO_3 (363ppm) as compared to NaCl (250ppm) and Na_2SO_4 (203ppm) although they share the same ionic strength. The current generated for NaNO_3 was observed to be higher than the other two electrolytes which might kill more *E. coli* initially due to stronger electric field and generation of more disinfecting agents. Therefore, one possible future work is to investigate the *E. coli*

inactivation in the electrolytes with similar concentration. The study might provide us with a clearer picture of the effects of electrolytes where the concentration and current generated is similar among the electrolytic solutions.

For this thesis, only 3 types of electrolytes have been studied for the *E. coli* inactivation by platinized titanium. This range can be extended to include other electrolytes such as phosphates, bicarbonates, carbonates, etc. In addition, the effect of different types of cations can also be studied such as magnesium sulfate (MgSO_4) which is available commercially in the form of Epsom salt.¹ If favourable results are obtained for MgSO_4 , the electrolyte can be easily incorporated into the portable water purifier product and enhance the purification of water without generating chlorine. Investigation of a wider range of electrolytes might provide a broader insight on the effects of electrolytes and assist us in determining the most suitable alternative electrolyte to NaCl for the water purifier product.

Another future study that can be performed is the effect of potentials on the *E. coli* inactivation by platinized titanium. The potential used for the disinfection study in chapter 2 was -10 V to ensure maximum disinfection of *E. coli*. Therefore, there is a possibility to investigate the *E. coli* inactivation at lower potential range e.g. -5 V to -10 V. This is to examine whether there is a significant difference in the % *E. coli* inactivation between the lower potential range and -10 V. If result shown to be favourable, a lower potential can be applied to the water purifier system which can save energy and resources e.g. batteries.

For the *E. coli* inactivation study of different electrolytes in chapter 2, it was observed that the difference in the % *E. coli* inactivation between Na_2SO_4 and NaCl is not significant despite no chlorine species generated for Na_2SO_4 . The significance of this result is that Na_2SO_4 might be a promising non-chloride electrolyte alternative to NaCl. Therefore, further studies can be conducted on the *E. coli* inactivation using platinized titanium in Na_2SO_4 such as varying the concentration of Na_2SO_4 . Moreover, future studies can also explore on the residual effect of electrolyzed Na_2SO_4 . Na_2SO_4 can be electrolyzed for a particular duration and then poured into a solution of *E. coli* to observe its residual effects. This opens up a wide area of investigation including the effect of electrolysis duration, concentration of electrolyzed Na_2SO_4 and duration of disinfection.

For all of the disinfection experiments, a high concentration of *E. coli*, approximately $\sim 10^9$ CFU/mL was studied. Therefore, future studies can investigate the inactivation by platinized

titanium in lower *E. coli* concentrations. Furthermore, the types of bacteria can be extended to include *Salmonella typhi*, *Legionella* and *Pseudomonas aeruginas*. This study might provide a broader insight on the effects of electrolyte and inactivation ability of platinized titanium electrodes for various bacteria.

For the study of the *E. coli* inactivation by individual electrodes; anode and cathode, the electrolytes employed had relatively low concentrations. To gain better understanding of the inactivation capability by each electrode, a higher range of concentrations (0.01 – 0.1M) of electrolytes can be studied.

In chapter 3 of this thesis, the % *E. coli* inactivation achieved for the water purifier prototype is 32% in 6 h with a $\log(N/N_0)$ of -5. Although there is a certain degree of *E. coli* inactivation by the water purifier prototype, further exploration on other possible designs can be carried out to create a prototype with greater *E. coli* inactivation capability. One possible idea is to incorporate the set-up of the *E. coli* inactivation experiments in chapter 2 as a design for the water purifier prototype. As shown in figure 1, the two electrodes will be parallel to each other and attached to the lid of the water purifier. The stir bar and magnetic stirrer can still be integrated at the bottom of the purifier. This design was inspired by a commercially available product in the form of a glass bottle with tea infuser displayed in figure 2.²

Figure 1. A possible alternative design for the water purifier prototype

One possible benefit of this design is that there is a large exposure of the electrodes to the bulk of the water. As the water purifier is turned on, current will be passed through the electrodes and the stir bar will stir the water which ensure that there is a maximum contact between the electrodes and the water. In addition, maximum amount of disinfecting agents can be generated due to the large exposure which will be well-distributed throughout the water by the action of the stirrer bar. This might allow the maximum inactivation of bacteria by the action of both electrodes either through direct contact with electric field or formation of disinfecting agents. Furthermore, study of the electrolyte effects can add value to the water purifier prototype. Once a suitable non-chloride electrolyte and its concentration has been determined, it can be added to the water system to enhance the purification process without generating chlorine species.

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Appendix

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Figure 1. Autodesk Fusion 360 3D design of water purifier prototype design 1

Figure 2. Autodesk Fusion 360 3D design of water purifier prototype design 2

Figure 3. Autodesk Fusion 360 3D design of water purifier prototype design 3