# NATURALLY OCCURRING METAL OXIDES FROM ROCKS AS CAPACITIVE DEIONIZATION ELECTRODE MATERIALS FOR ANTIBACTERIAL ACTIVITIES

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

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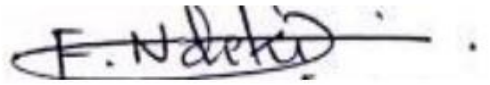
## ABSTRACT

The availability of clean and safe drinking water remains a prominent challenge in most parts of the world. Drinking water should be free from harmful microorganisms, salt as well as other organic and inorganic contaminants that need attention as they have health impacts on human beings. In the present study, naturally occurring metal oxides from rocks embedded in activated carbon (AC/MO) electrodes were evaluated for desalination and anti-bacterial activities against gram-negative (*Escherichia coli*) and gram-positive (*Salmonella aureus*) bacteria using capacitive deionization (CDI) technique. The AC/MO electrodes were fabricated for desalination and disinfection of natural and synthetic water with the CDI method. The AC/MO electrode materials were characterized by Scanning Electron Microscope (SEM), Energy Dispersive X-Ray (EDX), X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF), and Fourier-Transform-Infrared spectroscopy (FTIR), and Transmission Electron Microscope (TEM) which affirm the formation of disinfecting electrode materials. The desalination and disinfection CDI experiments were conducted by carrying out batch mode laboratory CDI system using natural water collected from the Nduruma stream (natural water) while applying a potential difference of 1.2V for 4 h. It was found that the AC/MO CDI electrodes achieved 100 ± 0.42% *E. coli* and 60 ± 0.53% *S. aureus* bacteria removal and 46.85 ± 0.49% salt removal efficiency. The bacterial disinfection mechanism is through the CDI process and physical adsorption. Therefore, this study presents the AC/MO electrode material which can be considered as an appreciable anti-bacterial agent for the CDI performance.

## DECLARATION

I, Furaha Ndeki Alphonce 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 been concurrently submitted for the degree award in any other institution.



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## CERTIFICATION

The undersigned certify that they have read and hereby recommend for acceptance by The Nelson Mandela African Institution of Science and Technology a dissertation entitled "*Naturally occurring metal oxides from rocks as Capacitive Deionization electrode material for antibacterial activities*" in partial fulfillment of the requirements for the degree of Master of Science in materials science and Engineering of The Nelson Mandela African Institution of Science and Technology.

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## DEDICATION

This work is dedicated to my family members specifically my lovely son Chrispin Furaha Ndeki and my daughter Cleopatra Furaha Ndeki.

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## LIST OF ABBREVIATION AND SYMBOLS

| | |
|---|---|
| AC | Activated Carbon |
| AgNPs | Silver Nanoparticles |
| AuNPs | Gold Nanoparticles |
| AAS | Atomic Absorption Spectroscopy |
| BET | Brunner-Emmett-Teller |
| BJH | Barrett-Joyner-Halenda |
| BSA | Bismuth Agar |
| CB | Carbon Black |
| CC | Constant Current |
| CDI | Capacitive Deionization |
| CDID | Capacitive Deionization-Disinfection |
| CuO | Copper Oxide |
| DC | Direct Current |
| DI | Deionized Water |
| DNA | Deoxyribonucleic Acid |
| ED | Electrodialysis |
| FP | Flame Photometer |
| FTIR | Fourier-Transform-Infrared Spectroscopy |
| GO | Graphene Oxide |
| HEA | Hichrome *E. coli* Agar |
| IE | Ionic Exchange |
| MO | Metal Oxides |
| PTFE | Polytetrafluoroethylene |
| PUFA | Polyunsaturated fatty acids |
| QC | Quartenized Chitosan |
| RNA | Ribonucleic Acid |
| RO | Reverse Osmosis |
| ROS | Reactive Oxygen Species |
| SEM-EDX | Scanning Electron Microscope- Energy Dispersive X-Ray |
| $SnO_2$ | Tin Oxide |
| TBMF | Thermal-Based-Multistage Flash |
| TD | Thermal Distillation |

| | |
|---|---|
| TEM | Transmission Electron Microscope |
| $TiO_2$ | Titanium Oxide |
| WHO | World Health Organization |
| XRD | X-Ray Diffraction |
| XRF | X-Ray Florescence |

# CHAPTER ONE

# INTRODUCTION

## 1.1 Background of the Problem

Freshwater availability for agricultural, industrial, and domestic use is a great challenge in developing countries. The strained demand for freshwater by the increasing world population threatens its availability in the near future (Liu *et al.,* 2013). Water scarcity and contamination are becoming more widespread worldwide, posing a severe threat to human health and ecological sustainability. Fresh water can be contaminated by organic and inorganic compounds such as industrial by-products, personal care products, pesticides, heavy metals, microbes, parasitic protozoa, and even the enteric virus (Gordon, 2016). According to a report published by the World Health Organization (WHO) in 2021, around 2.8 billion people worldwide do not have access to safe and clean water, and 3.6 billion people do not have adequate sanitation (WHO, 2021). Clean and safe water means water without any toxic chemicals and pathogens or microbes (Diallo *et al.,* 2005). To date, several techniques such as reverse osmosis (RO), ion exchange resin (IE), electrodialysis (ED), thermal distillation (TD), thermal-based-multistage flash (TBMF), and multi-effect distillation (MED) have been employed by researchers for water treatment and purification (Saleem *et al.,* 2016). Most of these techniques can achieve high water purification efficiency with excellent stability, but have drawbacks including high energy consumption, secondary wastes generation, high maintenance cost, and equipment fouling problem (Díaz Baizán *et al.,* 2014). Also, reverse osmosis (RO) plants require significant upfront costs and become uneconomical at larger scales, and they are ineffective in treating low-salinity water (Anderson *et al.,* 2010). Therefore, to overcome such shortcomings new water treatment technologies are required (Chen *et al.,* 2020).

Capacitive deionization (CDI) is a promising and rapidly growing technology that is easy to operate, environmentally friendly, and energy efficient for water purification, especially for the removal of microbes (Suss *et al.,* 2015), and heavy metals (Chen *et al.,* 2023). Furthermore, the CDI technology uses low pressure and non-membrane processes making it a viable water treatment technique (Yan *et al.,* 2018). The CDI working principle is based on the electric double layer capacitors (EDLs) principle, whereby the charged ions from the aqueous solution are adsorbed and electrostatically stored on the oppositely charged surfaces of electrodes through the application of potential difference from an external source of power (Zouli, 2022). When the external potential difference is removed or reversed, the adsorbed ions released back to the solution, which resulting in the regeneration of electrodes (Ahualli *et al.,* 2018).

The chemical and physical properties of electrodes materials play a significant role in (CDI) performance (Han *et al.,* 2018). Recently, polydopamine/polyhexamethylene guanidine co-deposited activated carbon (AC-PDA/PHMG), porous carbon, aerogels, activated carbon, carbon nanotubes, carbon nanofibers, and graphene are different carbon materials which have been studied for microbes removal (Folaranmi *et al.,* 2020). These materials have suitable properties such as high specific surface area (SSA), good wettability, high adsorption capacity, chemical inertness, high electrical conductivity, suitable pore size distribution, and high capacitance (Rambabu *et al.,* 2020).

Capacitive Deionization has been employed in many investigations for water treatment, however the presence of microbes in desalinated water remains a significant challenge. Various conventional antibacterial agents have been used to overcome such challenges including hypochlorite, chlorine, peroxides, ozone, and zeolite (Liu *et al.,* 2021; Takayama, 1998) have been used to remove microbes in water. However, they faced with limitations such as production of hazardous by-products that are carcinogenic, mutagenic, highly irritating, and damaging to human health and the environment (Diana, 2019; Stalter, 2016). Recently, activated carbon (AC) embedded with different nanomaterials have been studied in CDI for antibacterial activity including silver nanoparticles (AgNPs) (Tang *et al.,* 2018), gold nanoparticles (AuNPs) (Sathiyaraj *et al.,* 2021), carbon nanotubes (CNTs) (Mohammed *et al.,* 2020), and graphene oxide (GO) (Folaranmi *et al.,* 2020). Abdallah *et al.* (2019) uses the silver nanoparticles embedded with activated carbon (AC/AgNPs) for antimicrobial activities using CDI and achieved to kill 100% of *Escherichia coli* and 98% of *Salmonella enteritidis* after charging for 3 h during the CDI process (Abdallah *et al.,* 2019). Also, Yasin *et al.* (2017) uses nitrogen doped tin oxide intercalated activated carbon non composite (N-AC/$SnO_2$) and composite nitrogen-$TiO_2$/$ZrO_2$ nanofibers incorporated activated carbon (NACTZ) electrode materials which show good antibacterial effects as well as desalination performance (Yasin *et al.,* 2017). Wang *et al.* (2015) also uses capacitive deionization disinfection (CDID) electrode made by coating an activated carbon (AC) with cationic non hybrid of graphene oxide-graft-quaternized chitosan (GO-QC), (GO-QC/AC CDID electrode) achieved to kill 99.9999% (6 log reduction) of *Escherichia coli* in water (Wang *et al.,* & Boom, 2015). Although activated carbon (AC) electrodes modified with nanomaterials are effective on inhibiting bacterial activity in desalinated water, their implementation on a broad scale is challenging due to their high cost, rigid reaction conditions, and challenging fabrication methods (Hou *et al.,* 2018; Yoon *et al.,* 2021). Additionally, various studies have reported the toxicity effects of nanomaterials including AgNPs (Stensberg, 2011), AuNPs (Albanese *et al.,* 2011), CNTs (Cheng, 2009), and GO (Duch, 2011) on rat liver and murine stem cells, human nerves, and its poisonous impacts on aquatic organisms in nanomolar concentration. But metal oxides (MO),

including $TiO_2$, ZnO, CuO, $SnO_2$, and MnO are recently attracted special attention due to their unique properties and noticeable effect against bacterial activities in water (Chavali *et al.,* 2019). Furthermore, MO are renowned for being affordable, plentiful, non-toxic, and eco-friendly (Sawai *et al.,* 2004). Rocks are naturally occurring materials which containing MO including $SiO_2$ abundantly (Tian *et al.,* 2021) which showing appreciable anti-bacterial activity without use of chemicals and low cost. Furthermore, it is noteworthy that rock materials containing MO are abundantly accessible throughout various regions of Tanzania, with particular emphasis on the Singida region, and they are available at highly cost-effective rate. Therefore, this study was intended to investigate the effectiveness of the naturally occurring MO from rock materials modified AC (AC/MO) as an alternative low-cost electrode with high antibacterial activity in water using the CDI method.

## 1.2 Statement of the Problem

Many studies employed CDI technology for desalination and removal of ionic contaminants in water, however, the issue of microorganisms in the desalinated water persists as a formidable challenge. According to the report of World Health Organization (WHO) of 2021, reveal that approximately five billion people lose their lives because of waterborne diseases caused by microbes present in drinking water each year (WHO, 2021). Hence, developing new, green, and cos-effective biocidal materials for water treatment, especially for microbial removal using CDI technique is of significant importance. As bactericidal materials, rock powder containing metal oxides (MO) can be employed in water treatment and purification for domestic use (Stanić *et al.,* 2020). It is largely known that naturally occurring metal oxides are effective material for killing bacteria such as *Escherichia coli* and *Salmonella aureus* and are non-toxic to human being when consumed below the recommended concentrations levels (Stanić *et al.,* 2020). Since metal oxides can kill microbes and show a significant effect against microbial activity, they can be used as a CDI electrode material to increase efficiency in microbial removal from water as well as desalination. Thus, this study intended to use electrodes made with AC loaded with rock powder containing metal oxides (AC/MO) in CDI for bacterial and salt removal from simulated and natural water.

## 1.3 Rationale of the Study

For human consumption and life in general, clean and safe water is a crucial need. Waterborne diseases, including cholera, typhoid fever, amoebiasis, hepatitis A, and giardiasis are attributable due to the ingestion of water contaminated with pathogenic microorganisms. To ensure the eradication of these harmful microbes from drinking water, which persists as a significant peril to

human well-being, a diverse range of techniques can be implemented. Capacitive deionization (CDI) technology presents a promising approach for effectively eliminating pathogenic microorganisms from water. Its chemical-free operational modality, energy efficiency, and compatibility with existing infrastructure render it a valuable option for mitigating waterborne diseases. Incorporating naturally occurring metal oxides (MO) derived from rocks as electrode materials for their inherent antibacterial properties offers a reliable and sustainable solution for microbial removal in water treatment processes, encompassing cost-effectiveness and eco-friendliness. Therefore, it is necessary to use these cutting-edge technologies for water purification. To provide safe and clean water, this study was implemented to address the issue of microbial-contaminated water and concurrent challenge of salt removal. It focused on harnessing the potential of metal oxides obtained from rocks through application of CDI technique. The proposed solution encompasses significant advantages, including the mitigation of health concerns associated with the consumption of bacteria-contaminated drinking water, as well as the enhancement of water quality overall. By effectively removing harmful microbes and reducing the salt content, this approach holds promise in safeguarding public health, and ensuring access to safer, high-quality water resources.

## 1.4 Objectives

### 1.4.1 General Objective

The general objective of this study is to investigate the efficacy of AC loaded with naturally occurring MO from rocks as CDI electrode materials for microbes and salt removal from water.

### 1.4.2 Specific Objectives

(i) To characterize the pristine AC, rock powder, and AC loaded MO (AC/MO) CDI electrode materials.

(ii) To fabricate the CDI electrodes from the AC/MO materials.

(iii) To evaluate performance of developed electrode (AC/MO) for microbes and salt removal from water.

## 1.5 Research Questions

(i) What are the characteristics of AC and rock composition that make them effective in disinfection and desalination?

(ii) What is the efficiency of AC loaded with MO (AC/MO) electrodes in CDI for bacterial and salt removal?

(iii) Can AC/MO remove bacteria without affecting the CDI performance on salt removal?

## 1.6 Significance of the Study

The significant demand for water increases as the population keeps increasing. There are now several techniques such as reverse osmosis (RO), ion exchange resin (IE), electrodialysis (ED), thermal distillation (TD), thermal-based-multistage flash (TBMF), and multi-effect distillation (MED) used to desalinate water and remove ionic impurities to reduce water crisis. However, these technologies suffer from various drawbacks including high energy consumption during the purification process. Capacitive deionization technique is a promising method which has the advantage of utilizing low energy during purification process desalination and it is environmentally friendly. Therefore, this study used AC impregnated with naturally occurring MO (AC/MO) as a CDI electrode material for bacterial and salt removal from water, which serves to make a meaningful contribution towards mitigating the problem of saline water contaminated with bacteria, and ultimately facilitating the provision of clean and safe drinking water. Through the proficient elimination of microbes and salts from water, this study significantly enhances the water quality, rendering it safe for human consumption while concurrently extending its applicability to diverse agricultural and industrial purposes. Such improvements have a significant impact on public health and environmental sustainability.

## 1.7 Delineation of the Study

This chapter explains the background of the problem of the study, 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 efficacy of naturally occurring metal oxides (MOs) from rocks in capacitive deionization (CDI) as anti-bacterial agent for water treatment and completed with three specific objectives in which the rock sample in powder form was characterized to determine the metal oxides present and mixed with the activated carbon (AC) to synthesize the electrode followed by characterization of electrode materials, finally performance of the CDI electrodes for microbes removal and desalination was evaluated. This study covered a wide part of desalination, encompassing the removal of both gram-positive and gram-negative bacteria specifically *Salmonella aureus* and *Escherichia coli*. Additionally, the removal of other ionic impurities by using the CDI technique with an electrode developed using AC loaded with rock powders enriched with metal oxides (MO). This electrode (AC/MO) exhibits promise for

deployment within large-scale water treatment plant systems, offering potential solutions to global challenges related to waterborne issues.

# CHAPTER TWO

# LITERATURE REVIEW

## 2.1 Introduction

Access to safe and clean drinking water is a major global challenge of 21st century because of pollution created by both natural and human activities. To overcome this problem, low-cost and effective technologies for water purification should be a fundamental focus of recent studies. Because of its low-cost, high energy efficiency, cost-effectiveness, and ease of material regeneration compared to conventional technologies such as ion-exchange resin, electrodialysis (ED), thermal distillation (TD), multi-effect distillation (MED), thermal based multi-stage flash (TBMSF), and reverse osmosis (RO), capacitive deionization (CDI) has attracted significant attention as a promising technology for water desalination and disinfection (Sabir *et al.,* 2015).

Various materials have been reported to be employed as electrode materials in CDI for water desalination and disinfection. Nwanya *et al.* (2019)used mixed oxide nanoparticles ($TiO_2$-ZnO-MgO) and activated carbon electrode materials for disinfection against *Artemia salina* and the results show good antibacterial effects as well as desalination performance. Yasin *et al.* (2017) used N-doped and $SnO_2$ (N-AC/$SO_2$) incorporated activated carbon for water desalination and bio-decontamination and enhance the electrosorption capacity of 3.42 mg/g and the desalination efficiency of 61.13% and good antibacterial performance, and Motshekga *et al.* (2015) used an activated carbon (AC) electrode with cationic nanohybrids of graphene oxide-graft-quartenized chitosan (GO-QC), (GO-QC/AC CDID electrode) and achieve to kill 99.9999% of *Escherichia coli* in water.

Recently, activated carbon electrodes embedded with silver nanoparticles (AC-AgNPs) have been used in CDI technologies for water desalination and disinfection, improving electrosorption capacity and desalination efficiency by 2 to 5.3 mg/g and 42 to 67%, respectively (Yoon *et al.,* 2017). However, the availability of novel electrode materials for CDI technology is still a challenge. To overcome the challenges, effective CDI electrode materials that are low in cost and readily available are required to improve CDI performance.

## 2.2 Basic Principle of CDI

Capacitive deionization studies emerged in the 1960s, with a porous electrode made of activated carbon powder (ACP) used for water desalination in the inflow through mode. Under the effect of inherent chemical surface charges, ions from electrolytes (aqueous solution) are adsorbed on the electrode in CDI (Alencherry *et al.,* 2017).

An electric field is generated across the aqueous solution due to potential differences between the two surfaces. Electrosorption of ions occurs on oppositely charged electrodes due to the electric field generated, with cations adsorbed to the negative electrode and anions adsorbed to the positive electrode (Saleem *et al.*, 2016). The presence of an electronic charge at the solid surface and an ionic charge in the nearby solution forms the electric double layer (EDL) (Fig. 1) (Lu *et al.*, 2021). Ion storage in the electric double layer (EDL) can be reversed. Because electrons travel from the negative electrode to the positive electrode when the potential difference between two electrodes is adjusted to zero, the surface charge is lowered. Because the entire interface region stays electrically neutral, the counter ions migrate back into the bulk solution (Zhang *et al.*, 2018).

The surface layer and the diffuse layer are the two layers that exist at the surface of the solid-liquid interface and are referred to as the EDL. The nearest surface layer to the solid (carbon matrix) is the Helmholtz Outer Layer, which comprises counter-ions interacting with the surface via chemical interactions. In contrast, the diffuse layer comprises of ions drawn to the surface by electrostatic charge. The electrodes' electrical capacity to store energy is determined by the capacity of both EDL components (Saleem *et al.*, 2016; Yoon *et al.*, 2017).

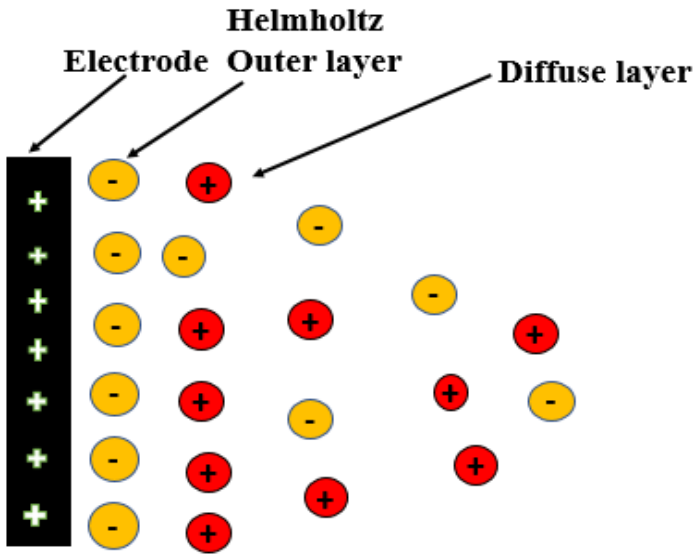


**Figure 1: Electric double layer (EDL) structure**

Electrodes become less efficient at removing ions from aqueous solutions when the electrode surface area is saturated with ions. The electrode can be regenerated by reversing the charges, which causes ions to repel from the electrode's surface to the interstitial region, where they are

evacuated as a highly concentrated solution from the cell unit (Fig. 2) (Yasin *et al.,* 2017; Zhao *et al.,* 2012). The electrode can be regenerated and start a fresh cycle of electrosorption of ions. Typically, the highly concentrated effluent is discarded, but it can also be utilized to recover or sample components that are very dilute in the influent water (Saleem *et al.,* 2016).

### 2.3 CDI Cell Design

The flow-in mechanism and the flow-by mechanism are the two mechanisms that allow water to flow through the CDI cell. Water flows through the pores of the CDI cell's electrode in the flow mechanism, whereas water flows via the flow channel or gap between the electrodes in the flow-by mechanism (Ahualli *et al.,* 2018). The flow in through electrodes, also known as flow through CDI, has the benefit of eliminating the need for a spacer in the area where the solution/water flows. The electrode/separator/electrode assembly, on the other hand, lowers the cell's internal resistance and speeds up the desalination process (Saleem *et al.,* 2016).

### 2.4 CDI Operational Process

Capacitive deionization systems can be operated with either constant current (CC) or constant voltage (CV), with the latter being more common. The effluent concentration drops to a minimum when a constant voltage (CV) is applied to the porous electrode of the CDI cell, then begins to rise again when the feed concentrations equal the effluent concentration, indicating that the CDI cell is saturated with ions or the micropores of the porous electrode reach the maximum value of storage or saturation point (Saleem *et al.,* 2016). Constant current mode (CC) achieves a constant ionic conductivity (salinity composition) at the CDI cell's output, allowing the CC to be used when a specific effluent concentration is required (Porada *et al.,* 2013).

According to several studies, adding a membrane to the CDI cell improves ion adsorption by enabling only ions with opposite charges to the polarized electrode (counter ions) to pass through and be absorbed by the electrode (Sufiani *et al.,* 2019). The co-ions are instead ejected from the micropore but retained on the electrode by the membrane, which attracts more counter ions to the electrode's surface (Sun *et al.,* 2021). The advantage is that more ions can be absorbed on the electrode than with regular CDI, but parts of the ions are retained on the electrode during the purge (Abdallah *et al.,* 2019). Furthermore, the use of ion exchange membranes (IEM) inhibits ions adsorbed during the purification cycle from adsorbing to the electrode of opposite charge during the purge step, while standard CDI allows the ions to be adsorbed and desorbed more easily.

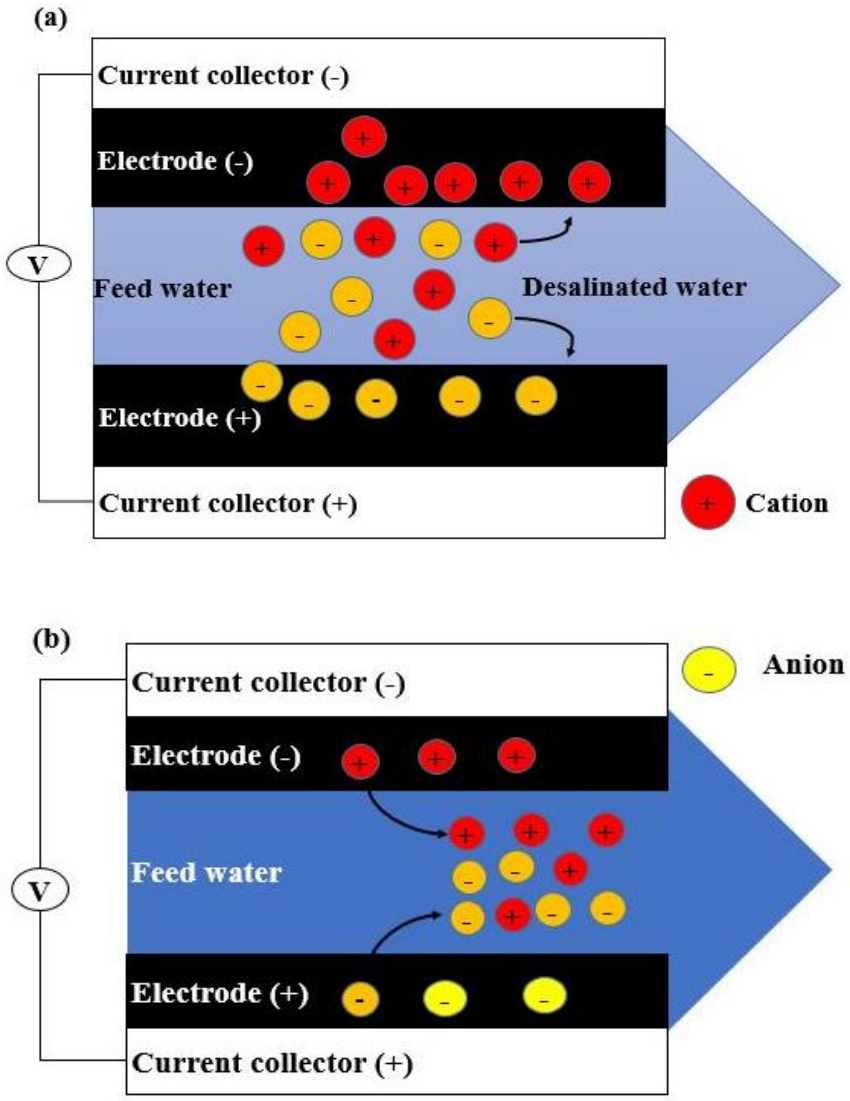


**Figure 2:** **Schematic representation of basic principle of CDI (a) Adsorption (b) Desorption**

**Table 1: Existing technologies for salt and bacteria removal**

| Existing technology | Advantages | Disadvantages | References |
|---|---|---|---|
| Microbial desalination cell (MDC). | Doesn't use external source of power (electricity). | High internal resistance which decreasing performance of the system. | Cao *et al.* (2009) |
| Nanofiltration (NF). | Selective removal of salts and some microorganisms. | Less effective against smaller microbes. | Singh *et al.* (2020) |
| Ozonation (O). | Effective over a broad range of microorganisms. | High cost, limited residual disinfection. | Xi *et al.* (2017) |
| Chlorination (C). | Widely used, effective against many microorganisms. | Formation of disinfection byproducts. | Nielsen *et al.* (2022) |
| Electrochemical disinfection (ED). | Low energy consumption, effective microbial inactivation. | Limited scalability, need for skilled operation. | Zhang *et al.* (2023) |
| Reverse osmosis (RO). | Effective removal of microbes and salt. | High energy consumption, membrane fouling, and production of brine waste. | Li *et al.* (2023) |
| Capacitive deionization (CDI). | Chemical-free, low energy consumption, no secondary waste generation. | Limited removal of charged species. | Shocron *et al.* (2022) |

## 2.5 Electrode Material for CDI

Good electrical conductivity, a high specific surface area with adequate pore sizes and distributions, electrolyte wettability, chemical stability, and a porous structure are all requirements for CDI electrode materials (Yasin *et al.*, 2017). Activated carbon (AC), carbon nanofibers, carbon nanotubes (CNTs), reduced graphene oxide (RG), carbon aerogels (CAs), macro and mesoporous carbon (MC), fullerenes, activated carbon fiber cloth, and carbon black are commonly utilized as electrode materials for CDI to suit these requirements (CB) (Abdallah *et al.*, 2019). Because of their high specific area (1000-2000 $m^2/g$) and porosity, activated carbon materials are commonly utilized as electrode materials and are attractive options for CDI cells (Chen *et al.*, 2020), relatively good electrical properties (Yasin *et al.*, 2017), and its low cost (Abdallah *et al.*, 2019). Activated carbon (AC) has poor capacitance, which results into limited ion removal, as well as hydrophobicity, which prevents it from being widely used in the CDI procedure (Yasin *et al.*, 2017). As a result, several studies have been conducted to overcome the AC electrode's shortcomings and improve its desalination performance and efficiency (Alencherry *et al.*, 2017). As a result, by incorporating the AC with organic and inorganic materials to perform surface

modification on the AC electrode, the capacitance and desalination efficiency can be improved (Yasin *et al.,* 2017). Inorganic materials, particularly metal oxides such as zinc oxide (ZnO), manganese oxide ($MnO_2$), and Titanium oxide ($TiO_2$) on carbon electrodes, can facilitate excellent CDI desalination performance with their high physiochemical characteristics and significantly improve electrode capacitance as well as electrochemical performance, in addition to the incorporation of organic matter and surface modifications.

In CDI, modified carbon porous electrodes made of nanoparticles oxide were also used to improve electrosorption capacity and salt removal efficiency (Alencherry *et al.,* 2017). Some of these materials are bio-decontaminated and can kill microbes found in desalinated water (Yasin *et al.,* 2017). Yasin *et al.* (2017) used nitrogen-doped tin oxide intercalated activated carbon nanocomposite (N-AC/$SnO_2$) and composite nitrogen-$TiO_2$/$ZrO_2$ nanofibers incomporated activated carbon (NACTZ) electrode materials which shows good anti-microbial effects as well as desalination performance. Wang *et al.* (2015), also used CDI disinfection electrode made by coating an activated carbon (AC) with cationic nanohybrid graphene oxide-graft-quaternized chitosan (GO-QC), (GO-QC/ACCDID electrode) and achieved to kill 99.9999% of *Escherichia coli* in water. (Abdallah *et al.,* 2019), using activated carbon electrode embedded with silver nanoparticles (AC/AgNPs) for water treatment and disinfection and achieves to kill 100% of *Escherichia coli* and 98% *Salmonella enteritidis* with the desalination efficiency of 45% using AC electrode embedded with silver nanoparticles (AC/AgNPs).

### 2.6 Nanoparticles as Anti-Microbial Agents

Nanoparticles have recently gotten a lot of press because of their unusual qualities, making them valuable in various scientific fields. They are used in catalysts, plasmonic, optoelectronics, biological sensors, medicines, and water treatment, among other things (Chen *et al.*, 2020). These particles have distinct features because of their smaller size relative to the bulk form. Since, more electrons are confined at the surface of nanoparticles at the nanoscale, the particle's characteristics change, making it more reactive (Ahmed *et al.,* 2016). As a result, as materials' sizes approach the nanoscale, their properties change, and atom confinement at the material's surface becomes more important, as opposed to the bulk material, where atom confinement at the surface becomes less important because more atoms are found within the bulk material's structure (Abdallah *et al.,* 2019). To date metallic nanoparticles are prepared mostly from noble metals including; silver, gold, copper, zinc, titanium, cadmium, iron, and alignate (Deshmukh *et al.,* 2019). Among the noble metals from which nanoparticles prepared, silver (Ag) is the metal of choice in the field of biological system, living organisms, water treatment and medicines (Sulaiman *et al.,* 2013). Various nanoparticles have been tested as bactericides including; $TiO_2$, ZnO, CuO and carbon

nanotubes (CNTs) (Liu *et al.*, 2013). Although these nanoparticles are efficient bactericides against microbial activities, their activity gradually takes, taking around 4 hours to kill microorganisms effectively (Kumar *et al.*, 2013). Some of these antimicrobial nanoparticles have been examined in CDI technology and exhibit good improvement in electrosorption capacity and desalination efficiency (Sondi *et al.*, 2004).

Silver metal compounds and silver ions ($Ag^{+}$) are poisonous to bacteria and are used to inhibit microbial growth in various applications, including medicine, dentistry, and wound burns (Abdallah *et al.*, 2019). Silver metal based compounds are widely used as antimicrobial agents against microbial activities because silver metal ions adhere to the cell wall of bacteria and damage cell wall permeability, leading to the destruction of cellular DNA and protein via the interaction of silver ions with phosphorus in DNA and Sulphur-containing amino acids in protein (Elumalai *et al.*, 2010). Silver-based metal compounds have already been investigated in biological science, drug delivery, water treatment, and antibacterial agents against Gram positive and Gram negative bacteria by several researchers (Theivasanthi *et al.*, 2011). Although silver nanoparticles (AgNPs) effectively inhibit bacterial activity in desalinated water, their implementation on a broad scale is challenging due to their high cost, rigid reaction conditions, and challenging fabrication methods (Hou *et al.*, 2018). Additionally, various studies have reported nanomaterial's toxic effects, including AgNPs on rat liver and murine stem cells, human nerves, and its poisonous impacts on aquatic organism in nanomolar concentration (Albanese *et al.*, 2011; Stensberg, 2011). Therefore, this study aims to investigate the application of naturally occurring MO from rock powders mixed with AC as an alternative low-cost CDI electrode material to high-cost antibacterial agents in microbes and salt removal from water.

## 2.7 Current Applications of CDI

Capacitive deionization is increasingly being employed as a rival to current desalination technologies such as reverse osmosis (RO), thermal distillation (TD), electrodialysis (ED), and ion exchange (IE) (Cai *et al.*, 2014). The CDI is now widely acknowledged as a cost-effective and efficient method for desalinating brackish water (up to 10g/L NaCl) (Abdallah *et al.*, 2019). When compared to current desalination technologies such as reverse osmosis (RO), which uses high pressure to force only permeable water through the membrane, RO is a pressure-driven membrane separation technique. The CDI is also regarded as a low-energy, cost-effective, no-secondary-waste-generation, and ecologically acceptable approach for the desalination of salt water (Chen *et al.*, 2020), and also having the electrode which can be regenerated which lowers the energy costs (Liu *et al.*, 2013). Additionally, RO and ED have concerns with membrane fouling (biofouling), scaling (salt precipitation), and maintenance, which reduces the electrode's regenerative ability

(Ahualli *et al.*, 2018). The energy accumulated during the adsorption process can also be recovered through electrode regeneration, although the efficiency of recovery is varied and requires further adjustment (Khan *et al.*, 2018). Anderson *et al.* (2010) suggests that capacitive deionization is more energy efficient than electrodialysis (ED) for brackish water desalination below 500 mg/L of salt.

## 2.8 Contaminants Removed using CDI Process

To present, most CDI study has concentrated on removing ions from various solutions. the removal of simple ions from a variety of solutions. Sun *et al.* (2021), used the kelp hierarchal porous carbon (KHPC) for the simultaneous removal of tetracycline (TC) and water hardness ions ($Ca^{2+}$ and $Mg^{2+}$) in natural water using capacitive deionization technique (Sun *et al.*, 2021). Kim *et al.* (2010), examined the effect of octanol on the removal of salt from brackish water. They observed that the compound partly adsorbed and desorbed to the ion-exchange membrane overlying the electrode (Kim *et al.*, 2010).

The CDI has mostly been used to remove tiny charged chemicals from various types of water. It has not been thoroughly evaluated for biological contamination elimination. Negative charges are imposed on microorganisms such as bacteria and viruses by nucleic acid and proteins located on the cell membrane in water with a neutral pH (Abdallah *et al.*, 2019). The ability of positively porous carbon electrode to remove bacteria such as *E. coli* from the liquid suspension have been recognized for many years (Feng *et al.*, 2018). Some of the early tests using graphite mesh removed 85-95% of bacteria, depending on the strain of *E. coli* used (Golub *et al.*, 1987). Some researchers revealed that *E.coli* could be successfully desorbed from the electrode by flushing during the CDI process (Chen *et al.*, 2020). This feature is particularly valuable for applying a CDI system used to remove salts and microorganisms from surface water.

# CHAPTER THREE

# MATERIALS AND METHODS

## 3.1 Materials and Reagents

The rock samples were collected from Singida region in Iramba district in a village called Ibaga which is 50 Km from Iramba town. The natural water was collected from Nduruma stream located near the Nelson Mandela African institution of Science and Technology (NM-AIST). The commercial AC was purchased from Finar Co. Ltd. Other materials used were beaker, test tubes, petri dishes, falcon tubes, aluminium foil, filter papers, filter funnel, magnetic stirrer hot plate, stirer bar, droppers, Erlenmeyer flask, and oven. Sodium chloride (NaCl) purchased from Loba Chemie pvt. Ltd, polytetrafluoroethylene (PTFE), Carbon black (CB), 100% Ethanol purchased from Chem-lab, NV Belgium, Hi Chrome *E. coli* agar purchased from Hi-media Co. Ltd, deionized water produced at NM-AIST, cellulose nitrate filter paper with pore size of 0.45 μm, and Bismuth Sulfite agar (BSA) purchased from Sartorius Stedim Biotech GmbH. All reagents were of analytical grade and used without any modification.

## 3.2 Characterization of Rock Samples and Synthesis of Electrodes

### 3.2.1 Characterization of Rock Samples

The elements and MOs present in the rock materials were characterized by X-Ray Florescence (XRF) (EZ5001XSV) and the crystallinity, structure and crystal size of the rock materials were determined by X-Ray Diffraction (XRD) using a Rigaku (Tokyo, Japan) Miniflex X-ray diffractometer with Cu-$K_\alpha$ radiation source ($\lambda$ = 0.15406 nm) at 50 kV and 30 mA, and reflection geometry at 2$\theta$ values range from 5 to 90 degree. The diffraction peaks were assigned through the comparison with the Joint Committee on Powder Diffraction Standards (JCPDS) powder diffraction files. The crystallite average size of the rock material was calculated by using Scherrer Equation (1).

$$D = \frac{K\lambda}{\beta Cos\theta} \quad (1)$$

Whereby, D is the average crystallite size in nm, K is known as Scherrer's constant, which is 0.94 for spherical crystal, $\lambda$ is the wavelength, $\beta$ is the full width at half maximum (FWHM) of high intensity diffraction peak in radians and $\theta$ is the angle of diffraction in degrees.

### 3.2.2 Synthesis of AC/MO Electrodes

The rock samples were washed with deionized water several times to remove some impurities and oven dried at 60$^{o}$C for 1h. Then the rock samples were grinded into powder form followed by a sieve of 180 μm and a sieve of 90 μm for removing large particles. The fine powder obtained was used for synthesizing the CDI electrodes for microbes and salt removal from water, in which the rock powder mixed with AC mechanically, together with CB, and PTFE in the ratio of 3:5:1:1 respectively were mixed in a beaker of 100 mL with ethanol and then stirred for 60 minutes using a magnetic stirrer at a temperature of 80$^{o}$C until all ethanol evaporated and then the dough slurry obtained. Then the obtained slurry (dough like paste) was pressed using a presser machine to a specified thickness of 1 mm, then cut into 4 x 4 $cm^2$ and oven dried at 60$^{o}$C overnight to remove the remaining organic solvent (Fig. 3). After drying, the real weight of the electrode was measured.

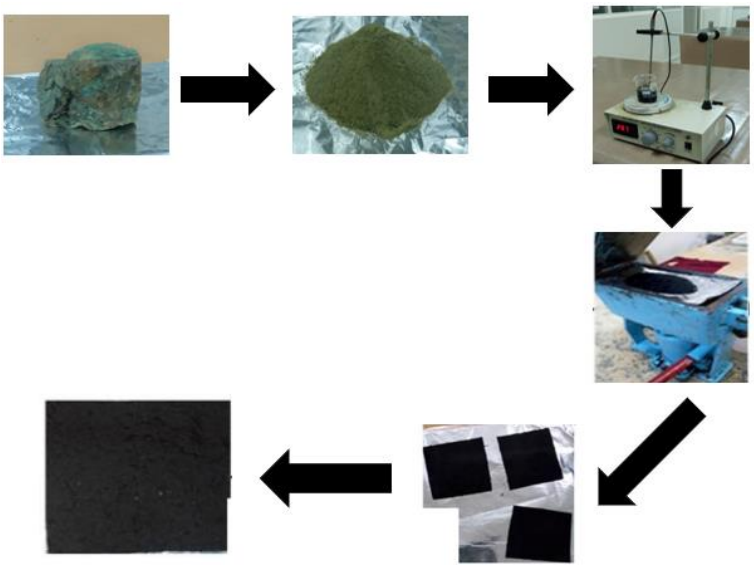

**Figure 3: Summary of the procedures for the synthesis of the electrodes (AC/MO)**

## 3.3 Characterization of AC and AC/MO Electrode materials

The surface morphology of AC, MO and AC/MO electrode was examined using the Scanning Electron Microscope (SEM) coupled with the Energy Dispersive X-Ray (EDX). The specific surface area of the AC powder was measured based on $N_2$ adsorption isotherms using BET surface area analyzer. The pore size distribution was obtained by using the Barrett-Joyner-Halenda (BJH) method. The functional groups of AC and AC/MO were investigated using Fourier-Transform-Infrared spectroscopy (FTIR) using Tensor 27 spectrometer fitted with high through-put screening device (HTS-XT). The test was conducted in absorbance mode in spectral range of 4000 –500 $cm^{-1}$.

### 3.4 Desalination and Disinfection of Water with CDI using the Developed Electrodes

The desalination and disinfection CDI experiments of AC, MO and AC/MO electrodes were evaluated by batch mode experiment as shown in Fig. 4. The CDI cell comprises of two electrodes placed parallel to each other and connected with the IVIUM STAT (Vertex. 1A. EIS 1A/10V/1MHZ EIS, Ivium Technologies, the Netherlands) together with the peristaltic pump. Then 30 mL of field bio-contaminated water collected from Nduruma stream with an initial conductivity of 405.6 µS/cm pumped between the two electrodes at a flow rate of 5 mL/min for 4 h at a potential difference of 1.2V to the cell.

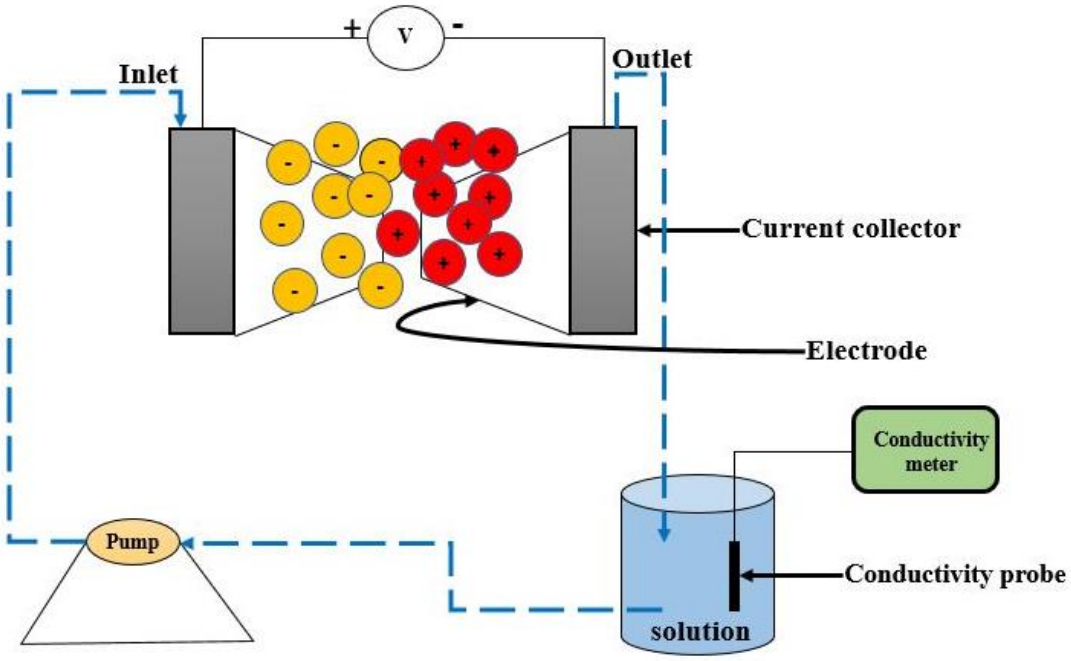


**Figure 4: Schematic diagram of the CDI experiment setup**

The conductivity of the effluent was recorded after every 10 minutes. The concentration of salts present in water sample was obtained, and the selected ionic concentration present in the water were measured before and after experiments. Flame photometer (FP6440) was used to measure concentrations of cations ($Na^+$, $K^+$, $Ca^{2+}$, and $Mg^{2+}$) and the titration method was used to measure the concentration of anions ($PO_4^{3-}$, $NO_3^-$, and $Cl^-$). The removal efficiency (η) in %, salt adsorption capacity (SAC) in mg/g, and salt adsorption rate (SAR) in mg/g $min^{-1}$ were calculated using the Equation 2, 3 and 4 respectively (Chen *et al.*, 2020).

$$\eta = \left(\frac{C_i - C_f}{C_i}\right) x\ 100 \qquad (2)$$

Where:

$C_i$ = Initial concentration (at inlet) in mg/L and

$C_f$ = Final concentration (at outlet) in mg/L.

$$SAC = \left(\frac{C_i - C_f}{m}\right) x\, V \quad (3)$$

Where: $C_i$ and $C_f$ = the initial and final concentrations in mg/L, respectively.

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

m = mass of the active components in the working electrodes in gram (g).

$$SAR = \left(\frac{SAC}{t_{ch}}\right) \quad (4)$$

Where: $t_{ch}$ = charging time in minutes.

Membrane filtration method (MF) was used for microbes culturing, in which the 30 mL of field bio-contaminated water was filtered using the membrane filter (cellulose nitrate filter paper with pore diameter of 0.45 µm) before and after treatment and then the filter placed onto the surface of Hi chrome *E. coli* agar plates for enumeration of gram-negative bacteria *Escherichia coli*, then another 30 mL of bio-contaminated water was filtered using the membrane filter and the filter placed onto the surface of bismuth sulfite agar plates (BSA) for enumeration gram-positive bacteria *Salmonella Aureus.* The plates (Hi chrome *E.coli* agar plates and Bismuth sulfite agar plates) were incubated at 37$^{o}$C for 24 h (Fig. 5). The colonies formed were counted using digital colon counter and the percentage removal was detemined using the Equation 5:

$$Bacterial\ removal = \left(\frac{A - B}{A}\right) x\ 100 \quad (5)$$

Where: A = Number of microbial viable cells before treatment

B = Number of microbial viable cells after treament

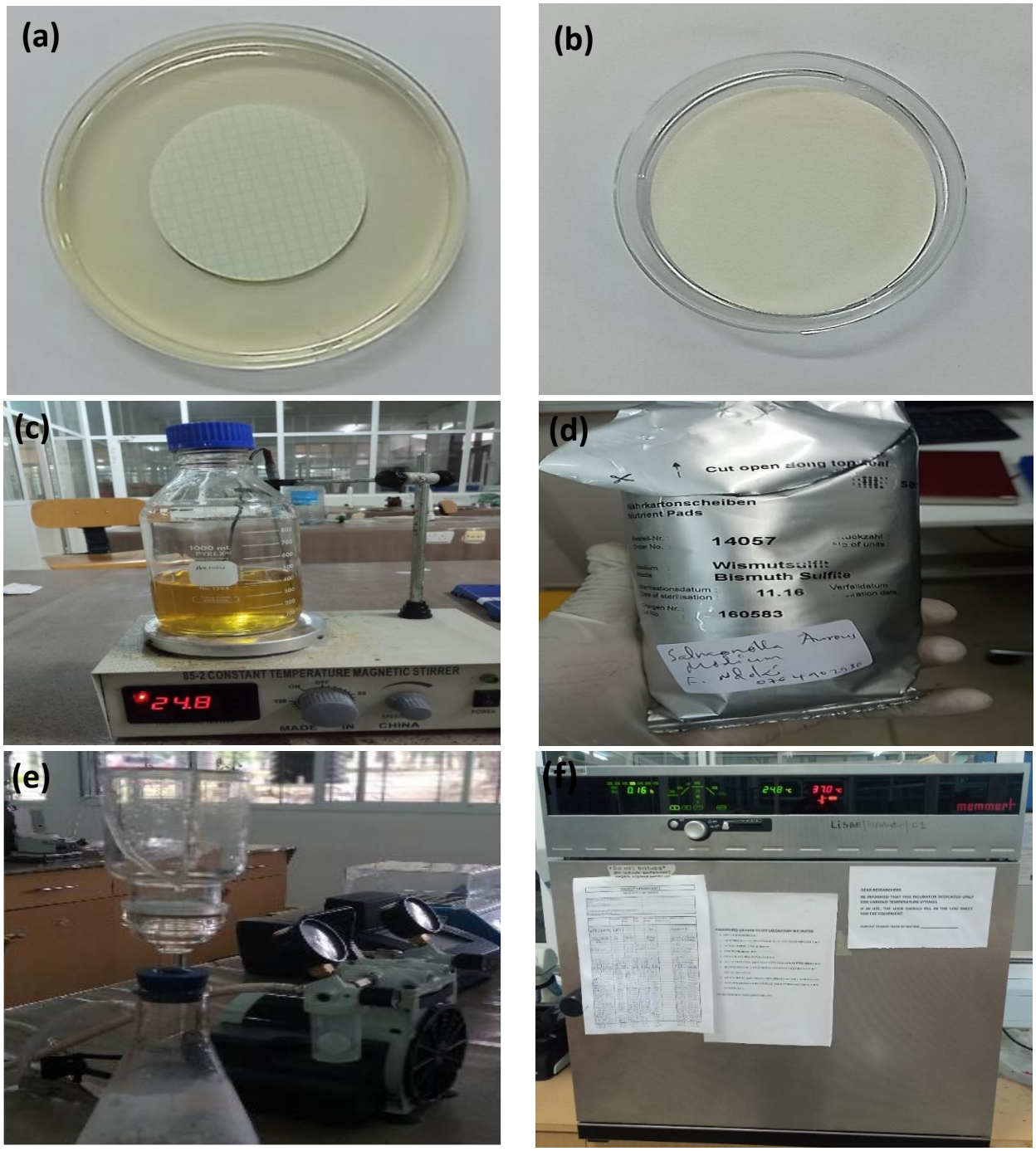


**Figure 5:** **(a) Hi chrome *E. coli* agar plates (b) Bismuth sulfite agar plates (c) Hi chrome agar media (d) Bismuth sulfite agar media (e) Membrane filtration technique (f) Incubator**

# CHAPTER FOUR

# RESULTS AND DISCUSSION

## 4.1 Introduction

This chapter presents and discusses the characterization of the prepared electrode materials, desalination, and disinfection performance of water during the CDI experiments. The chapter presents the removal efficiency of different selected ions (cations and anions) and the removal efficiency of bacteria (*Escherichia coli* and *Salmonella aureus*). The prepared AC, rock powders and AC/MO electrodes were tested in the CDI cell unit to evaluate the salt and bacterial removal efficiency, electrosorption capacity and adsorption rates.

## 4.2 Characterization of Electrode Materials

### 4.2.1 XRF and XRD Analysis

The X-Ray Fluorescence (XRF-EZ5001XSV) instrument with uniquant software was used to analyze MO present in the rock samples. The XRF results show that the rock samples containing higher concentration of silicon dioxide ($SiO_2$) with a mass composition of 53.25% compared to other metal oxides identified, as shown in Table 1.

**Table 2: X-Ray Fluorescence analysis results of rock samples containing MO with their mass composition (%)**

| Metal oxides (MO) | Mass composition (%) |
|---|---|
| $SiO_2$ | 53.25 |
| $Al_2O_3$ | 15.45 |
| CuO | 10.45 |
| $Fe_2O_3$ | 9.36 |
| MgO | 4.90 |
| $Na_2O$ | 1.98 |
| CaO | 0.73 |
| $TiO_2$ | 0.55 |
| $K_2O$ | 0.47 |
| ZnO | 0.19 |
| $P_2O_5$ | 0.12 |
| MnO | 0.006 |

The rock samples' crystallinity analysis was investigated by using X-Ray Diffraction (XRD). The XRD pattern of the rock materials is shown in Fig. 6. The diffraction peaks at $2\theta = 21.34°$, 25.57°, 26.59°, 35.45°, 37.90°, 40.02°, 42.76°, 50.78°, 55.45°, 61.38°, 67.38°, 75.63°, 80.42°, and 82.74° are assigned to (223), (110), (101), (002), (240), (200), (220), (211), (103), (215), (222), (202),

(104), and (244) crystallographic planes (*hkl*) of $K_2O$, $Al_2O_3$, $SiO_2$, CuO, $Fe_2O_3$, MgO, $Na_2O$, MnO, CaO, $TiO_2$, ZnO, and $P_2O_5$ which are matched with the JCPDS card number 75-0576. The average crystallite size of the rock materials was calculated using the Scherrer equation (Equation 1) and found to be 30.43 nm. The average crystallite size depicts that the rock powders are nano-size which enhances the high surface area of the MO contained in the rock materials against the bacterial activities for both gram positive (*E. coli*) and gram negative (*S. aureus*).

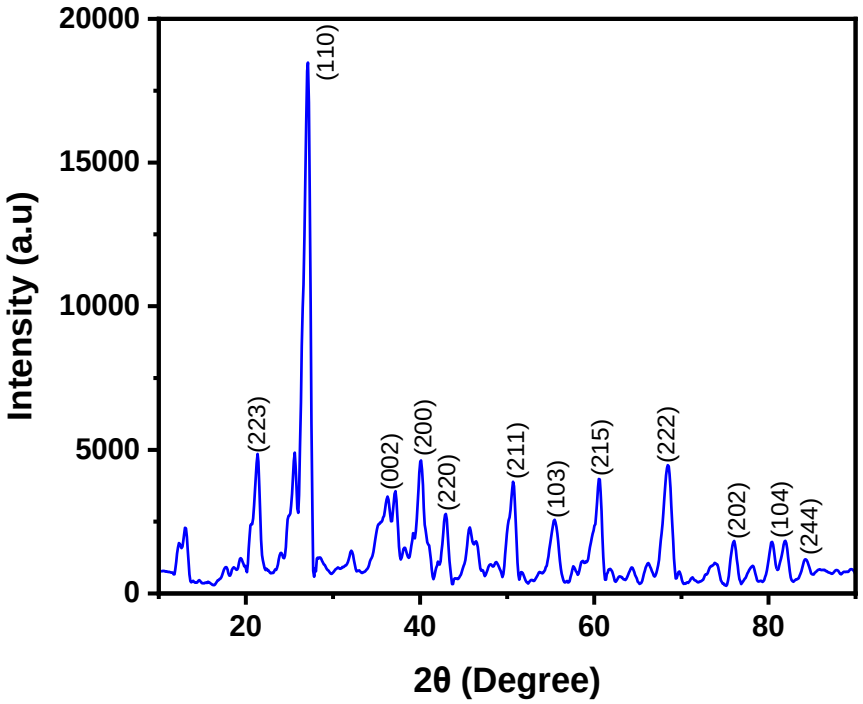


**Figure 6: XRD spectra of rock samples (MO)**

### 4.2.2 BET Analysis

The BET surface area of the AC and AC/MO was 1287 and 1037 $m^2/g$ respectively, with a pore volume of 0.65 and 0.45 $cm^3/g$ as presented in Table 2. The pore diameter varied from 2.5 to 3.0 nm. According to International Union of Pure and Applied Chemistry (IUPAC), classification of the pore size can be divided into three categories: macropores, mesopores, and micropores. Macropores are pores with a diameter greater than 50 nm, mesopores are pores with diameter range between 2 and 50 nm, and the micropores are pores with a diameter less than 2 nm (Zdravkov *et al.,* 2007). The results in Fig. 7 (a) and (c) demonstrates that AC and AC/MO composed of mesopores exhibiting type IV isotherms. Figure 7 (b) and (d) shows the pores size distribution of AC and AC/MO calculated by using the BJH method. The graph shows that many pores were distributed between 2 and 18 nm which agrees well with the mesopores region. Thus, the presence of mesopores leads to a highly active surface area available for ions adsorption (García-Quismondo *et al.,* 2013; Huang *et al.,* 2014).

Pore structure and size are significant factors in electrosorption because they affect ion transport and the formation of an electric double layer (EDL). On one hand, smaller pores produce a greater

surface area because of the surface area to volume ratio. On the other hand, when the pore size begins to approach the size of ion diameters in solution, the electric double layer can overlap, hence reduce the electrosorption efficiency (Porada *et al.*, 2013). 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.*, 2015). Some theoretical and experimental studies show that the correlation between micropores and electrosorption is greater than that of mesopores (Porada *et al.*, 2012). Also, it is observed that the presence of PTFE binder and rock particles containing MO in AC tends to reduce the BET surface area and pore volume significantly. This is because the PTFE binder provides the internal resistance which blocks some pores of electrodes (Chang *et al.*, 2012), as a result, decreasing capacitance due to the decrease of surface wettability (Anderson *et al.*, 2010). Also, loading the rock particles containing MO into AC surface might slightly affect the electrosorption performance of AC/MO electrodes.

Table 3: BET surface area, pore volume, pore size and diameter of the materials.

| **Sample ID** | **BET surface area ($m^2/g$)** | **Pore volume ($cm^3/g$)** | **Pore diameter (nm)** |
|---|---|---|---|
| Commercial AC | 1300 | 0.78 | 3.00 |
| AC/PTFE | 1287 | 0.65 | 2.85 |
| AC/MO/PTFE | 1037 | 0.45 | 3.57 |

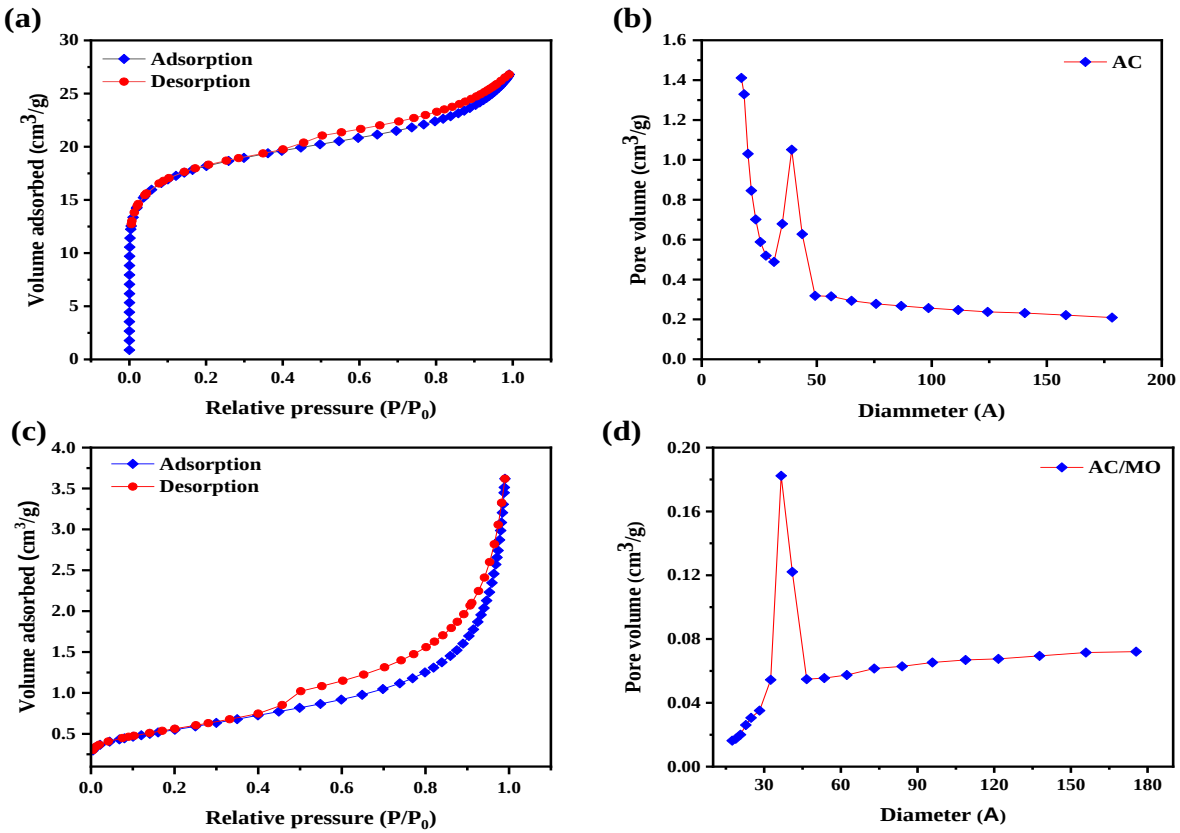


**Figure 7:** **(a, c) Nitrogen adsorption-desorption of AC and AC/MO electrode materials (b, d) Pore size distribution calculated from $N_2$ adsorption-desorption isotherms using BJH method for electrode materials**

### 4.2.3 SEM-EDX Analysis

The surface morphology of AC and AC/MO was characterized by the SEM. The resulting images demonstrated that rock and AC electrode have rough like surfaces as depicted in Fig. 8 (a). These observations suggest that the AC electrode is capable of effectively adsorbing ionic impurities during the deionization process (Tay *et al.,* 2009). The SEM image presented in Fig. 8 (b) illustrates that the surface of the fabricated AC/MO electrode exhibits a mesh-like structure composed of hollow tubes. This observation implies the presence of the rock particles containing MO on the surface of the AC electrode, which was further confirmed by the EDX analysis. This might suggest the presence of metal oxides from the rock powders. The particle size and morphology of the synthesized AC/MO electrode and the rock powder containing MO were analyzed using TEM, as presented in Fig. 8 (c) and (d). The resulting TEM micrographs demonstrates that the AC/MO electrode is composed of spherical rock particles with average particle size ranging from 20 to 35 nm (Figure 17 in Appendix 1), which is consistent with an average particle size estimated using Scherrer equation based on the XRD pattern. The spherical shape of the rock particles containing MO contributes to their increased reactivity, owing to their high surface area-to-volume ratio and high-atom-density surfaces, resulting in heightened antimicrobial activity of AC/MO (Guzman *et al.,* 2012). Moreover, the positive surface charge of MO from rock particles facilitates their binding to the negatively charged surface of the bacteria, potentially enhancing the bactericidal effects of AC/MO electrode (Seil *et al.,* 2012). As reported by Dizaj *et al*. (2014) the shape of the metal oxides nanoparticles (MO-NPs) plays a significant role in their antimicrobial properties as it promotes greater contact with bacterial cells. Hence, the nano size of the rock particles containing MO were found to exhibit detectable antibacterial activity during the CDI process.

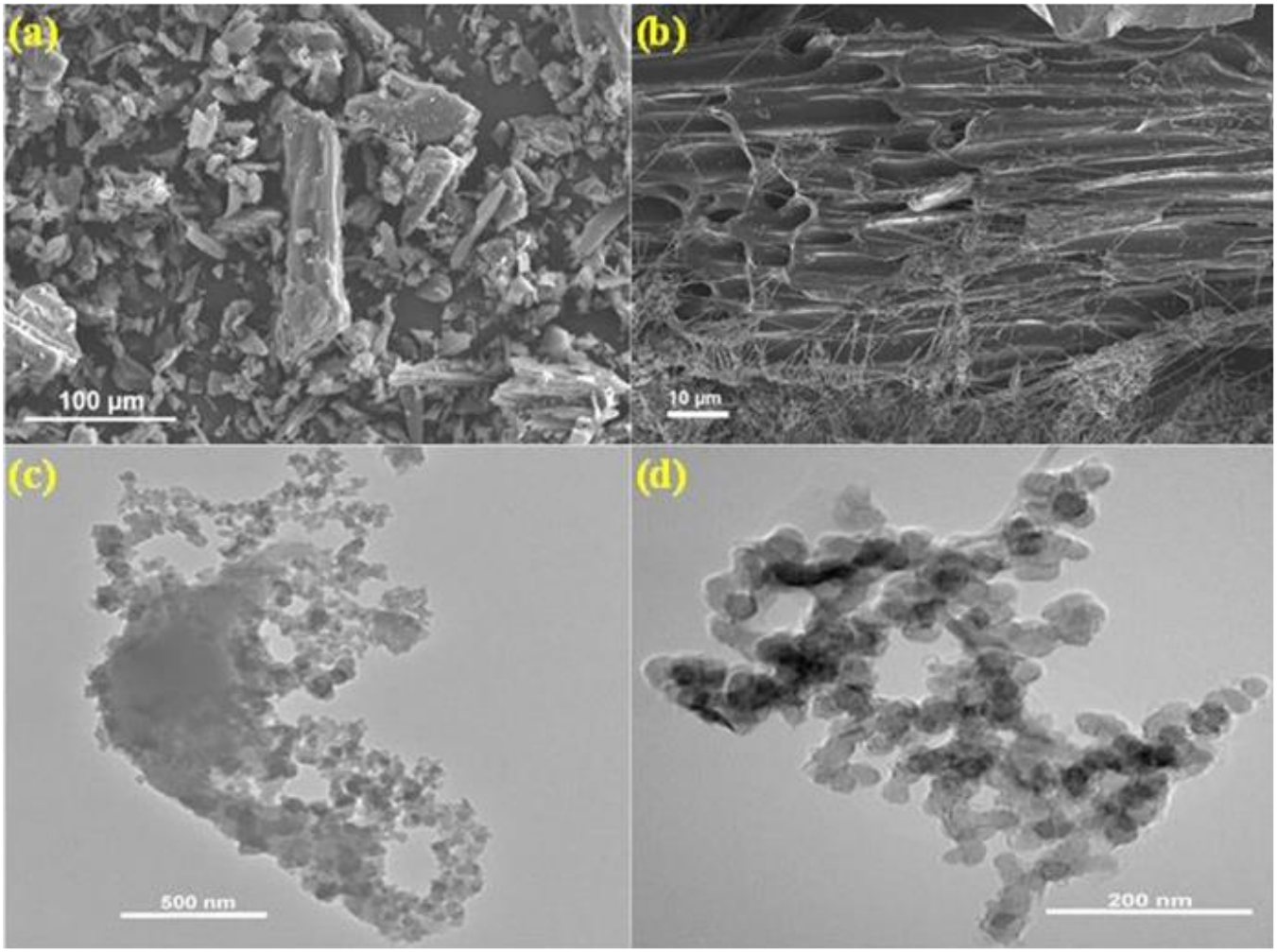


**Figure 8: (a) SEM of AC (b) SEM of composite AC/MO electrode (c) TEM of AC/MO electrode and (d) TEM of rock powder containing MO**

The elemental composition of AC/MO electrode material was confirmed by the EDX analysis (Figure 18in Appendix 2) which shows the presence of silicon (43.97%), Magnesium (0.66%), Aluminum (2.76%), Sulphur (0.09%), iron (2.04%), nickel (0.27%), copper (1.52%), zinc (0.25%), and oxygen (47.8%). Additionally, the EDX analysis results of AC depict that Oxygen (O), Silicon (Si), Sulphur (S), Nickel (Ni), Aluminum (Al), Chlorine (Cl), and Calcium (Ca) existed in the AC alongside with Carbon (C) which indicating the presence of impurities within the AC powder (Table 7 in Appendix 3).

### 4.2.4 FTIR Analysis of AC and AC/MO Electrodes

The FTIR analysis was conducted to characterize the functional group present on AC and AC/MO electrode materials and results were presented in Fig. 9. It was observed that AC revealed the strong characteristic wide peak at 3285 $cm^{-1}$ which is attributed to the stretching vibration of O-H bond, peak at 2889 $cm^{-1}$ which is attributed to C-H bond, peaks at 2358 $cm^{-1}$ which is attributed to stretching and vibration of C-OH bond in carboxyl group (COOH) and peak at 1206 $cm^{-1}$ and 1790 $cm^{-1}$ which is attributed to C-O and C=O bond. On the other hand, AC/MO reveal the strong

characteristic wide peak at 3684 $cm^{-1}$ which is attributed to stretching and bending vibration of O-H bond, peak at 2093 $cm^{-1}$ attributed to stretching and vibration of C-H bond, peaks at 1000 $cm^{-1}$ and 1407 $cm^{-1}$ which is attributed to stretching and vibration of C-O and C=O bond. These results shows that the presence of hydrophilic groups such as carboxyl and hydroxyl on the surface of electrodes enhance the wettability and electrosorption capacity of carbon materials (Chang *et al.*, 2012). Mohammed *et al.* (2019), reported that the presence of the phenolic and carboxyl functional group have significant effect against the bacterial activities when interacting with the cell membrane of bacteria (Mohammed *et al.*, 2019). Furthermore, the FTIR analysis was systematically undertaken to facilitate a comparative analysis between AC and AC/MO electrodes. This analysis serves the crucial purpose for elucidating the impact of MO impregnation on the chemical structure of the electrodes in the context of their functional performance, with a particular focus on their efficacy against bacterial activities as well as ionic adsorption during the CDI process.

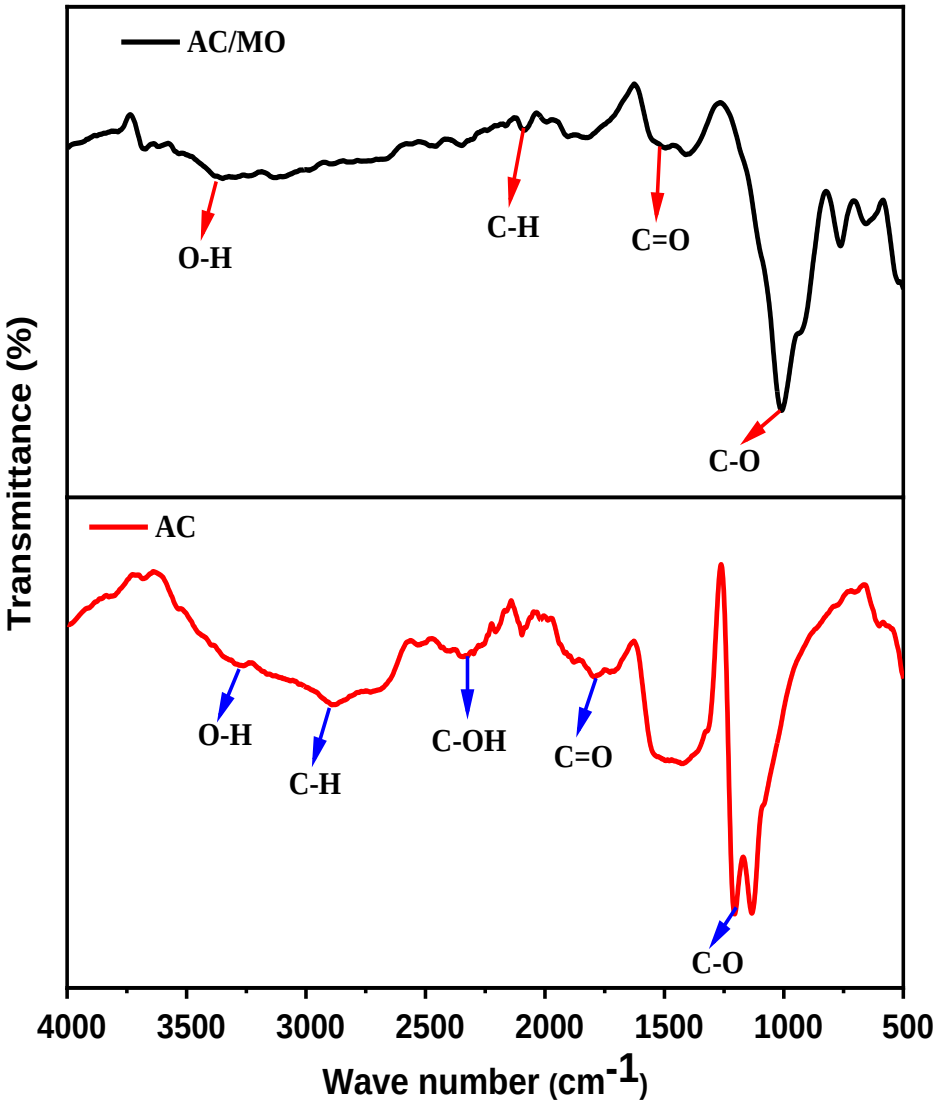


**Figure 9: FTIR spectra of pristine AC and AC/MO electrodes**

### 4.3 Salt Removal from Water using CDI with AC and AC/MO Electrodes

The water employed in this study was characterized before conducting the salt removal performance with CDI. Table 8, located in the Appendix, provides a comprehensive summary of the water quality used in this study. The desalination efficiency of pristine AC and AC/MO electrodes were performed in batch mode experiment during the CDI process. Figure 10 (a) and (b) shows the conductivity change of water when pristine AC and AC/MO were used at 1.2V. Initially, the conductivity decreased rapidly, indicating that the ions were adsorbed more onto the opposite charged electrodes under the applied potential difference, then after 120 minutes the conductivity tends to remain constant, indicating that the electrode is already saturated with the adsorbed ions. The pristine AC electrode shows higher adsorption capacity compared to AC/MO electrode due to the presence of rocks particles which are in large size leading to the decrease of the pore size and volume of the electrode, hence the electrosorption capacity of AC/MO decreased.

Figure 10 (c) shows that the salt removal efficiency (RE) of the pristine AC electrode was higher reaching 62.40 ± 0.64% compared with the AC/MO which had a desalination efficiency of 46.85 ± 0.49%. The pristine AC electrode has higher salt adsorption capacity (SAC) and salt adsorption rate (SAR) of 6.21 ± 0.17 mg/g and 0.0259 mg/g $min^{-1}$, respectively, in comparison to AC/MO electrode which 3.34 ± 0.13 mg/g and 0.0139 mg/g $min^{-1}$ as calculated from equations (3) and (4) and presented in Figure 10 (d). This is due to the reduced surface area pore volume during the mixing process of the rock powder, activated carbon, carbon black and polytetrafluoroethylene as shown in Table 2. The higher adsorption capacity of the pristine AC electrode indicates that more ions are adsorbed compared to that of AC/MO electrode. The results reveal that (Fig. 10c and 10d) the salt removal efficiency is directly proportional to the electrosorption capacity of the material.

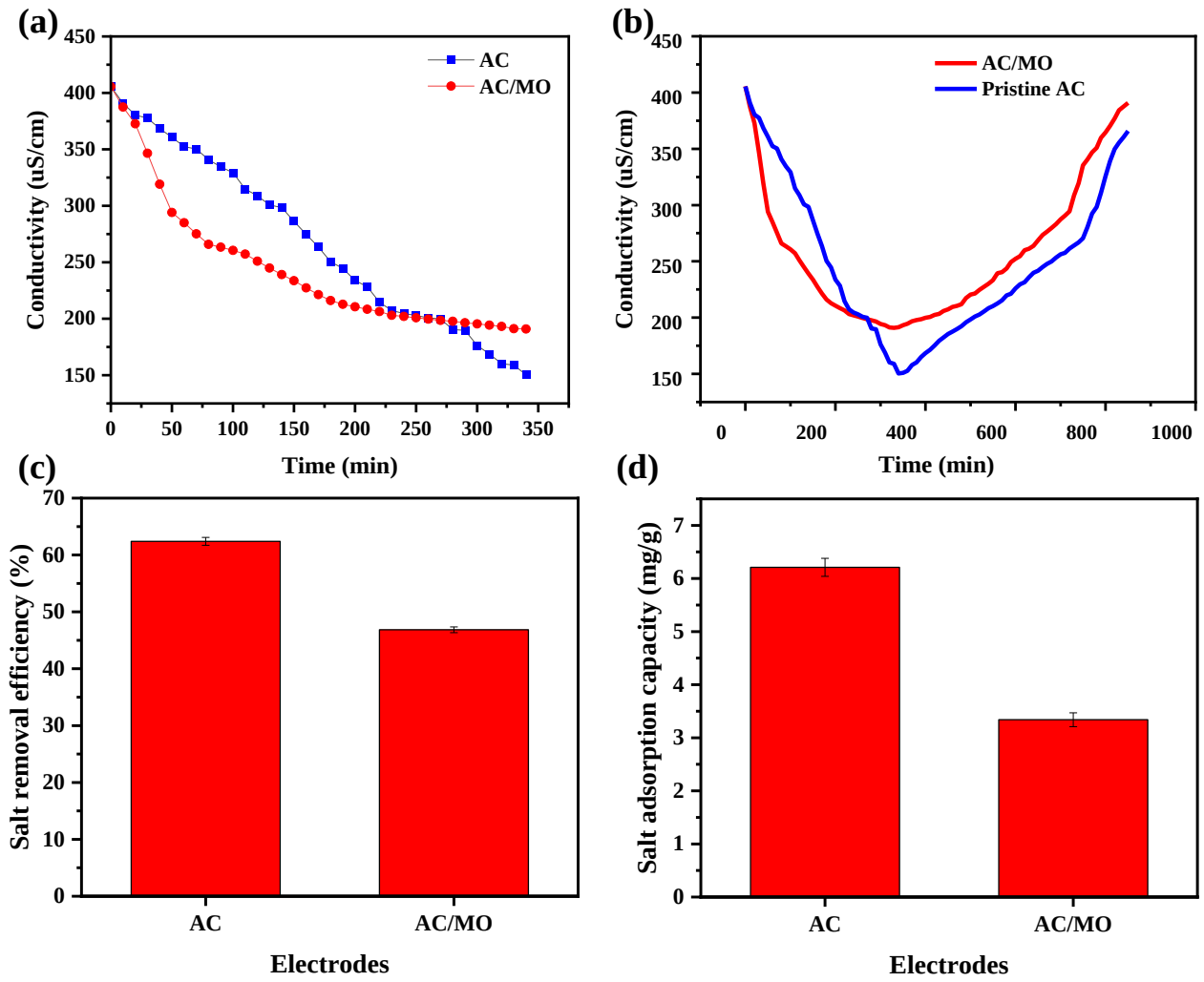


**Figure 10: CDI performance for the fabricated electrode in salt solution, curve (a) and (b) Conductivity change. Histogram (c) Salt removal efficiency and (d) Electrosorption capacity**

The regeneration experiment for both AC and AC/MO electrodes were performed by repeating the charge-discharge experiment for 2 h by applying a constant potential difference of 1.2V during adsorption and 0V during desorption. Figure 11 shows the conductivity and time profile over five charge-discharge cycles. In the first cycle, conductivity dropped to 318 µS/cm for AC and 275 µS/cm for AC/MO and dropped further to 250 µS/cm in the fifth cycle. It was observed that the ions were released rapidly after desorbed but the conductivity of the solution does not reach the initial value. These reveal that upon the removal of the applied potential difference, some of the ions were not released back into the solution, and there was no decrease in desalination performance observed after the first cycle, thus indicating that the AC and AC/MO electrodes can be re-used without compromising its capacity.

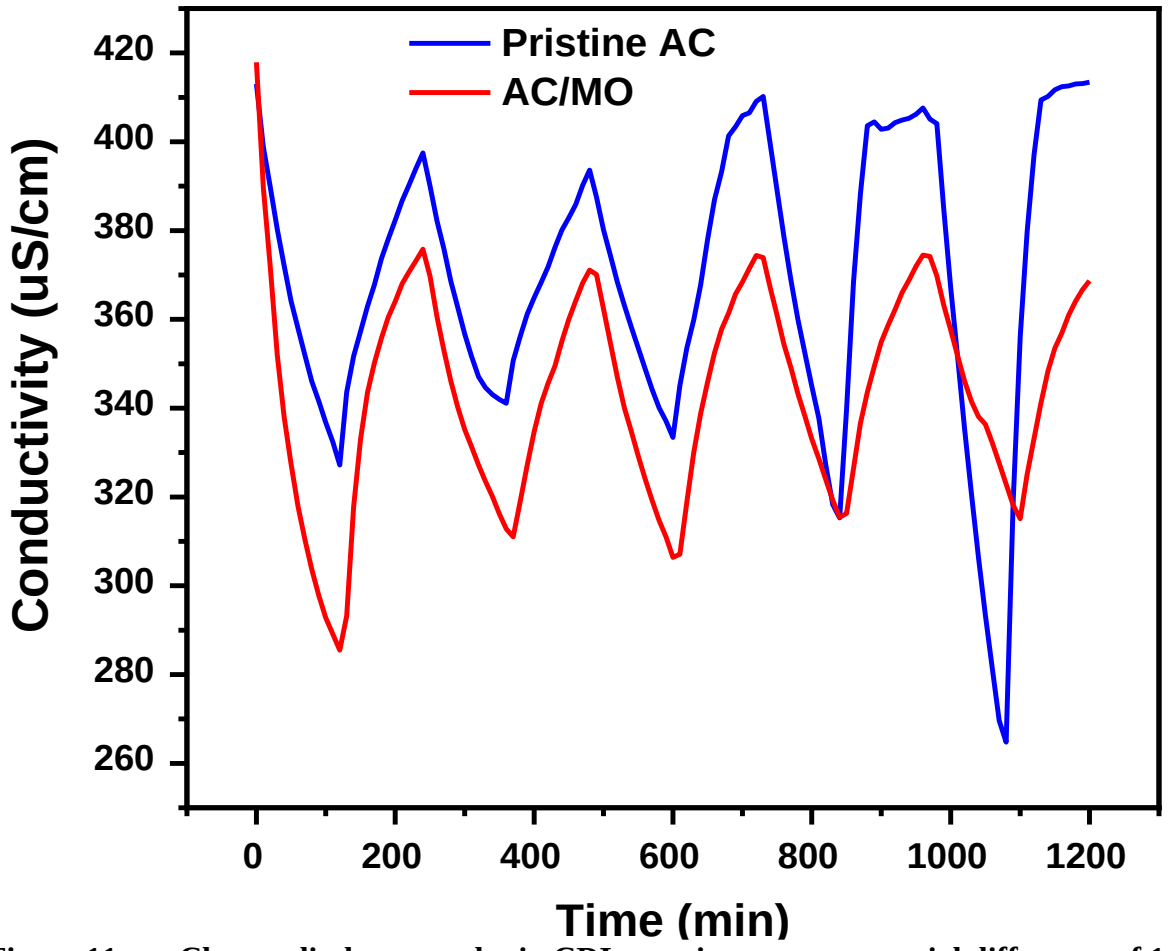


**Figure 11: Charge-discharge cycles in CDI experiment at a potential difference of 1.2V**

The results of ionic composition of bio-contaminated natural water before and after treatment with CDI using AC and AC/MO electrodes are presented in Table 3. Field water comprises of a mixture of selected cations ($Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$) and anions ($PO_4^{3-}$, $NO_3^-$, $Cl^-$) with different concentrations as shown in Table 3 whereby each ion was having the salt adsorption capacity (SAC) that varies depending on the valence of the ionic species.

**Table 4: Ionic concentration of field water ($C_0$), ionic radius (IR), hydration radius (HR), removal efficiency (η) and salt adsorption capacity (SAC)**

| Ion type | $C_0$ (mg/L) | V (Charge) | IR[a, b] (pm) | HR[c] (pm) | η (%) | | SAC (mg/g) | |
|---|---|---|---|---|---|---|---|---|
| | | | | | AC | AC/MO | AC | AC/MO |
| $Na^+$ | 14.54 | +1 | 116 | 358 | 96 | 43 | 0.69 | 0.26 |
| K+ | 41.05 | +1 | 133 | 331 | 82 | 36 | 1.66 | 0.60 |
| $Ca^{2+}$ | 37.97 | +2 | 65 | 428 | 39 | 30 | 0.74 | 0.36 |
| $Mg^{2+}$ | 33.60 | +2 | 86 | 412 | 46 | 27 | 0.78 | 0.37 |
| $PO_4^{3-}$ | 0.34 | -3 | 223 | 339 | 74 | 50 | 0.012 | 0.07 |
| $NO_3^-$ | 19.20 | -1 | 264 | 335 | 81 | 51 | 0.77 | 0.40 |
| $Cl^-$ | 0.25 | -1 | 332 | 332 | 60 | 24 | 0.7 | 0.002 |

[a, b,c :] Reference (Huang *et al.,* 2014; Tansel, 2012; Uwayid *et al.,* 2022)

The results of the ionic composition of the field water after treating with CDI using AC and AC/MO electrodes are presented in Fig. 12. Generally, the ions adsorption rate was higher in AC compared to AC/MO electrode since AC has larger BET surface area and pore volume compared with AC/MO as shown in Table 2. Porada *et al.* (2012), and Nadakatti *et al.* (2011), 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 (Nadakatti *et al.,* 2011; Porada *et al.,* 2012).

Field water comprises of a mixture of selected cations ($Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$) and anions ($PO_4^{3-}$, $NO_3^-$, $Cl^-$) with different concentrations as presented in Table 3 whereby each ion was having the salt adsorption capacity (SAC) that varies depending on the valence of the ionic species. From Table 3 both the porous AC and AC/MO electrodes of the CDI shows the removal of monovalent cations ($Na^+$ and $K^+$) to a larger extent compared to the divalent cations ($Ca^{2+}$ and $Mg^{2+}$) because monovalent cations have large ionic radius which enhance penetration through the pores and attachment on the surface of electrode easily while larger size and small ionic radius of the divalent cations suppress the passage of ions through the electrode deeply (Gao *et al.,* 2009), but both ions are thermodynamically favored for adsorption during the deionization process (Avraham *et al.,* 2008; Tansel, 2012). Figure 12 and Table 3 shows the salt adsorption capacity of various ions and reveals that selectivity of ions depends on the valency, concentration and the size of ions present in water.

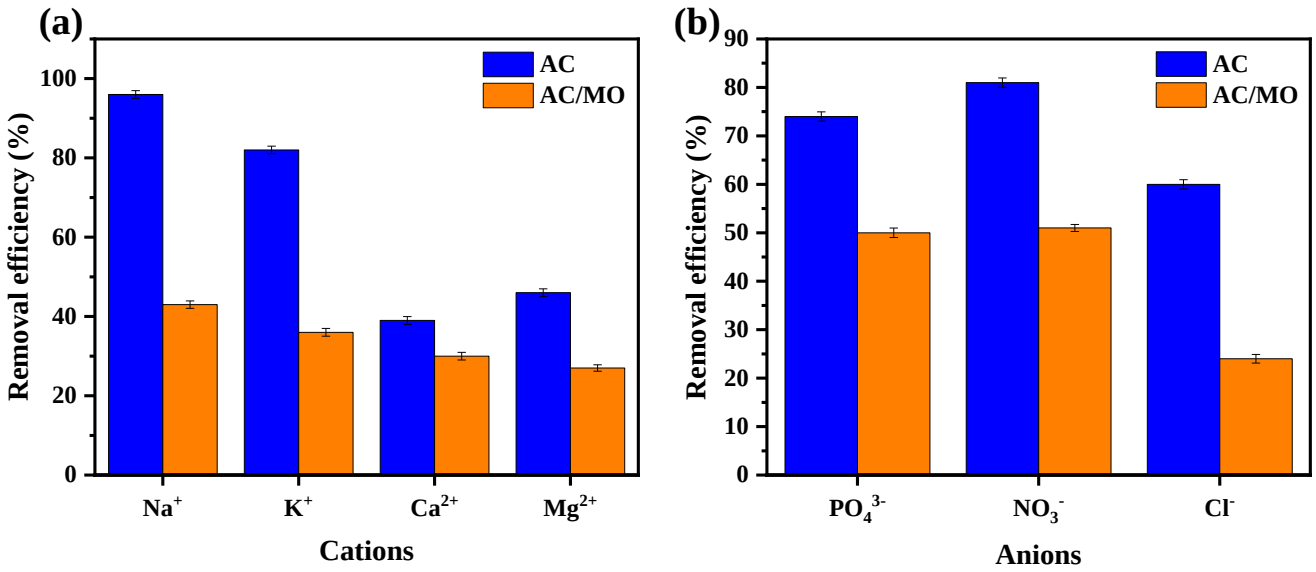


**Figure 12: Removal efficiency of ionic impurities in natural water**

### 4.4 Bacterial Removal with CDI

The field bio-contaminated water was characterized before treatment in CDI testing and was found to have gram-negative (*Escherichia coli*) and gram-positive bacteria (*salmonella aureus*) as indicated in Fig. 13 (a) and (d), which were discovered as the model pathogens in investigating the antibacterial activities. After circulating the water in CDI cell with AC and AC/MO electrodes the results indicate the reduction of both gram-negative (*Escherichia coli*) and gram-positive (*Salmonella aureus*) bacteria (Fig. 13 (b) and (e)).

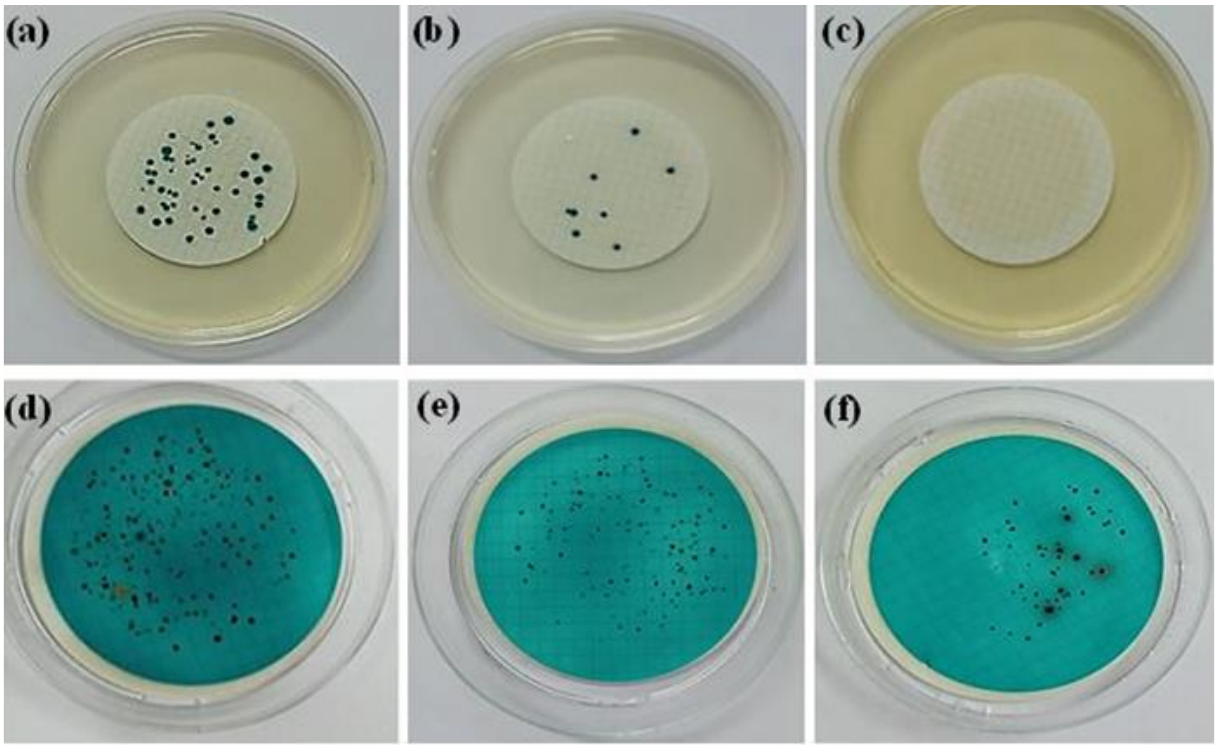


**Figure 13: Plates showing bacteria growth (a) and (d) before treatment, (b) and (e) treated with AC electrode, (c) and (f) treated with AC/MO electrodes (Blue colonies indicates *Escherichia coli* and the black colonies indicates *Salmonella aureus*)**

Figure 13 (c) and (f) shows that, AC/MO electrode have excellent antibacterial effect towards both gram-negative (*Escherichia coli*) and gram-positive (*Salmonella aureus*) bacteria and their removal efficiency is 100 ± 0.42% and 60 ± 0.53% respectively after 4 h of charging without dilution. During the charging process in CDI, the bacteria were electrically attracted towards the positive electrode due to the presence of negative charges attributed by thiol (-SH), amino (-NH) and carboxylic (-COOH) groups of proteins present on their cell wall and then killed by the embedded MO from the rocks by physical contact (Wang *et al.*, 2015). The effectiveness of MO against anti-bacterial activities was due to the release of metal ions and regeneration of reactive oxygen species (ROS) (Fig. 14). The released metal ions interact with membranes proteins which leading to a drastic change in the permeability of the membrane through the degradation of lipopolysaccharide resulting to the intracellular leakage which causing the death of bacterial cell and also the metal ions released interact with nucleic acid which preventing replication of DNA and translation process which leading to the death of bacterial cell (Stanić *et al.*, 2020). The reactive oxygen species (ROS) generated by metal oxides (MO) in aqueous solution including singlet oxygen ($O_2$), hydroxyl radical ($OH^-$) and the superoxide ($O_2^-$) radical interact with the vital cell biomolecules like polyunsaturated fatty acids (PUFA), proteins, nucleic acids and carbohydrate to a lesser extent (Zhang *et al.*, 2013). ROS induces severe oxidative stress and damage to the cell's macromolecules which overall cause lipid peroxidation, alterations of proteins, inhibition of enzymes and RNA/DNA damage (Zhang *et al.*, 2023). This severe oxidative stress also forms holes or pits within the bacterial membrane which alter the intrinsic membrane properties like fluidity and lysis of bacterial cells which leading to death of microbial cell (Dahiya *et al.*, 2021; Zhang *et al.*, 2013).

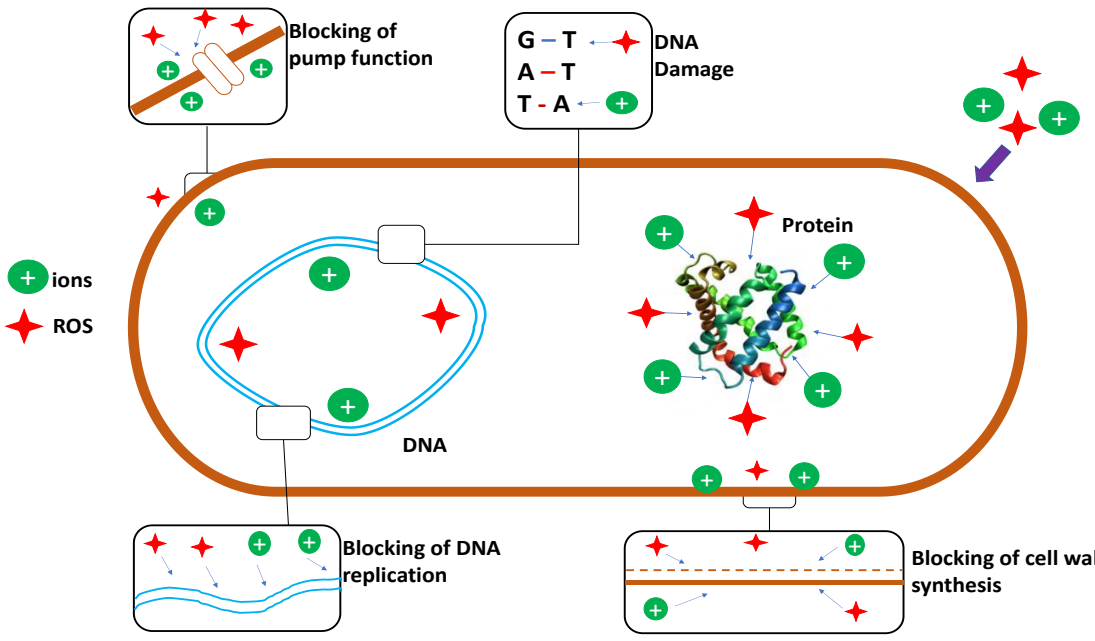


**Figure 14: Effects of metal ions ($M^{n+}$) and reactive oxygen species (ROS) on the bacterial cell**

Furthermore, bacteria cell death could be due to cell wall rupture upon exposure to the high electric field generated between the electrodes during CDI process (Hou *et al.,* 2013). Bacterial cell wall has negative charge due to the presence of phosphates and lipopolysaccharides (Deng *et al.,* 2015) which can be electrosorbed onto the positive electrode (anode) (Oren *et al.,* 1983) along with anions, bringing them into proximity to each other. The high concentration of anions in the vicinity at the electrode surface creates a hypertonic environment which leading to dehydration of bacterial cell and eventually leading to cell death of bacteria (Kristian Stevik *et al.,* 2004). Thus, bacterial removal during the CDI process could be due to electro-adsorption of bacteria cell (temporary reduction) or cell death (permanent reduction). To better understand the mechanism the AC/MO electrode was washed with ultrapure water to facilitates removal of any electro-adsorbed bacteria cell on the electrode surface without application of the potential difference on CDI cell, and the effluent was filtered with cellulose membrane filter paper with pore size of 0.45 µm and cultured for bacterial growth. The results (Fig. 15) showed that the number of bacteria colonies formed was lower than that examined prior to the CDI process, which indicating that some of bacteria cells were just electro-adsorbed onto electrode surface, and some were permanently killed due to high concentrations of anions released from the MO during CDI process.

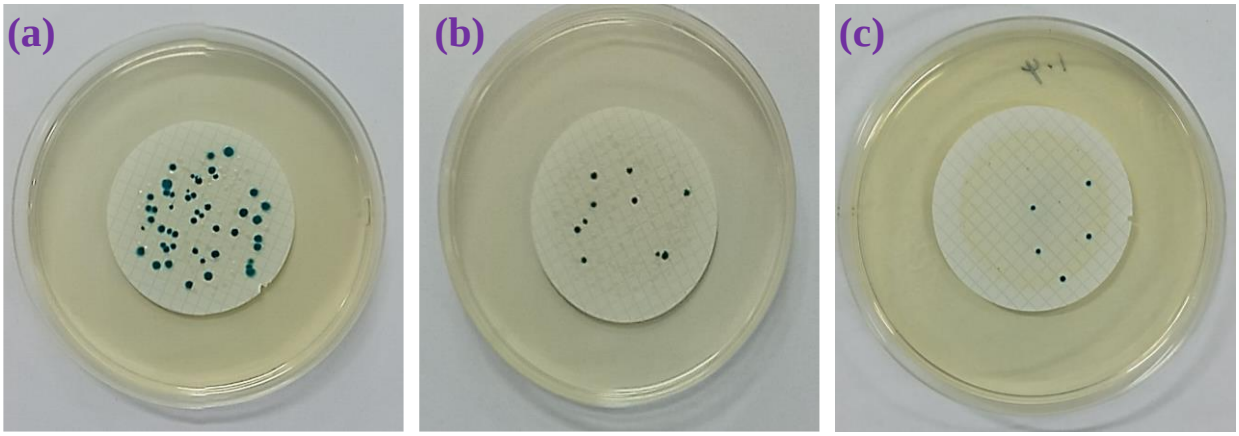


**Figure 14: Plates showing bacteria growth (a) Before CDI (b) and (c) bacteria colonies formed when AC/MO electrode washed with ultrapure water without applying voltage in CDI cell**

The gram-negative bacteria (*Escherichia coli*) having thin cell wall which can be penetrated easily by the ions released by the metal oxides (MO) in physical contact and during the CDI process, hence being killed for 100% (Gold *et al.,* 2018) and on the other hand gram-positive bacteria (*Salmonella aureus*) were not removed all due to the presence of the hard thick peptidoglycan layer which prevent easy penetration of metal oxide ions released from the electrode (AC/MO) (Paul *et al.,* 2020). The AC electrodes only remove bacteria by absorbing 92 ± 0.68% and 30 ± 0.59% for *Escherichia coli* and *Salmonella aureus* respectively.

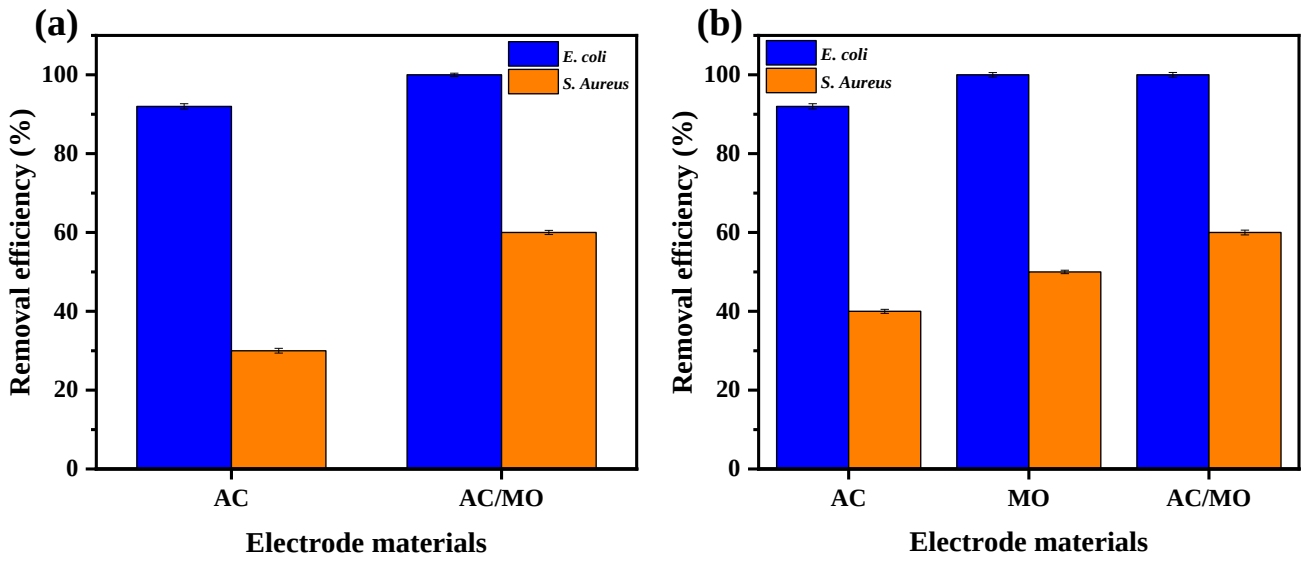


**Figure 15: Bacterial removal efficiency (a) during CDI process (b) by physical contact**

Further we studied if the metal oxides (MO) from rock sample and AC/MO can remove the bacteria by physical contact without undergoing the CDI process (i.e., without applying the potential difference to the CDI cell). The effluent water was taken and filtered using the cellulose nitrate filter paper with the pore diameter of 0.45 µm for microbiological analysis. After the culturing process there were no bacteria which grow in the agar plates which contain effluent from AC/MO materials, but the bacteria tend to grow in the agar plates which contain the effluent water from the AC electrodes with 25 to 87% bacterial removal efficiency as shown in Fig. 16 (b). This reveals that AC electrodes may result in a decrease in the CDI life span as the microorganisms do not die in the cell.

### 4.5 Effect of salt concentration on bacterial removal

The concentrations of salt ions in bio-contaminated water were analyzed prior to the experiment using Flame Photometer (FP 6440) in which 14.54 mg/L for $Na^+$, 41.05 mg/L for $K^+$, 37.97 mg/L for $Ca^{2+}$, and 33.60 mg/L for $Mg^{2+}$ were determined as presented in Table 3. The total concentration of the salt ions in the solution was 246.95 mg/L. However, it was observed that this concentration had no appreciable effects on the death of bacteria during the CDI process. This observation can be attributed to the fact that salinity is one of the factors that facilitate bacteria growth, and the ideal salt concentration for bacteria to survive typically ranges between 200-500 mg/L (Chapman *et al.*, 2009; Lytle, 1999). Therefore, the presence of MO significantly impacts the disinfection of saline water, as it can effectively reduce the number of bacteria present in bio-contaminated water. Recent CDI-AC electrodes material present in literature for water desalination and disinfection are summarized in Table 4.

**Table 5: Salt and bacterial removal efficiency and electrosorption capacity reported in the literature and the findings of this study**

| Electrode material | Volt (V) | Flow rate (mL/min) | Initial concentration (mg/L) | Salt removal efficiency (%) | Electrosorption capacity (mg/g) | Bacterial removal (%) | Reference |
|---|---|---|---|---|---|---|---|
| AC/ZIF-9 | 1.2 | 5 | 584 | 78 | 55.4 | 95 *E. coli* | Cao (2021) |
| AC/GO/G5/Ag | 1.2 | 30 | 500 | 80 | 46.29 | 99.9 *E. coli* | (Janpoora (2021) |
| ACC | 1.6 | 10 | 1000 | 32 | 10.5 | 66 *E. coli* | Laxman *et al.* (2015) |
| 3DAPGr | 1.4 | 20 | 300 | 75 | 18.43 | 98.55 *E. coli* | El-Deen *et al.* (2016) |
| AC-PDA/PHMG | 1.2 | 10 | 250 | 76 | 10 | 99.11 *E. coli*<br>98.67 *P. aeruginosa* | Liu *et al.* (2021) |
| AC | 1.2 | 5 | 246.95 | 62.40 | 6.21 | 92 *E. coli*<br>30 *S. aureus* | This study |
| AC/MO | 1.2 | 5 | 246.95 | 46.85 | 3.43 | 100 *E. coli*<br>60 *S. aureus* | |

From Table 4, it is observed that Cao *et al.* (2021) uses cobalt benzimidazole framework (ZIF-9) derived carbon composite with unique quasi-microcubic as an electrode for desalination and antimicrobial activities using CDI and achieved to kill 95% of *Escherichia coli* after charging for 3 h during the CDI process, Janpoora *et al.* (2021) used graphene oxide dendrimer-silver coated electrode (AC/GO/G5/Ag) for water desalination and disinfection using CDI technology and achieved to kill 99.9% *Escherichia coli* bacteria as well as desalination efficiency of 80%. Laxman *et al.* (2015) also uses activated carbon cloth (ACC) electrode with electrosorption capacity of 10.5 mg/g and achieved to remove salt for 32% as well as killing 66% of *Escherichia coli* during the CDI process. El-Deen *et al.* (2016) using microporous activated 3D graphene electrode (3DAPGr) with electrosorption capacity of 18.43 mg/g water disinfection via CDI and achieved to kill 98.55% of *Escherichia coli*. Also, Liu *et al* (2021) uses polydopamine hexamethylene guanidine co-deposited activated carbon electrode (AC-PDA/PHMG) with electrosorption capacity of 10 mg/g and achieved to remove 99.11% *Escherichia coli* and 98.67% *P. aeruginosa* using CDI. This study used an electrode developed using rock powders containing MO (AC/MO) and achieved to completely kill 100% *Escherichia coli* (gram-negative bacteria) and 60% *Salmonella aureus* (gram-positive bacteria) after 4 h of charging without dilution of the original sample during the CDI process.

### 4.6 The Effect of applied voltage

The effects of different voltages (0.6, 0.8, 1.0 and 1.2V) applied during the CDI process on the bacterial removal (*E. coli* and *S. aureus*) were studied using the AC/MO electrode. The 30 mL of bio-contaminated water was filtered using a cellulose membrane filter paper with pore size of 0.45 µm for enumerating the number of microbes before and after the CDI process for both gram-positive and gram-negative bacteria. Figure 17 shows that effective removal of bacteria was increased as the voltage increased from 0.6 to 1.2V. The *E. coli* bacteria were removed for 40 ± 0.95% at 0.6V and was increased further to 100 ± 0.45% at a potential difference of 1.2V, but *S. aureus* bacteria were removed for 5 ± 0.69% at 0.6V and increased to 60 ± 0.74% at a potential difference of 1.2V. This depicts that *S. aureus* bacteria cannot be effectively removed at lower potential differences during CDI process in comparison to gram-negative bacteria. This is attributed to the presence of thick peptidoglycan layer on cell wall of *S. aureus*, which resist the electrostatic force and limits the penetration of metal ions and reactive oxygen species (ROS) released from AC/MO electrodes during charging process in CDI system (Gil *et al.*, 2019). The *E. coli* bacteria were observed to be completely removed to 100%, which could be attributed to

presence of thin cell wall composed of lipopolysaccharides that impart a strong zeta potential ranging from -23 mV to -50 mV. This significant zeta potential can greatly aid their migration toward the positive electrode surface (Martins, 2013).

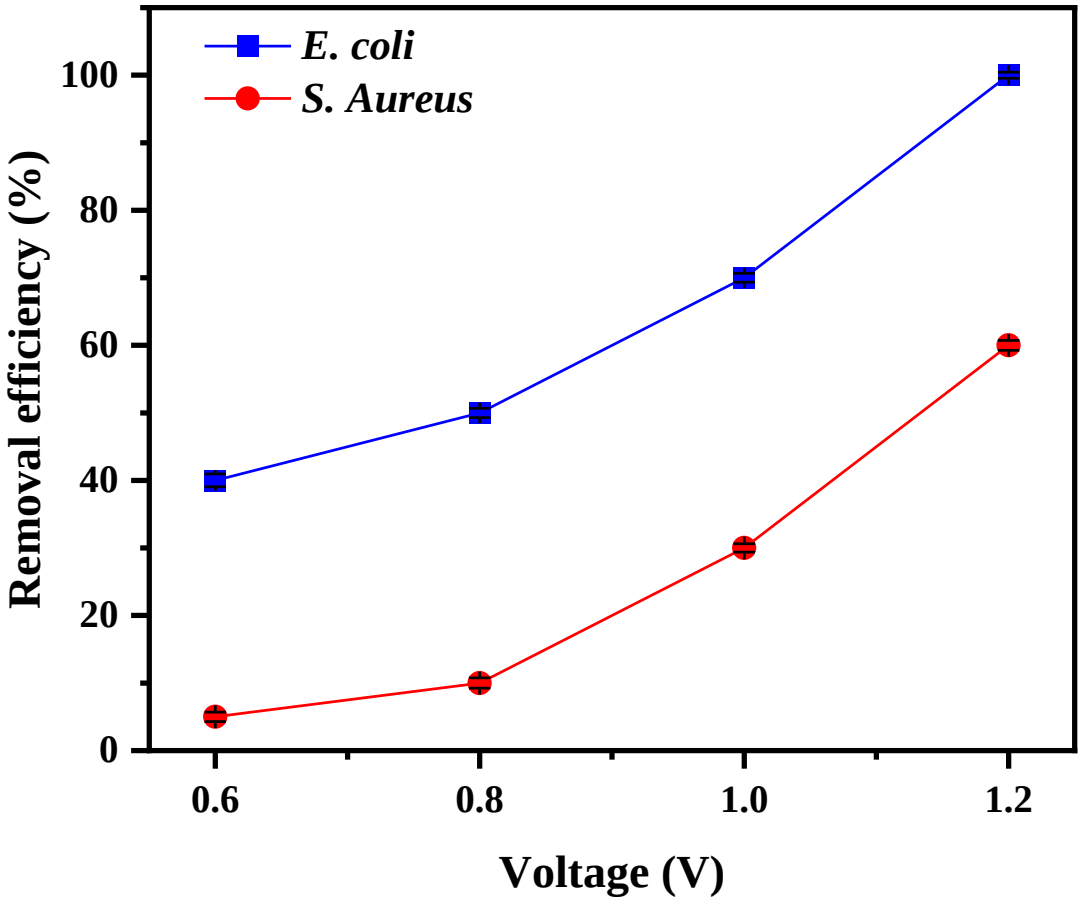


**Figure 16: Effect of applied voltage on bacterial removal during the CDI process**

### 4.7 The Effect of charging time

The impact of varying contact time on the removal of bacteria was studied using bio-contaminated water with a concentration of 246.5 mg/L. The 30 mL of natural water was passed through the CDI cell at a potential difference of 1.2V at different intervals of time ranging from 60 to 240 min. The findings revealed a positive correlation between charging time and bacterial removal, with increasing charging time leading to a higher removal rate. Specifically, the highest removal rate of 80 ± 0.75% for *E. coli* bacteria was attained after a charging time of 3 h during the CDI process, while a removal rate of 30 ± 0.59% was achieved for *S. aureus* bacteria following the same charging time. Upon extending the charging time to 4 h, the bacteria removal rate increased to 100 ± 0.46% for *E. coli* and 60 ± 0.54% for *S. aureus* bacteria. The results presented in Table 5 demonstrate that as the charging time was increased, the rate of bacteria removal increased for

both gram-negative and gram-positive bacteria. Therefore, it can be concluded that the charging time has a significant impact of the CDI system in removal of bacterial contaminants.

**Table 6: Effects of charging time on bacterial removal rate during CDI process at 1.2V**

| Charging time (h) | Bacteria removal rate (%) | |
|---|---|---|
| | ***E. coli*** | ***S. Aureus*** |
| 1 | 30 ± 0.60 | 10 ± 0.47 |
| 2 | 50 ± 0.77 | 20 ± 0.53 |
| 3 | 80 ± 0.75 | 30 ± 0.59 |
| 4 | 100 ± 0.46 | 60 ± 0.54 |

During the CDI process, the positive and negative charges present on the cell wall of gram-positive and gram-negative bacteria mediate their adsorption onto the oppositely charged electrode surface through electrosorption processes. The interactions of temporary reactive oxygen species (ROS) generated from MO increases with an increase in charging time, resulting in oxidative stress on the cell walls, and ultimately leading to cell death (Marugán *et al.*, 2010). Additionally, the electric field generated during the CDI process may also affect the electrosorbed bacterial cells (Del Pozo *et al.*, 2009).

### 4.8 Leaching Experiment

To investigate the optimal leaching of the metal ions from the electrodes into water, 30 mL of ultra-pure water was circulated through the CDI cell containing the electrodes fabricated with the rock powders containing MO exclusively, and that made with the activated carbon (AC/MO) for 4 h of charging without dilution at a potential difference of 1.2V and flow rate of 5 mL/min. The presence of potential metal ions in water from the rock powder electrodes during the CDI process was analyzed using the Atomic Absorption Spectroscopy (AAS). The obtained results, as presented in Table 6, indicated a significant leaching of metal ions in high concentrations for the electrodes made solely with rock powders. Conversely, the leaching concentration of metal ions was significantly reduced for the electrodes composed of AC and rock powder (AC/MO). This observation suggests that the addition of activated carbon to the electrode synthesis process can substantially reduce metal ions leaching in the CDI process. The concentration of leached metal ions from the electrodes was compared against the standard guideline established by WHO. The findings reveal that the concentration of leached metal ions from the electrodes made solely with rock powders (MO) exceeded the recommended limit set by WHO. In contrast, the concentration of leached metal ions from AC/MO electrodes was within the acceptable limits established by WHO. The incorporation of AC and MO during the synthesis of electrodes could help to reduce potential health risks associated with metal ions leaching in water during the CDI process.

**Table 7: Concentration of metals leached in 4 h of charging without discharging at 1.2V**

| Elements | Symbol | Concentration (mg/L) | | WHO standards (mg/L) |
|---|---|---|---|---|
| | | MO | AC/MO | |
| Aluminum | Al | 0.877 | 0.078 | 0.2 |
| Calcium | Ca | 4.00 | 3.60 | * |
| Copper | Cu | 3.44 | 0.29 | 2 |
| Iron | Fe | 1.73 | 0.06 | 0.3 |
| Magnesium | Mg | 3.36 | 0.09 | * |
| Manganese | Mn | 0.92 | 0.01 | 0.1 |
| Nickel | Ni | 2.88 | 0.009 | 0.07 |
| Potassium | K | 82.09 | 16.34 | * |
| Silicon | Si | 9.60 | 1.265 | * |
| Sodium | Na | 2.00 | 0.077 | 20 |
| Titanium | Ti | 8.30 | 0.28 | * |
| Zinc | Zn | 7.20 | 0.03 | 3 |

Reference (WHO, 2021) (* Not found)

# CHAPTER FIVE

# CONCLUSION AND RECOMMENDATIONS

## 5.1 Conclusion

The main objective of this study was achieved as mentioned in chapter 1. This dissertation focused on the performance of AC and AC loaded with naturally occurring MO from rock powders AC/MO as CDI electrode materials for disinfection and desalination.

In this study, the effect of metal oxides (MO) from rock sample loaded on activated carbon (AC) electrodes for desalination and microbial removal from the natural water was successfully using CDI method. The results revealed that the MO from rocks was found to be appreciable disinfectant and significantly can remove both gram-positive (*Salmonella aureus*) and gram-negative (*Escherichia coli*) bacteria during the CDI process as well as by physical contact, but AC alone cannot kill the bacteria by physical adsorption. The salt and bacterial removal efficiency of 46.85 ± 0.49% and 100 ± 0.42% for *E. coli*, and 60 ± 0.53% for *S. aureus* was achieved. The salt adsorption capacity (SAC) for pristine AC was 6.21 ± 0.17 mg/g and that of AC/MO was 3.43 ± 0.13 mg/g when 30 mL of field bio-contaminated water was used. Compared with the pristine AC, the AC/MO electrode depicted the appreciable disinfection performance for both gram-positive (*Salmonella aureus*) and gram-negative (*Escherichia coli*) bacteria. The AC/MO electrode has the potential for disinfection as the bacteria contact-killing process is fast and continuous. Importantly, this anti-microbial capability can be harnessed without the need for intricate or resource-intensive infrastructure. Moreover, the durability and longevity of AC/MO remain substantial as the electrodes have a long operational lifespan and do not require frequent replacements. This inherent longevity not only mitigates the operational cost but also establishes a compelling case for the economic feasibility of the CDI technology. Also, the efficiency of AC/MO electrodes against bacteria activities is essential. The improved performance of AC/MO reduces the need for secondary treatment and ensures a more cost-effective overall water treatment process using CDI technique. Therefore, this study developed a cost-effective AC loaded MO derived from rock powder as a highly favorable CDI material for CDI performance in large-scale industries to effectively eliminate bacteria from real water during the treatment process.

## 5.2 Recommendations

Even though the metal oxides (MO) contained in the rock sample shows appreciable antibacterial activity against both gram-positive (*S. aureus*) and gram-negative (*E. coli*) bacteria during the CDI

process as well as by physical contact, further techniques for extracting the potential selective metal oxides (MO) in nano size from the rocks and investigating their efficacy against microbial contaminants in desalinated water is more significant. Furthermore, the molecular techniques are required to confirm the exact mechanism of bacterial killing during the CDI process.

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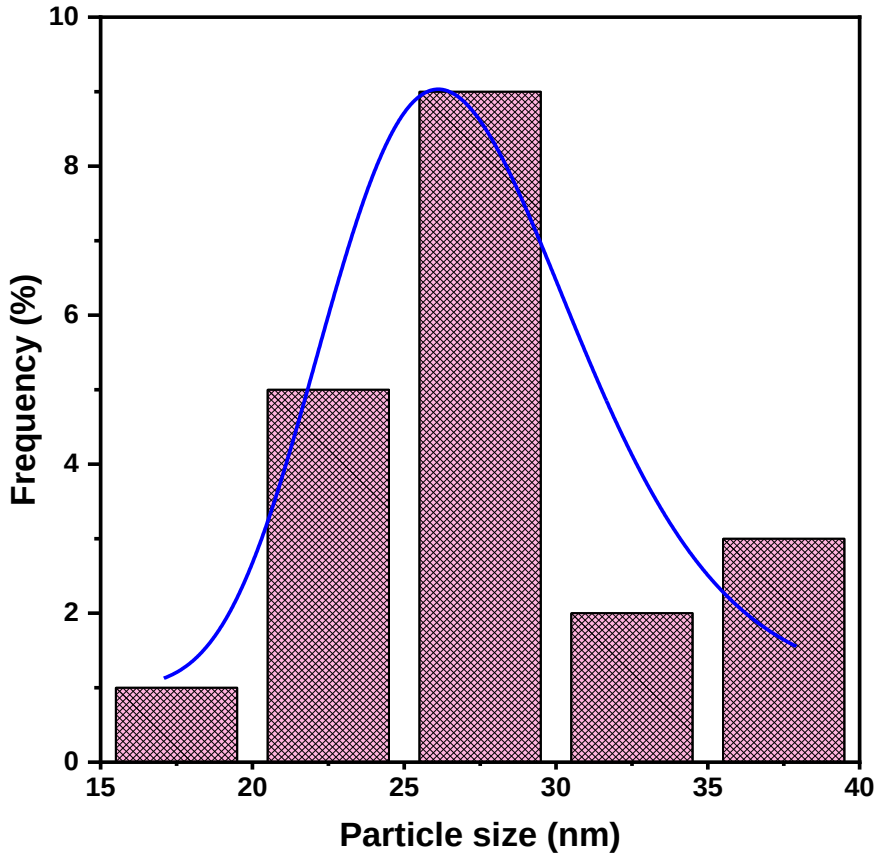
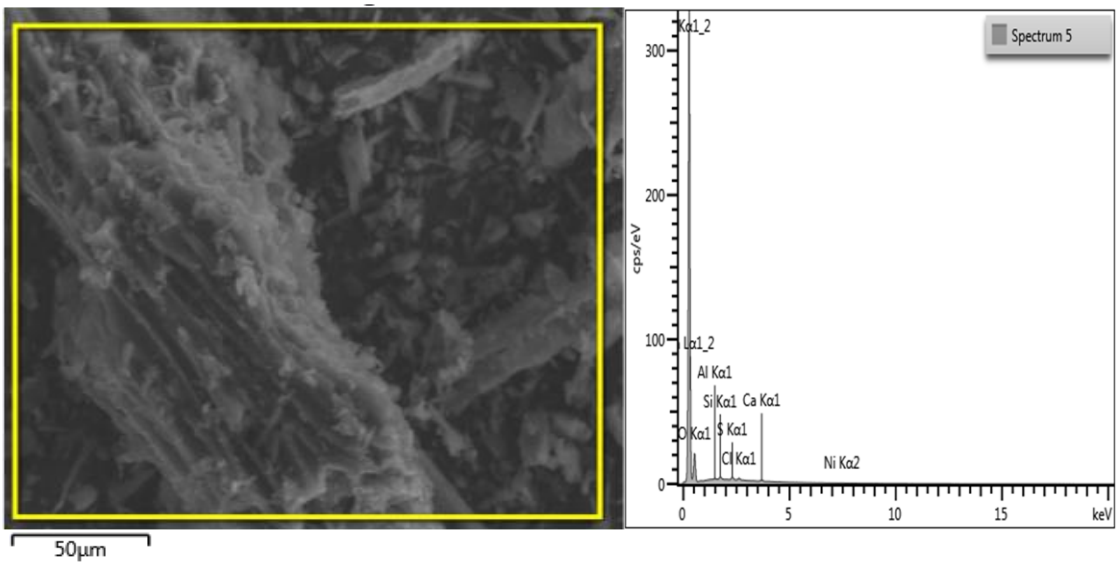
# APPENDICES

## Appendix 1: Histogram of particle size distribution



## Appendix 2: EDX analysis of AC powder



**Appendix 3: Percentage weight of impurities present in AC material during EDX analysis**

| Element | Percentage weight (wt. %) | Weight percent (Wt.% Sigma) | Atomic % |
|---|---|---|---|
| O | 82.54 | 0.49 | 90.96 |
| Al | 1.17 | 0.19 | 0.77 |
| Si | 3.47 | 0.18 | 2.18 |
| S | 4.55 | 0.19 | 2.50 |
| Cl | 3.38 | 0.19 | 1.68 |
| Ca | 3.16 | 0.20 | 1.39 |
| Ni | 1.73 | 0.37 | 0.52 |

**Appendix 4: Water quality parameters before treatment with CDI**

| Parameters | EC (uS/cm) | pH | TDS | Initial concentration (mg/L) | | | | | | | *Escherichia Coli* | *Salmonella Aureus* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | $Na^+$ | $K^+$ | $Ca^{2+}$ | $Mg^{2+}$ | $Cl^-$ | $NO_3^-$ | $PO_4^-$ | | |
| Units | 415.06 | 7.68 | 395 | 14.54 | 41.05 | 37.97 | 33.60 | 0.25 | 19.20 | 0.34 | TNTC | TNTC |

EC = Electrical Conductivity, TNTC = Too Numerous to Count, TDS = Total Dissolved Solids.

## RESEARCH OUTPUTS

### (i) Publication

Alphonce, N. F., Alfredy, T., Hilonga, A., Jande, C. A. Y. (2023). Naturally occurring Metal oxides from rocks as capacitive deionization electrode material for antibacterial activities. *Desalination and Water Treatment*, 294(2023), 172-184.

### (ii) Poster presentation

# NATURALLY OCCURRING METAL OXIDES FROM ROCKS AS CAPACITIVE DEIONIZATION ELECTRODE MATERIAL FOR ANTIBACTERIAL ACTIVITIES

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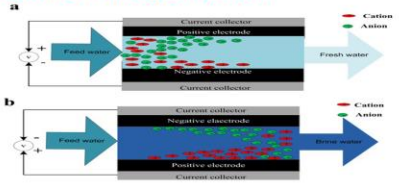
## Introduction

- Access to clean and fresh water is becoming the most severe challenges facing the world as population keeps increasing
- Water can be contaminated by an organic and inorganic compound, bacteria, parasitic protozoa, and even enteric virus.
- About billion people worldwide lack access to clean and safe drinking water.
- Due to scarcity of fresh water, desalination and disinfection of water becoming more significant (UNICEF, 2012).

## Desalination and Disinfection methods

- Some desalination metods are; Reverse osmosis, thermal distillation, electrodialysis and ion exchange resin and capacitive deionization (CDI).
- Disinfection methods are chlorination and ozonation.
- CDI is a promising and rapidly growing technology due to; it is easy to operate, environmentally friendly method and energy efficient for brackish water.
- Their electrode materials can be regenerated easily.
- Though AC loaded with silver nanoparticles (AgNPs) and graphene oxides used as biocidal materials, their application is hindered by their high cos and toxicity effects.

## Basic Principle of CDI




## Objectives

- To investigate the efficacy of AC loaded with naturally occurring MO from rock as CDI electrode material for microbes and salt removal from water.

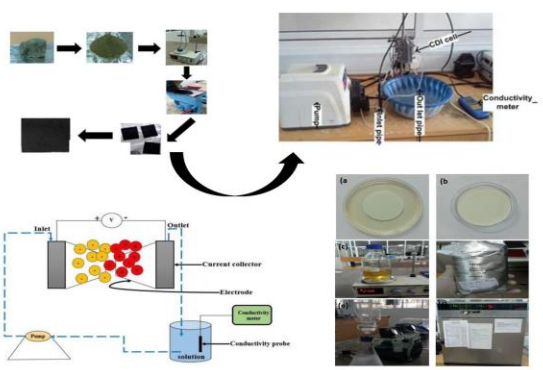
## Specific objectives

I. To characterize the pristine AC, rock powder, and AC loaded MO (AC/MO) CDI electrode materials.

II. To fabricate the CDI electrode from the AC/MO materials.

III. To assemble the electrode in the CDI cell and evaluate performance of developed electrode (AC/MO) for microbes and salt removal from water.

## Methods




## Results

**Table 1: Ionic concentration of field water before and after desalination.**

| Ion type | $C_0$ (mg/L) | V | IR[a,b] (pm) | HR[c] (pm) | η (%) | | SAC (mg/g) | |
|---|---|---|---|---|---|---|---|---|
| | | | | | AC | AC/MO | AC | AC/MO |
| $Na^+$ | 14.54 | +1 | 116 | 358 | 96 | 43 | 0.69 | 0.26 |
| $K+$ | 41.05 | +1 | 133 | 331 | 82 | 36 | 1.66 | 0.60 |
| $Ca^{2+}$ | 37.97 | +2 | 65 | 428 | 39 | 30 | 0.74 | 0.36 |
| $Mg^{2+}$ | 33.60 | +2 | 86 | 412 | 46 | 27 | 0.78 | 0.37 |
| $PO_4^{3-}$ | 0.34 | -3 | 223 | 339 | 74 | 50 | 0.012 | 0.07 |
| $NO_3^-$ | 19.20 | -1 | 264 | 335 | 81 | 51 | 0.77 | 0.40 |
| $Cl^-$ | 0.25 | -1 | 332 | 332 | 60 | 24 | 0.7 | 0.002 |

[a, b]Reference (Huang *et al*., 2014; Tansel. 2012; Uwavid *et al*., 2022)

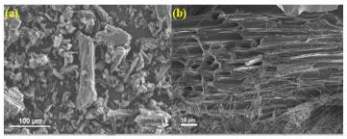



**Figure 1: SEM images (a) Pristine AC and (b) AC/MO electrode.**

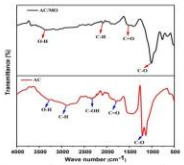



**Figure 2: FTIR spectra of AC and AC/MO electrodes.**

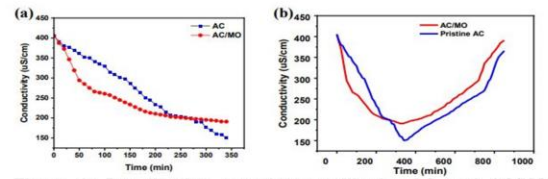



**Figure 3: Desalination experiment with the AC and AC/MO electrodes: (a) and (b) Conductivity change.**

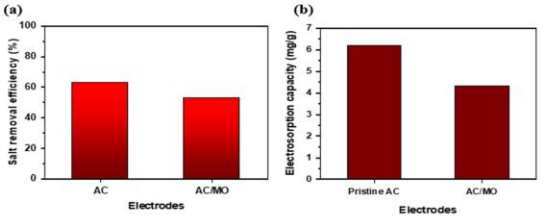



**Figure 4: (a) Salt removal efficiency; (b) Electrosorption capacity.**

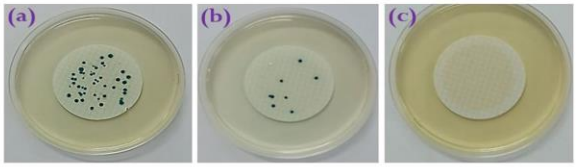



**Figure 5: Plates showing bacteria growth: (a) Before treatment; (b) Treated with AC; (c) Treated with AC/MO electrode.**

## Conclusion

- The AC/MO electrodes prepared by mixing AC with rock powder containing MO mechanically.
- The electrodes achieved 100% *E. coli* and 60% *S. aureus* removal and 46.85% salt removal efficiency, and electrosorption capacity of 3.34 mgg$^{-1}$

## References:

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