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Efficacy of silver nanoparticles in capacitive deionization electrodes as antimicrobial agents

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EFFICACY OF SILVER NANOPARTICLES IN CAPACITIVE DEIONIZATION ELECTRODES AS ANTIMICROBIAL AGENTS

Amina Said Abdallah

**A Dissertation Submitted in Partial Fulfilments of the Requirements for the Degree of
Master of Science in Environmental Science and Engineering of the Nelson Mandela
African Institution of Science and Technology**

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ABSTRACT

The availability of clean and safe water is still a big challenge in most parts of the world. Drinking water should be free of harmful microorganisms and should contain the required amount of minerals based on the set standards. In this study, silver nanoparticles (Ag-n) embedded in Activated Carbon (AC) electrodes for capacitive deionization (CDI) were evaluated for desalination and also for anti-microbial activities against *Escherichia coli* and *Salmonella enteritidis*. The novel AC/Ag-n electrodes were prepared by mixing Activated Carbon powder together with silver nanoparticles. The morphology, surface functional groups, and porosity were characterized by Scanning Electron Microscope (SEM), Fourier-transform infrared (FT-IR), and nitrogen adsorption studies which affirm the formation of disinfecting electrode material. The desalination and disinfection performance of the fabricated electrodes were evaluated by Capacitive Deionization batch mode experiment using natural water collected from the Ngaranana stream while applying the potential of 2 V for 3h. The AC/Ag-n Capacitive Deionization (CDI) electrodes achieved 100% *Escherichia coli* and 98% *Salmonella enteritidis* removal and 45% salt removal efficiency, and electrosorption capacity of 2.56 mg/g and the ions removal efficiency of 89%, 40%, 2.4%, 57.9%, 50%, 8% and 33% for Na^+ , K^+ , Ca^{2+} , Mg^{2+} , PO_4^{3-} , NO_3^- and Cl^- respectively. The microbial disinfection mechanisms were through electrosorption process and physical contacts with the embedded Ag-n. Thus, it is possible to disinfect the water while also removing salt simultaneously using Capacitive Deionization. Therefore, AC/Ag-n are considered as novel electrode material with an excellent antimicrobial agent for the Capacitive Deionization process.

DECLARATION

I, Amina Said Abdallah do hereby declare to the Senate of The Nelson Mandela African Institution of Science and Technology that this dissertation is my own original work and that it has neither been submitted nor being concurrently submitted for degree award in any other institution.

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Date

The above declaration is confirmed by

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Dr. Yusufu Abeid Chande Jande
Name and signature of supervisor 1

.....
Date

.....
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Name and signature of supervisor 2

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CERTIFICATION

The undersigned certify that they have read and hereby recommend for examination by The Nelson Mandela African Institution of Science and Technology a dissertation entitled: “Efficacy of Silver nanoparticles in Capacitive Deionization electrodes as antimicrobial agents” submitted in (partial) fulfillment of the requirements for the degree of Masters of Science in Environmental Science and Engineering of The Nelson Mandela African Institution of Science and Technology Tanzania.

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DEDICATION

This work is dedicated to my family members especially my lovely daughters Faidha Mwalim Khamis and Khairat Mwalim Khamis

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LIST OF ABBREVIATIONS AND SYMBOLS

AC	Activated Carbon
Ag	Silver
Ag-n	Silver Nanoparticles
AgNO ₃	Silver Nitrate
BET	Brunauer-Emmet-Teller
BJH	Barret-Joyner-Halender
CC	Constant Current
CDI	Capacitive Deionization
CDID	Capacitive De-Ionization Disinfection
CuO	Copper Oxide
CV	Constant Voltage
DC	Direct Current
DI	Deionized Water
ED	Electrodialysis
EDL	Electrical Double Layer
FE SEM	Field Emission Scanning Electron Microscope
FP	Flame Photometer
FTIR	Fourier-Transform Infrared
GO	Graphene Oxide
HEA	Hicrome <i>E. coli</i> Agar
IE	Ion Exchange
NaBH ₄	Sodium Borohydride
PDV	Potential Different Voltage
PTFE	Polytetrafluoroethylene

PVA	Polyvinyl alcohol
PVP	Polyvinylpyrrolidone
QC	Quartenized Chitosan
RO	Reverse Osmosis
SEM-EDS	Scanning Electron Microscopy – Energy Dispersive X-rays
SnO ₂	Tin Oxide
TD	Thermal Distillation
TDS	Total Dissolved Solids
TiO ₂	Titanium Oxide
WHO	World Health Organization
ZnO ₂	Zinc Oxide

CHAPTER ONE

INTRODUCTION

This chapter explains the background of the problem about capacitive deionization technique, statement of the problem, rationale of the study, objectives, research questions and significance of the study. The general objective of this study is to investigate the viability of silver nanoparticle in CDI electrodes as anti-microbial agent for water purification and completed with the three specific objectives in which silver nanoparticles (Ag-n) was synthesized and coated into the Activated Carbon (AC) electrode during fabrication process followed by characterization of the materials, finally the performance of CDI electrodes for salt and bacterial removal was evaluated.

1.1 Background of the Problem

The availability of safe and clean water is a worldwide problem. Clean water is that water which doesn't contain any toxic chemicals and pathogens (Savage & Diallo, 2005). Water can be contaminated by an organic and inorganic compound such as industrial by-products, personal care products, pesticides, heavy metal, bacteria, parasitic protozoa and even enteric virus (Gordon, 2016). Also, water from underground can have higher salinity compared to the recommended value, which is not suitable for human consumption (Porada *et al.*, 2013). According to the World Health Organization report 2012, about 780 million people worldwide lack access to clean and safe drinking water and 2.5 billion lack improved sanitation (WHO, 2012). Since clean and safe water is essential to human health, reliable access to clean and affordable water remains a major global challenge for the 21st century (Laxman *et al.*, 2015). Due to the scarcity of fresh water sources, the desalination of water is becoming more important.

To remove salts and specific ions from water, a wide range of technologies can be used (Limpt *et al.*, 2010). The main desalination technologies are distillation, reverse osmosis (RO), electrodialysis (ED) and ion exchange (IE), but these technologies have some limitations, for example, more energy consumption for desalinating brackish water using RO (Jande *et al.*, 2014), ED and IE may cause fouling hence they require pre-treatment such as coagulation, flocculation and filtration (Anderson *et al.*, 2010; Xu *et al.*, 2008) hence their operation consume high cost. New desalination technique needed to overcome those limitations of existing desalination technologies.

Capacitive Deionization (CDI) is an emerging technique used for desalination of low saline (brackish) water with concentration is below 10 g/L to obtain fresh water (Porada *et al.*, 2013). This process involves the application of two porous electrodes using direct current (DC) power (Jande *et al.*, 2013). The electrodes are made of carbon-based materials that are highly porous and have a large surface area. The electrode plates are separated by an ionic solution, which transmits an electrical current. Ions suspended in the solution are attracted to the electrodes of opposite charge and are absorbed into the pores of the electrodes, while the solution elutes from the cell with a lower ionic concentration (Huang *et al.*, 2013).

Several studies use CDI electrode materials for desalination and removal of ionic impurities in water, but the problem of microbes in the desalinated water still challenges. Some antimicrobial agents such as hypochlorite and ozone commonly used in water disinfection produce harmful by-products which can be carcinogenic, mutagenic and are extremely irritant and toxic to human health and environment (Wang *et al.*, 2015), so there is great interest in finding ways to create new types of safe and cost-effective biocidal materials. Antimicrobial tests in the form of nanoparticles can be used as effective bactericidal materials (Sondi & Sondi, 2004). Nanoparticles with antimicrobial activity have been studied in CDI and show the improvement of electrosorption and efficiency for salt removal.

Yasin *et al.* (2017) used nitrogen-doped tin oxide intercalated activated carbon nanocomposite (N-AC/SnO₂) electrodes for disinfection and the results show good antibacterial performance. Wang *et al.* (2015) also use capacitive deionization disinfection (CDID) electrode made by coating an activated carbon (AC) with cationic nanohybrids of graphene oxide-graft-quaternized chitosan (GO-QC), (GO-QC/AC CDID electrode) and achieve to kill 99.9999% of *Escherichia coli* in water. It is widely known that silver ions and it's compound are highly toxic to microorganisms (Kim *et al.*, 2007) such as *Escherichia coli* and *Staphylococcus aureus* and nontoxic to human body at low concentration (Abdel Hameed *et al.*, 2013; Mavani *et al.*, 2013; Theivasanthi *et al.*, 2011; Xu *et al.*, 2008). Since Ag-n can kill microbes and shows strong biocidal effect hence they can be embedded in AC to make AC/Ag-n electrodes and used as CDI electrodes which can be applied to increase efficiency and enhance bacterial removal in treated drinking water without compromising its salt removal efficiency. Therefore, this study was intended to investigate electrodes made by AC embedded with Ag-n (AC/Ag-n) in CDI electrodes for bacteria removal.

1.2 Statement of the Problem

Many studies use CDI for desalination and removal of ionic impurities in water, but the problem of microbes in the desalinated water is not yet solved. Some antimicrobial agents are extremely irritant and toxic and there is great interest in finding ways to create new types of safe and cost-effective biocidal materials. Antimicrobial tests in the form of nanoparticles can be used as effective bactericidal materials (Sondi & Sondi, 2004). It is widely known that silver ions and its based compound are highly toxic to microorganisms (Kim *et al.*, 2007) such as *Escherichia coli* and *Salmonella enteritidis* and nontoxic to human body at low concentration (El-Aassar *et al.*, 2013; Harikumar *et al.*, 2011; Theivasanthi *et al.*, 2011). Since Ag-n can kill microbes and shows the strong biocidal effect it can be used in CDI electrodes to increase the efficiency of salt and bacterial removal in treated drinking water. So, this study is intended to use electrodes made by AC coated with Ag-n (AC/Ag-n) in CDI for desalination and bacteria removal.

1.3 Rationale of the Study

Water is very important for human consumption and for life in general. Capacitive deionization technology and silver nanotechnology are easy to use, has high efficiency, utilize low energy and environmentally friendly. Therefore, there is a need to apply these new and modern technologies for water purification. This study will solve the problem of saline water and water contaminated with microbes for the production of safe and clean water.

1.4 Objectives

1.4.1 General Objective

The general objective of this study is to investigate the viability of silver nanoparticle in CDI electrodes as an anti-microbial agent for water purification.

1.4.2 Specific Objectives

- (i) To synthesize and characterize silver nanoparticles (Ag-n)
- (ii) To synthesize and characterize CDI electrodes coated with silver nanoparticles (Ag-n)
- (iii) To evaluate the performance of the CDI electrodes in salt and bacterial removal.

1.5 Research Questions

- (i) What are the characteristics of Ag-n that make them effective in desalination and disinfection?
- (ii) What is the efficiency of AC coated Ag-n (AC/Ag-n) electrodes in CDI for salt and bacteria removal?
- (iii) Can Ag-n remove bacteria without affecting the performance of CDI AC electrodes in salt removal?

1.6 Significance of the Study

The potential demand for water increases as the global population increases. Currently, there are many methods used for desalination and removal of other ionic impurities, but researchers still try to find alternative methods to overcome the constraints. Other desalination methods have high energy consumption for brackish water desalination such as Reverse Osmosis. Capacitive deionization technology is a novel method which has the potential of utilizing low energy during desalination and also it is environmentally friendly. Therefore, this study uses the modified AC/Ag-n electrodes as precursor materials for CDI application, which will help to solve the problem of saline water contaminated with microbes for the production of safe and clean water for domestic use.

1.7 Delineation of the Study

This study covered the wide part of desalination, removal of gram negative bacteria (*Escherichia coli* and *Salmonella enteritidis*) and removal of some other ionic impurities, hence using Capacitive Deionization technique with sufficient AC/Ag-n electrode materials can be used for large scale water treatment plantation which will help to solve the water demand challenges facing the worldwide.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

Water scarcity and water quality are the big issues facing the global population worldwide, in order to overcome these, low cost and energy efficient desalination technologies become the focal point of recent researches. Capacitive Deionization (CDI) is the one among the promising technologies for water desalination because it is safe, uses low energy, cost-effective, economic and environmentally friendly and the material can be regenerated easily, compared with other conventional desalination technologies, such as reverse osmosis, thermal distillation and electrodialysis (Limin *et al.*, 2012; Xu *et al.*, 2008; Yasin *et al.*, 2017). Recently, Ag-based AC electrode materials have been used in CDI and enhance the electrosorption capacity from 2 to 5.3 mg/g and salt removal efficiency from 42 to 67% (Alencherry *et al.*, 2017; Yoon *et al.*, 2017). However, the availability of novel CDI electrode materials with low-cost for salt and bacteria removal is still a challenge. Thus, in order to improve the CDI performance, suitable CDI electrode materials which have low cost and easily available are needed to overcome those challenge. This section describes different technologies used for desalination and different materials which have been used in the CDI technology for salt, bacteria and ionic contaminant removal and their challenges on CDI application.

2.2 Basic Principle of CDI

Capacitive Deionization (CDI) studies started since the 1960s, using the porous electrode made by activated carbon powder (ACP) in which inflow through mode applied for water desalination. CDI adsorb salt ion in electrical double layer (EDL) (Fig. 1) of high surface area electrodes with potential difference voltage (PDV) applied across the electrodes (Saleem *et al.*, 2018). Electrical Double Layer (EDL) are the two layers exist at the surface of the solid and liquid interface; those layers are the surface layer and diffuse layer. The surface layer called the Helmholtz Outer Layer is closest to the solid (carbon matrix) and is made up of counter-ions interacting with the surface via chemical bonds, and the outside surface layer is diffuse layer which is made up of ions attracted to the surface by electrostatic charge. The electrical capacity of the electrodes to store energy depends on the capacity of both

components of the EDL (Anderson *et al.*, 2010; Gordon, 2016; Oren, 2008; Porada *et al.*, 2013).

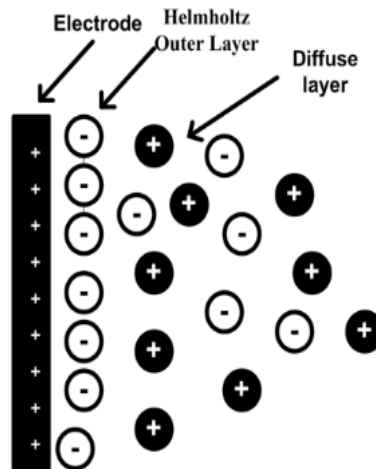


Figure 1: The structure of an electrical double layer

As the electrode surface areas become saturated with ions, the electrodes become less efficient at removing ions from the solution. The electrodes can be regenerated by reversing the charges, which repels the ions from the surface of the electrode to the interstitial space and are subsequently removed from the cell as a highly concentrated solution (Fig. 2). Following regeneration, the electrodes can then begin a new cycle of ionic adsorption. The concentrated effluent is typically discarded, but it can also be used for the recovery or sampling of components which may be very dilute in the influent water (Jande & Kim, 2014; Limin *et al.*, 2010; Porada *et al.*, 2013).

The passage of water through the CDI cell can occur through two different mechanisms: flow-through mode or flow-by mode. In flow-through mode, water passes through the pores of the electrode whereas, in flow-by mode, water passes through the gap or flow channel between the electrodes (Suss *et al.*, 2015). Capacitive Deionization units can be operated using either constant current (CC) or constant voltage (CV), the latter being more commonly used. CC can be used when a specified effluent concentration is required (Jande & Kim, 2014; Oren, 2008; Porada *et al.*, 2013).

Some studies thought that, the addition of membranes to the cell will improve ion adsorption by allowing only ions which has the opposite charge as the polarized electrode (counter ions) to go through and finally being absorbed by the electrode (Porada *et al.*, 2013; Saleem & Kim, 2018). Instead, the co-ions are expelled out of the micropores but are retained on the

electrode by the membrane, which attracts more counter-ions on to the surface of the electrode (Porada *et al.*, 2013). The advantage of this is that more ions can be absorbed on to the electrode than using standard CDI, but during the purge step some of the ions are retained to the electrodes. Additionally, the use of IE membranes prevents the ions adsorbed during the purification cycle from adsorbing to the electrode of opposite charge during the reversal of charge which occurs during the purge step but the standard CDI allows the ions to be adsorbed and desorbed more easily.

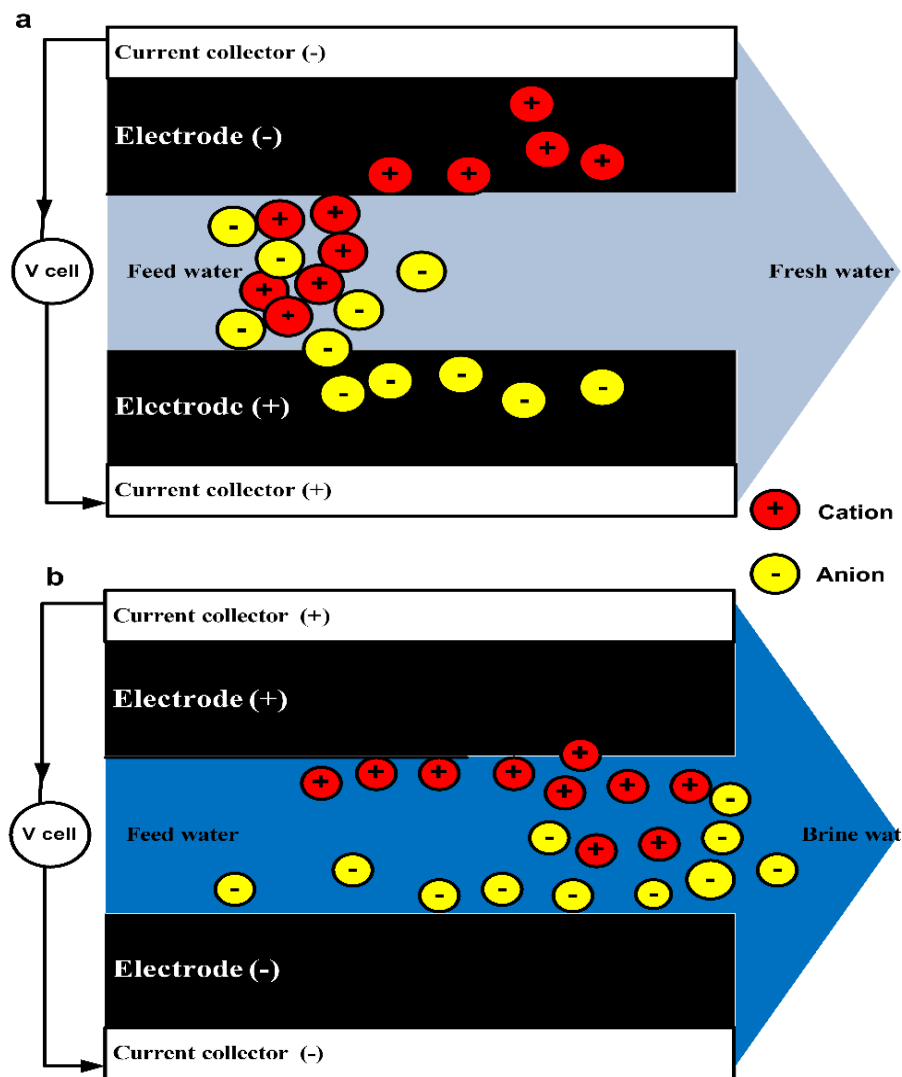


Figure 2: Schematic representation of basic principle of CDI purification (a) Adsorption (b) Desorption

2.3 Electrode Materials for CDI

Good electrode materials for CDI should have good electrical conductivity, high specific surface area with suitable pore sizes, excellent electrolyte wettability and also be chemically stable (El-Deen *et al.*, 2014). Porous carbon materials are the most electrode materials used for CDI; these materials include activated carbon (AC), carbon aerogel, ordered mesoporous carbon, carbon nanotube (CNT) (Zhang *et al.*, 2012), graphene, fullerene (Gaikwad *et al.*, 2016) and activated carbon fibre cloth (Alencherry *et al.*, 2017). Activated Carbon is the most widely used carbon materials for CDI since 1970s due to its high surface area, electrical conductivity, very high adsorption capacity (Zou *et al.*, 2008) and has the low cost.

Also modified carbon porous electrodes prepared from nanoparticle oxide were used in CDI to improve the electrosorption capacity as well as salt removal efficiency (Alencherry *et al.*, 2017; Yasin *et al.*, 2017). Some of these materials are bio-decontaminated and can kill microbes. Yasin *et al.* (2017) used nitrogen-doped tin oxide intercalated activated carbon nanocomposite (N-AC/SnO₂) and composite nitrogen-TiO₂/ZrO₂ nanofibers incorporated activated carbon (NACTZ) electrode materials which shows good antimicrobial effects as well as desalination performance (Yasin *et al.*, 2017; Yasin *et al.*, 2018). Wang *et al.* (2015) also used CDI disinfection (CDID) electrode made by coating an activated carbon (AC) with cationic nanohybrids of graphene oxide-graft-quaternized chitosan (GO-QC), (GO-QC/AC CDID electrode) and achieves to kill 99.9999% of *Escherichia coli* in water (Wang *et al.*, 2015).

2.4 Nanoparticles as Antimicrobial Agent

Nanoparticles are of great scientific interest as they are effective bridge between bulk materials and atomic or molecular structures. These materials have constant physical properties without consideration of its size, but it was observed that, at the nanoscale, the size of the particles depends on their properties. Thus, the properties of the materials change as their size approaches the nanoscale and the percentage of atoms at the surface of a material becomes significant. For bulk materials larger than one micrometer the percentage of atoms at the surface is insignificant as compared to the number of atoms in the bulk of the material (Mavani & Shah, 2013). Various nanoparticles were being tested as bactericides including TiO₂ (Kim *et al.*, 2009), ZnO (Ghosh *et al.*, 2012), CuO (Pandey *et al.*, 2012) and carbon nanotubes (Yang *et al.*, 2010). Though many of these materials work as good antimicrobial

agents, their activity is slow, taking a minimum of 4 h for the effective killing of bacteria (Kumar *et al.*, 2013). Some of these nanoparticles with antimicrobial activity have been studied in CDI and shows the improvement of electrosorption and efficiency for salt removal (Sondi & Sondi, 2004).

Silver (Ag) ions and silver-based compounds are highly toxic to microorganisms and are currently used to control bacterial growth in a variety of applications, including dental work, catheters, and burn wounds (Kim *et al.*, 2007). Silver nanoparticles (Ag-n) are widely used as antimicrobial nanomaterials (Haibo *et al.*, 2010) because they have strong antimicrobial activities, broad antimicrobial spectrum, low human toxicity and are easy to use. Various researchers have already tested Ag-n in various field of biological science, drug delivery, water treatment and an antibacterial compound against both Gram (+) and Gram (-) bacteria (Theivasanthi *et al.*, 2011). So, the application of Ag-n for CDI electrodes can be used to reduce bacteria and biofilms in water and increase its performance in both salt and microbe's removal. Therefore, this study evaluated the performance of Ag-n in CDI as an antimicrobial agent.

2.5 Current Applications

Capacitive Deionization (CDI) has been increasingly tested as a competitor for current desalination technologies, such as Ion Exchange (IE), Electrodialysis (ED), thermal distillation (TD) and Reverse Osmosis (RO) (Haibo *et al.*, 2010). It is an attractive alternative because CDI does not require the use of membranes under high pressure, as RO does. As well, CDI has electrodes with a regenerative capacity, which lowers energy costs (Anderson *et al.*, 2010). Additionally, RO and ED have issues with membrane fouling and maintenance, which the regenerative capacity of the electrodes reduces (Porada *et al.*, 2013). The electrode regeneration is also able to recover the energy stored during the adsorption step, though the efficiency of recovery is variable and is in need of further optimization (Anderson *et al.*, 1999). One model suggests that even with energy efficiency as low as 70%, Capacitive Deionization is more energy efficient than ED for brackish waters desalination - below 5000 mg/L of salt (Anderson *et al.*, 2010).

Currently, CDI is used for the removal of dissolved ions from different water sources. The CDI cell was used to remove salt ions from contaminated groundwater and surface water system. The contaminated water contained 137 mg/L of nitrate, which after undergoing CDI,

was reduced to 42.5 mg/L of nitrate. The Electrostatic discharge (ESD) was able to reduce the concentration of Total Dissolved Solid (TDS) by 92% from a surface drinking water source in Sudbury, Ontario (Oren, 2008). A test of a bench top CDI unit was able to remove an average of 80.3% of ions (by weight) from greenhouse leach water, with 83.9% water recovery; the energy usage was 2.517 kWh/m³ of treated water for comparison, RO energy usage is 2.9– 3.7 kWh/m³ of water treated (Anderson *et al.*, 2010). Capacitive deionization has also been used to recover water from RO brines produced during purification of wastewater through the NE Water initiative in Singapore. Capacitive deionization was able to reduce the RO brine from a conductivity of 2060 µS/cm to 277.4 µS/cm, and the amount of TDS from 1275 mg/L to 176.5 mg/L, while operating with 85% water recovery (Tao *et al.*, 2011). The potential for CDI to remove TDS from wastewater produced during natural gas extractions has also been identified, as these waters usually have ion concentrations of less than 6000 ppm. Bench-scale tests using these waters have shown TDS removals of 75-90% (Christen, 2006).

2.6 Contaminants Removal Through CDI Process

Currently, studies of CDI have focused primarily on the removal of simple ions from different types of solutions. Kim *et al.* (2010) examined the effect of octanol on the removal of salt from brackish waters. They observed that the compound partly adsorbed and desorbed to the ion-exchange membrane overlaying the electrode (Kim *et al.*, 2010). Zhou *et al.* (2015) examined the removal of salt from both simulated and real wastewaters, as well as the removal of organic compounds, by using electro adsorption by measuring the chemical oxygen demand. Under optimized conditions, 76% removal of organic compounds was observed from refined cotton wastewater (Zhou *et al.*, 2015).

Although CDI has been used primarily for the removal of small charged chemical compounds from different types of waters, it has not been extensively tested for the removal of biological substances. Microorganisms, such as bacteria and viruses, carry net negative charges in the water at neutral pH, imparted on them by nucleic acids and proteins present on the cell membrane. The ability to positively charged porous carbon electrodes to remove *E. coli* from liquid suspension has been known for many years (Oren *et al.*, 1983). Some of the early tests using graphite mesh were able to remove 85-95% of bacteria, depending on the strain of *E. coli* used (Golub *et al.*, 1987). Some of the researchers demonstrated that *E. coli* can be desorbed successfully from the electrodes by flushing during the CDI process (Gordon,

2016). This feature is particularly valuable for the application of a CDI system used for removal of salts and microorganisms from surface water.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials and Reagents

Natural water was collected from Nganana stream located near the institution and the commercial AC powder was purchased from Finar Co.Ltd. Other materials used were small Erlenmeyer flask, beaker, test tube, large dish of ice, stirrer hotplate, 1" stir bar, droppers, filter paper, filter funnel, aluminium foil, and oven. The reagents used were silver nitrate (AgNO_3), sodium borohydride (NaBH_4), sodium chloride (NaCl) were of analytical reagent grade, polyvinyl pyrrolidone (PVP), polyvinyl alcohol (PVA) was purchased from Loba Chemie Pvt. Ltd, polytetrafluoroethylene (PTFE) and Carbon black, 99.9% ethanol were purchased from Sigma Aldrich, Hi Chrome *Escherichia coli* agar was purchased from Hi-media Co. Ltd, cellulose nitrate filter with a pore size of $0.45\mu\text{m}$ purchased from Sartorius Stedim Biotech GmbH and deionized (DI) water produced within the institution.

3.2 Synthesis of Silver Nanoparticles (Ag-n) using Reduction Method

Figure 3 below shows the summary of the Procedures for the synthesis of Ag-n, the method was adopted from Mavani *et al.* (2013) with some modifications, in which 30 mL of 0.002 M NaBH_4 were added into an Erlenmeyer flask. The solution was made fresh right before the experiment. Then a magnetic stir bar was added and the flask placed in an ice bath on a stir plate. Keeping the NaBH_4 on ice reduced the rate of decomposition during the experiment. Then 2 mL of 0.001 M AgNO_3 added into the stirring NaBH_4 solution at one dropwise. The stirring stopped as soon as all of the AgNO_3 was added.

A small portion of the solution transferred to a test tube followed by the addition of a few drops of 1.5 M NaCl solution causes the suspension to turn darker yellow, then grey as the nanoparticles aggregate. After that, the remaining portion of the solution transferred into beaker followed by the addition of a few drops of 0.3% PVP which prevents aggregation. Finally, enough solid PVA was added slowly into the stirred, hot colloidal solution until it reaches 4% in order to allow to dissolve completely, then mixture decanted into mold leaving air bubbles and undissolved PVA in the beaker and the silver nanoparticles (Ag-n) mixture evaporated in the oven for about 30 minutes to remove the unwanted impurities (Mavani *et al.*, 2013).

The silver nitrate reduction reaction can be written as;

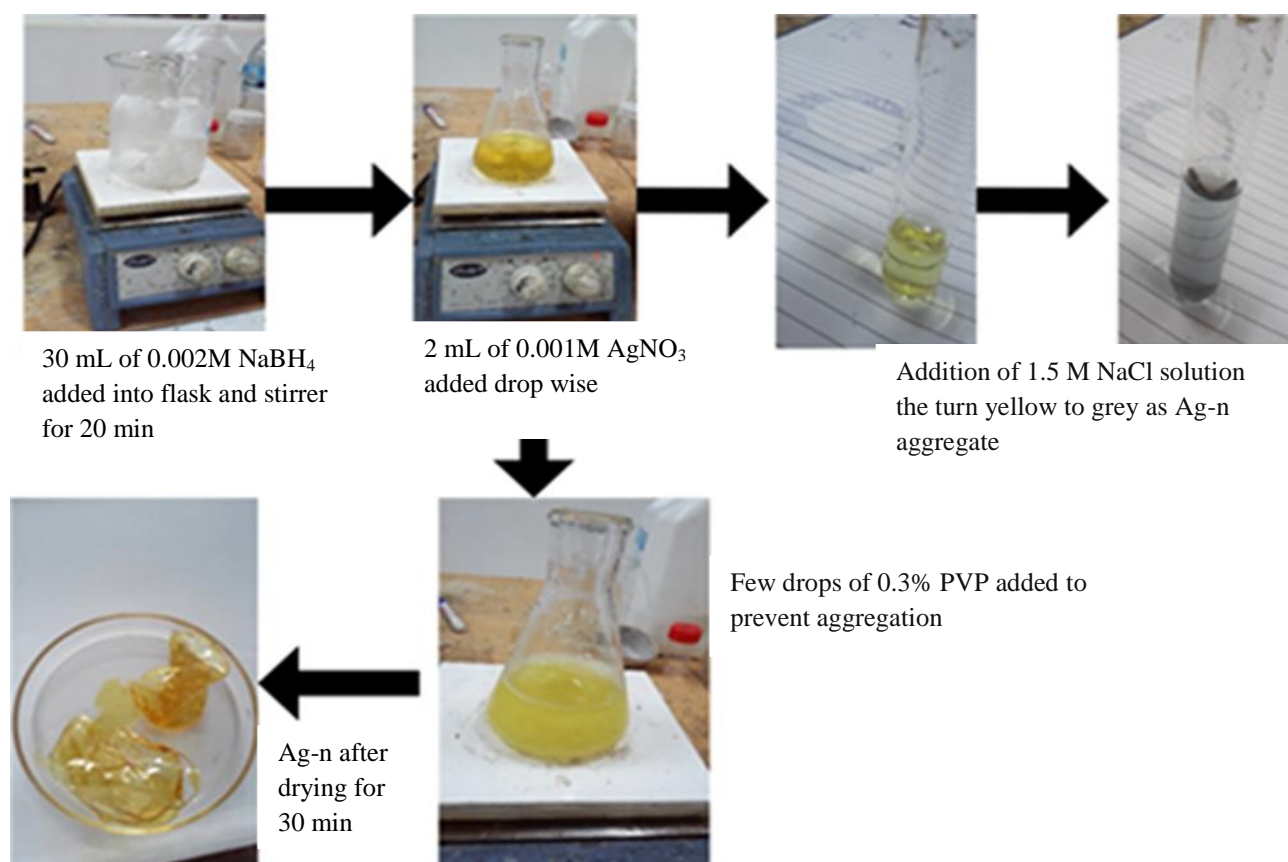
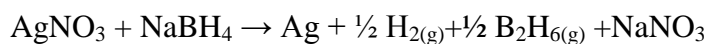


Figure 3: Summary of the procedures for the synthesis of Ag-n

3.3 Synthesis of AC/Ag-n

The Commercial AC powder with BET Surface area of $\sim 1300 \text{ m}^2/\text{g}$ was mixed with synthesized Ag-n then stirred for 2 h and dried into the oven overnight. The dried mixture was then washed with DI water until the pH of 7 and the conductivity close to that of DI water was attained; then dried again at oven overnight. Then the mixture of AC/Ag-n, carbon black (CB) and PTFE in the ratio of 8:1:1 respectively mixed with 99.9% ethanol and stirred at 100°C until all ethanol evaporated and the uniform slurry was obtained. The produced slurry (dough like structure) was pressed using presser machine into a specific thickness of about 1 mm then cut into $4 \times 4 \text{ cm}^2$ and oven dried at 60°C overnight to remove the remaining organic solvent as shown in Fig. 4. After drying the actual weight of the electrodes were measured (1.02 g for AC and 0.988 g for AC/Ag-n).

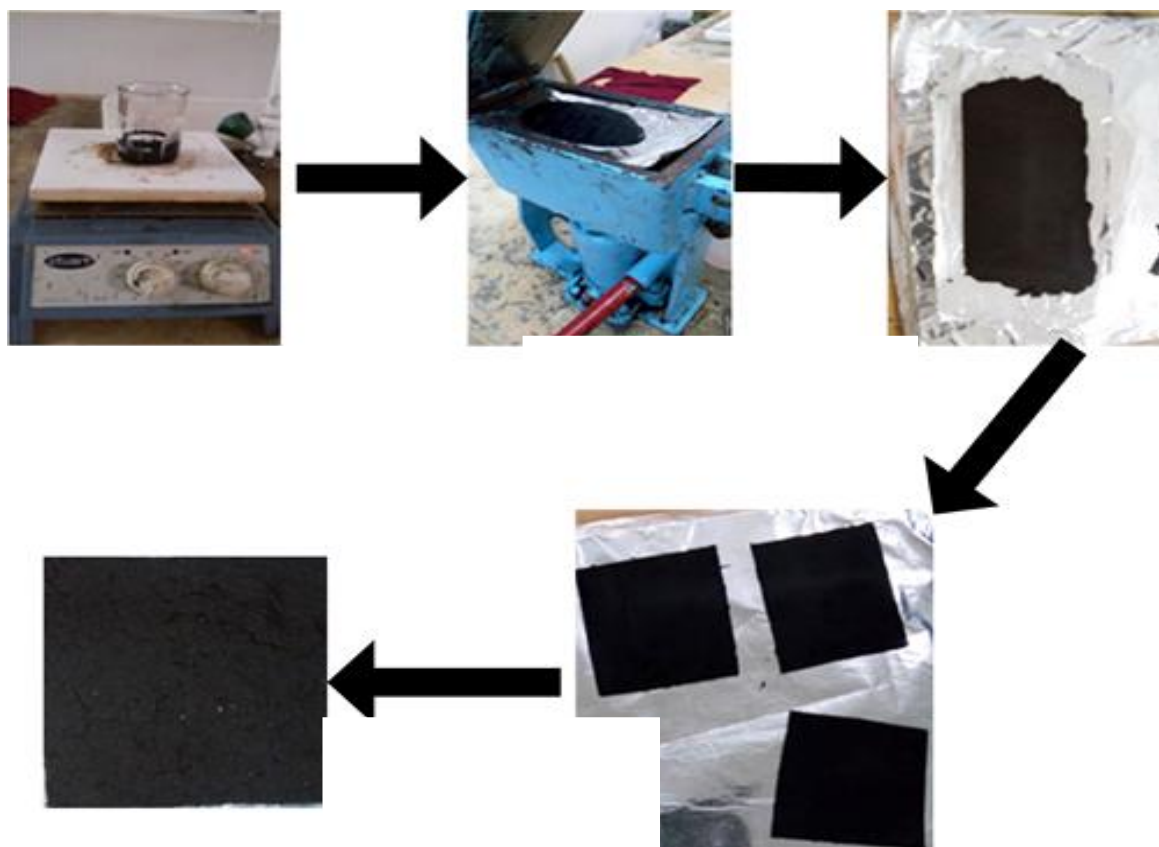


Figure 4: Summary of the procedures for the fabrication of the electrodes

3.4 Characterization of AC and Ag-n Electrodes Materials

The surface morphology of the AC Ag-n and AC/Ag-n was examined using a field-emission scanning electron microscope (FESEM) (JSM-7600F Thermo NORAN System7) with energy dispersive X-ray (EDX) analysis. The specific surface area of the AC powder was measured based on N₂ adsorption isotherms at 77 K using NOVA 4200e, Quanta chrome, UK porosimeter. Brunauer-Emmet-Teller (BET) was used to obtain surface area while the pore size distribution was obtained by the Barret-Joyner-Halender (BJH) method. The functional groups of AC and AC/Ag-n were investigated using Fourier-transform infrared spectroscopy (FTIR) using Tensor 27 spectrometer fitted with a high-throughput screening device (HTS-XT). Tests were conducted in absorbance mode in a spectral range of 4000 - 500 cm⁻¹ and cationic concentration of field water measured by using flame photometer (FP 6440).

3.5 Desalination and Disinfection Performance

The desalination and disinfection performance of AC/Ag-n electrode was evaluated by batch mode experiment as shown in Fig. 5. Capacitive Deionization cell comprises of two AC/Ag-n electrodes placed parallel to each other and connected with IVIUM STAT together with a peristaltic pump. Then, 30 ml of field bio contaminated water collected from Nganana river with initial conductivity of 425 $\mu\text{S}/\text{cm}$ was pumped between the two electrodes at a flow rate of 2.5 ml/min for 3 h while applying DC potential difference of 2 V to the cell, the conductivity meter was calibrated before starting each experiment.

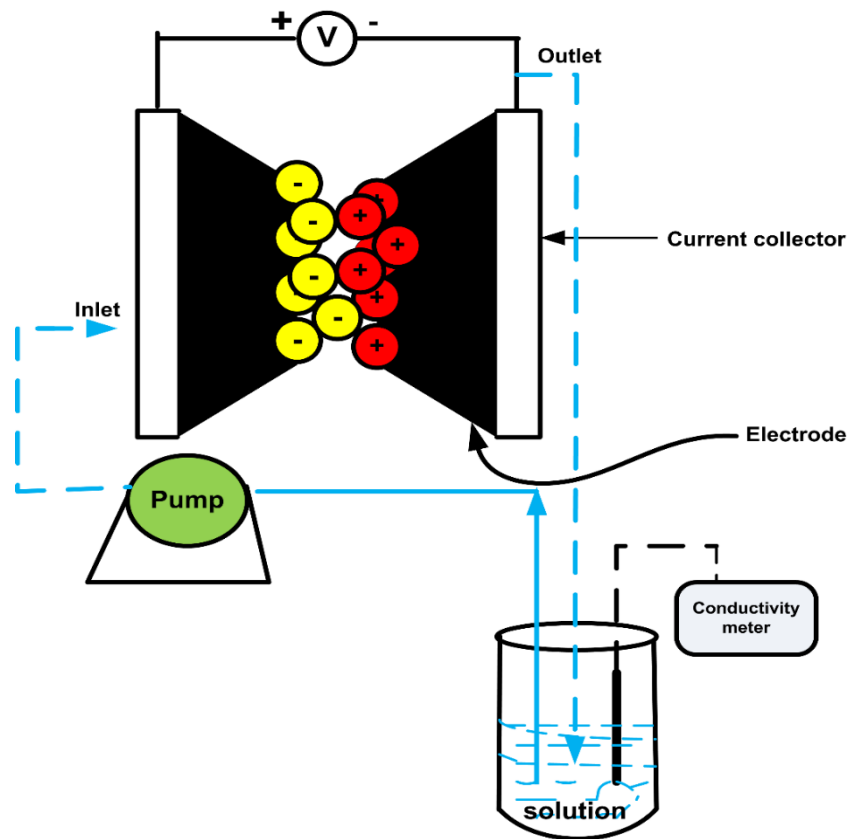


Figure 5: Schematic diagram of the capacitive deionization experiment setup

The conductivity of the outlet was recorded every 10 min. Amount of salts present in the water samples were obtained and the selected ionic concentration present in the water were measured before and after the experiments. Flame photometer (FP 6440) was used to measure the concentration of cations (Na^+ , K^+ , Ca^{2+} and Mg^{2+}) and titration methods were used to measure the concentration of anions (Ascorbic acid method for PO_4^{3-} , Cadmium reduction method for NO_3^- and Silver nitrate method for Cl^-). Removal efficiency (η) in % and adsorption capacity (S_c) in mg/g were calculated using equation 1 and 2 below (Yasin *et al.*, 2017)

$$\eta = \left(\frac{C_0 - C_1}{C_0} \right) \times 100 \quad (1)$$

Where:

C_0 = Initial Concentration (at inlet) in mg/L

C_1 = Final Concentration (at outlet) in mg/ L

$$Sc = (C_o - C_1)V/m \quad (2)$$

Where: C_0 and C_1 = the initial and final concentrations in mg/L, respectively.

V = the total volume of the aqueous salt solutions in L.

m = represents the mass of the active components in the working electrodes in g.

Membrane filtration method (Fig. 6 (c)) was used to culture bacteria, in which 30 mL of field bio contaminated water was filtered using membrane filter (cellulose nitrate filter with diameter 0.45 μ m) (Fig. 6 (b)) before and after treatment and the filter placed onto the surface of Hi Chrome *Escherichia coli* agar plates (Fig. 6 (a)). The plates were incubated at 30°C for 4 h and then at 44°C for 18 h. The colonies formed were counted and the percentage removal determined using the equation 3 below;

$$Bacteria\ removal = \left(\frac{A - B}{A} \right) \times 100 \quad (3)$$

Where: A =Number of microbial viable cells before treatment

B = Number of microbial viable cells after

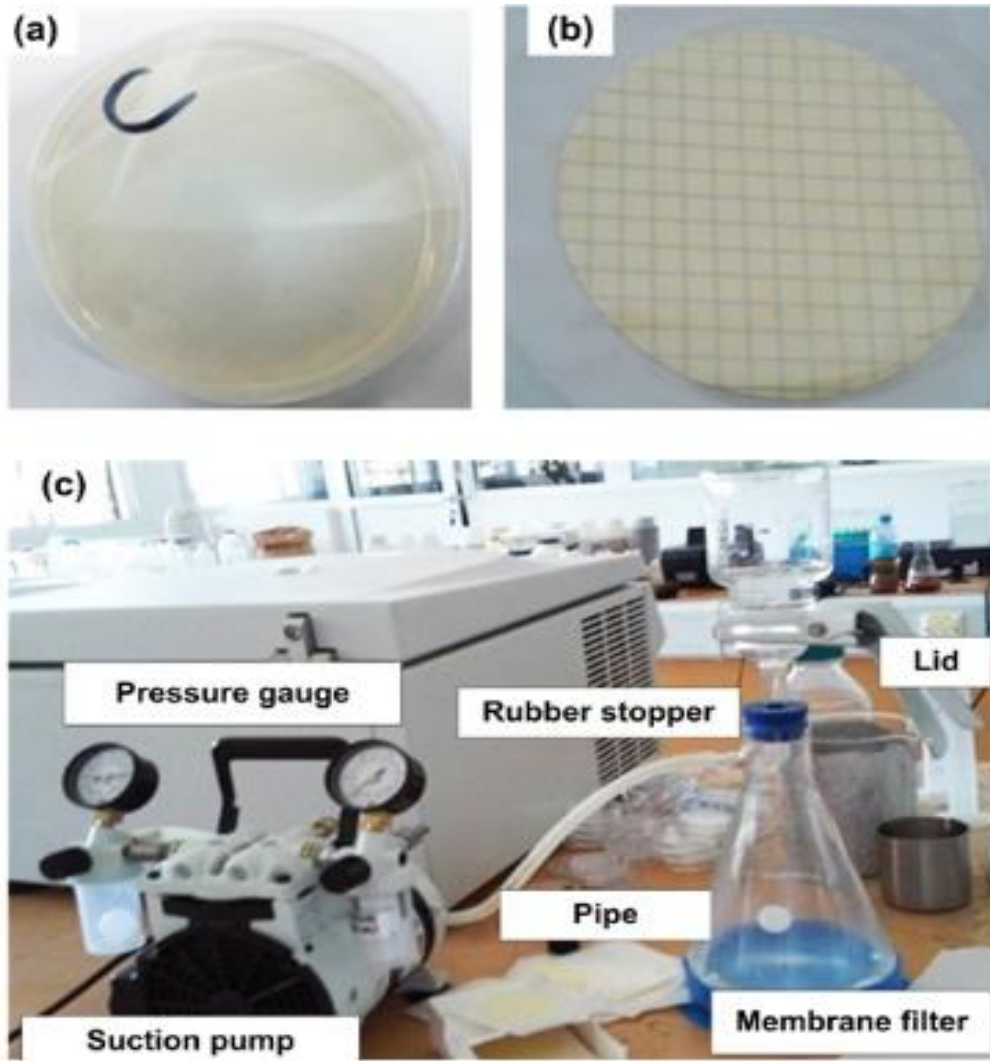


Figure 6: (a). Hi Chrome *Escherichia coli* agar plates, (b). Cellulose nitrate filter, (c) Membrane filtration technique

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Introduction

This chapter discusses the characterization of the prepared electrode materials, desalination and disinfection efficiency during CDI performance. The chapter describes the removal efficiency of different selected ions (cation and anions) and the bacteria (*Escherichia coli* and *Salmonella enteritidis*) removal efficiency. The prepared AC/Ag-n electrodes tested in the CDI cell unit to evaluate the salt and bacteria removal efficiency and their electrosorption capacity and adsorption rates.

4.2 Characterization of Electrode Materials

The BET surface area of AC and AC/Ag-n were 1037 and 786 m²/g respectively, with a pore volume of 0.65 and 0.35 cm³/g respectively as shown in Table 1. The pore diameter varied from 3 to 4.2 nm. According to the International Union of Pure and Applied Chemistry (IUPAC), pore sizes can be divided into three categories which are macropores, mesopores, and micropores. By definition, macropores are pores with diameters greater than 50 nm, mesopores are between 2 to 50 nm and micropores are less than 2 nm (Zdravkov *et al.*, 2007). The results in Fig. 7 curves show that, AC and AC/Ag-n electrodes composed of mesopores which exhibit type IV isotherms. Figure 8 shows the pore size distribution calculated by using the BJH method. The graph show that many pores were distributed between 3 to 4.2 nm which agrees well with the isotherms that indeed the samples have many pores in the mesopores region. Hence the presence of mesopores leads to a highly active surface area available for ions absorption (Garcia-Quismondo *et al.*, 2013; Huang *et al.*, 2013).

Pore size and structure are crucial to electrosorption because they affect ion transport and the formation of EDLs. On one hand, smaller pores produce a greater surface area because of the surface area to volume ratio. On the other hand, if the pore sizes begin to approach the size of the ion diameters in solution, there is the possibility for EDL to overlap and thus electrosorption efficiency reduced (Tsouris *et al.*, 2011). It was found that mesopores had the greatest contribution to electrosorption efficiency because of the accessibility of ions to the surface adsorption sites (Wang *et al.*, 2013). Some theoretical and experimental studies show that the correlation between micropores and electrosorption is greater than that of mesopores (Porada *et al.*, 2013).

Also, it is observed that the presence of PTFE binder and Ag-n in AC tend to reduce the BET surface area and the pore volumes significantly. This is because the binder provides internal resistance which blocks some pores of electrodes. As a result, the capacitance decreases due to the decrease of its surface wettability (Byeong-Hee *et al.*, 2010; Limin *et al.*, 2012). Also, embedding Ag-n into the carbon materials might slightly affect electrosorption performance of AC/Ag-n electrodes.

Table 1: BET surface area, pore volume, pore size and pore diameter of the materials

Sample ID	BET surface area	Pore Volume (cm ³ /g)	Pore Diameter (nm)
Comm.AC powder	1300	0.78	3.0
AC/Ag-n +PTFE	786	0.35	4.2
AC /PTFE	1037	0.65	3.0

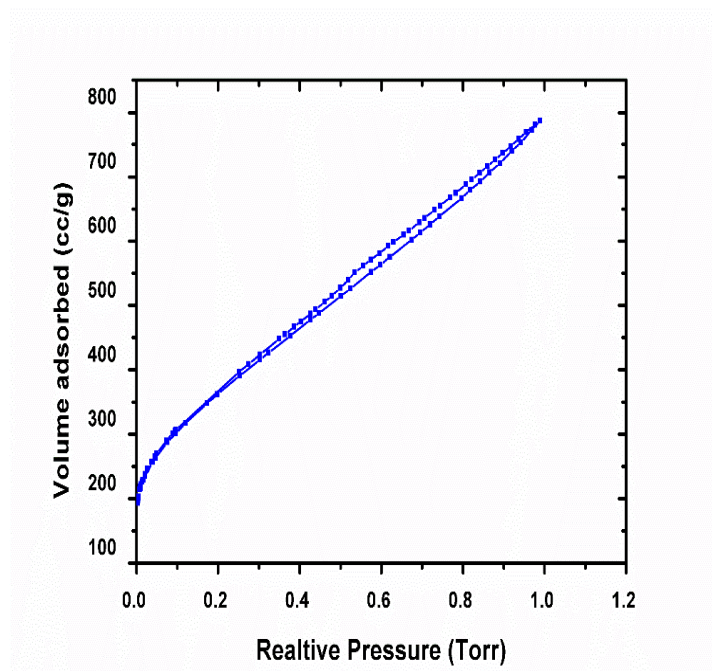


Figure 7: Nitrogen adsorption-desorption isotherms of electrode materials

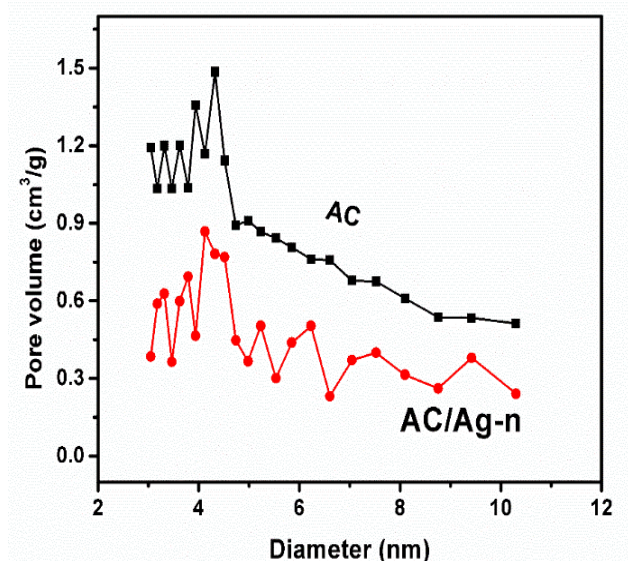


Figure 8: Pore size distribution calculated from N₂ adsorption-desorption isotherms using BJH method for electrode materials

The morphology of AC and AC/Ag-n was characterized by the SEM. Figure 9 (A) shows the rock and rough like structure thus reveals irregular surface morphology of AC, hence AC powder plays an important role in the adsorption of ionic impurities during the deionization process. Figure 9 (B) displays the EDS results of the AC. It can be clearly observed that Oxygen (O), Silicon (Si), Sulphur (S), Chlorine (Cl) and Calcium (Ca) were existing in the AC alongside with Carbon (C) and Potassium (K) (Table 4 in Appendix) indicating the presence of impurities within AC powder.

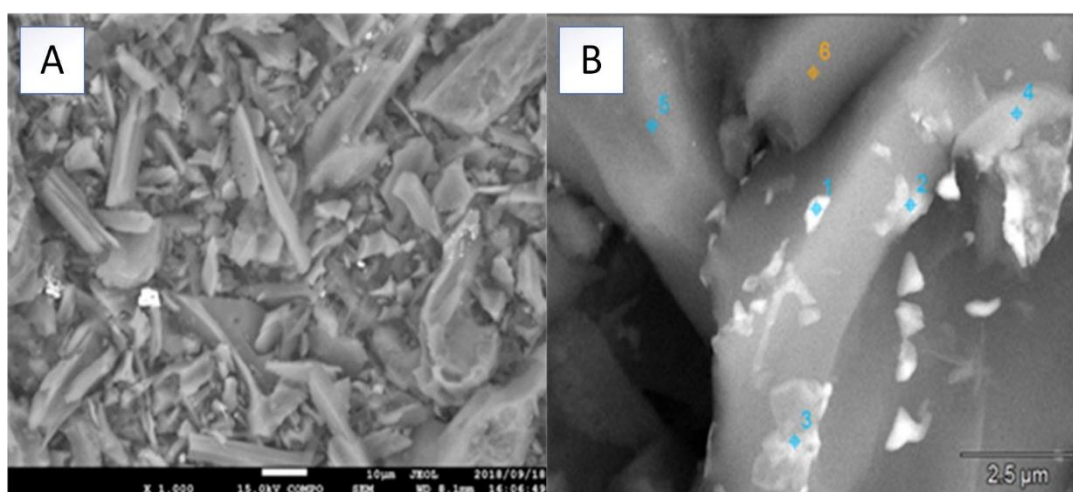


Figure 9: (A) FE SEM images of Activated Carbon powder structure, (B) SEM-EDS analysis

Figure 10 shows the FTIR spectra of AC and AC/Ag-n. AC revealed the strong characteristic wide peak of 3388 cm^{-1} which was attributed to the stretching vibration of O–H bond, peak at 2915 cm^{-1} attributed to stretching vibration of C–H, a peak at 1041 cm^{-1} attributed to C–O and a small peak of 2350 cm^{-1} attributed to C=O. On the other hand, AC/Ag-n revealed the strong characteristic wide peak of 3388 cm^{-1} is attributed to stretching and bending vibration of O–H bond, peaks at 1550 and 2915 cm^{-1} attributed to stretching vibration of C=C and C–H respectively. The strong absorption peak at 1394 cm^{-1} is caused by the stretching vibration of C–O–C. These results show that the reaction of the surface Ag-n was hindered due to the reaction of the active groups, such as C–O–C (Zou *et al.*, 2016) and the reductive group like C=C around the surface of Ag-n can react with oxidizing substance which protect the Ag-n from oxidation to the surrounding environment (Wang *et al.*, 2014). Presence of these surface hydrophilic groups such as phenolic, carboxyl and hydroxyls will enhance wettability and electrosorption capacity of carbon materials (Limin *et al.*, 2012).

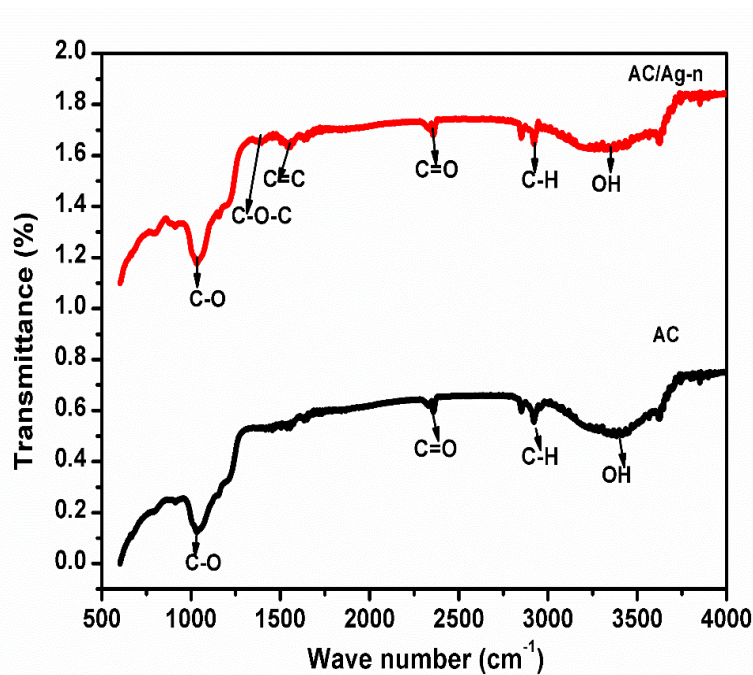


Figure 10: FTIR spectra of pristine AC and AC/Ag-n

4.3 Salt Removal Efficiency

Before studying salt removal efficiency, natural water was characterized. Table 5 in the Appendix summarizes the quality of water used in this study.

Figure 11 (a and b) show the conductivity change of water when pristine AC and AC/Ag-n electrodes were used at 2.0 V. Initially the conductivity dropped quickly, indicating that the ions are adsorbed on the oppositely charged electrodes under the applied voltage. After 150 minutes the conductivity tends to be stable, indicating the electrodes are saturated. When the electrodes become saturated, the CDI system become short circuited (zero voltage is applied), the conductivity increases rapidly, in which the ions are desorbed from the electrodes and concentrated effluent stream is produced from the CDI cell. Noticeably, pristine AC electrode reveals the higher adsorption capacity compared to AC/Ag-n as they reduce the pore sizes and volumes when Ag-n embeds AC hence the electrosorption capacity decreases.

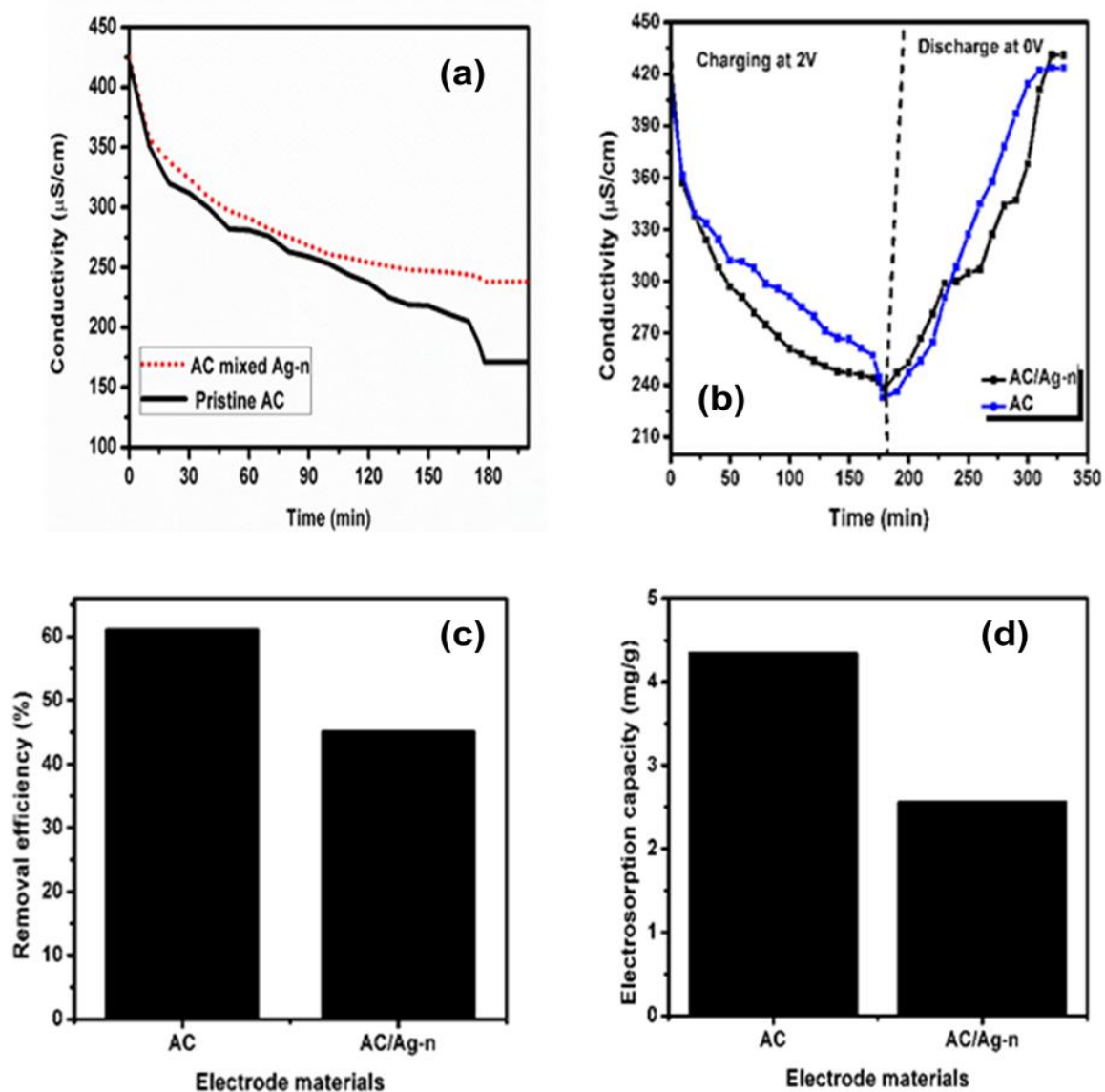


Figure 11: CDI performance for the fabricated electrodes in the salt solution, Curve (a) and (b) Conductivity change. Histogram (c) salt removal efficiency and (d) Electrosorption capacity

Figure 11 (c) shows that the salt removal efficiency (η) of the pristine AC electrode was higher reaching 61% compared to the AC/Ag-n which has desalination efficiency of 45%. The pristine AC electrode has a higher electrosorption capacity (4.34 mg/g) than AC/Ag-n (2.56 mg/g) Fig. 11 (d). This is due to the reduced surface area and pore size during embedded (mixing) process as revealed by BET and BJH method of pore size distribution shown in Table 1.

The regeneration performance of both AC and AC/Ag-n electrodes was conducted by repeating the charge-discharge experiment for 6 h by applying a constant voltage of 2 V during charging and 0 V during discharge. Figure 12 shows the conductivity and time profile over 3 charge-discharge cycles. In the first cycle, conductivity dropped to 40 min for AC and 30 min for AC/Ag- and dropped further to 180 min in the second cycle. It was observed that the ions were released rapidly after discharged but the conductivity of the solution doesn't reach the initial value. These results show that upon the removal of the applied voltage, some of the ions were not released back to the solution, and there was no decline in desalination performance observed after the first and second cycle, thus indicating that the AC and AC/Ag-n electrodes can be re-used without affecting its capacity.

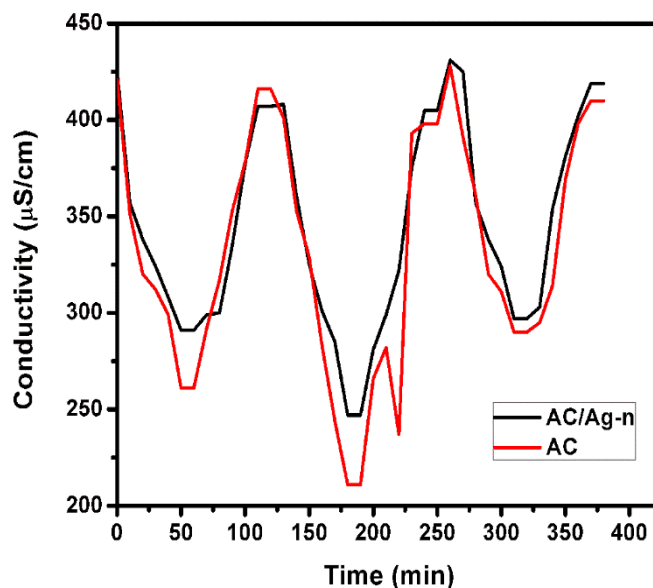


Figure 12: Charge-discharge cycles in a CDI experiment at 2V

The results of the ionic composition of bio-contaminated natural water before and after treating with CDI using AC and AC/Ag-n electrodes are presented in Table 2. Field water comprises of a mixture of selected cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) and anions (PO_4^{3-} , NO_3^- and Cl^-) each having an adsorption rate corresponding to the valance of the ionic species.

Table 2: Ionic concentration for the feed field water before and after desalination (C0 and C1), Ions charge (Valence) (V), ionic radii (IR) and hydrated radii (HR), Removal efficiency (η) and electrosorption capacity (Sc)

Ion type	V	IR (pm) ^{a,b}	HR (pm) ^c	C ₀ (mg/L)	C ₁ (mg/L)		RE (%)		Sc (mg/g)	
					AC	AC/Ag-n	AC	AC/Ag-n	AC	AC/Ag-n
Na ⁺	+1	116	358	14	0	0.5	100	96	0.43	0.40
K ⁺	+1	133	331	40	6	24	85	40	0.99	0.47
Ca ²⁺	+2	65	428	31	25	31	19	0	0.18	0
Mg ²⁺	+2	86	412	44	16	18	63	59	0.83	0.79
PO ₄ ³⁻	-3	*	*	2.35	0.54	1.17	77	50	0.053	0.035
NO ₃ ⁻	-1	264	335	22.4	9.8	20.6	56	8	0.37	0.054
Cl ⁻	-1	181	332	0.3	0.1	0.2	67	33	0.06	0.03

C₀= Initial concentration C₁=Final concentration after treatment, RE =Removal Efficiency, Sc = Electrosorption capacity, ^{a,b,c} References (Gabelich *et al.*, 2002; Nightinga, 1959; Yang *et al.*, 2009),* Not found

Figure 13 presents the ion removal efficiency. Generally, the ions adsorption rate were higher in AC than in AC/Ag-n electrodes, due to the fact that AC has larger BET surface area and pore volume compared to AC/Ag-n as shown in Table 1. Seo *et al.* (2010), Gabelich *et al.* (2002) and Xu *et al.* (2008) previously reported that, surface area, pore size and pore structure of the electrodes are important parameters to consider during ion adsorption/desorption process because they affect electrosorption capacity as well as removal efficiency of the ions during water purification (Gabelich *et al.*, 2002; Seo *et al.*, 2010; Xu *et al.*, 2008).

Field water comprises of a mixture of selected cations (Na⁺, K⁺, Ca²⁺, and Mg²⁺) and anions (PO₄³⁻, NO₃⁻ and Cl⁻) with different concentrations as presented in Table 2 whereby each ion was having an adsorption capacity corresponding to the valency of the ionic species. It can be observed that, using both CDI porous AC and AC/Ag-n electrodes, monovalent cations (Na⁺ and K⁺) were removed to the large extent from the solution over divalent cation (Ca²⁺ and Mg²⁺) because monovalent cations have smaller hydrated radii hence can penetrate through the pores and attached on the surface of electrode more easily while divalent cation have

larger hydrated radii, thus it was difficult to pass the ions through the pores of the electrode deeply (Avraham *et al.*, 2008; Yang *et al.*, 2009). Conversely, monovalent anions (NO_3^- and Cl^-) were removed to a smaller extent compared to trivalent anions (PO_4^{3-}), but those ions (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) are thermodynamically favored for adsorption during the deionization process (Kim *et al.*, 2016; Laxman *et al.*, 2015). From Table and Fig. 13, the adsorption capacity of the various ions in natural water shows that the selectivity of the ions depends on the valency, concentration and the size of the ions present in water.

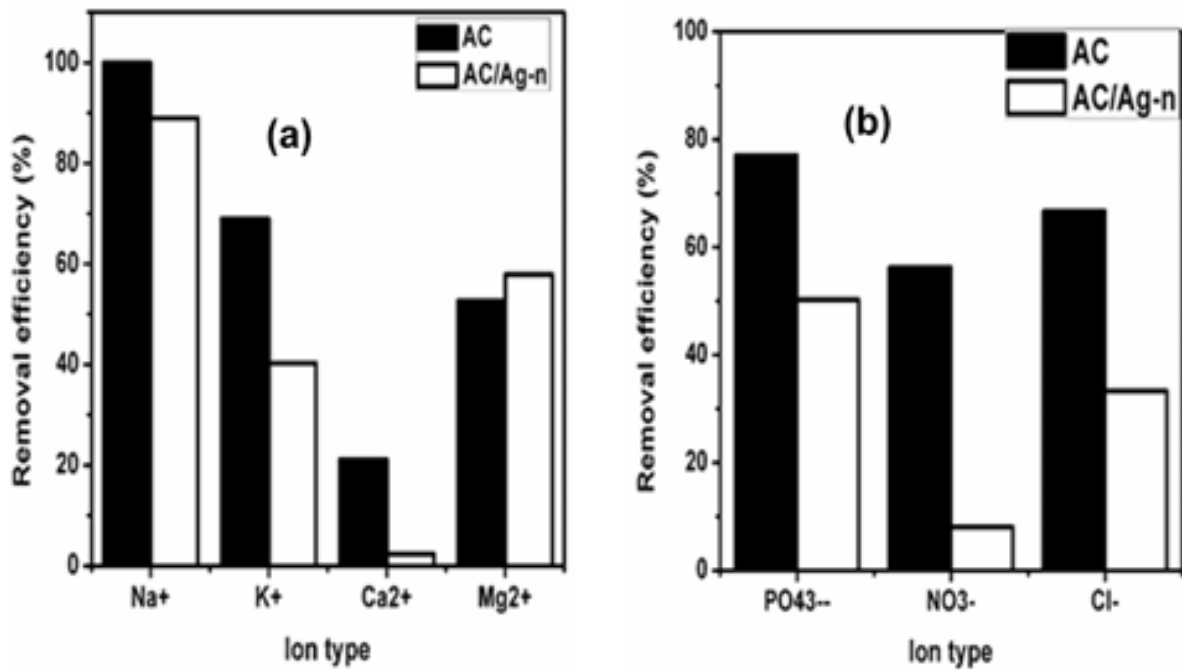


Figure 13: Removal efficiency of ionic impurities in natural water

4.4 Bacteria Removal Efficiency with CDI

Natural water was characterized before treatment and found to have *Escherichia coli* and *Salmonella enteritidis* as indicated in Fig. 14 (a), which were detected as model pathogens in testing antimicrobial activities. After circulating the water in CDI cell with AC and AC/Ag-n electrodes the result indicates the reduction of those two-gram negative (*Escherichia coli* and *Salmonella enteritidis*) bacteria (Fig. 14 (b) and (c))

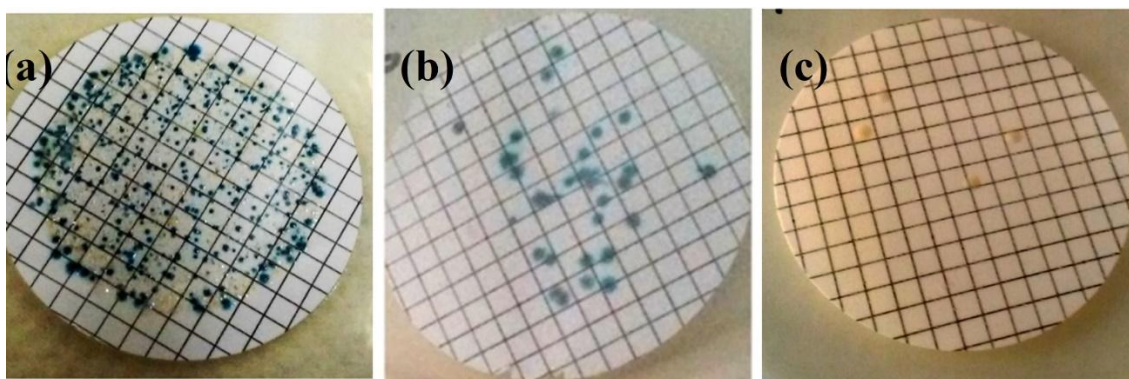


Figure 14: Plates showing bacteria growth (a) before treatment and (b) treated with AC and (c) treated with AC/Ag-n electrodes, (Blue colonies indicate *Escherichia coli* and cream colonies indicates *Salmonella enteritidis*)

Figure 15 (a) shows that, AC/Ag-n electrodes have excellent antimicrobial effect toward both bacteria *Escherichia coli* and *Salmonella enteritidis* and their removal efficiency is 100% and 98% respectively after 3 h of charging without dilution. During CDI process the bacteria were electrically attracted toward the positive AC/Ag-n electrodes, this was due to the presence of negative charges on their cell envelope (Wang *et al.*, 2015) and then killed by the embedded Ag-n when in physical contact. AC electrodes only remove bacteria by absorbing 91% and 87% for *Escherichia coli* and *Salmonella enteritidis* respectively.

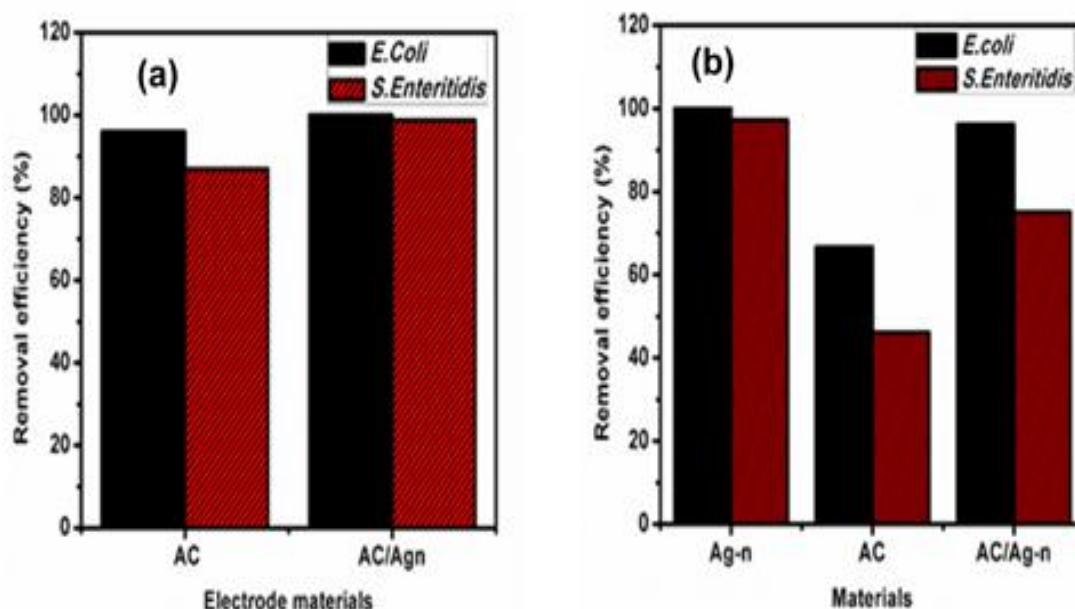


Figure 15: Bacteria removal efficiency (a) during the CDI process (b) by physical contact.

We further studied if Ag-n and AC/Ag-n can remove bacteria by physical contact [Fig. 15 (b)] without CDI process (i.e without applying electric potential to the CDI cell). Effluent water was taken and filtered for microbiological analysis. After culturing there were no bacteria which grow in the agar plate which contain effluent from AC/Ag-n materials, but bacteria grew in plates with effluent from AC electrodes with 87 to 91% bacterial removal efficiency as shown in Fig. 15 (a). This implies that AC electrodes may result in a decrease in the CDI life span as the microorganisms do not die in the cell.

Furthermore, it was noted that the concentration of salt ions in this study which was 250 mg/L in the solution has no significant effect on the bacteria-killing because the salinity is the one among the factors which favor the bacteria growth. The optimum salt concentration for bacteria to survive is about 200 to 500 mg/L as previously reported by Chapman *et al.* (2009), hence the presence of Ag-n have critical effects for disinfection of saline water. Table 3 presents different studies in which nanomaterials have been used as an antimicrobial agent in CDI-AC electrodes.

From Table 3, it can be observed that Yasin *et al.* (2017) uses nitrogen-doped tin oxide intercalated activated carbon non composite (N-AC/SnO₂) and composite nitrogen-TiO₂/ZrO₂ nanofibers incorporated activated carbon (NACTZ) electrode materials which show good antimicrobial effects as well as desalination performance (Yasin *et al.*, 2017; Yasin *et al.*, 2018). Wang *et al.* (2015) also uses capacitive deionization disinfection (CDID) electrode made by coating an activated carbon (AC) with cationic non hybrids of graphene oxide-graft-quaternized chitosan (GO-QC), (GO-QC/AC CDID electrode) and achieve to kill 99.9999% of *Escherichia coli* in water (Wang *et al.*, 2015). This study achieved 100 % *Escherichia coli* and 98% *Salmonella enteritidis* removal using AC/Ag-n electrode after 3h without dilution of the original sample.

Table 3: Salt and bacterial removal efficiency and electrosorption capacity reported in the literature and the findings of this study.

Electrode materials used	Volt (V)	Flowrate (ml /min)	Initial concentration (mg/l)	Salt removal efficiency (%)	Electrosorption capacity (mg/g)	Bacteria removal (%)	Reference
AC	2	2.5	250	61	4.34	91- <i>E.coli</i>	<i>This study</i>
						87 <i>S. Enteritidis</i>	
AC /Ag-n	2	2.5	250	45	2.56	100 <i>E.coli</i>	
						98 <i>S. Enteritidis</i>	
AC	2	1	100	66	-	82 (6 log reduction)	<i>Wang et al. (2015)</i>
			200	63	-		
AC/GO-QC	2	1	100	73	-	99.9999 (6 log reduction)	
			200	69	-		
N-AC/SnO ₂	1.2	0.8	50	61.13	3.42	Good	<i>Yasin et al. (2017)</i>
NACTZ	1.2		50	71.19	3.98	Good	<i>Yasin et al. (2018)</i>

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

To conclude, the main objectives of this study were achieved as mentioned in Chapter 1. This dissertation focused on the fabrication of AC/Ag-n electrodes for the CDI desalination and disinfection.

Capacitive Deionization (CDI) is a potential technology which can be used to remove multiple classes of contaminants from different types of water. In this study, effect Ag-n on AC electrodes for salt ion and bacteria removal from surface water (river water) was investigated. Ag-n have been embedded in AC and used as novel CDI electrode. The fabricated AC/Ag-n was tested for desalination and antimicrobial performance. The Ag-n are excellent disinfectant and can remove bacteria gram-negative species (*Escherichia coli* and *Salmonella enteritidis*) by physical contact as well as during CDI process against representative but AC alone cannot kill bacterial by physical adsorption. The salt and bacteria removal efficiency of 45% and 100% respectively were achieved. The electrosorption capacity of pristine AC was 4.43 mg g^{-1} and that of AC/Ag-n was 2.56 mg g^{-1} when 30 mg L^{-1} of field bio contaminated water was used compared to the pristine AC, AC/Ag-n revealed high disinfection performance for gram-negative bacteria (*Escherichia coli* and *Salmonella enteritidis*). The AC/Ag-n electrode is considered the potential for disinfection as bacteria contact killing process was fast, continuous and do not require complicated infrastructure. Therefore, this study presents a novel AC/Ag-n composite electrode material which can be considered as an excellent antimicrobial agent for the CDI process.

5.2 Recommendations

Even though this technique performs better to remove bacteria after culturing into agar plate but further techniques (such as molecular technique) are needed to confirm the exact mechanisms of bacteria-killing during CDI process. Furthermore, the efficacy of removing diverse contaminants in isolation as well as simultaneously in different water types should be studied to better model CDI application in natural water treatment.

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