KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY,

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PERFORMANCE ANALYSIS OF ELECTRODE MATERIALS (BIOCHAR AND PETROLEUM COKE) IN MICROBIAL FUEL CELLS USING INDUSTRIAL WASTEWATER

by

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MASTER OF PHILOSOPHY

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CERTIFICATION

I hereby declare that this submission is my own work towards the Master of Philosophy degree and that, to the best of my knowledge, it contains no material previously published by another person, nor material which has been accepted for the award of the degree of the University, except where due acknowledgment has been made in the text.

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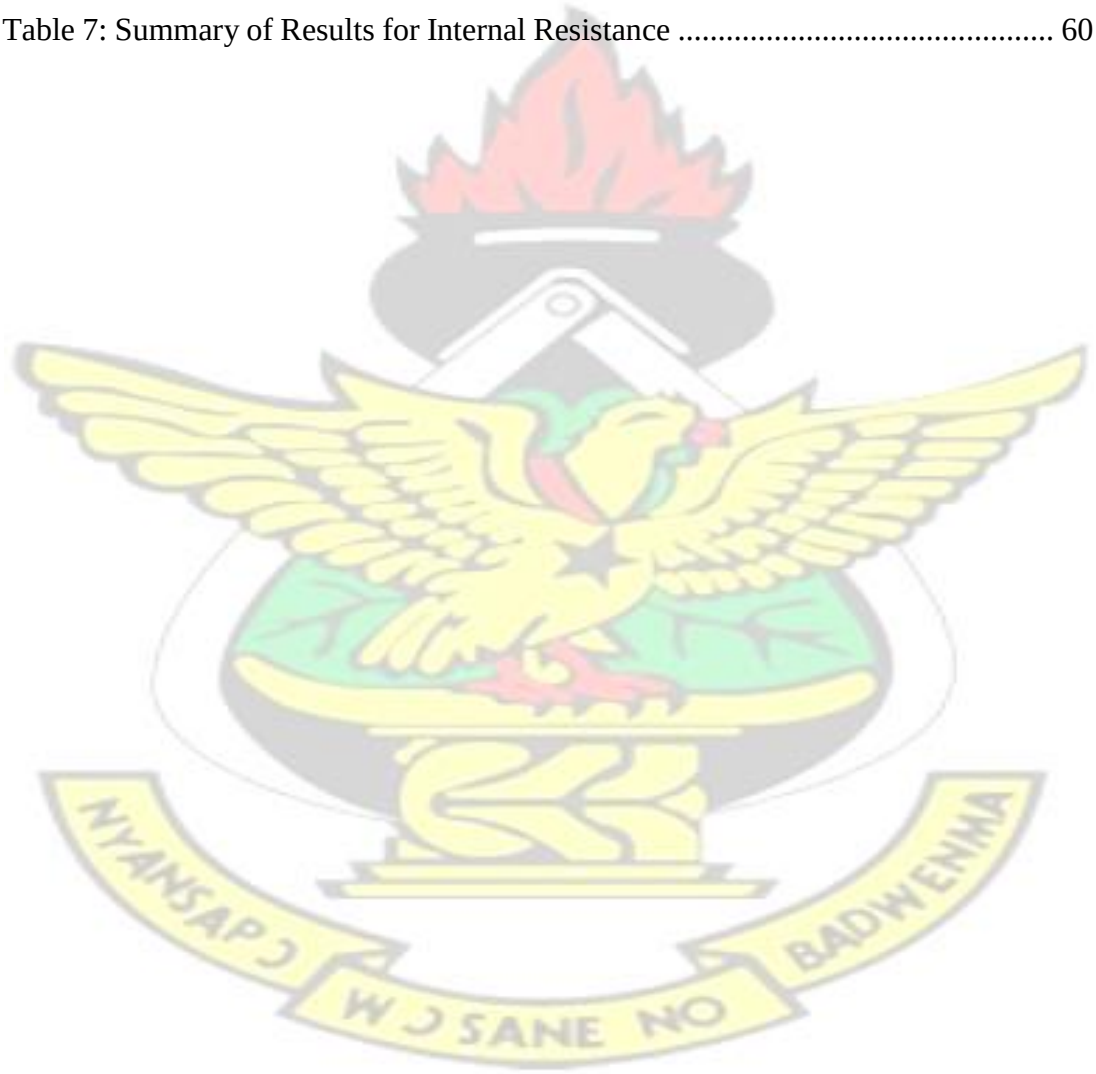
ABSTRACT

Increasing global energy demand coupled with the problem of global warming have necessitated the need for alternatives to fossil fuels. One possible alternative is the use of Microbial Fuel Cells. Microbial Fuel Cells have the potential to provide decentralized power generation and wastewater treatment systems which is especially needed in many rural households and schools. This study investigated the performance of biochar from palm kernel shells and petroleum coke as electrode materials in microbial fuel cells running on brewery and abattoir wastewater. This study sought to examine the power generation and wastewater treatment potential of the selected electrode materials when used as microbial fuel cell. When carbon paper was run on brewery wastewater and abattoir wastewater the maximum power densities achieved were 1.40 ± 0.34 Wm^{-3} and 1.35 ± 0.02 Wm^{-3} respectively. Biochar achieved power densities of 0.78 ± 0.045 Wm^{-3} and 0.54 ± 0.01 Wm^{-3} in brewery wastewater and abattoir wastewater respectively. When abattoir wastewater was used carbon paper removed 39.65 ± 14.30 % of chemical oxygen demand content and that of biochar was 21.92 ± 7.13 %. When brewery wastewater was used biochar had the higher percentage of 59.19 ± 20.67% and carbon paper removed 36.41 ± 2.54 % of chemical oxygen demand content. Petroleum coke granules proved to be unsuitable electrode materials to be used in microbial fuel cells. Petroleum coke granules failed inoculation and also failed to acclimate when both wastewaters were used. The maximum power density achieved during the entire study when using petroleum coke was 0.01 Wm^{-3}. Biochar achieved up to 55% of the power density achieved by carbon paper. However, lower material expenses made their power output cost cheaper than that of carbon paper making it a suitable replacement for the more extensively used carbon paper.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES



ABBREVIATIONS AND NOMENCLATURE

16S rRNA-DGGE	16S Ribosomal Ribonucleic Acid- Denaturing Gradient Gel Electrophoresis
AC	Alternating Current
ADP	Adenosine diphosphate
AFC	Alkaline Fuel Cell
ATP	Adenosine triphosphate
BES	Bioelectrochemical System
BET	Brunauer–Emmett–Teller
BOD	Biochemical Oxygen Demand
CE	Coulombic Efficiency
CEM	Cation Exchange Membrane
CI	Current Interrupt
COD	Chemical Oxygen Demand
DGGE	Denaturing Gradient Gel Electrophoresis
DNA	Deoxyribonucleic Acid
DOE	Department of Energy
ECG	Electricity Company of Ghana
EFC	Enzymatic Fuel Cell
EIS	Electrochemical Impendence Technique

FRA	Frequency Response Analyzer
LED	Light Emitting Diode
LSV	Linear Sweep Voltammetry
MCFC	Molten Carbonate Fuel Cell
MDC	Microbial Desalination Cell
MEC	Microbial Electrolysis Cell
MFC	Microbial Fuel Cell
MSC	Microbial Solar Cell
MW	Megawatt
MXC	Microbial Electrochemical Cell
NREL	National Renewable Energy Laboratory
NSF	National Science Foundation
OCP	Open Circuit Potential
OCV	Open Circuit Voltage
PAFC	Phosphoric Acid Fuel Cell
PEM	Proton Exchange Membrane
PEMFC	Proton Exchange Membrane Fuel Cell
RVC	Reticulated Vitreous Carbon

SEM	Scanning Electron Microscopy
SOFC	Solid Oxide Fuel Cell
TOC	Total Organic Carbon
VALCO	Volta Aluminium Company Limited
VRA	Volta River Authority

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CHAPTER 1: BACKGROUND OF STUDY

1.1 Introduction

Due to population growth and technological advancement there is the increased demand for energy and energy sources. The use of fossil fuels, especially oil and gas, in recent years has accelerated and this has triggered a global energy crisis (Du et al, 2007). The current leading energy source (fossil fuels) is unsustainable due to pollution and finiteness of supply and in the light of further global population growth this creates the need to discover renewable alternatives to our current energy sources. Also, the threat of climate change by the problem of greenhouse gas emissions from the combustion of fossil fuels has rendered necessary the need for the search for alternative non-polluting, reliable, renewable and sustainable sources of energy such as solar energy and its derivatives (Nwokocha et al, 2012). In addition to the global energy insecurity there is environmental concern such that there is emergent interest in developing sustainable green or environmentally friendly energy sources which require the use of zero or minimal hydrocarbons (Singh et al, 2010).

Ghana has an established power production limit of 2813.5MW from 12 production era plants. Of the 12 generation plants, 8 of them are thermal plants running on fossil fuels. These 8 generate a total of 1229.5 MW of power making up 43.7 % of the total electricity generation capacity. The remaining 4 power production plants incorporates 3 Hydro plants specifically the Akosombo, Bui and Kpong Power Plants which create a sum of 1580MW. A Solar facility is additionally accessible, producing 2MW of electricity (VRA, May 2013). In 2010, rural electrification was estimated by the Ministry of Energy to be at 70 %. As at 2008, 66.7% national coverage had been achieved, covering 4,070 electrified communities with a total population of 16 million. About 82,000 communities, covering 8 million people, remained without access to

electricity. As at 2011, the national coverage had risen to 72%. Ghana has recently enacted the enabling legislation "to provide for the utilisation, sustainability and adequate supply of renewable energy for electricity and heat generation and for related matters" (Energy Commission, 2012). One of its main objectives is to increase the share of renewable energy in the energy mix in line with national policy, which sets target share of 10% in 2020. The current share of renewable energy in the energy mix is 0.13% (2010), mainly derived from solar photovoltaic energy and co-generation plants of oil palm and wood processing mills. The Renewable Energy Act, 2011(Act 832), provides the enabling legal framework for Government to institute a licensing regime for renewable energy producers, a feed-in tariff scheme feed into electricity and a renewable energy development fund. Ghana has set itself the target of achieving Universal Access to Electricity by the year 2020, in line with its National Energy Strategy of 2010. Be that as it may, the real tests to utility suppliers in Ghana extends to; expanding request by existing clients, high client populace development, fast growth of rural networks, inaccessibility of natural gas and increment in distribution material expenses. These difficulties obstruct the extension to cover the 30% remainder (ECG, June 2013). People in these unreached rural communities are forced to either live without electricity or find expensive off-grid alternatives.

Ghana also faces problems in wastewater treatment. Wastewater treatment in Ghana is exceptionally low with fewer than 8% of the entire wastewater created undergoing any sort of treatment. It is additionally assessed that Ghanaian wastewater generation will experience an increment between the years 2000 and 2020 from a rate of 530,346 m^3/day to 1,452,383 m^3/day (Agodzo, 2003). Though much research has gone into the discovery of alternative energy sources it does not appear as though a single solution would be able to replace fossil fuel in its entirety (Franks and Nevin,

2010). This therefore implies that a number of different alternatives would be required, providing energy for specific tasks in specialised ways in different situations (Franks and Nevin, 2010). One such specialised means of providing energy for a specific task is the use of microbial fuel cells (MFCs) in treating waste water (Franks and Nevin, 2010). This uses microbes to reuse or re-circulate the otherwise removed microbial nutrients in the production of electricity to offset part if not all the high energy demands of waste water treatment.

As of late the MFC power yield has been enhanced, however one primary difficulty for MFCs in being utilized as a large scale wastewater treatment option is the high cost when juxtaposed with other wastewater treatment options (Lovley et al, 2011). Electrode materials remain a noteworthy factor in the high cost of MFCs, which is evaluated to sum to 20-50 % of the general cost (Rozendal et al, 2008). Be that as it may, electrode assume a major part in encouraging bio-film development and electrochemical reactions, and are imperative in enhancing the usefulness and productivity of MFCs (Huggins et al, 2014). The majority of electrode materials utilized as a part of MFCs are carbon based; either granular activated carbon or graphite granules, particularly in large scale frameworks (Zhou et al, 2011), on the grounds that granular activated carbon has high level of micro porosity and catalytic activity, graphite granules tend to be less costly with higher conductivity, despite the fact that the surface area density is much lower. The expenses of granular activated carbon or graphite granules cathodes range from 500-2500 US$ per US tonne, which is much lower than carbon cloth or carbon paper which is evaluated to be between 100,000-500,000 US$ m^{-2} (Huggins et al, 2014). Therefore cheaper alternatives are required if MFCs are to be used commercially in the treatment of wastewater while generating electricity.

1.2 Problem Statement

Though recent works on MFCs show improvement in power output, the challenge of its high cost contrasted with other wastewater treatment options still remains as 20-50 % of the general expense of MFCs is controlled by the decision on electrode material will be used. The majority of materials utilized as electrodes in MFCs are carbon based granular activated carbon or graphite granules and their costs are considered high for large scale applications and are not readily available within the Ghanaian setting. Therefore a cheaper alternative is required if MFCs are to be used commercially in the treatment of wastewater while generating electricity to meet sanitation and energy demands.

The current study is intended to investigate the feasibility of using petroleum coke and biochar produced from agricultural waste as an alternative electrode material within an MFC anode. The success of the research will help to reduce the overall cost of MFCs.

1. 3 Objectives of the Research

1.3.1 Main Objective

The aim of the research is to assess the performance of some chosen electrode materials in MFCs for the purpose of electricity generation and wastewater treatment.

1.3.2 Specific Objectives

1. To determine the feasibility of the use of biochar and petroleum coke as electrodes materials in microbial fuel cells.

2. To determine and compare the generated electrical power of an MFC operating with biochar and petroleum coke as electrode materials with the more extensively used carbon paper.

3. To measure and compare the rate of organic substrate removal when the selected electrodes are used with that of carbon paper.

1.4 Research Questions

1. What cheaper alternative carbonaceous materials are yet to be tested as electrode materials within microbial fuel cells?
2. Which carbonaceous material can be used effectively in a MFC?
3. Are the selected electrode materials sustainable and cost effective?
4. How well do the chosen materials perform in a functioning MFC perform?

1.5 Justification for Research

Cost of electrode materials aside, the effect on the environment of the lifecycle of the electrode material may very well be a huge contributor to the decision of feedstock, manufacturing method, and electrode material waste disposal method to be employed. For instance, granular activated carbon is most usually made from the pyrolysis of coal preceding activation. Graphite granules is mined from naturally occurring stores or artificially fabricated through the heat treatment (>3000°C) of carbon based materials. Such feedstock extraction and fabrication strategies utilized for the production granular activated carbon and graphite granules can be very energy demanding and bring about the release of contaminants such as greenhouse gasses. Moreover, the frequency of reuse and recycle of granular activated carbon and graphite granules are low, and the waste materials are customarily landfilled after a few times of use.

An alternative which is relatively cheaper is petroleum coke which is a byproduct of refinery coking process and costs between US$ 170 per tonne to US$ 800 per tonne. Its method of manufacturing is relatively less energy intensive than granular graphite or granular activated carbon and results in the release of less environmental pollution. With the specific end goal of advancing the utilization of sustainable and less expensive lectrode materials certain variables, for example, raw material, manufacturing process, and end-of life alternative uses will have to be considered. Biochar fulfils all the before expressed factors of consideration since it is fabricated from locally accessible bio wastes, for example, agricultural residue, which brings down the expense and environmental impact while guaranteeing an unfaltering supply. Production is by pyrolysis or gasification, which uses the chemical energy present within the feedstock to fuel the carbonization of the material. In addition, biochar can be reused as an agrarian soil amendment. This utilization has been demonstrated to improve crop yield, and increment microbial variety and wealth of the soil, and reduce soil emissions such as nitrogen dioxide while remaining environmentally stable for years.

1.6 Limitations of study

1. The current research work hereby discussed is restricted to the use of a two chambered microbial fuel cell configuration only. The results obtained and parameters calculated will differ from those performed in reactors of different configurations and even those of the same configuration but of different dimensions.

2. The chosen wastewater sources are from industrial sources. There may be variations sample from other similar sources not included in this research.

Thus the work does not quantify the variations in results obtained from other sources.

3. The determination of the characteristics of wastewater samples is restricted to the parameters most pertinent to the study.

1.7 Method of the Research

This stud involves the collation of data on the chosen electrode materials for usage in an MFC. Certain parameter values would be derived from calculations performed on empirical data. Research conclusions would be based on patterns detected in data together with the empirical and other calculated parameters pertinent to the study.

CHAPTER 2: LITERATURE REVIEW

2.1 History of Microbial Fuel Cells

A Microbial Fuel Cell (MFC) is a system that uses by microorganisms to produce power by converting organic and inorganic substrates. Through the use of electrodes, electrons from bacteria can be collected and used to produce electrical current across a resistor. In 1911, M.C. Potter observed the electrical current that can be produced by bacteria. He demonstrated a current flow between two electrodes emerged in a bacterial culture and in sterile medium (Potter, 1911). However, very little interest was shown in the idea of electron transfer through the use of microbes thus resulting in few advances made in the technology from 1911-1967 (Biffinger and Ringeisen,2008).

The first actual MFC was constructed by Barnett Cohen in 1931 (Lewis, 1966), he operated a potentiostat-poised half-cell and obtained a current of 0.2 mA by

applying +0.5 V. He also found that the capacity of this device could be improved by introducing potassium ferricyanide or benzoquinone as artificial electron mediators in the anode (Cohen, 1931). The first patent to describe microbial fuel cell technology was issued to John Davis in 1967 (Biffinger and Ringeisen, 2008). MFCs attained prominence in the 1960s through the study of biological corrosion (Lewis, 1966) however research truly began on microbial fuel cells and their possible applications in the 1990's (Biffinger and Ringeisen, 2008). Since 1967, there have been very few patents given with most of them being given in the 2000's the preferred choice within the field is to publish research, methods, and designs in scientific journals rather than apply for a large number of patents (Biffinger and Ringeisen, 2008).

2.2 Fuel cells Bioelectrochemical Systems and Microbial Fuel Cells

A fuel cell is a device that converts the chemical energy in a fuel into electricity directly, generating power with high efficiency and low environmental impact. It usually consists of two units, the anode and the cathode compartments both separated by a proton exchange membrane. Fuel cells can be divided into two main groups: biological fuel cells and Chemical fuel cells. The classification of fuel cells is shown in Figure 1.

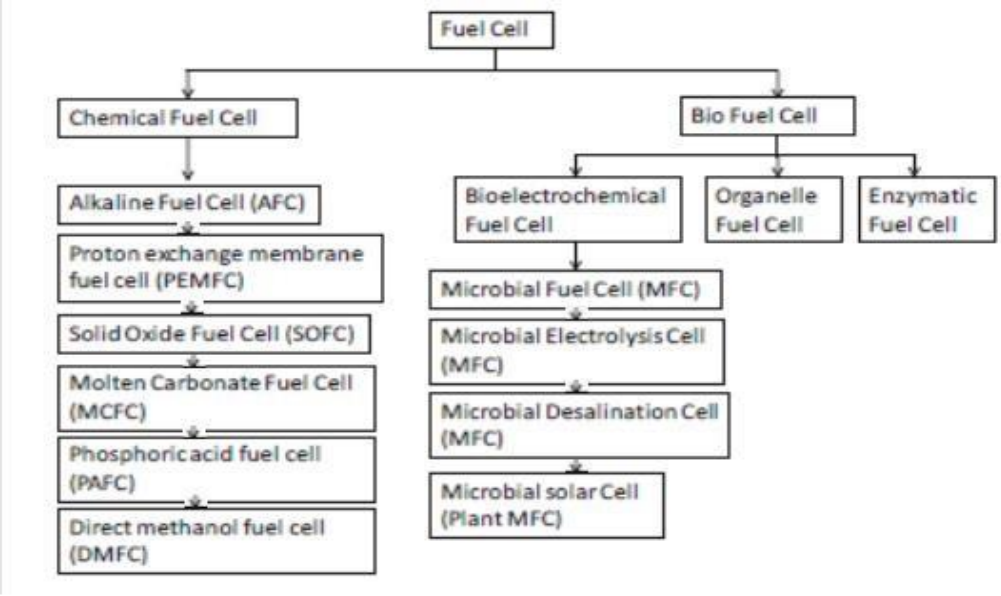

Figure 1: Classification of Chemical and Biofuels (Pant et al, 2012)

Biological fuel cells are electrochemical devices in which organic material is biologically oxidized at an anode, producing carbon dioxide, electrons and protons. The biological fuel cell can be further categorized into bioelectrochemical systems (BES) or enzymatic fuel cells (EFC), depending on the respective catalyst used in the system, i.e. either a living cell or enzyme (Pant et al, 2012).

Chemical Fuel cells are divided into two chambers with each chamber containing an electrode. On the surface of the anode an electron donor is oxidized resulting in the formation of electrons and cations. The electrons then reduce the anode and generate current in the circuit. The voltage difference that is developed across the circuit is the driving force for the reaction. The created cations at the anode surface then travel across a cation selective membrane to the cathode of the fuel cell, in order to equalize the charge transferred by the electrons. In some fuel cells, anions transfer occurs from the cathode to the anode in place of the cation transfer. The second part of the redox reactions that create power in fuel cells is the oxidation of the cathode by

the electrons created on the anode; this requires some oxidized electron acceptor (Bockris and Srinivasan, 1969). There is the absence of biological activity within the cell.

BESs generate electrical energy through the action of microbes at anode sites. BESs are divided into MFCs, microbial electrolysis cell (MEC), microbial desalination cells (MDCs) and microbial solar cells (MSC), depending on their mode of application. Harnisch and Schröder (2010) recently coined the term MXC for these systems, the X standing for the different types and applications. If the electric current created is utilized to push the cathodic with the use of external energy to produce an alternate product the set-up is termed as a microbial electrolysis cell however the setup is called MFC when the produced electrical energy is utilized straightforwardly as an energy source. (Logan et al, 2006).

Because of the availability of electrolytes chemical fuel cells show larger power densities than BES. Power densities of CFCs have been observed to be in the scope of 10-150 kW/m3 (Sundmacher et al. 2010; Arends and Verstraete, 2012). The non-renewable nature of CFCs makes BES a feasible option later on if further strides are made in improving power densities.

BES can and are regularly contrasted with anaerobic digestion systems because of their similitude as far as the substrate that is utilized and their abilities as a part of wastewater treatment systems. Both systems transform fluid biomass by use of micro-organisms. Be that as it may, BES can transform waste directly to power while anaerobic digesters demand a combined heat and power module to change over methane to power (Pham et al, 2008). The potential of BES in power generation, wastewater treatment and formation of useful products is being well researched globally.

2.3 Working Principle

A MFC is a BES that generates electric energy from the catalytic action of electrogenic micro-organisms on organic compounds and/or metals (Nwokocha et al, 2012). In much simpler terms Microbial fuel cells (MFCs) are bioreactors that convert chemical energy in the chemical bonds in organic compounds to electrical energy through catalytic reactions of microorganisms under anaerobic conditions (Du et al, 2007; Singh et al, 2010). The conversion of bio-convertible substrates directly into electricity by the action of these microbes occurs during microbial metabolism of the substrates (Das and Mangwani, 2010; Rabaey and Verstraete, 2005).

The microbial decomposition of sugars in aerobic conditions produces carbon dioxide and water as illustrated by the equation below.

$$C_6H_{12}O_6 + 6O_2 + 6H_2O \rightarrow 6CO_2 + 12H_2O$$

Equation 1: Aerobic Decompositions of Sugars by Microbes (Nwokocha et al, 2012)

However, in anaerobic conditions, carbon dioxide, protons and electrons are produced since oxygen is not available to take up the electrons as illustrated by the equation below (anodic half-cell reaction).

$$C_6H_{12}O_6 + 6H_2O + 6O_2 \rightarrow 6CO_2 + 24H^+ + 24e$$

Equation 2: Anaerobic Decompositions of Sugars by Microbes (Nwokocha et al, 2012)

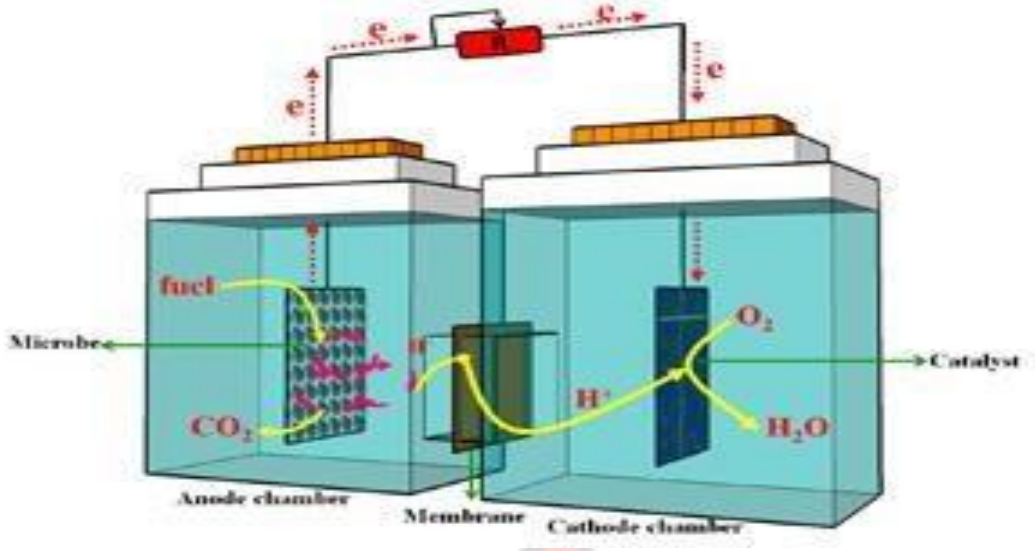

Figure 2: A diagram depicting the parts of a microbial fuel cell (Zhou et al, 2011)

The production and transfer of electrons to the anode by bacteria under anaerobic conditions serves as the principle of operation in MFCs. This can be achieved when bacteria switch from the natural electron acceptor, such as oxygen or nitrate, to an insoluble acceptor, such as the MFC anode (Rabaey and Verstraete, 2005). To utilize these electrons in electricity generation, the electrons produced have to be moved from the electron transport chain of the cell and be deposited on an anode (Nwokocha et al, 2012). This transfer can occur either via bacteria membraneassociated components, or soluble electron shuttles (Nwokocha et al, 2012). The liberation of electrons by the action of microbial catalysis at the anode and the following electron consumption at the cathode, are the defining characteristics of an MFC when both processes are sustainable (Logan et al, 2006).

A standard MFC consists of two terminals, anode and cathode these are separated by a proton exchange membrane (PEM) or salt bridge (Das and Mangwani, 2010). Electrons produced by the bacteria from the substrates are transferred to the anode (negative terminal) and flow to the cathode (positive terminal) linked by a conductive material containing a resistor, or operated under a load (an external

circuit). The protons produced from the breakdown of the substrate move across the PEM or salt bridge to be oxidized in the formation of pure water (cathodic half-cell reaction) at the cathode as electrons are deposited on them to complete the circuit.

2.4 Electron transfer mechanisms in MFCs

Transport of electrons is by 2 main means. They are direct transfer (mediatorless MFC) and indirect transfer (Yan-ping, 2008).

2.4.1. Direct electron transfer:

Here electrons are sent from the cell interior to electron acceptors by use of special cell structures and the formation of biofilms (Lovley, 2008). The microbes develop as biofilms on the anode and transfer electrons directly to the anode (Chaudhuri and Lovley, 2003; Kim et al., 2002). MFCs that operate using this electron transfer mechanism are called mediatorless MFCs.

2.4.2. Electron transfer by use of mediators:

Here, electrons are transferred to the anode by a mediator produced by the microorganism or by added mediators. The mediators facilitate extracellular electron transfer. The MFCs that use mediators as electron shuttles are called mediator MFCs. Mediators provide a means for the microorganisms to generate electrochemically active reduced products. When the mediator is reduced it is able to permeate into the cell, accept electrons and transport them to the anode (Lovley, 2006). Common compounds used as mediators in MFCs include neutral red, thionine, methylene blue, anthraquinone-2, 6-disulfonate, phenazines and iron chelates (Du et al., 2007). An effective mediator must permeate cell membranes with ease, enhance electron

transport, and last during extended periods of redox cycling and while remaining harmless to the micro-organisms in use (Du et al., 2007; Ieropoulos et al., 2005a; Osman et al., 2010).

2.5 MFC Components

2.5.1 Anode

The anodic chamber of a MFC houses the anode and wastewater (anolyte). Within the anode occurs substrate oxidation and electron transfer. Some anodes may or may not contain electron mediators depending on the electron transfer mechanism occurring within the anode. Electron mediators utilized as a part of microbial fuel cells are namely methylene blue and neutral red. Analysis has been performed on the behaviour of both mediators in a single compartment microbial fuel cell. The OCP of methylene blue doubled that generated by neutral red (Daniel et al. 2009). Some heterogeneous large molecules of organic compounds discovered principally in aquatic environments showed support for the transport electrons (Thygesen et al 2009).

Phosphate buffer solutions are sometimes added to the anode of MFCs to steady the needed pH level for the development of microbes. It can also be used to increase solution conductivity. Nevertheless, phosphate buffers in large scale application is unsustainable due to requirements of high concentrations resulting in higher operational costs (Fan et al. 2007).

2.5.2. Cathode

The MFC cathode contains the electron acceptor. One generally used electron acceptor is oxygen due to low expense and abundant occurrence in the atmosphere.

However, oxygen shows slow reduction reaction rates resulting in poor overall MFC performance (Gil et al 2003, Pham et al., 2004). Permanganate can also be used in solution as electron acceptors due to its high oxidation rate. Also Ferricyanide is also used for the same reason (Rabaey and Verstraete 2005, You et al. 2006).

Platinum coated carbon cathode together with oxygen, carbon electrode (no platinum) with oxygen and ferricyanide have been tested within MFC cathodic chambers (Oh and Logan 2006). The use of platinum catalyst additives to carbon cathodes is prominent in the use air cathode MFCs. Platinum is employed to improve the slow electron reduction rate of oxygen.

The possibility of bio-cathodes which uses aerobic bacteria as cathode catalysts is also being explored but a careful study of its biofilm development is needed (He and Angenent, 2006). Through the photosynthesis of some plants employed, bio-cathodes gain oxygen for electron and proton reduction (Clauwert et al. 2007). Low fabrication expenses and enhancement of in de-nitrification processes constitute some of the advantages of bio-cathodes (He and Angenent, 2006).

2.5.3. Microbial Fuel Cell Separator (membrane)

Membranes are required to physically separate the two chambers. This stops the anolyte and catholyte from mixing and helps to control the transfer of ions in a MFC. A membrane should ideally be able to prevent the exchange of oxygen and electrolyte between chambers while enabling efficient proton transfer. Several materials have been evaluated as membranes in MFCs with varying results.

The cation exchange membrane (CEM) which is can be called a proton exchange membrane (PEM) controls the flow of protons between the anodic chamber

to the cathodic chamber while inhibiting the transfer of oxygen to the anode from cathode. The most frequently employed CEM in microbial fuel cells is Nafion 117. This is because of its high conductivity with several cations (Mauritz and Moore, 2004). Ultrex CMI 7000 (Membranes Inc., USA) is comparable with Nafion in terms of proton mass transfer and durability but has a higher ohmic resistance (Harnisch et al. 2008). Other CEMs used include: Biomax (Millipore Corp., Germany), Isopore (Millipore, USA), Polytetrafluoroethylene (Sartorius Stedim, Germany), Selemion (Asahi Glass Co., Japan) and Zirfon (Pant et al. 2010).

The salt bridge is a separator commonly used in electrochemical cells which has also been applied MFCs. The salt bridge is less expensive as compared to the Nafion and has very low oxygen permeability. It has the disadvantage of a low power density as a result of its high internal resistance (Min et al., 2005).

Microporous filtration membranes have also been applied in MFCs. They allow charge species to pass across anodic and cathodic solutions when used as a separator. The ionic species transport is possible through movement through a permissible pore size favourable mainly for protons (Zuo et al. 2007). Microporous layer is a lower cost alternative as compared to ion exchange membranes. However, leakage of oxygen and substrate and also it's associated Ohmic resistance. Examples of the Microporous filtration membranes include nylon mesh, cellulose filters and polycarbonate filters (Biffinger et al., 2007). Jcloth have been used effectively as separator in an MFC to regulate proton mass transfer (Fan et al., 2007; Zhuang et al., 2009).

Though separators are needed in regulating proton transfer and substrate losses MFCs have been tested without them. A single chamber air cathode MFC using CEM

showed a maximum power density of 10mW/m^2 while the maximum power density without CEM was 21mW/m^2. A reduction in internal resistance was proposed to be the reason behind the large increase in power density in the absence of CEM.

Coulombic efficiency reported was 40-55% with the CEM and 9-12% with the CEM removed. The low coulombic efficiency recorded without CEM was attributed to large oxygen diffusion into the anode chamber causing losses in substrate. The substantial increase in oxygen diffusion favoured the activity of aerobic bacteria in substrate consumption reducing the coulombic efficiency (Liu and Logan, 2004).

2.6 Microbes in MFCs

Many microorganisms possess the ability to transfer electrons derived from the metabolism of organic matter to an electron acceptor and a large range of them have been identified and utilised in MFCs. They are often referred to as electrogenes or electrogenic microbes. Bacteria that have been found in MFCs have either been aerobes or facultative anaerobes and their tolerance to reaction temperature determine the operating MFC temperature (Logan, 2008; Rabaey and Verstraete, 2005). Activated sludge, fresh water sediment, marine sediment, soil, and wastewater are known sources for these electrogenes (Niessen et al., 2006, Zhang et al., 2006). The list of identified microbes with the ability of direct substrate to energy conversion is growing with researchers still finding new species. Several and varying bacterial communities have been discovered to be electrogenic. Logan et al. (2005) along with some other publications have discussed screening and identifying electrogenes and the construction of a chromosome library (Holmes et al., 2004; Back et al., 2004).

In MFCs the bacteria gain energy from the transfer of protons across the separator to form a gradient in proton concentration that acts as a driving force in the

production of adenosine triphosphate (ATP) from adenosine diphosphate (ADP). The energy required for growth and the many metabolic processes of the organism is obtained by the production of ATP (Franks and Nevin, 2010). *Geobacter* is one of the commonly used bacteria in mediatorless MFCs and belongs to dissimilatory metal reducing microorganisms; they produce energy in the form of adenosine triphosphate during the dissimilatory reduction of metal oxides under anaerobic conditions. In soils and sediments electron transfer is by direct contact between the bacteria and a final electron acceptor such as Fe_2O_3 (Lovley et al., 2004; Vargas et al., 1998). When metal reducing bacteria belonging to the families of *Shewanella, Rhodoferax,* and *Geobacter* are used in mediatorless MFCs the anodic reaction is similar to that in the soil or sediment however in an MFC the anode acts as the final electron acceptor just as the solid mineral oxides (Du et al. 2007). Most mediator-less MFCs are operated with dissimilatory metal reducing microorganisms however one exception was reported with *Clostridium butyricum* (Oh and Logan, 2006; Park et al., 2001). When mediators are used they have some effects on the mediator-less MFC especially in the early stage of biofilm formation even though the anodophiles can transfer the electrons to the anode directly (Park and Zeikus, 2002). *Dessulfobulbus propionicus, Rhodopseudomonas palustris and Klebsiella pneumonia* are other bacteria that were obtained from the wastewater samples that demonstrated promise of possible use in microbial fuel cells (Sharma and Kundu, 2010).

Mediators are vital in the transfer of electrons for microbes that are unable to transfer the electrons to the anode (Lovley et al., 1996, 2004; Ieropoulos et al., 2005a). Mediators shuttle between the anode and the bacteria while transferring the electrons. They receive the electrons from microbes and discharge them at the surface of the anode.

2.6.1. Choice of inoculums

MFC inoculum choices lie between pure bacterial cultures or mixed cultures (Cheng et al., 2005). Mixed cultures have been shown to handle the break down of complex substrates occurring in wastewater samples (Kim et al, 2007). MFCs using mixed cultures usually have good performances and those using complex mixed cultures allow much wider substrate utilization this implies that the MFCs have much wider substrate specificity when mixed than do pure cultures (Du et al., 2007). Mixed culture performance in microbial fuel cells is not easily disturbed by process disturbances and frequently produces higher power outputs when compared with pure cultures (Rabaey et al., 2005). MFCs inoculated with marine sediments or anaerobic sludge often contains mixed cultured microbes within the anode chamber (Du et al., 2007). Present in MFCs inoculated with anaerobic sludge are both electrophiles/anodophiles and groups that use natural mediators together in the same chamber. The relationship between power output and levels of Sulphur compounds were studied in MFCs. Since there are always some naturally occurring levels of Sulphur containing material in sludge, they showed that up to 70–80% of the power was due to sulphate/sulphide mediated system and only 20–30% due to electrophiles(Ieropoulos et al., 2005b). Some pure cultures capable of producing current in an MFC include *Saccharomyces cerevisiae* and *Hansenula anomala* (Bond and Lovley, 2005; Zhang et al, 2008; Prasad et al, 2007).

2.7 Substrate in MFC

In any biological process the substrate in use is an important factor as it acts as an energy and carbon source (Pant et al, 2010). The substrate supplies not just energy responsible for microbial growth but also affects parameters like power density

and coulombic efficiency of MFCs. A variety of substrates can be used in MFCs ranging from pure compounds to complex mixtures of organic matter present in waste water. Properties of the substrate such as composition and concentration influence the diversity and abundance of the microbial community present and the overall power production of the MFC (Cheng and Logan, 2011; Pant et al, 2010). There is some difficulty in comparing from literature MFC performances, due to differences in methods and operating conditions, this difficulty also extends to the performance of different substrates for the same reasons (Pant et al, 2010). Though several substrates have been tested and their columbic efficiencies and power outputs evaluated by many researchers, the economics of substrate utilization still remains unknown (Lee et al., 2008; Niessen et al., 2004; Pant et al, 2010; Zuo et al., 2006). A few of the substrates that have been used in MFCs are discussed hereafter.

2.7.1 Acetate

Most MFC studies so far use acetate as the substrate of choice for electricity generation. Acetate is a simple substrate more commonly used in research asa carbon source for the induction of electroactive bacteria (Pant et al, 2010). In the standardizing novel MFCs and varying working conditions, it remains the substrate of choice due to its low tendency towards fermentation and methanogenesis at room temperature (Pant et al, 2010). In a review by Pant et al. (2010) it was cited that Liu et al. (2005) using a single-chambered MFC, generated power with acetate that was 66% higher than power produced with butyrate. In the very same review it was stated that the work of Chae et al. (2009) compared the performance of four different substrates in terms of coulombic efficiency and power output. MFC using acetate showed the highest coulombic efficiency, then butyrate, propionate and glucose in descending order of coulombic efficiency. In the work of Liu et al., (2009) acetate was

evaluated in comparison to a protein-rich wastewater as fuel within a MFC, the biofilm feeding on acetate obtained more than two times the maximum power, and lower internal resistance compared to the MFC using protein-rich wastewater(Pant et al, 2010) .

2.7.2 Glucose

Another alternative commonly used as substrate within MFCs is glucose. The work of Pant et al, (2010) provides some information concerning the performance of glucose as a substrate for MFCs. Citing the work of Hu (2008) it states that the performance of anaerobic sludge and glucose as substrates were compared in a bafflechamber membrane-less MFC, the glucose-enriched MFC provided a larger power density. The energy conversion efficiencies of both glucose and acetate within MFCs were compared with acetate showing the higher conversion efficiency (Lee et al, 2008). When glucose was used in an MFC, the MFC generated the lowest coulombic efficiency as a result of electron loss due to competing bacteria (glucose is a fermentable substrate, which means that it is consumed by competing metabolisms such as fermentation and methanogenesis that do not result in the production of current), nevertheless it enabled much wider substrate utilization and the greatest power density due to its relatively diverse bacterial structure (Chae et al. 2009; Pant et al. 2010).

2.7.3 Brewery wastewater

Due to its low strength, suitability for electricity generation in MFCs as a result of the food-derived nature of the organic matter and the lack of high concentrations of inhibitory substances, wastewater from breweries has been a favourite among researchers as a substrate in MFCs (Feng et al., 2008; Pant et al., 2010). Brewery wastewaters usually have concentrations in the range of 3000–5000 mg of COD/L

which is approximately 10 times more concentrated than domestic wastewater (Vijayaraghavan et al., 2006). Adding to the already stated properties brewery wastewaters can also be an ideal substrate for MFCs due to its nature of high carbohydrate content and low ammonium nitrogen concentration (Pant et al., 2010). Feng et al. (2008) reported a maximal power density of 528 mW/m^2 , this occurred when 0.05M solution of phosphate buffer was mixed with beer brewery wastewater treatment using air cathode MFC. When both brewery wastewater and domestic wastewater were compared at similar strengths the maximum power produced by brewery wastewater was lower than that achieved using domestic wastewater. Difference in conductivities of two wastewaters was determined to be the cause; a decrease in solution conductivity was the result of the wastewater being mixed with deionized water (Feng et al., 2008). The main contributors to the internal losses of the MFC running on brewery wastewater appeared to be reaction kinetic loss and mass transport loss (Wen et al., 2009). These losses can be minimized by augmenting the solution concentration, raising the operation temperature and employing the use of a rough electrode for the purpose of increase surface area.

2.8 Electrode Materials in MFCS

One of the key components in deciding the performance and cost of MFCs is the electrodes employed within the MFC. This is due to their influence in microbial attachment, biofilm formation and electron transfer. Electrodes make up construction cost by up to 50% (Rozendal et al. 2008). Electrodes are used in both the anodic and cathodic chamber of MFCs and are made from different materials. Electrode materials may differ in their physical and chemical properties e.g. surface area, electric

conductivity and chemical stability. They also vary in microbial attachment, electron transfer, electrode resistance and the rate of electrode surface reaction.

2.8.1. Anode Materials

Electrode materials used within the anode are classified into two main categories carbon based and metal based electrode materials. Characteristics of a good anode material include:

1. High electrical conductivity
2. Reduced surface resistance
3. It should be compatible with microbial life forms
4. Non-reactive and corrosion proof
5. Must possess large specific surface area and micro-porosity
6. Its mechanical strength must support it use as an electrode (Zhou et al. 2011).

Because they corrode easily, are expensive and harmful to micro-organisms electrode materials from metals are seldom utilized in MFCs despite their higher conductivites. Stainless steel plate recorded a power density of 23mW/m^2 (Dumas et al. 2007). In a test using *Geobacter sulfurreducens* as inoculum gold was used as the anode with producing a steady current of 0.4mA to 0.7mA (Richter et al., 2008).

Carbon based electrodes are more frequently used in research because they possess good electrical conductivity and while remaining chemically stable. In some cases they reduce the spacing between while possessing a large surface. This is true in the case of carbon cloth and carbon paper. However, carbon cloth is more expensive while carbon paper is fragile (Zhang et al., 2010). Though graphite fibre brush has a high specific surface area with low electrode resistance it gets clogged by waste

material. Despite the fact that it has a small specific surface area, graphite rod remains electrically conductive, chemically stable and cheap (Logan et al., 2005). In a single chamber air-cathode MFC with continuous flow, graphite fibre brush as the anode yielded a maximum power density of 422mW/m2 (Ahn and Logan, 2010). When carbon cloth and brewery wastewater were used together in a single chamber MFC a maximum power density of about 483mW/m2 was obtained (Wang et al., 2009). RVC is hardly used in MFCs since it gives a large internal resistance and is very fragile making handling difficult even though it has good conductivity (He et al., 2005)

2.8.2. Cathode Materials

Cathode materials greatly affect the power outputs of MFCs. The most sought after properties in cathode materials are a high reduction-oxidation potential and the ability to capture protons easily. One of the most frequently used catalysts in cathodes is platinum because it is able to lower the requisite activation energy for the reduction of oxygen thereby improving the rate of reaction in the cathode chamber and reducing the energy losses due to reaction kinetics. Nevertheless, platinum remains too expensive to be practical in large scale applications (Zhou et al.,2011).

2.9 MFC designs

Using the same operating principles different types of reactors have been built. There are different types or configurations of MFCs that have been fabricated employing a wide range of materials

1. **Two chamber MFC**: This construct consists of two compartments. Anodic and cathodic chambers are physically separated by a PEM. It is more commonly utilized in labs of the purposes of research. Reported power outputs from these systems tend to be lower than other designs because of their their complicated design, high internal resistance due to the distance between

electrodes (Du et al., 2007; Logan and Regan, 2006; Nwogu, 2007). Systems which use a bio-cathode for oxygen reduction have been developed as a possible replacement for chemical electron acceptors (Clauwert et al, 2007).

2. **Single chamber MFC**: In this design only one compartment contains both the anode and the cathode. The anode is either placed away or close to the cathode separated by ion exchange membrane. When the anode is closer to the cathode by avoiding the use of a catholyte as a result of two chambers; there is reduced internal ohmic resistance as a result of the reduced distance and this in turn increases the power density achieved in a single chamber MFC (Liang et al, 2007). They have the added advantage of sustainability with air as its catholyte (Kim et al, 2008).When the single chamber is contrasted with the double chambered microbial fuel cell, it provides a simpler, cheaper design (Du et al., 2007). Single chamber MFC without a PEM is a cheaper alternative and is more practical for large scale applications (Kim et al, 2008). In this design though the presence of microbes on the cathode and the leaking of oxygen onto anode are some of the challenges encountered (Kim et al, 2008). Also the membrane-less MFC has the disadvantage of electric short-circuiting when the cathode is placed too close to the anode (Liu and Logan, 2004).

3. **Up-flow MFC**: Here, the MFC is designed as a cylinder. The anode is placed at the bottom and the cathode is placed at the top. Both electrodes are separated by two layers. These include a glass wool layer and a glass bead layer. The influent is through the base bottom and the flow is vertical. The effluent is through the top. A diffusion barrier occurs between the anode and the cathode.

This creates a concentration difference that is needed for optimal working of the MFC (Du et al., 2007; Kim et al., 2008; Schwartz, 2007). Due to the design and the absence of a PEM there are no proton transfer related difficulties and is suitable for large scale applications. However, it still faces the difficulty of oxygen leakage (Kim et al., 2008; Moon et al. 2005).

4. **Stacked MFC**: This design combines a number of MFCs in a circuit to produce and increased output (Du et al., 2007). Parallel connections demonstrate better outputs when compared to series connection due to higher electrochemical reaction rate. However, parallel connections tend to short circuit more often than serial connection (Aelterman et al., 2006; Schwartz, 2007).

2.10. Electrochemical or Electroanalytical techniques

New mechanisms are gradually being made clearer to understand and electrochemical methods play an important role. They are very much needed to pinpoint and assess the upper bounds of a new component's performances in order that the MFC operation may be optimised, and to also allow for continued innovation within the field. The electrochemical methods presently employed in MFC research were already in practise in traditional electrochemical systems research. However, the electron transport mechanisms and the different metabolic processes brought on by the use of microbes in MFCs make MFCs appear more complicated. The major distinction between CFCs and MFCs is in electricity generation. In MFCs electricity generation is from the cellular metabolisms, this needs the MFCs to be operated

continuously for extended periods under optimum conditions microbial growth (Zhao et al, 2009).

The output of a MFC is evaluated in terms of electrical power (the product of the potential difference and the current generated). The open circuit voltage (OCV) is the voltage of a MFC when the circuit connection between anode and cathode is left open. This parameter is determined using a voltmeter or *a* potentiometer. Open circuit potential (OCP) means the electrode potential determined against a requisite standard electrode (Zhao et al, 2009).

2.10.1 MFC polarization techniques

Polarization alludes to the variation of electrode potential (or MFC voltage) with current. The data gotten from polarization tests is used to plot curves which are graphs that show the variation of electrode potential (or MFC voltage) when current or current density is varied (Zhao et al, 2009). Polarization curves provide a plethora of needed information that can be used to assess and understand the behaviour and performance of a MFC. There are four methods to determine MFC polarization curves:

1. Constant resistance method: The load across the MFC is varied and voltage is recorded.
2. Potentiodynamic method: Here, voltage is varied at a slow rate of $1mVs^{-1}$
3. Galvanostatic method: Current is varied in this method while voltages are recorded.
4. Potentiostatic method

A MFC polarization curve yields the overall fuel cell performance under specific operating conditions, but does not provide information on the performances

of the individual electrodes (anode or cathode), thus it is difficult to determine the limiting factor of MFC performance. However, a reference electrode can be easily introduced in one or more of the MFC chambers so that it is possible to record the individual potentials of anode or cathode. The overpotentials of a MFC is the total of the anode overpotential, cathode overpotential and internal ohmic overpotentials of the MFC. Analysis of the potential changes that occur at the anode and the cathode while varying currents can bring to light what the limiting factor of a MFC's performance is(Zhao et al, 2009).

2.10.2. Current interruption (CI)

Current interruption methods have been more commonly utilised to determine the internal ohmic resistance of CFCs and in recent times MFCs. The basic principle of the CI is to interrupt the current flow and to observe the resulting voltage changes. The MFC is operated at a current at which no concentration losses occur. Next the electrical circuit is opened and a sharp potential rise is initially observed, and then a slower increase of the potential to the OCV (Zhao et al, 2009). When a break in the flow of current occurs the ohmic irreversibilities immediately vanish producing a sharp increase in voltage that is proportional to the ohmic resistance and the current generated immediately before the break. The potential continues to increase slowly afterwards until the OCV is attained. This slower potential rise can be used to determine the electrode overpotentials produced when the MFC was in operation (Zhao et al, 2009).

Current interrupt can be performed with cheap electronic equipment, and output data can be interpreted with ease. The main demerit is that near instantaneous measurements (< 10 μsec) of the disturbance to the system are needed for precision

and accuracy. The difficulty in differentiating between charge transfer and mass transfer impedances adds to the demerits of CI (Zhao et al, 2009).

2.10.3. Electrochemical Impedance Spectroscopy (EIS)

EIS is a method employed in the characterization of fuel cell limitations and the optimization/improvement of their performances. During an EIS test, a frequency response analyzer (FRA) is used to impose a small amplitude AC signal to the fuel cell through the load. The AC voltage and current response of the fuel cell is analyzed by the FRA to determine the impedance of the cell at that particular frequency. The physicochemical processes occurring within the cell have different characteristic time-constants and are therefore exhibited at different AC frequencies. When conducted over a broad range of frequencies, impedance spectroscopy can be used to identify and quantify the impedance associated with these various processes (Zhao et al, 2009).

It is possible to deduce information such as ohmic losses, and transport losses, from the analysis of data obtained by EIS. Ohmic resistance is determined by the intercept of the curve with the real impedance axis. Information concerning a MFC internal ohmic loss obtained by EIS is often more accurate than as compared to values obtained when simple single frequency resistance methods are employed. EIS just as current interrupt may occasionally produce larger internal ohmic resistances than the reality is. This is more frequent at large current densities though such current densities are unlikely to occur in MFCs (Zhao et al, 2009).

2.11 MFC Researchers and their Research

Many research projects have been initiated worldwide with the aim of exploring MFCs as an alternative source of energy. Due to this, the field of MFC

research has seen many rapid advances with many scientific articles being published. Between the years of 2002 to 2009 the number of citations on the title microbial fuel cell has experienced an increment from 2,415 to 10,700 (Logan, 2010). Also in order to explore the commercial applications of MFCs the field of MFC research has seen a multitude of startups and academic groups join forces. IntAct's lab (Cambrian Innovation) which is located in Cambridge acquired sponsorship from the U.S. Department of Agriculture and the National Science Foundation (NSF) to develop MFCs to treat wastewater. Its goal is to startup a pilot plant for treatment of wastewater. Craven (2010) reported that in a similar manner, Lebone, founded in 2007, also acquired a World Bank grant of two hundred thousand dollars to begin an initiative in Tanzania and Namibia employing MFCs to supply power to gadgets that do not require large amounts of power like cell phone chargers and LEDs. The University of Glamorgan received $1,000,000 for MFC studies t(Lane, 2010). Emefcy is producing MFCs for the purpose of electricity production from wastewater targeting that by 2012 commercial production of microbial fuel cells would have began (Clary, 2011). Bruce Logan leads a collective in the Penn state university being sponsored by ARPA-E for MFC production. This group is also in partnership with the National Renewable Energy Laboratory (NREL) and the Department of Energy (DOE). Below is a table containing a list of some researchers and their field of study.

Table 1: Some MFC Researchers and their Field

Full Name	Base Institution	Field
Bruce Rittmann	Biodesign Institute, Arizona state University	Anode electrochemistry
Largus Angenent	Cornell University, New York	Electron transfer mechanism
Bruce Logan	Penn State University	Reactor design and scaling up power generation
Harold May	Medical University of South Carolina	Bacterial community
Hong Liu	Oregon State University	Electrode development and performance
Arum Han	Texas A&M University	Screening electricigens
Keith Scott	Newcastle University	Anode biofilm and electrochemistry
Derek Lovely	University of Massachusetts	Electron transfer mechanism
Zhiyong Ren	University of Colorado	Anode biofilm and architecture

2.12 Challenges to MFC Scale-up

Microbial fuel cells have risen as a potential but challenge ridden technology to produce electricity. Though there is rapid progress in the field, there are still gaps in knowledge concerning MFC.

The major problem facing the in implementation of MFCs on an industrial scale is one of the reduction high capital costs, reduction of hazards in the meanwhile improving power production (Schwartz, 2007). Using a granular bed in a stacked MFC, the capital expenditure cost based on materials as presented by Tsuchiya and Kobayashi (2004) is estimated to be at a level 10 times that of anaerobic digestion processes, assuming a cost of €4000 per m3 of electrode compartment, and 1 kW power output per m3 anode (Rabaey and Verstraete, 2005).

Another difficulty in the large scale implementation of MFCs the problem of insufficient power density. Nevin et al (2008) achieved a power density greater than 2kW/m3, specific to reactor volume, which was less than 0.5ml. However, extrapolating laboratory scale performances to an industrial scale has not always considered the difficulties which need to be addressed to achieve scale-up. Dewan et al (2008) considered the assumption that an increased electrode surface area would most necessarily result in greater increased power density. They showed that there was not a direct linear relationship between specific power density and anode area, but a logarithmic relationship instead. This suggests that there are serious questions to address in relation to MFC scale-up. The current generation of electric current by MFCs is at 14mA (Saldago, 2009) while power generation is at a meagre 300 Wm^{-3} (Abhijeet el al., 2009) which is low for commercial applications.

There are also challenges on the laboratory scale which are yet to be overcome that hinder the scale-up of MFCs. Voltage reversal is a difficulty encountered in recent

MFC studies (Oh and Logan, 2007). Issue of large internal resistances is still unresolved (Nwogu, 2007). The inverse relation between power density and reactor size requires that more progress is needed to build very efficient reactors with minimal losses before large scale implementations can be considered (Cheng and Logan, 2011). Anode overpotentials and charge transfer losses due proton transport from the biofilm to cathode and the subsequent development inside the biofilm represses power creation (Franks and Nevin, 2010; Wen et al., 2009). The slow redox kinetics of oxygen reduction results in large losses. This is a restricting component in the pursuit of high current densities (Kim et al., 2008). Optimum MFC operating conditions should be assessed to decide the changes which are most influential to the performances of MFCs when scaled up (Osman et al., 2010)

CHAPTER 3: MATERIALS AND METHODS

3.1 MFC

Two two-chambered microbial fuel cells constructed from 2 acrylic cylinders each possessing a volume of 300 ml. A connection was made between the two

cylinders using an acrylic tube of diameter of 30 mm. The MFCs shaped like an 'H' were provided by Centre for Bioprocess Biochemical Engineering of the Danish Technical University, Denmark. Nafion™ N117 having an area of 9.62 cm^2 was used to separate the chambers.

Carbon paper with dimensions 4cm x 9cm x 0.35mm was common cathode to all reactors. Granular electrode materials (biochar and petroleum coke) 100 cm^3 were packed into the anode chamber and bound by the use of a plastic mesh. A stainless steel rod was employed as a charge collector.

Figure 3: Duplicate H-Tube MFCs

3.2 Electrode Material Manufacturing

For the purposes of this study the selected electrode materials were petroleum coke, biochar made from palm kernel shells and carbon paper. Carbon paper was chosen as the standard electrode material to which the performances of the other two electrode materials were to be compared because of its extensive use in MFC research. Toray carbon paper TGPH-120 was purchased from Permeas USA, Inc., E-TEK division. Petroleum coke which is a carbonaceous solid product obtained from petroleum cracking was obtained from the Volta Aluminium Company (VALCO),

Tema. They were obtained in particle sizes of 15-20cm in diameter. The petroleum coke particles were reduced to granules below 5mm in diameter to minimize void spaces.

The biochar sample was manufactured using a micro-furnace. Palm kernel shells were carbonized using a highest heating temperature of 700°C, a residence time of 1 hour and temperature readings were measured using a programmable thermocouple. Biochar was made from palm kernel shells, a locally available agricultural waste product.

Figure 4: Sample of Biochar Produced

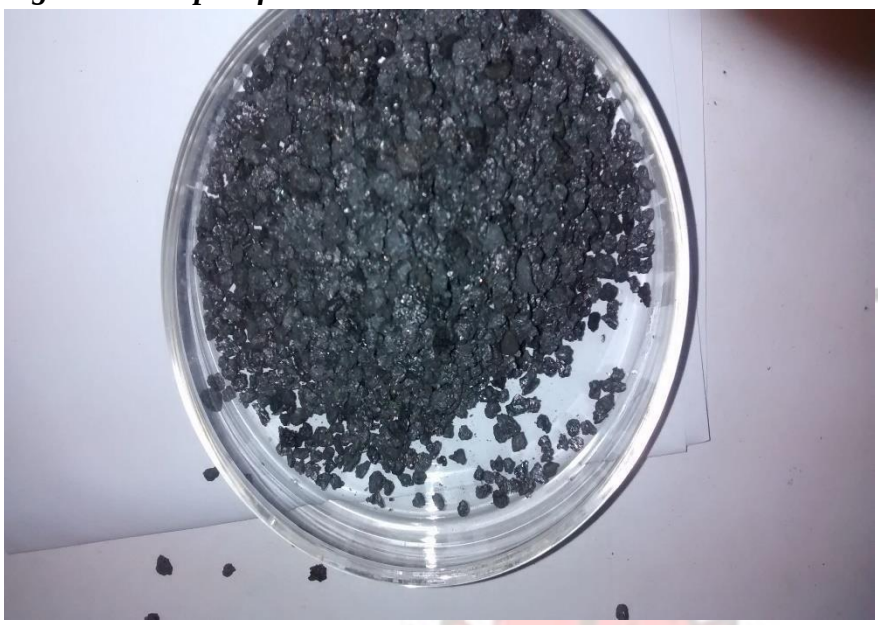

Figure 5: Sample of Petroleum Coke Used

3.3 Electrode Material Characterization

Proximate analysis was performed on petroleum coke samples and biochar samples to determine fixed carbon content, volatile matter content, moisture content and ash content. Brunauer–Emmett–Teller (BET) method that uses a multipoint N_2 gas adsorption technique was used to measure the specific surface of the petroleum coke and biochar samples. This was done at Pacific Surface Science Inc., California. The analyses were done in conformity with ASTM D 3174 for Ash content, ASTM D 3173 for moisture content, ASTM D 3175 for Volatile Matter and ASTM D 6556-10 for BET nitrogen adsorption specific surface area.

3.4 Wastewater Sampling

Industrial wastewater samples were obtained from two main sources; brewery wastewater from Guiness Ghana Breweries Limited and abattoir wastewater from

Kumasi Abattoir Company Limited. Both companies are located in Kumasi. Brewery wastewater was collected from the balancing tank within the wastewater treatment plant of Guinness Ghana Breweries Limited and abattoir wastewater was obtained from influent sump three within the wastewater treatment section of Kumasi Abattoir Company Limited. For the purposes of inoculation anaerobic sludge was obtained from Guinness Ghana Breweries Limited.

Wastewater samples were collected to inoculate MFCs and serve as substrate. Six samples of each wastewater type were collected for the purpose of characterization and use within the MFCs. 24-hour composite samples of brewery wastewater were obtained with the help of an on-site automatic sampler and plastic containers. Composite samples of abattoir wastewater were collected by collecting equal volumes of grab samples at an interval of 3 hours between 9 am to 6 am with the use of plastic containers.

3.5 Wastewater Sample Preparation and Characterization

Samples collected received no form of pre-treatment. The samples were characterized to determine Chemical Oxygen Demand (COD), solution conductivity, pH, total nitrogen, total phosphorus, ammonia content and total dissolved solids.

3.6 Inoculum Source testing

3.6.1 MFC Operation

MFCs were inoculated using anaerobic sludge, abattoir wastewater and brewery wastewater to help identify sources of electrogenic bacteria. Carbon paper was used as the anode during source testing.

The method of inoculation remained the same for each source used: 100ml of each inoculum source (anaerobic sludge, abattoir wastewater and brewery wastewater) was mixed with 100ml of a growth medium containing 0100mL of anaerobic sludge was mixed with 100mL of a growth medium containing 0.6 g of acetate, 0.003 g of ammonium chloride, 0.01 g of $NaH_2PO_4.2H_2O$, 0.03 g $CaCl_2$, 0.02 K_2HPO_4, and 0.0005g of $FeCl_2$. This mixture was used as anolyte. The growth medium was prepared by diluting 5 mL of a biological oxygen demand (BOD) test solution from HACH Chemical Industries to a volume of 1L. 0.6 g of acetate was then added to 100 mL of the solution. The catholyte used in each experiment was 200ml of 0.5 mM potassium ferricyanide. The MFCs were operated in a fed-batch mode under a 1000 ohm resistor.

The cell voltages monitored and recorded using a data logger (Picolog R5.22.8 from Pico Technology) every minute during the cycles. When the best source was identified the MFCs were then sterilized using an autoclave and then inoculated with the identified best source to be used for subsequent experiments.

3.6.2 Scanning Electron Microscopy (SEM)

In order to examine biofilms on the anode electrode surfaces, the anode electrode material was removed without touching its surface. A small piece was cut and heated in an incubator at 60 ^oC for 1 hour. It was then sent to the Danish Technical University for SEM analysis.

3.6.3 DNA Analysis

Samples of anodic biofilms in the MFCs were taken when inoculation ended and used in 16sRNA-DGGE analysis at Danish Technical University, Denmark

3.7 Electrode Performance Testing

3.7.1 Inoculation

100mL of anaerobic sludge was mixed with 100mL of a growth medium containing 0.6 g of acetate, 0.003 g of ammonium chloride, 0.01 g of $NaH_2PO_4.2H_2O$, 0.03 g $CaCl_2$, 0.02 K_2HPO_4, and 0.0005g of $FeCl_2$. This mixture was used as anolyte. The growth medium was prepared by diluting 5 mL of a biological oxygen demand (BOD) test solution from HACH Chemical Industries to a volume of 1L. 0.6 g of acetate was then added to 100 mL of the solution. The catholyte used in each experiment was 200 mL of 0.5 mM potassium ferricyanide. The MFCs were run in a fed-batch configuration under a 1000 ohm load. Inoculation ended when steady current generation was achieved with the MFC reaching a peak voltage and then descending.

3.7.2 MFC Operation

Three anolytes were chosen for the testing of the electrode materials. The first of was a prepared medium containing 100mL of anaerobic sludge was mixed with 100mL of a growth medium containing 0.6 g of acetate, 0.01 g of NH_4Cl, 0.52 g of $NaH_2PO_4.2H_2O$, 0.05 g $CaCl_2$, 0.04 g $MgSO_4$, 0.02 K_2HPO_4, 0.05 g of NaOH and 0.001 g of $FeCl_2$. This mixture was used as anolyte. The growth medium was prepared by diluting 5 mL of a biological oxygen demand (BOD) test solution from HACH Chemical Industries to a volume of 1L. 0.6 g of acetate, 0.5 g of $NaH_2PO_4.2H_2O$ and 0.05g NaOH was then added to 200 mL of the solution. Brewery wastewater and abattoir wastewater were used afterwards. The anode chamber was filled with 200ml anolyte.

The catholyte used in each experiment was 200ml of 0.5 mM potassium ferricyanide. Electrode materials which showed steady current generation during inoculation were tested on the different anolytes after inoculation. Twin MFC reactors were used for the purpose of establishing reproducibility and repeatability of results. The MFCs were sealed off tightly to create an anaerobic environment. The system ran in a fed-batch configuration at ambient conditions. The experiments were run in several fed-batch cycles using a 1000 ohm load. Each cycle lasted no less than 5 days. After each cycle both the anolyte and catholyte were replaced.

The cell voltages were monitored and recorded using a data logger (Picolog R5.22.8 from Pico Technology) every minute during the cycles. The electrochemical experiments performed on each material and corresponding reactor were conducted after the MFC had achieved similar peak voltages in three consecutive cycles and tests were repeated in order to determine the standard deviation.

3.7.3 MFC Polarization

Polarization curves were obtained by performing linear sweep voltammetry (LSV) using a potentiostat (Gamry G750, Gamry Instruments, NJ, USA) at a scan rate of 1mV/s from 0 mV to open circuit potential in the forward and reverse directions. The cathode was used as the working electrode, and the anode as the counter electrode and as the reference electrode.

3.7.4 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) was performed using a

Gamry potentiostat (Gamry G750, Gamry Instruments, NJ, USA) to measure total internal resistance utilizing the anode as the working electrode, and the cathode as the counter electrode and reference electrode.

3.7.5 Determination of Substrate Removal and Coulombic Efficiency

Chemical Oxygen Demand (COD) is a measure of the organic substrate concentration in the sample under analysis. COD removal efficiency was calculated using the equation below:

$$COD\ \% = \frac{Initial\ COD - Final\ COD}{Initial\ COD} \times 100\%$$

Coulombic efficiency (CE) is the ratio of the number of coulombs recovered as electric current to the ideal number of coulombs that should be obtained substrate. The coulombic efficiency was calculated by the ratio of total coulombs actually transferred to the anode from the substrate, to maximum possible coulombs if all substrate removal produced current. The total coulombs obtained is determined by integrating the current over time

The CE for a fed-batch configuration is calculated by:

$$CE = \frac{M \int_0^{t_b} I\ dt}{Fbv_{an}\Delta COD}$$

Where M is the molar mass of diatomic oxygen, F is Faradays' constant, ΔCOD is the difference in COD concentrations over a single cycle, t_b is the duration for the cycle, b is the stoichiometric ratio of electrons to oxygen (b=4), v_{An} is anode liquid volume and I is the total current generated (Logan et al., 2006).

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Characteristics of Electrode Materials

Table 2 Properties of Electrode Materials

Parameter	Biochar	Petroleum Coke
Volatile Matter	71.40 ± 10.71%	70.20 ± 14.04%
Ash Content	2.80 ± 0.39%	2.50 ± 0.3 %
Moisture Content	5.60 ± 0.84%	5.20 ± 0.78%
Fixed Carbon Content	20.90 ± 4.18%	20.50 ± 4.31%
Specific Surface Area	330.95 ± 17.74 m^2/g	0.7167 ± 0.001 m^2/g

Proximate analysis of both biochar and petroleum coke showed similar results as can be seen in the table above. Both samples showed similar amounts of fixed carbon content (20.90% for biochar and 20.50% for petroleum coke) which indicates the possible formation of graphitic layers within the carbon structure contributing to the electrical conductivity of the electrode. However, both samples show similarly high content of volatile matter (71.40% for biochar and 70.20% for petroleum coke) which is indicative of the presence of volatile matter on the surface of the electrode which would result in the interference of the electron transfer between bacteria.

BET surface area results showed that petroleum coke had a very low specific surface area. This indicates a very small surface area available for biofilm fixation and growth compared to biochar which had a specific surface area several orders larger than that of petroleum coke. Anodes within MFCs require large surface area for biofilm attachment needed for direct electron transfer; the results for specific surface area indicate that biochar would be more suitable as an MFC anode.

Scanning Electron Microscopy showed that the surface structure of biochar had a rough, non-uniform surface with very little crystal-like deposits; this is suitable

for biofilm adhesion. In Figure 6 below, a large number of pores can be seen in the surface of the biochar sample. The surface morphology of petroleum coke as seen in Figure 7, is smooth and uniform with presence of some pores. This is an indicator that bacterial attachment and stable biofilm formation on the surface of petroleum coke will be limited.

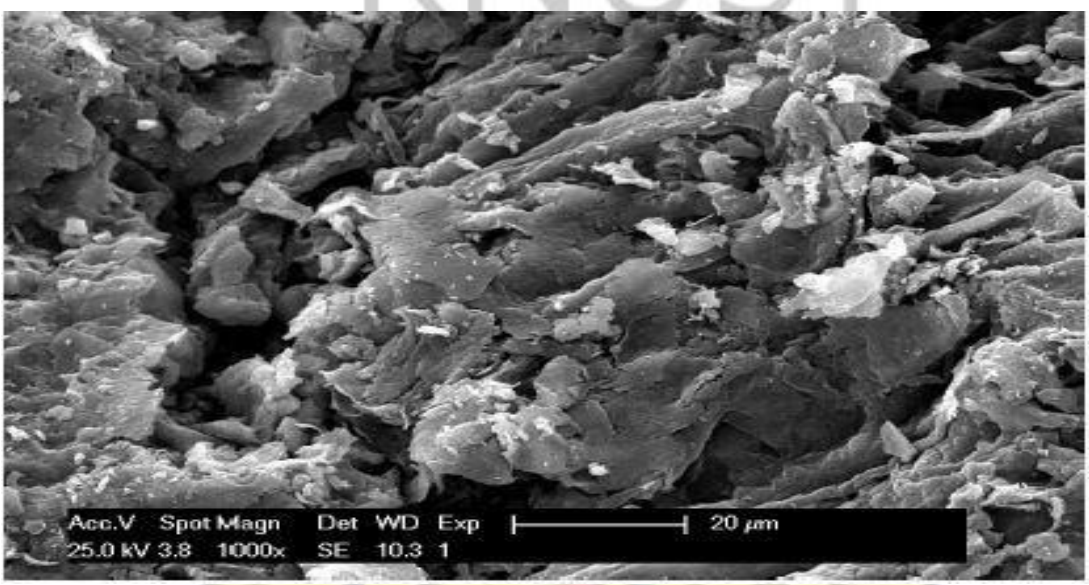

Figure 6: SEM Images of Biochar Surface

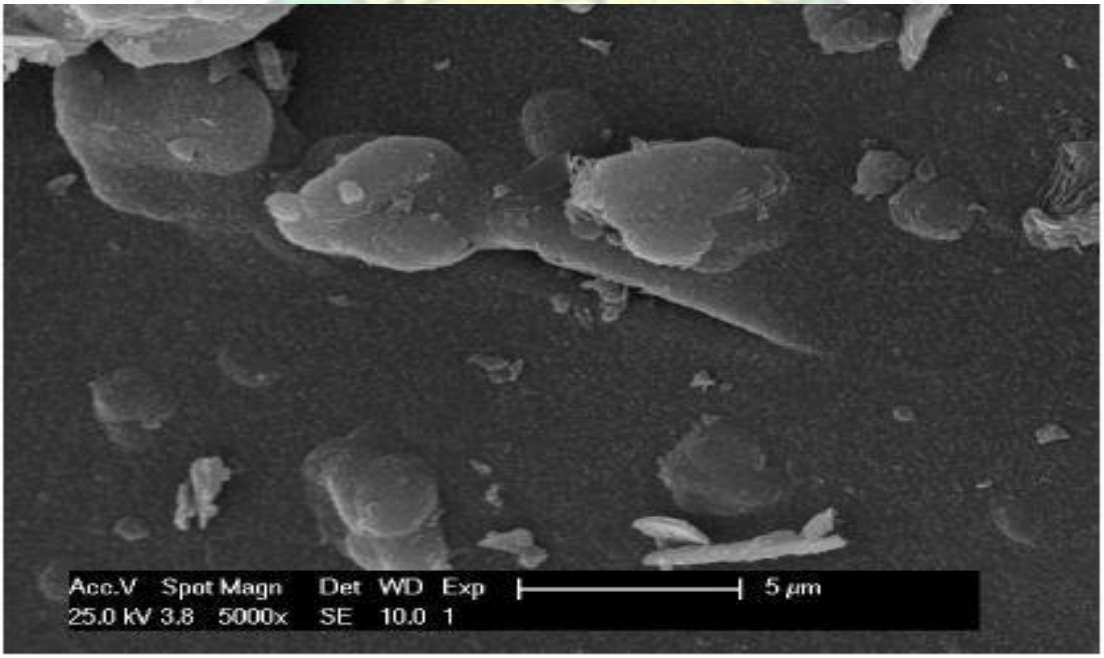

Figure 7: SEM Images of Petroleum Coke Surface

4.2 Inocula Testing and Microbial Analysis

The activity of electrogenic bacteria is central to the operation of an MFC. It is therefore necessary that the MFC is inoculated with bacteria. During inoculation electrochemically active biofilm is formed in the anode for electron transfer. In some MFC experiments, electrogenic bacteria are isolated from different sources, cultured and then introduced into the system. In Other studies, inoculation is achieved by running the MFC on the wastewater to be studied. The electrogenic bacteria within the wastewater develop a biofilm on the surface of the anode and the system is inoculated. Due to the fact that two sources of industrial wastewater are to be used in this study it was necessary that the best inoculum was identified and used for the rest of the experiments. Brewery wastewater and abattoir wastewater were the chosen sources of inocula in the study initially. However, both sources during two cycles of inoculation could not achieve a closed circuit voltage higher than 50mV which is considered the acceptable minimum in MFC research. A third inoculum was identified; anaerobic sludge.

During the period of inoculation the voltage-time profile of each MFC was observed to identify the best performing source. The voltage-time profiles of each source can be seen in Figure 9 for the second cycle of inoculation. The maximum voltage observed for both cycles was 616.39 mV for anaerobic sludge, 48.308 mV for brewery wastewater, and 42.162 mV for abattoir wastewater.

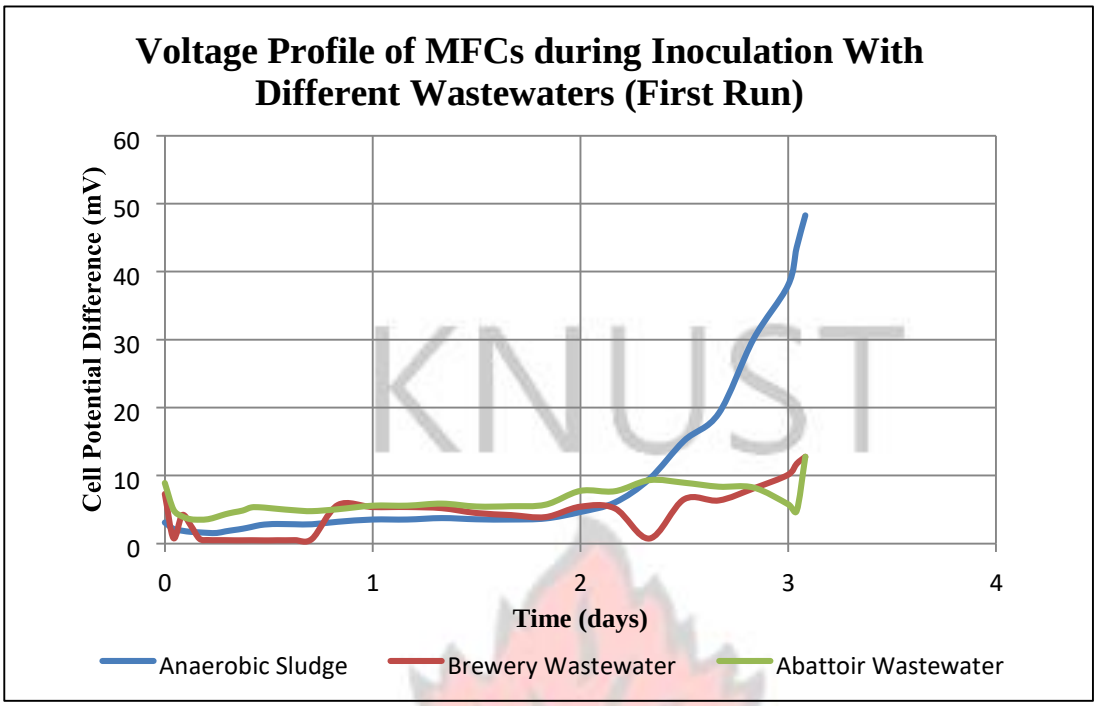

Figure 8: Voltage Profile of MFCs during Inoculation with Different Wastewaters (First Run)

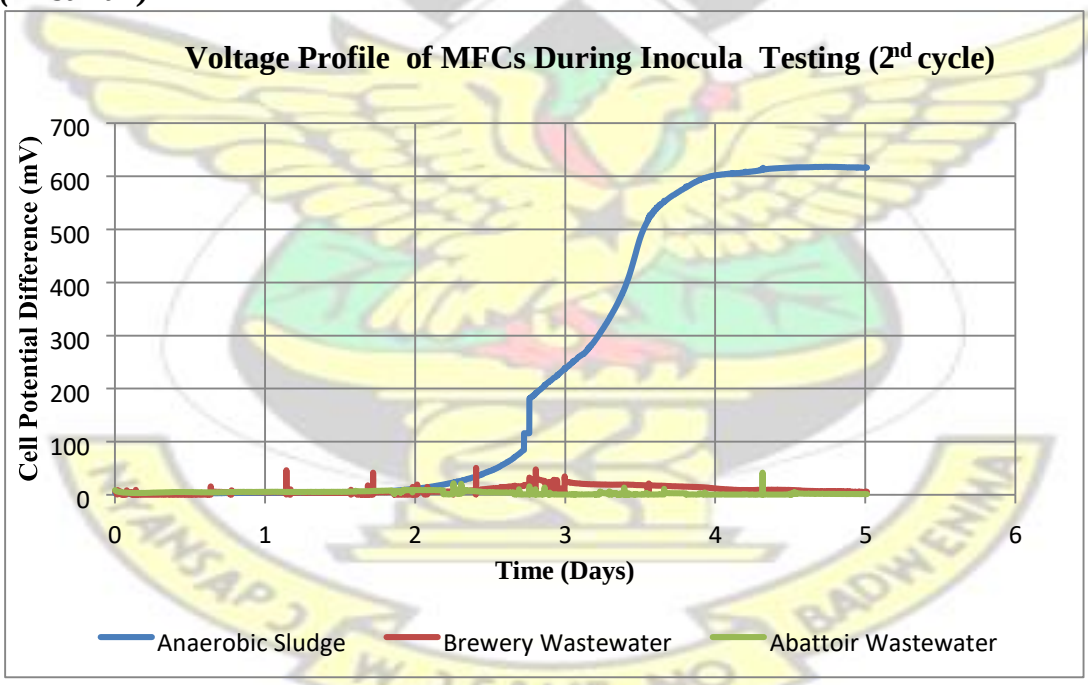

Figure 9: Voltage Profile of MFCs During Inoculums Testing (2nd cycle)

Scanning electron microscopy was performed on the anodes after inocula testing. The results conformed to the data observed in the voltage-time profiles of the

two cycles. Figure 10 is the control image of carbon paper before inoculation. Figure 11 and Figure 12 show poor biofilm formation on the anode for both brewery wastewater and abattoir wastewater corresponding to their low voltages. Figure 13 shows a good biofilm formed on the surface of the anode for anaerobic sludge corresponding to larger voltage observed.

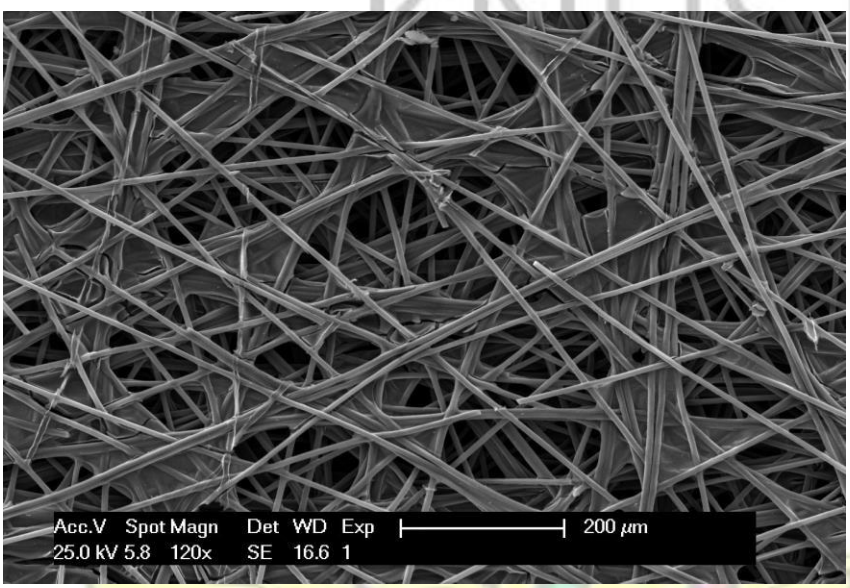

Figure 10: Control SEM Image of Carbon Paper Electrode

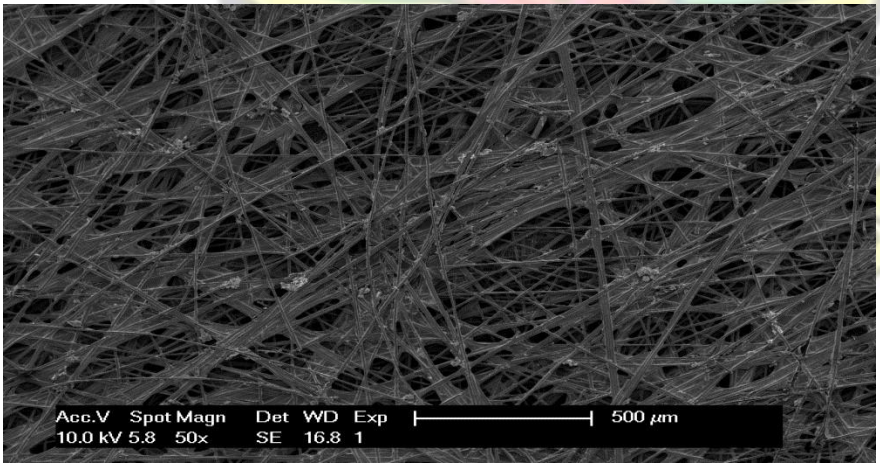

Figure 11: SEM Image of Biofilm Formation during Inoculation with Brewery

Wastewater

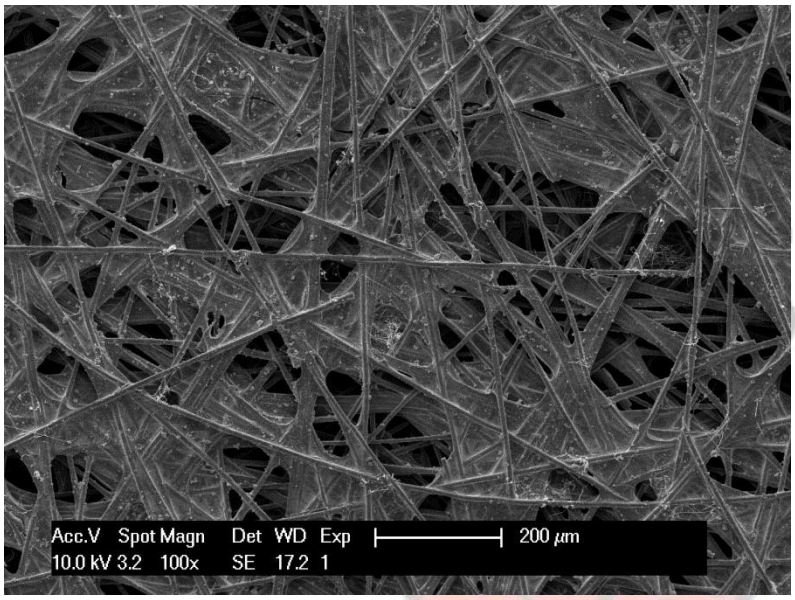

Figure 12: SEM Image of Biofilm Formation during Inoculation with Abattoir Wastewater

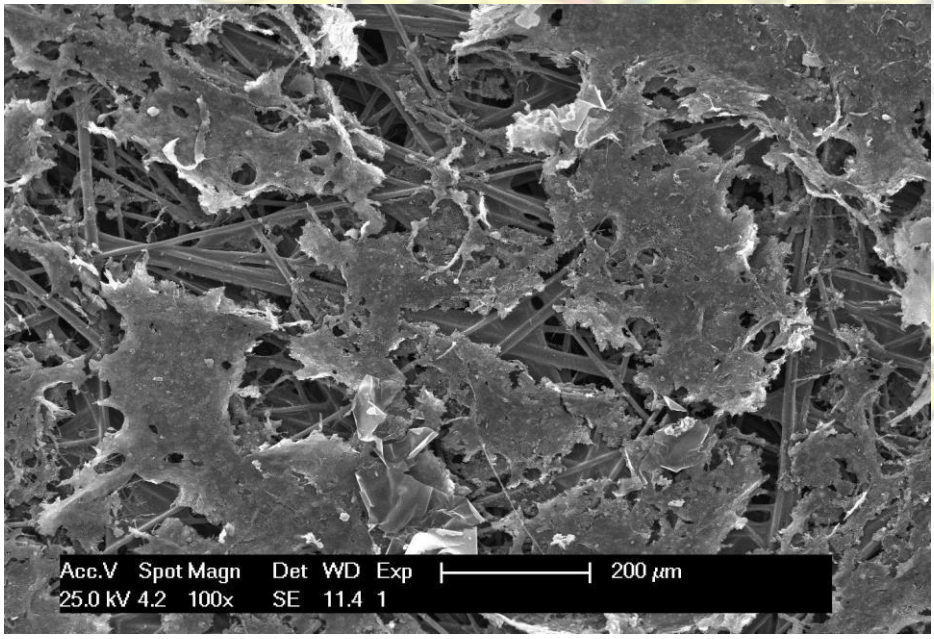

Figure 13: SEM Image of Biofilm Formation during Inoculation with Anaerobic Sludge

At the end of inoculation with anaerobic sludge the anodic biofilm formed on the surface of the electrode was sampled for analysis. The DGGE gene bank matches are in Table 3. The results were compared to marker containing of nine known bacterial species obtained from an existing biofilm. This was utilised as a standard to help identify bacteria present in biofilm samples from anaerobic sludge Microbial fuel cell inoculations. The bacteria identified as present in the biofilm formed from anaerobic sludge included *Shigella flexneri, Eubacterium tortuosum, Clostridium beijerinckii*. None of the bacteria identified are yet known for electrogenic behaviour. It is possible that the electrogenic bacteria present within the biofilm obtained from the anode inoculated with anaerobic sludge is absent in the marker for the reference biofilm, this is because newer species of electrogenic bacteria are constantly being identified in MFC research.

Table 3: Gene bank matches for samples tested

Sample	Gene Bank Match	Species Characteristics
Carbon Paper Inoculated with anaerobic sludge	*Shigella flexneri*	Facultative anaerobe which causes diarrhoea in humans
	Eubacterium tortuosum	Strict anaerobe found in human intestine

	Clostridium beijerinckii	Strict anaerobe producing a number of products.

Table 4: Summary of Inoculation Results

Inoculum	Cycle	Length of Cycle, days	Maximum Voltage, mV
Abattoir Wastewater	1	3	12
	2	5	42.162
Anaerobic Sludge	1	3	48
	2	5	616.39
Brewery Wastewater	1	3	12
	2	5	48.308

4.3 Inoculation of Electrode Materials

Prior to the testing of the performance of biochar from palm kernel shells and petroleum coke granules as electrode materials for MFCs, the materials are required to be inoculated. The selected electrode materials were inoculated with anaerobic sludge which performed better than the other inoculums tested. Biochar and petroleum granules were packed into the anodic chamber of the MFCs to a volume of 100ml. The granules were held together by a plastic mesh to maintain good inter-granular contact. A stain-less steel rod was used as a charge collector.

The inoculation of Carbon Paper yielded a maximum voltage of 535.063 mV whereas that of biochar granules made from palm kernel shells yielded a maximum voltage of 430mV and that of coke granules yielded a maximum voltage 45.373mV corresponding to a power density of 0.01Wm^{-3}.The voltage profile of the inoculation

of biochar and carbon paper both showed a steady rise to their maximum voltages indicative of steady biofilm growth and acclimation followed by a decline afterwards as a result of substrate depletion. However, the voltage profile of coke granules showed many fluctuations and no signs of steady biofilm formation and acclimation. The fluctuations indicate that the surface of the electrode was unsuitable for biofilm fixation resulting in constant loss of contact with the surface and reattachment to the surface of the electrode. The low maximum voltage is as a result of the small specific surface area available for electron transfer through direct contact between biofilm and electrode surface. Figure 10 shows the voltage profiles of each electrode during inoculation.

Inoculation of biochar and carbon paper was successful as shown by the voltages obtained seen in Figure 14. The inoculation of coke granules was determine to be a failure to the very closed circuit potential produced during operation. The significant amount of closed circuit voltage produced by the biochar and carbon paper was because of the proper development a biofilm on the electrode surface.

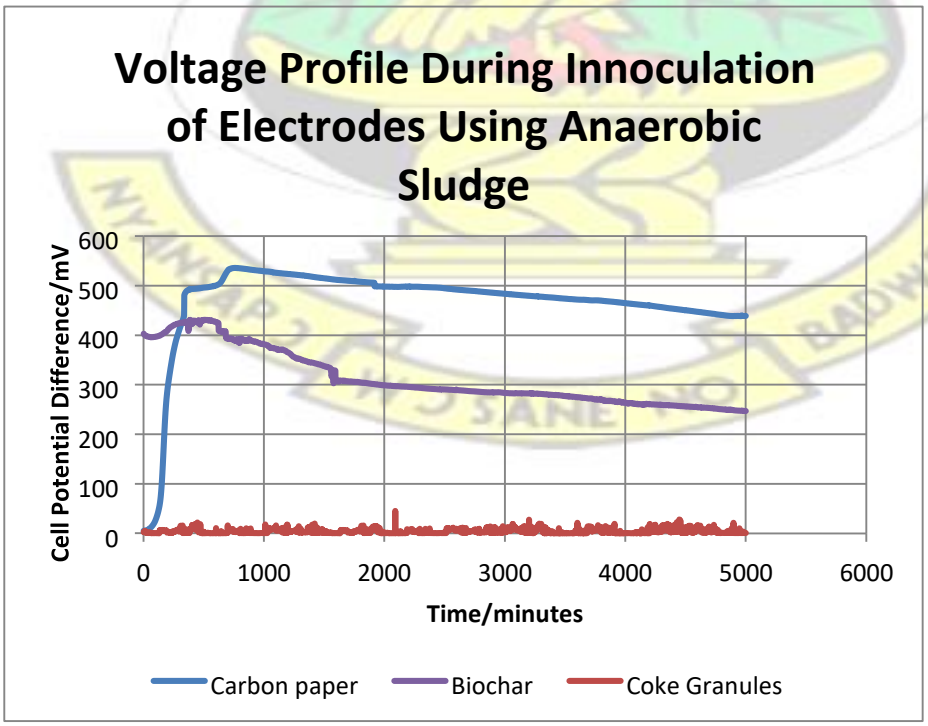

Figure 14: Voltage-Time Profile during Electrode Inoculation

4.4 Electrode Performance: Voltage Profile, Power Generation, Impedance and Substrate Removal

4.4.1 Voltage Profiles

In operating MFCs in a fed batch mode it is required that reproducible cycles of power generation be obtained over at least three consecutive fed batch cycles (each cycle must show the same peak voltage). When the MFC system fails to demonstrate reproducibility in this manner it then means that the reactor is not sufficiently acclimated for stable power generation. Electrochemical tests were performed after acclimation for stable power generation was achieved. Figure 15 shows the voltage profile of 3 cycles for each electrode running on a prepared acetate medium. Carbon Paper showed the largest peak voltage of about 530 mV and biochar had peak voltage of about 340 mV. Coke granules did not show any significant power generation or reproducible cycles of similar peak voltage. Fig 15 shows the 3 cycles of similar performance for the coke granules. However, these cycles were not consecutive cycles neither do they show similar peak voltage. The reproducible peak voltage is required in order to perform electrochemical tests since they must be performed when the MFC has reached its peak voltage. This is because at peak voltage the system has acclimatized and there are also minimum losses due substrate depletion.

Figure 16 shows the voltage profile of 3 cycles for each electrode running on a prepared brewery wastewater. Carbon Paper showed the largest peak voltage of about 450mV and biochar had peak voltage of about 360 mV. Similar to its operation during inoculation and its operations using acetate medium and brewery wastewater coke granules did not show any significant power generation or reproducible cycles

of similar peak voltage. Figure 16 shows the 3 cycles of similar performance for the coke granules. However, these cycles were not consecutive cycles neither do they show similar peak voltage.

Figure 17 shows the voltage profile of 3 cycles for each electrode running on a prepared abattoir wastewater. Carbon Paper showed the largest peak voltage of about 450mV mV and biochar had peak voltage of about 250 mV. Similar to its operation during inoculation and operations using acetate medium, brewery wastewater and abattoir wastewater, coke granules did not show any significant power generation or reproducible cycles of similar peak voltage. Figure 17 shows the 3 cycles of similar performance for the coke granules. However, these cycles were not consecutive cycles neither do they show similar peak voltage.

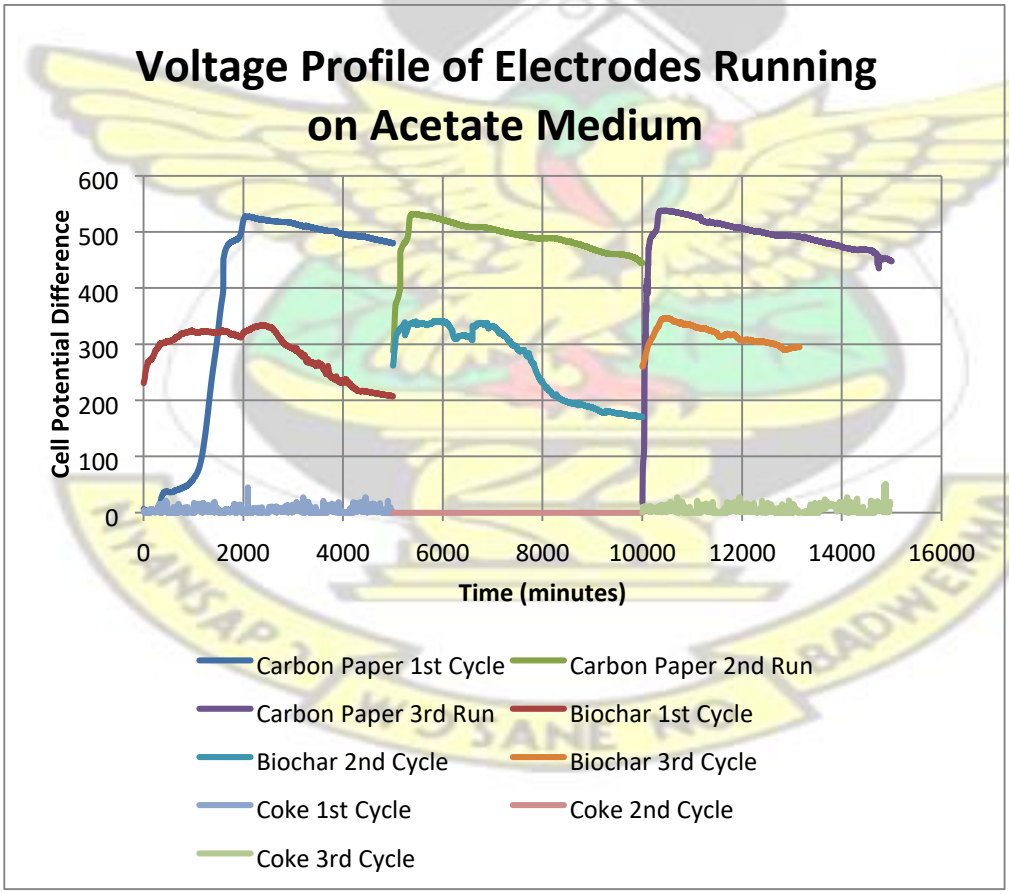

Figure 15: Voltage Profile of Electrodes Running on Acetate Medium

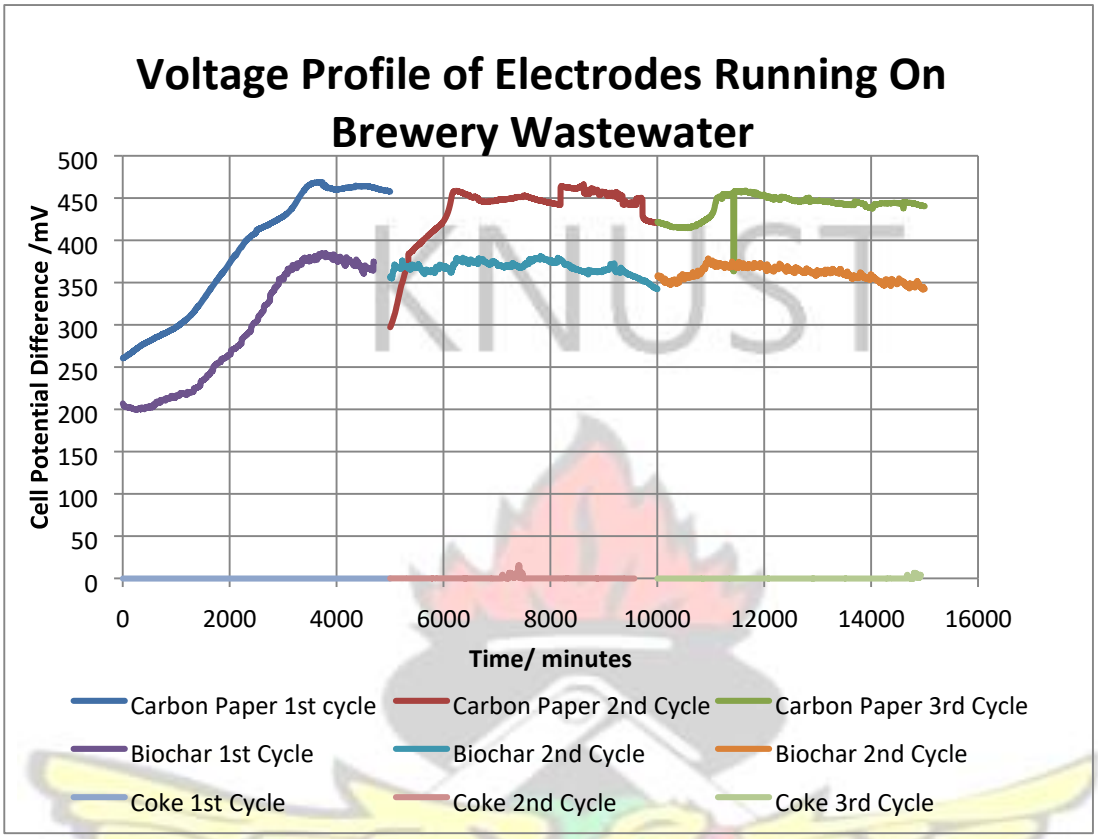

Figure 16: Voltage Profile of Electrodes Running On Brewery Wastewater

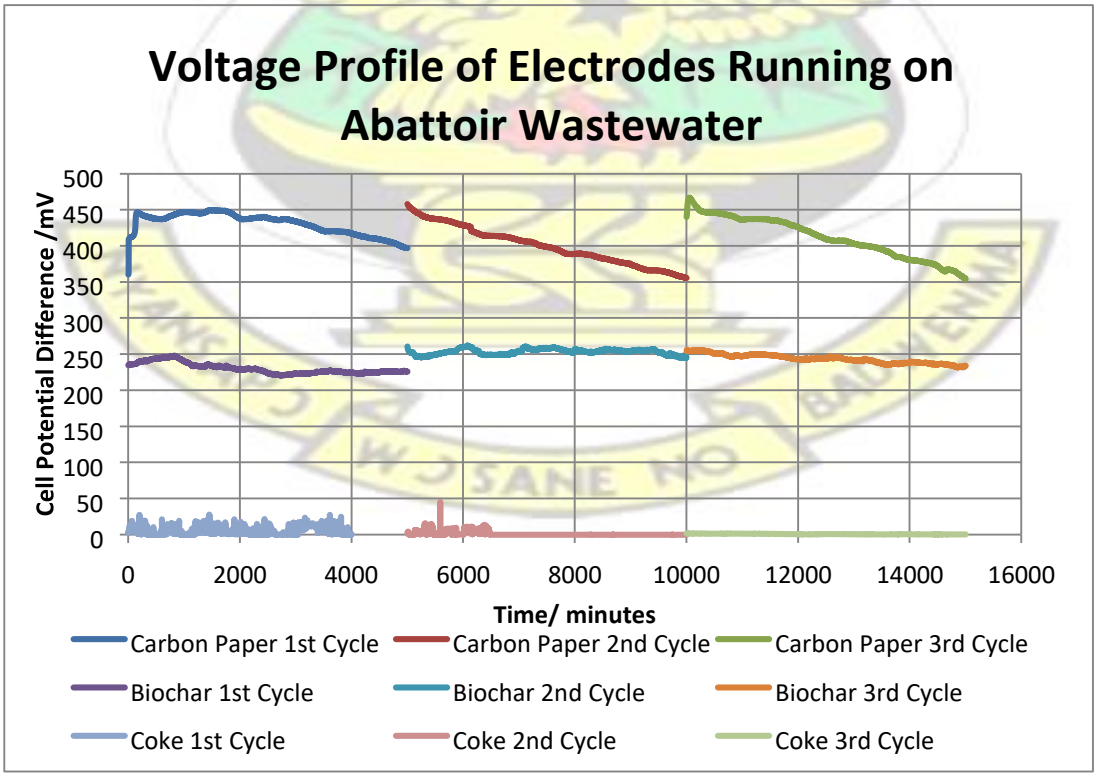

Figure 17: Voltage Profile of Electrodes Running on Abattoir Wastewater

4.4.2 Power Density and Coulombic Efficiency

Table 5: Summary of Power Density Results

	Carbon Paper	Biochar
Acetate Medium	1.76 ± 0.09 Wm^{-3}	0.85 ± 0.023 Wm-3
Brewery Wastewater	1.3967± 0.34 Wm-3	0.78 ± 0.045 Wm-3
Abattoir Wastewater	1.35±0.02 Wm-3	0.54 ± 0.01 Wm-3

Linear sweep voltammetry was used to obtain power density curves of the MFC. Power density curves of MFCs are typically parabolic and the maximum power density achievable by the MFC is that obtained at the apex of the parabola. Figure 18 shows the power density curves characteristic for each electrode running on acetate medium. The values of power density were normalized by anode liquid volume. The results of the power density curves corresponded with those of the maximum power density. Carbon paper in brewery wastewater achieved a Coulombic efficiency of 3.04 ± 0.001 % while that of biochar was 1.44 ± 0.003%. Using abattoir wastewater, that of carbon paper was 3.07 ± 0.01% and that of biochar was 2.97 ± 0.02 %. The electrodes which were able to convert substrate to electricity more efficiently achieved higher power densities.

The maximum power density values obtained for each electrode followed the pattern of the peak voltages; carbon paper showed the largest maximum power density of about 1.76 ± 0.09 Wm^{-3} followed by biochar with a maximum power density of about 0.85 ± 0.023 Wm^{-3} when using acetate medium. When using brewery wastewater carbon paper showed the largest maximum power density of about 1.3967±0.34 Wm^{-3} followed by biochar with a maximum power density of about 0.78 ± 0.045 Wm^{-3}. Carbon paper showed the largest maximum power density of about 1.35±0.02 Wm^{-3} followed by biochar with a maximum power density of about 0.54 ± 0.01 Wm^{-3} when using abattoir wastewater.

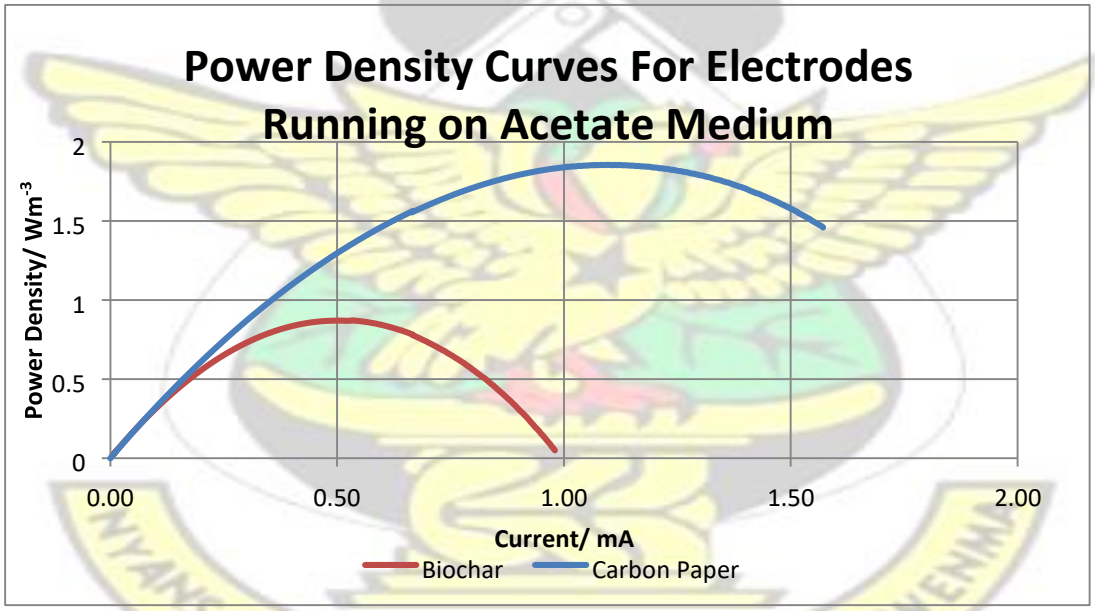

Figure 18: Power Density Curves for Electrodes Running on Acetate Medium

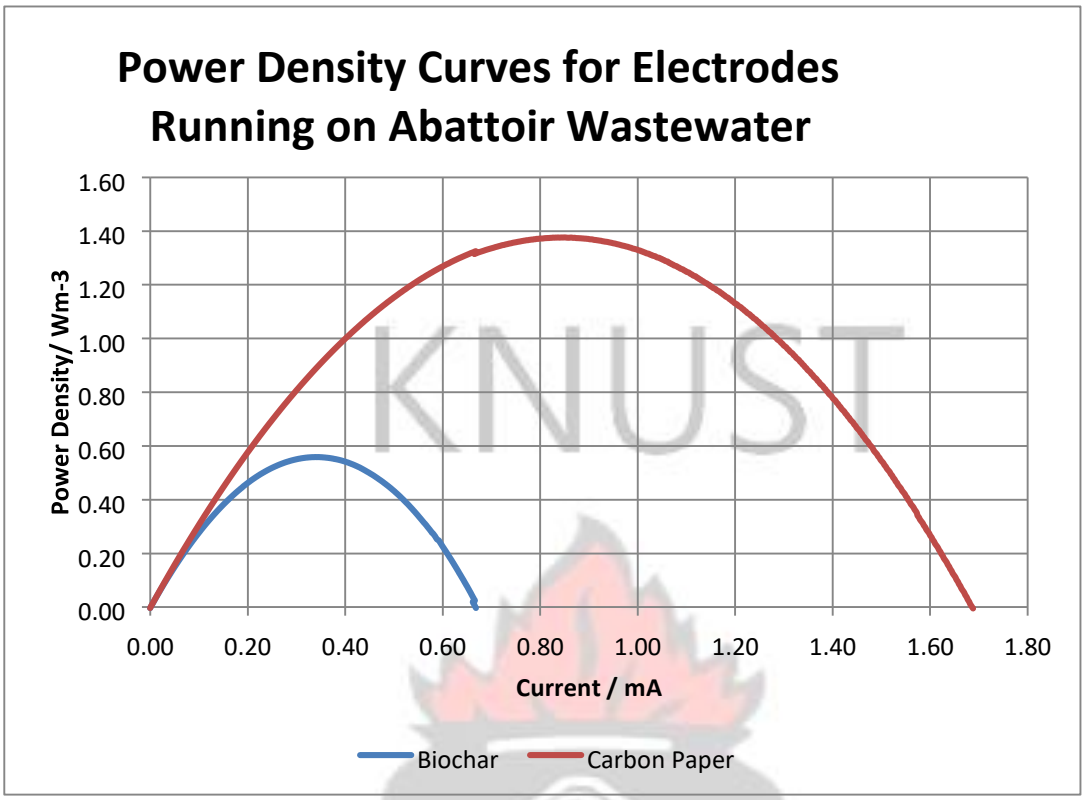

Figure 19: Power Density Curves for Electrodes Running on Abattoir Wastewater

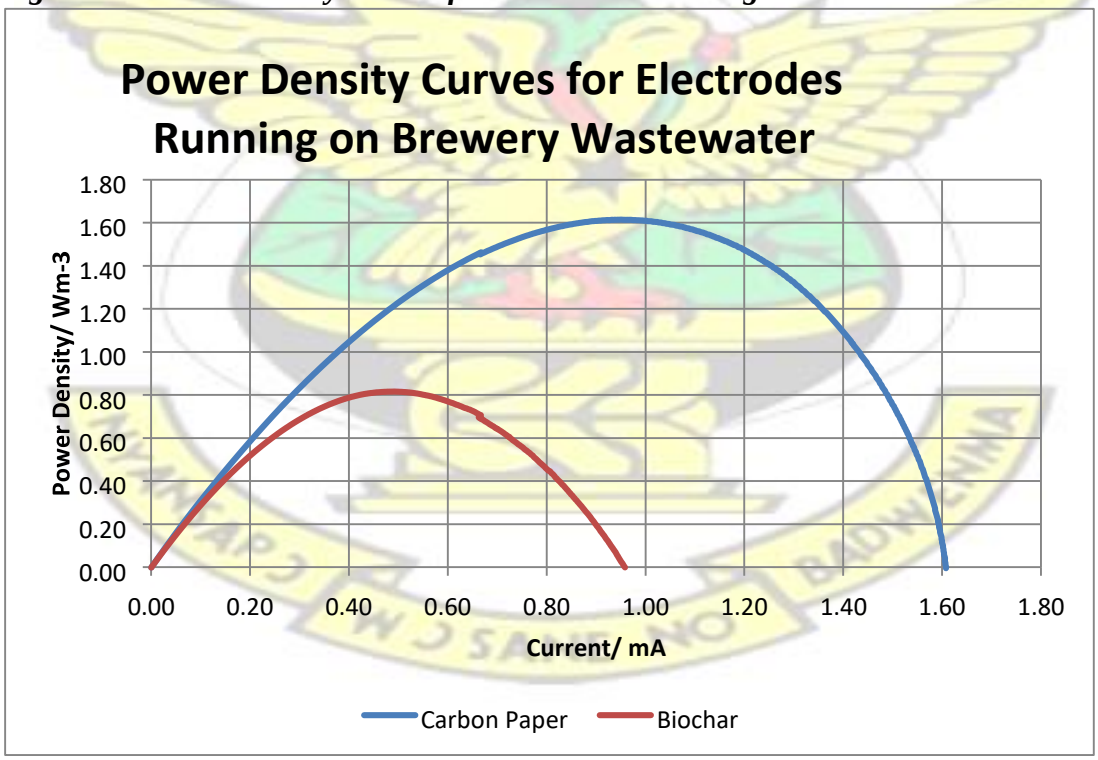

Figure 20: Power Density Curves for Electrodes Running on Brewery Wastewater

Though carbon paper achieved higher maximum power densities its current price

range of about US$ 1000 per square meter (Zhang et al, 2010) make its output cost of about US$ 3,461.41 per watt much higher than that of biochar which is estimated to be in the price range of US$ 51 to US$ 381 per metric tonne (Meyer et al, 2011) making its output cost about US$ 144.85 per watt.

4.4.3 Cell Impedance

Table 6: Summary of Results for Ohmic Resistance

	Carbon Paper	**Biochar**
Acetate Medium	178.17± 1.70 Ω	192.77 ± 0.25 Ω
Brewery Wastewater	174.97 ± 0.58 Ω	146.27 ± 1.67 Ω
Abattoir Wastewater	264.57 ± 0.152 Ω	288.5 ± 0.36 Ω

Table 7: Summary of Results for Internal Resistance

	Carbon Paper	**Biochar**
Acetate Medium	260.4 ±0.25 Ω	487± 38.88 Ω
Brewery Wastewater	293.97 ± 18.60 Ω	459.87 ± 2.27 Ω
Abattoir Wastewater	399.8 ± 2.17 Ω	789.17 ± 0.99 Ω

Electrochemical impedance spectroscopy was performed on the MFCs once they achieved peak voltage. The data of the impedance response of the system was

used in drawing a Nyquist plot which is a complex plane showing the imaginary impedance (indicative of the capacitive and inductive character of the cell) and the real impedance response of MFC. Figure 21 show the Nyquist plot for biochar running on acetate medium and carbon paper running on acetate medium respectively. The ohmic resistance of each MFC was obtained from the Nyquist plot by determining the intercept on the real impedance axis (z real axis) of the plot.

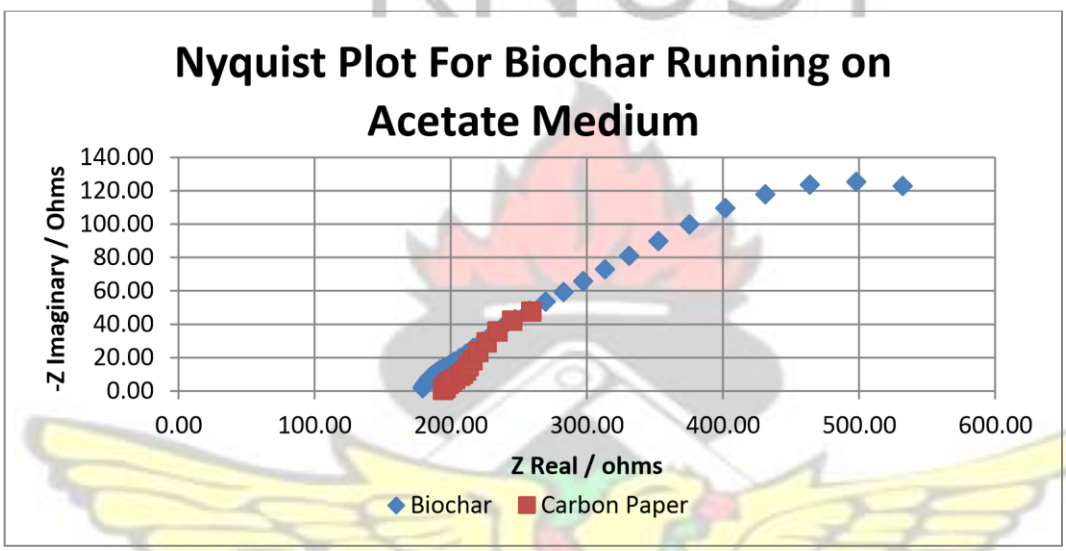

Figure 21: Nyquist Plot for Biochar Running on Acetate Medium

The total internal resistance of the cell was obtained by finding the real component of the last point of the Nyquist plot. Total internal resistance is made up of three components; the ohmic or solution resistance, charge transfer or kinetic resistance and the diffusion or mass transfer resistance. When acetate medium was used in the MFC the total internal resistance obtained by carbon paper was 260.4 ±0.25 Ω and that of biochar was 487± 38.88 Ω, more than double the internal resistance shown by carbon paper in the same medium. This corresponds to the maximum power density shown by carbon paper being more than double that of biochar in acetate medium. When brewery wastewater was used in the MFC a total internal resistance obtained by carbon paper was 293.97 ± 18.60 Ω and that of biochar was 459.87 ± 2.27 Ω. When abattoir

wastewater was used in the MFC a total internal resistance obtained by carbon paper was 399.8 ± 2.17 Ω and that of biochar was 789.17 ± 0.99 Ω.

The ohmic resistance is the resistance associated with electrons and ions transfer through the solution, electrodes, and separators. Since both the separators and solution remained the same in both experiments this implies that the contribution to the difference in ohmic resistance was as a result of the electrode materials used. Biochar showed an ohmic resistance of about 178.17± 1.70 Ω and carbon paper 192.77 ± 0.25 Ω when acetate medium was used. This implies that the biochar electrode showed a lower resistance to the conduction of electrons. This pattern was also observed when the MFCs were run on brewery wastewater, the MFC run with biochar showed a lower ohmic resistance of about 146.27 ± 1.67 Ω and that of carbon paper was 174.97 ± 0.58 Ω. However, when abattoir wastewater was used the biochar MFC showed a higher ohmic resistance of 288.5 ± 0.36 Ω and that of carbon paper was 264.57 ± 0.152 Ω. This is attributed to variations in the conductivity of biochar samples prepared. From the data it can be seen that when carbon paper was used the ohmic resistance obtained was about 66.57±7.26 % of the total internal resistance whereas when biochar was used as the anode the ohmic resistance was 36.50 ± 0.096 % of the total internal resistance. This implies that the large difference in the total internal resistance of the system when the different electrodes were used was mostly contributed by their differences in kinetic resistance and mass transfer kinetic resistance.

Charge transfer or activation resistance is the contribution to the total internal resistance associated with the different reactions happening at the electrodes and is often limited by the kinetics of the reactions taking place. The charge transfer resistance can be decreased by using catalysts or increasing surface area for reactions

(Hutchinson et al, 2011; Logan et al, 2006). The results from the Nyquist plot show that when using the biochar granules the surface area available for activity of bacteria on substrates was much lower than that of carbon paper.

Diffusion or concentration resistance encompasses diffusion of substrate to the anode, and protons and oxygen to the cathode and occurs when the rate of mass transport of a species to or from the electrode limits current production (Hutchinson et al, 2011; Logan et al, 2006). At the anode concentration losses are caused by either a limited discharge of oxidized or a limited supply of reduced species. In systems where there is no mixing concentration gradients may also arise in the bulk liquid (Logan et al, 2006). The differences in the diffusion resistances of the MFCs maybe as a result of the difference in electrode configuration with biochar's granular configuration providing more obstacles to the diffusion of species thus resulting in higher diffusion resistance and a higher overall internal resistance.

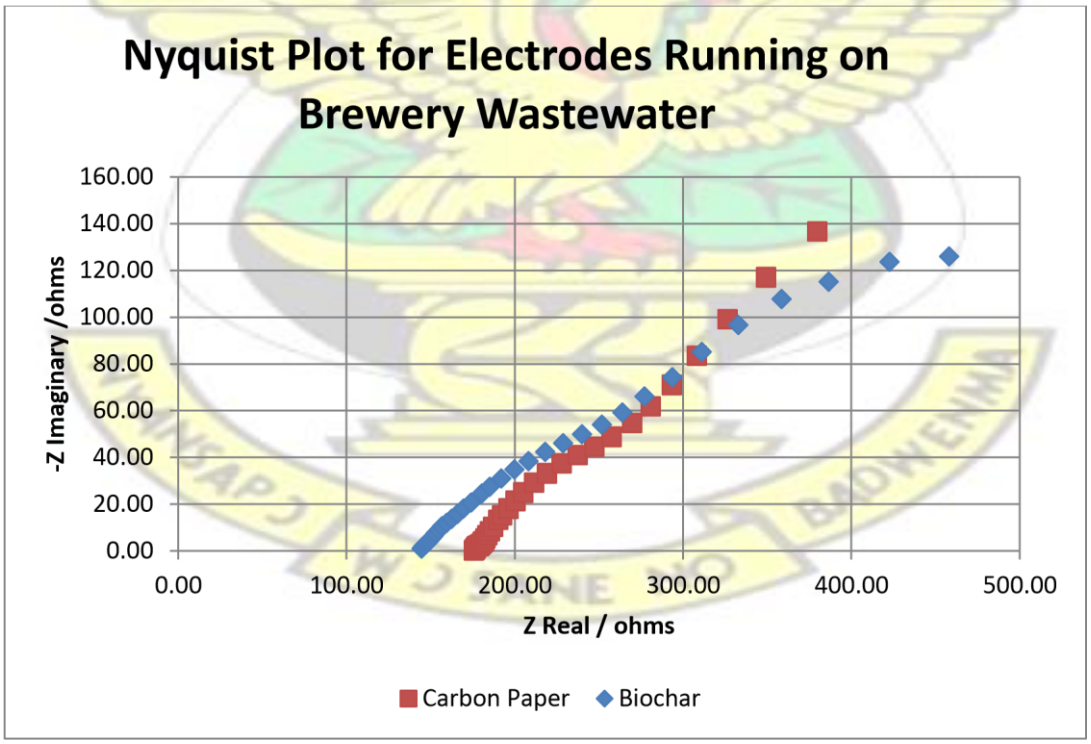

Figure 22: Nyquist Plot for Electrodes Running on Brewery Wastewater

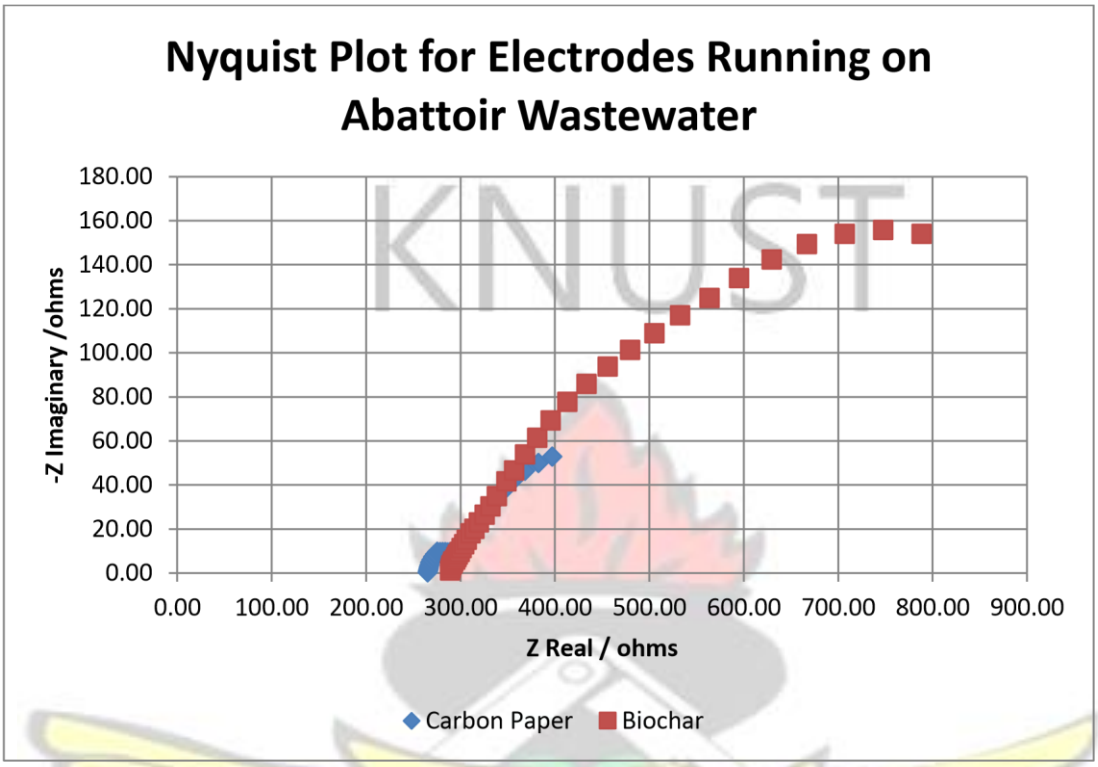

Figure 23: Nyquist Plot for Electrodes Running on Abattoir Wastewater

4.4.4 Treatment Efficiency

Since MFCs have been proposed as a method to treat wastewater it is therefore necessary to evaluate their treatment performance in terms of either biochemical oxygen demand (BOD), chemical oxygen demand (COD), or total organic carbon (TOC) removal (Logan et al, 2006). The wastewater treatment capabilities of the MFCs were determined by measuring the COD content of the wastewater before and after three cycles of equal length (6 days). This was performed after the MFCs had acclimated using the different wastewaters. When abattoir wastewater was used carbon paper achieved a higher COD removal efficiency of 39.65 ± 14.30 % at a rate of 320.476 ± 105.814 mg/day and that of biochar was 21.92 ± 7.13 % at a rate of 184.07 ± 61.84 mg/day. When brewery wastewater was used biochar had the higher

treatment efficiency of 59.19 ± 20.67% at a rate of 660.21 ± 270.18 mg/day and carbon paper had 36.41 ± 2.54 % at a rate of 418.47 ± 29.16 mg/day. When considering the average of the results of the treatment efficiencies using both industrial wastewaters, carbon paper had a treatment efficiency of 38.03 ± 8.54 % and biochar 40.55 ± 24.66 %. Carbon paper in brewery wastewater achieved a Coulombic efficiency of 3.04 ± 0.001 % while that of biochar was 1.44 ± 0.003%. Using abattoir wastewater, that of carbon paper was 3.07 ± 0.01% and that of biochar was 2.97 ± 0.02 %.

The Coulombic efficiency is diminished by utilization of alternate electron acceptors by the bacteria. Carbon paper achieved a higher coulombic efficiency because of its higher anode potential due to its lower total internal resistance making it more attractive than the alternate electron acceptors present within the anodic medium. It was also able to achieve higher treatment efficiency because of its larger specific surface area. However, the performance of biochar is comparable to carbon paper in terms of wastewater treatment.

CHAPTER FIVE: CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

Biochar made from palm kernel shells and petroleum coke granules were tested as electrode materials in microbial fuel cells. Biochar granules produced from palm kernel shells could produce a maximum power of up to 55% that of carbon paper and achieved treatment efficiencies comparable to the commonly used carbon paper. Electrochemical impedance spectroscopy results revealed that for biochar granules to achieve the power densities demonstrated by carbon paper improvements in its specific surface area would be required and an alternative electrode configuration other than the packed granules would be required.

Though the power densities obtained were significantly lower, biochar costs significantly less than carbon paper due to its feedstock and one-step manufacturing process. This makes biochar a suitable replacement for carbon paper. Also, biochar carries environmental benefits such as carbon sequestration potential, and its use as a soil amendment. However, more studies are needed to improve the manufacturing process of the biochar electrode in order to improve its performance.

Petroleum Coke is unsuitable as an electrode within the anode because of its smooth surface morphology, low specific surface area coupled with the presence of volatile matter which interferes with the electron transfer mechanism. As a result of this the system could not acclimate even after several cycles of operation.

5.2 Recommendations

The present study has identified that to improve upon the electrode performance of biochar, it is recommended that further research to identify alternative biomass feedstock for the production of biochar which would result in improved electrode properties such as increased conductivity, increased specific surface area and reduced volatile matter content. More studies are needed to improve the manufacturing process of the biochar electrode in order to improve its performance.

Limitations associated with petroleum coke granules were from its surface structure and its available surface area, these hindered biofilm formation and growth. It is recommended that a study into possible modifications to the surface structure be undertaken. Further carbonization and surface activation could be considered.

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APPENDICES APPENDIX A: **Supplementary Results for Sample Characterization APPENDIX A1:** Supplementary Results for Electrode Characterization

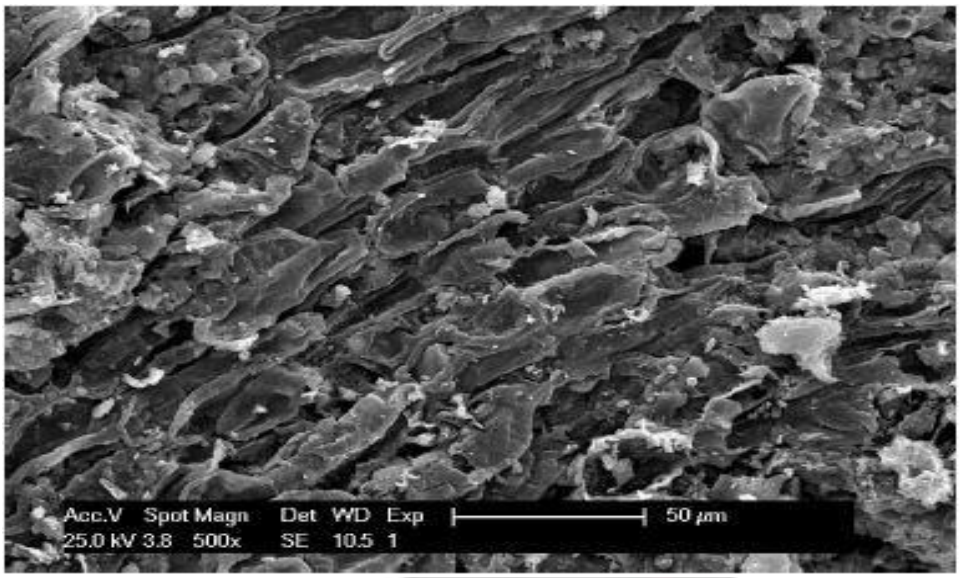

Figure A1.1: SEM control Image for Biochar

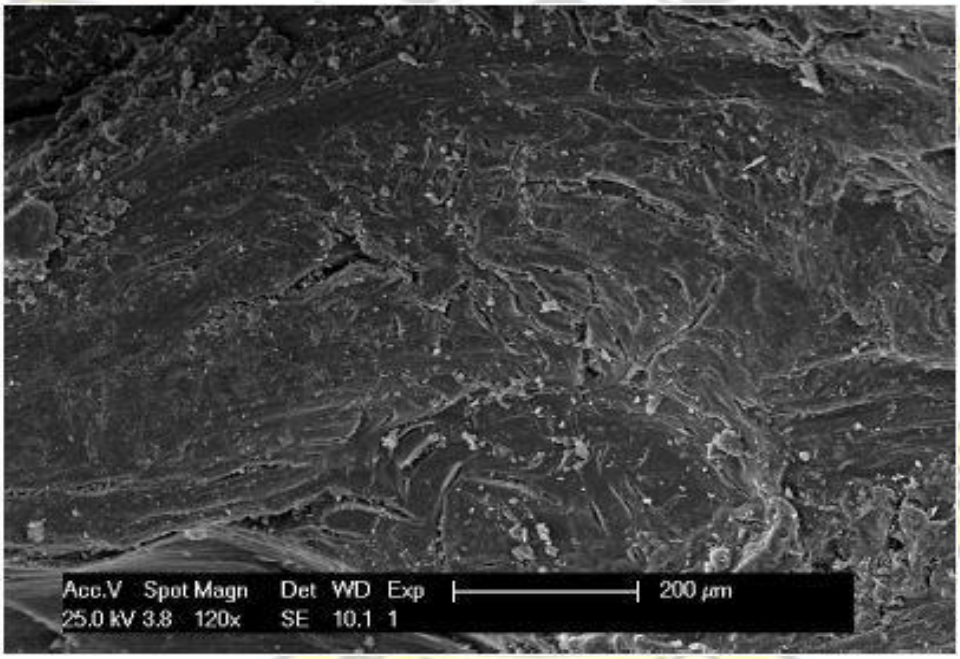

Figure A1.2: SEM control Image for Petroleum Coke

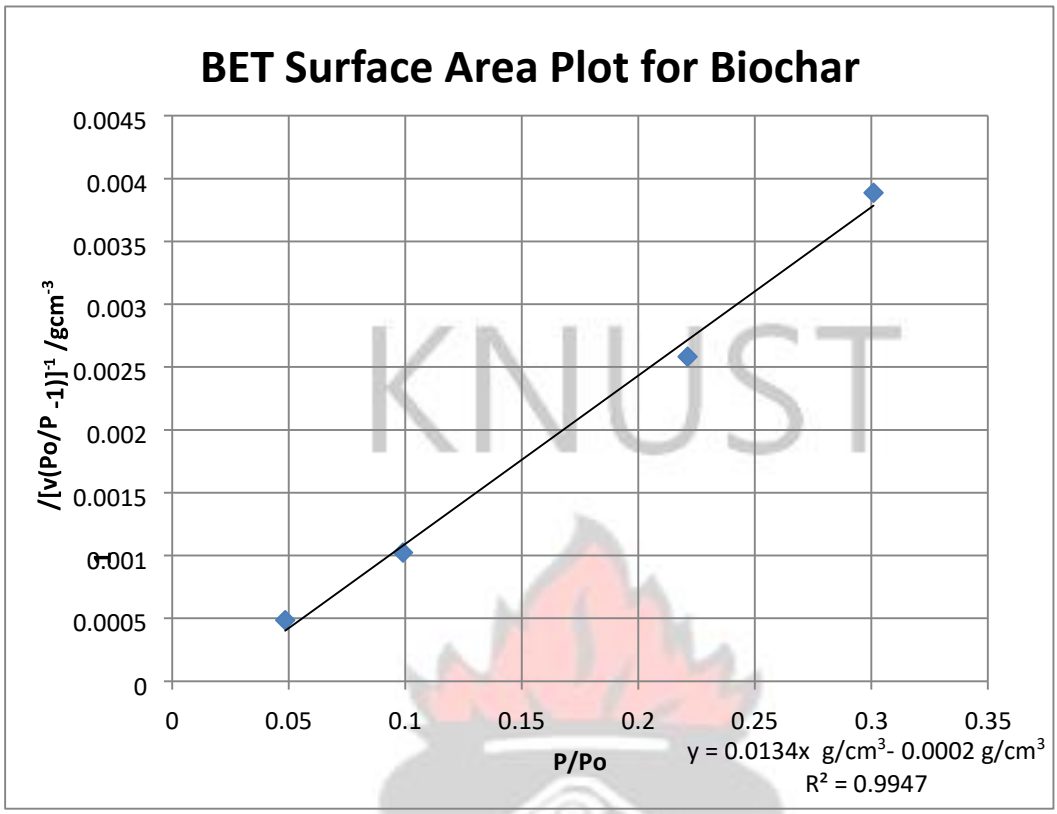

Figure A1.3: BET Surface Area Plot for Biochar

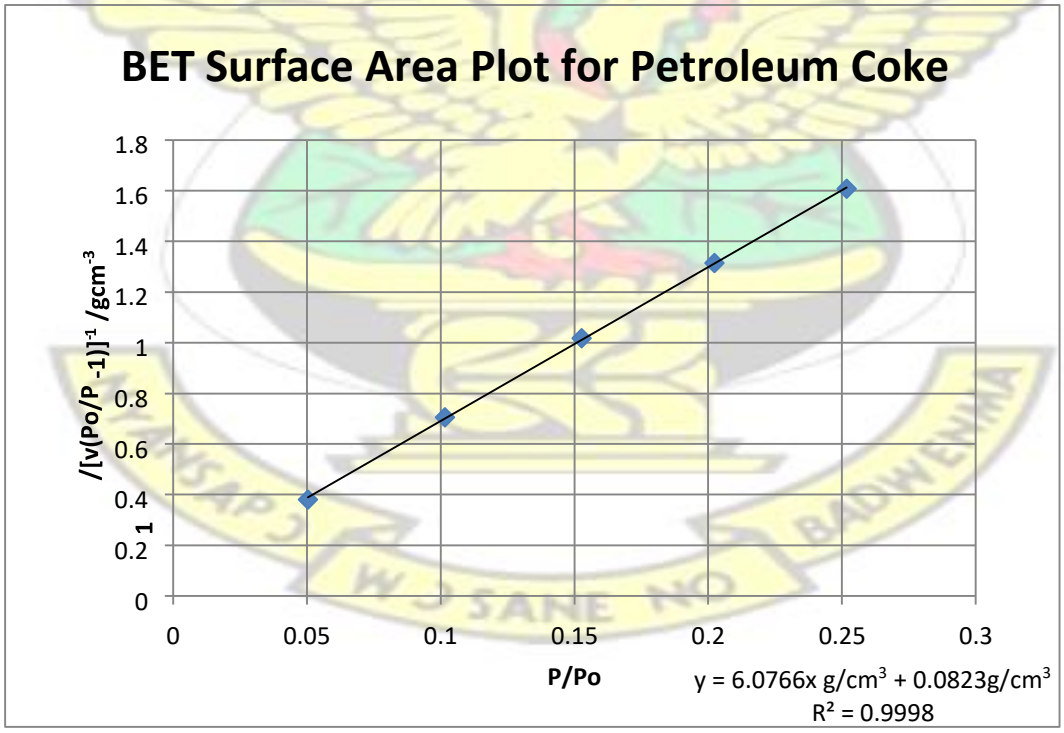

Figure A1.4: BET Surface Area Plot for Biochar APPENDIX A2: Results for Wastewater Characterization

Table A2.1: Results of Wastewater Characterization

Parameters	Brewery Wastewater	Abattoir Wastewater
Ph	4.62 ± 0.085	8.005 ± 0.49
COD/ mg/L	6575 ± 469.57	5296.67 ± 734.97
TDS/ mg/L	1197.67 ± 25.15	2109.75 ± 389.11
Conductivity/ µS/cm	1833.33 ± 29.57	3249 ± 593.98
Total Phosphorous/ mg/L	4.72 ± 1.02	8.7667 ± 3.93
Total Nitrogen/ mg/L	23.33 ± 5.13	128.5 ± 10.01
Ammonia/ mg/L	28.47 ±6.25	156.77±12.21
Nitrate/ mg/L	84.19 ± 11.74	552.59 ± 44.38
Salinity/ mg/L	0.9	2.2 ± 0.35

APPENDIX B: Supplementary Results for Electrode Performance Tests

APPENDIX B1: Supplementary Results for Power Generation

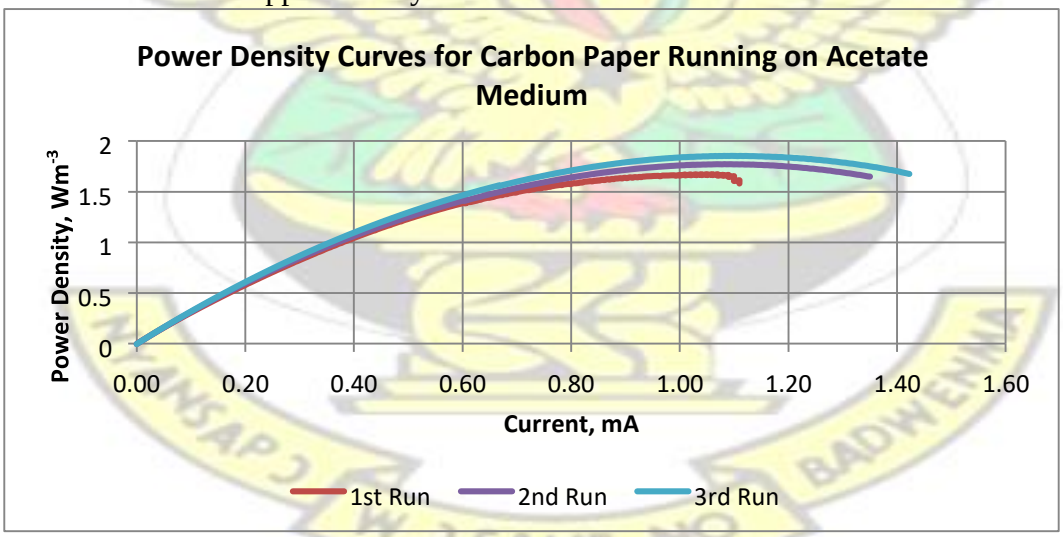

Figure B1.1: Power Density Curves for Carbon Paper Running on Acetate Medium

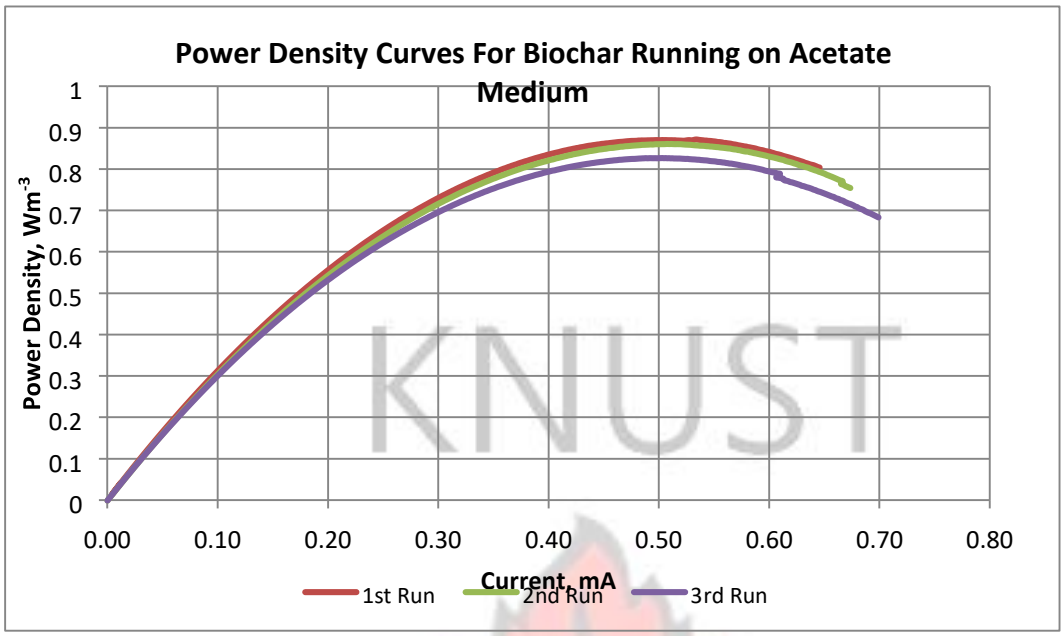

Figure B1.2: Power Density Curves for Biochar Running on Acetate Medium

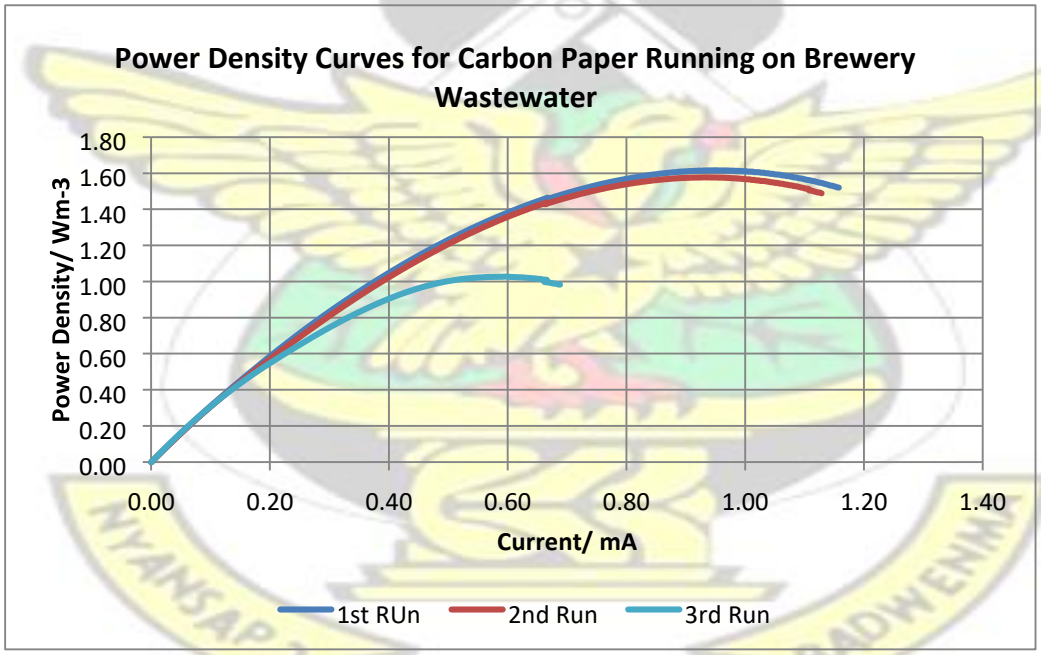

Figure B1.3: Power Density Curves for Carbon Paper Running on Brewery

Wastewater

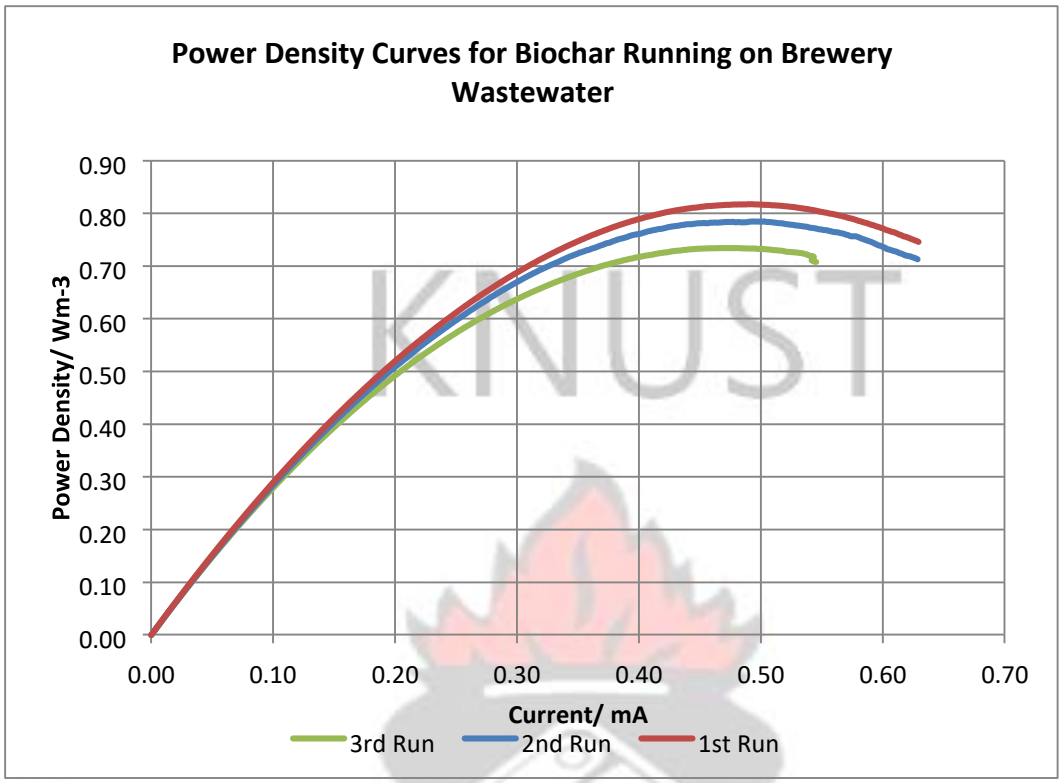

Figure B1.4: Power Density Curves for Biochar Running on Brewery Wastewater

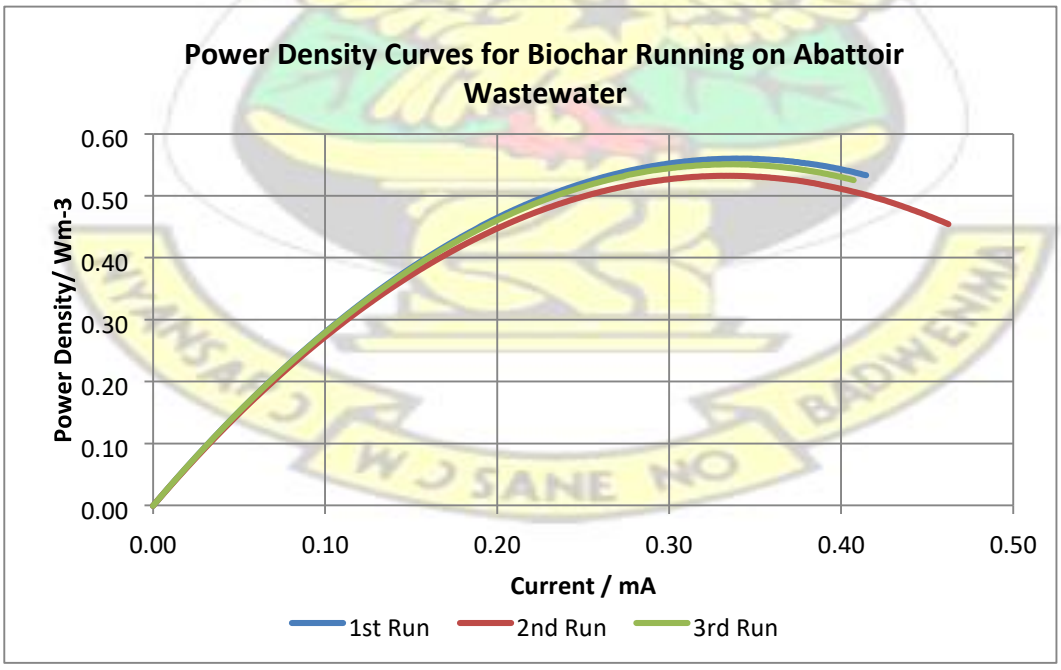

Figure B1.5: Power Density Curves for Biochar running on Abattoir Wastewater

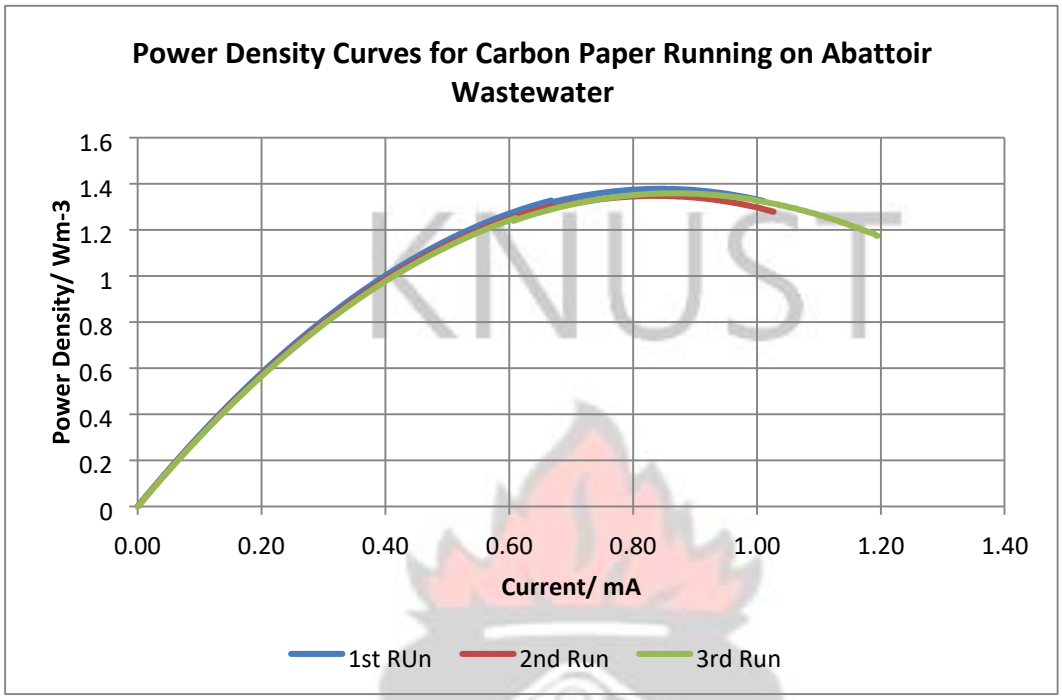

Figure B1.6: Power Density Curves for Carbon Paper Running on Abattoir Wastewater

Table B1.1: Power Density Curves Results for Carbon Paper

Run	Power Density / Wm^{-3}		
	Brewery Wastewater	Acetate Medium	Abattoir Wastewater
1	1.62	1.67	1.37
2	1.57	1.76	1.34
3	1	1.85	1.35

Average	1.40	1.76	1.35
Standard Deviation	0.34	0.09	0.02

Table B1.2: Power Density Curves Results for Carbon Paper

Run	Power Density / Wm^{-3}		
	Brewery Wastewater	Acetate Medium	Abattoir Wastewater
1	0.82	0.83	0.53
2	0.78	0.86	0.54
3	0.73	0.87	0.55
Average	0.78	0.85	0.54
Standard Deviation	0.05	0.021	0.01

APPENDIX B2 Supplementary Results for Cell Impedances

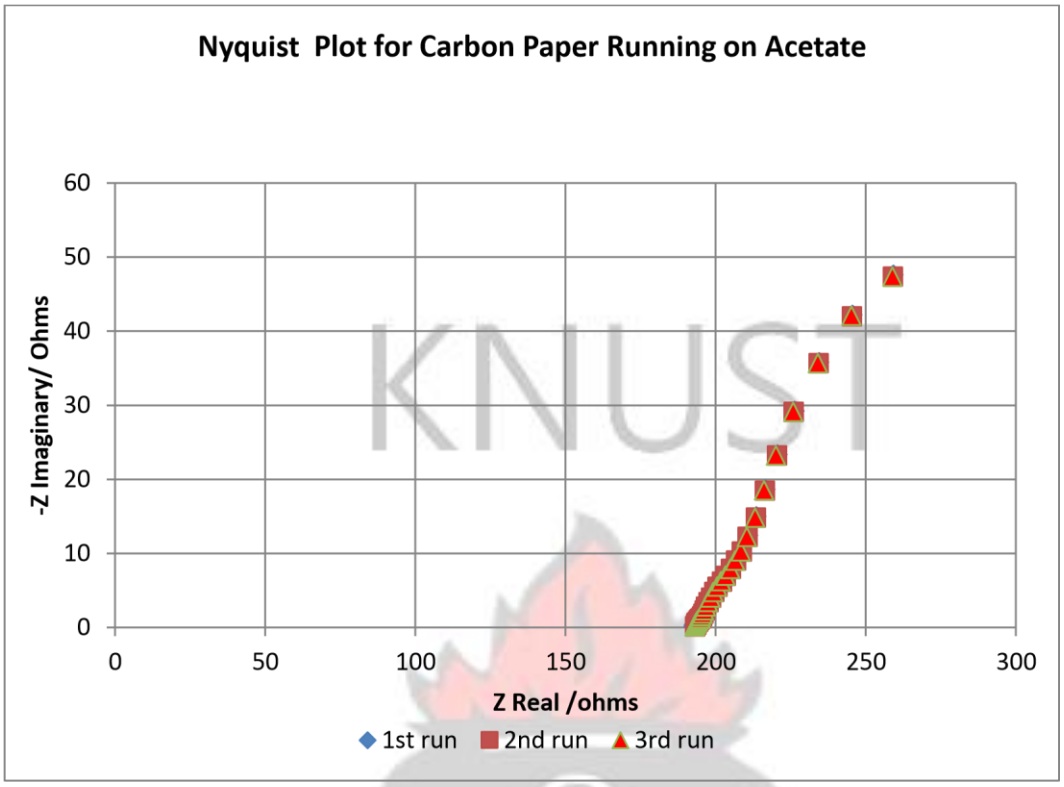

Figure B2.1: Nyquist Plot for Carbon Paper Running on Acetate

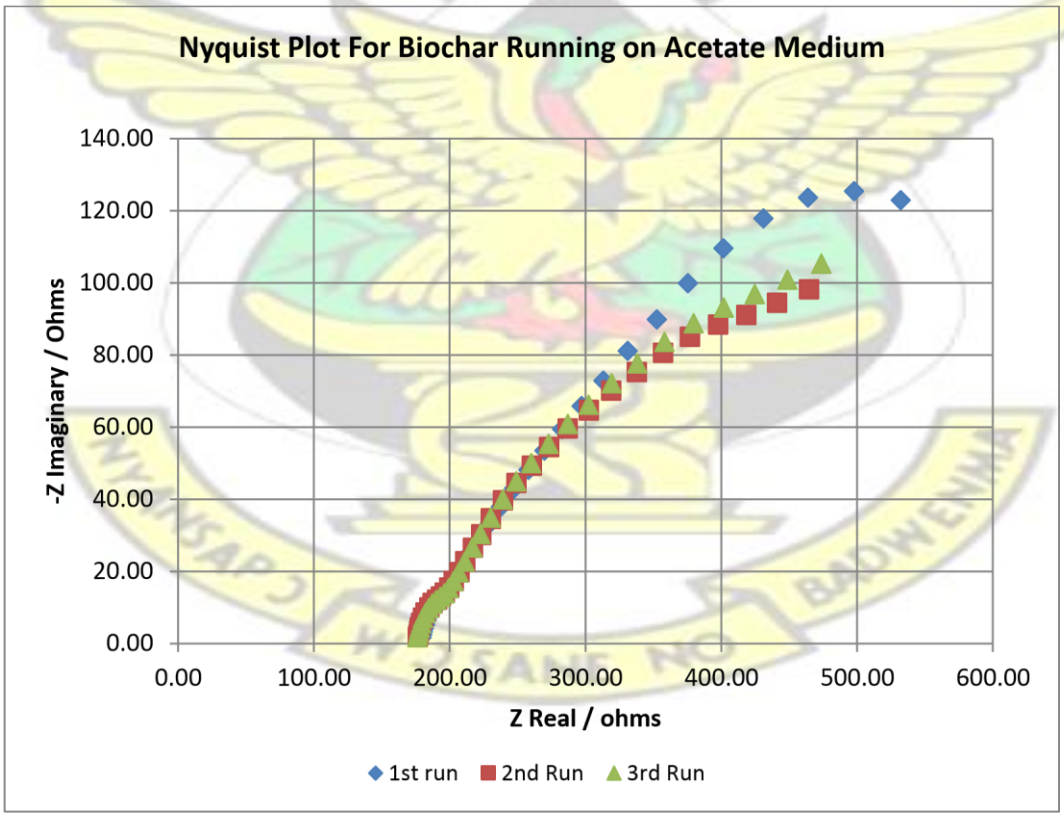

Figure B2.2: Nyquist Plot for Biochar Running on Acetate Medium

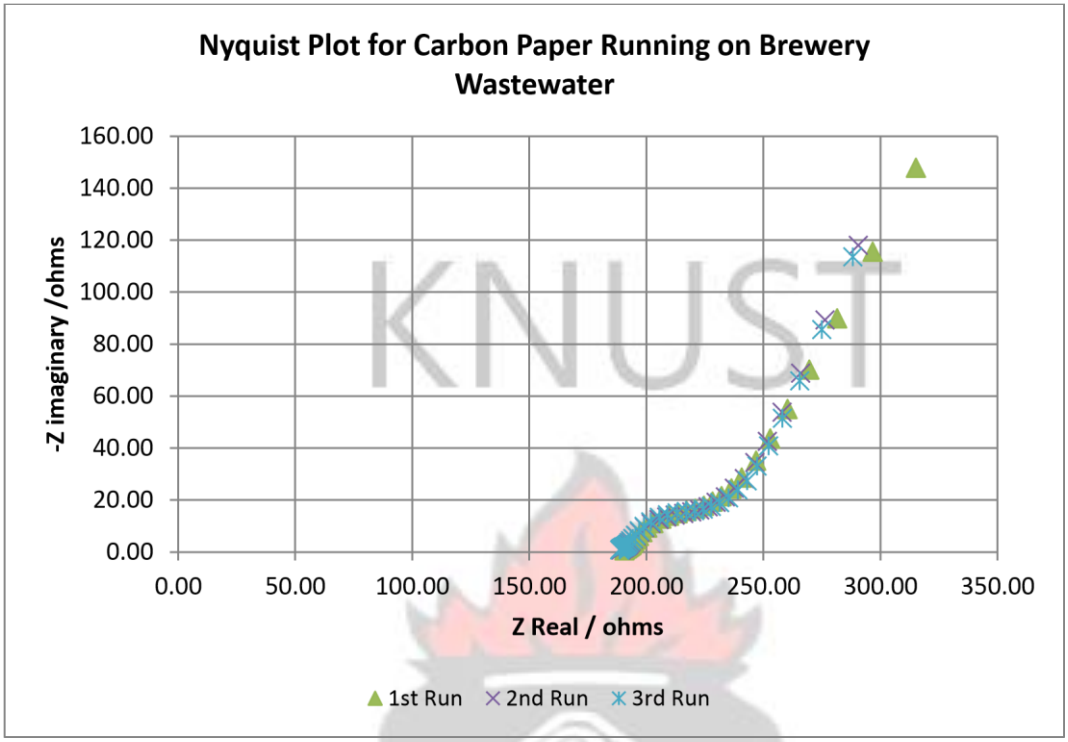

Figure B2.3: Nyquist Plot for Carbon Paper Running on Brewery Wastewater

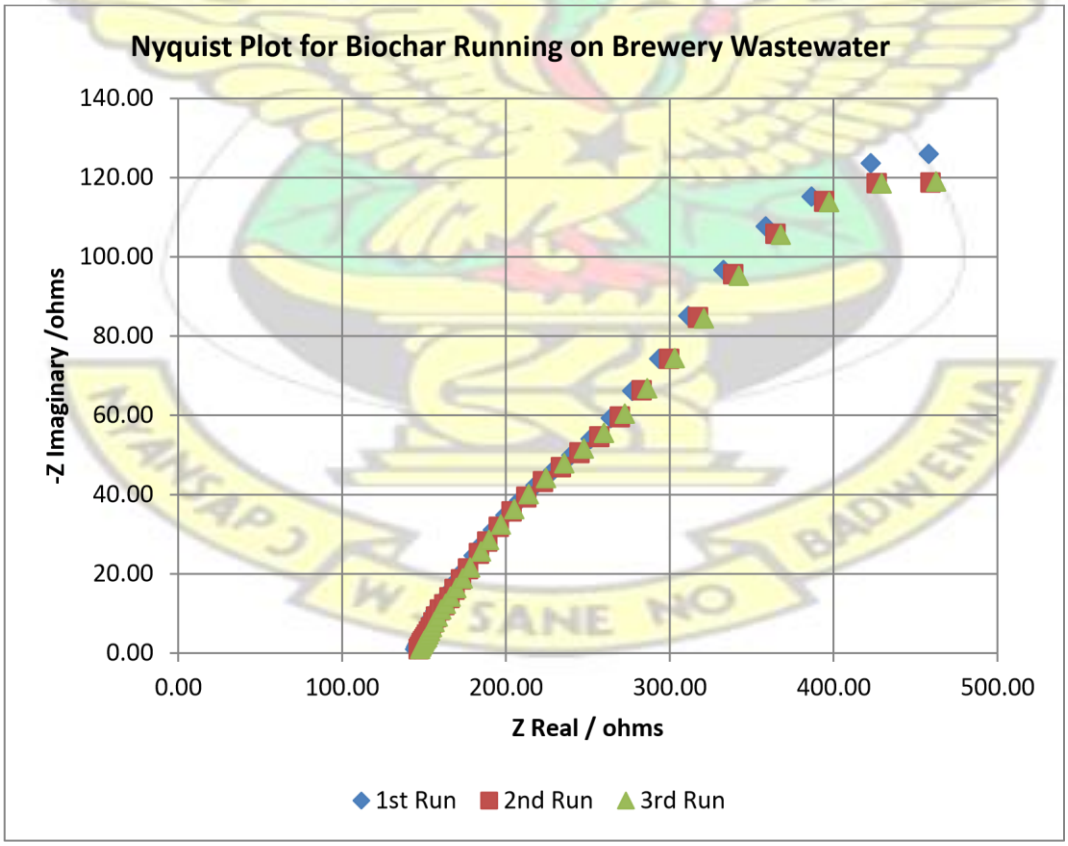

Figure B2.4: Nyquist Plot for Biochar Running on Brewery Wastewater

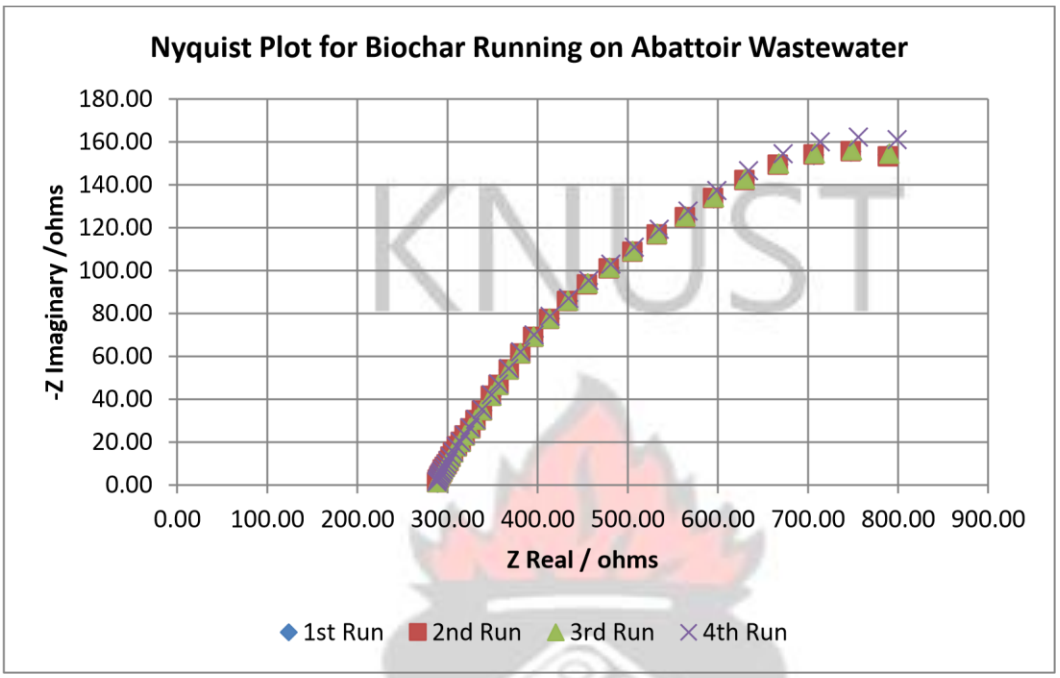

Figure B2.5: Nyquist Plot for Biochar Running on Abattoir Wastewater

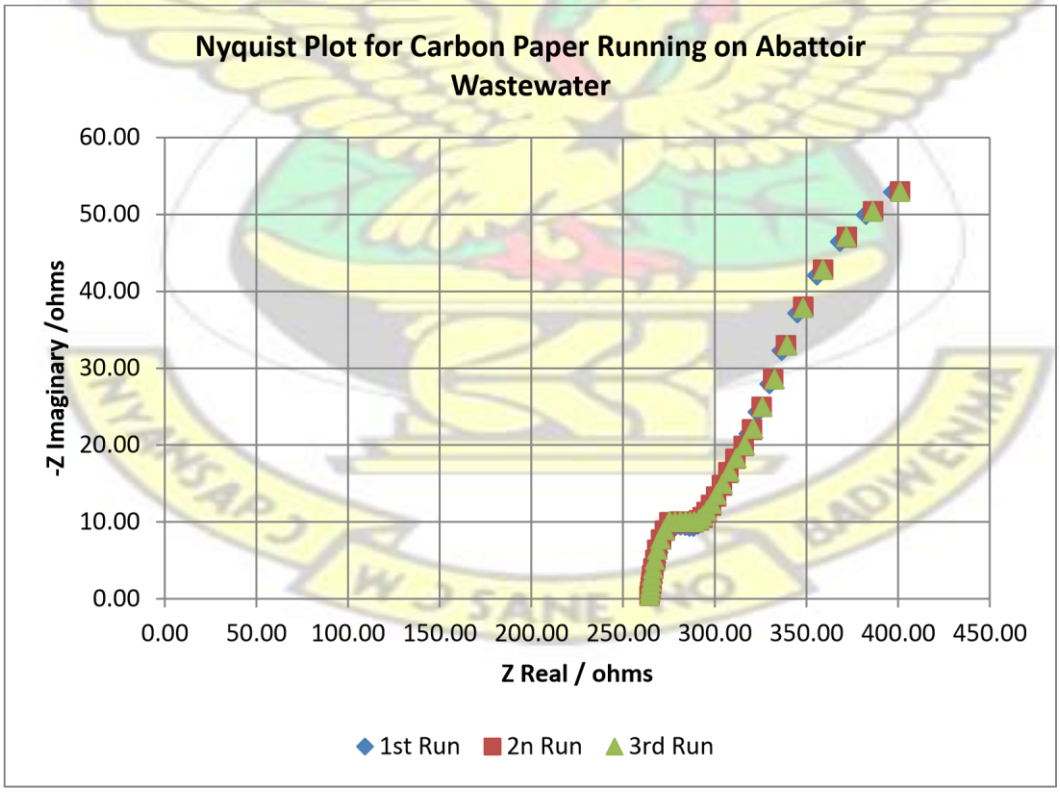

Figure B2.6: Nyquist Plot for Carbon Paper Running on Abattoir Wastewater

Table B2.1: Ohmic Resistance Carbon Paper

Run	Ohmic Resistance /Ω		
	Brewery Wastewater	Acetate Medium	Abattoir Wastewater
1	174.3	192.8	264.7
2	175.3	193	264.4
3	175.3	192.5	264.6
Average	174.9666667	192.7666667	264.5666667
Standard Deviation	0.577350269	0.251661148	0.152752523

Table B2.2: Internal Resistance Carbon Paper

Run	Internal Resistance / Ω		
	Brewery Wastewater	Acetate Medium	Abattoir Wastewater
1	278.70	263.10	397.30
2	315.10	259.00	401.10
3	288.10	259.10	401.00

Average	293.9666667	260.4	399.8
Standard Deviation	18.89585492	2.338803113	2.165640783

Table B2.2: Ohmic Resistance Biochar

Run	Ohmic Resistance / Ω		
	Brewery Wastewater	Acetate Medium	Abattoir Wastewater
1	144.4	176.3	288.9
2	146.8	179.2	288.2
3	147.6	176.1	288.4
Average	146.2666667	177.2	288.5
Standard Deviation	1.6653328	1.734935157	0.360555128

Table B2.3: Internal Resistance Biochar

Run	Internal Resistance / Ω

	Brewery Wastewater	Acetate Medium	Abattoir Wastewater
1	458.00	464.50	788.70
2	459.20	464.60	788.50
3	462.40	531.90	790.30
Average	459.8666667	487	789.1666667
Standard Deviation	2.274496281	38.88457278	0.986576572

APPENDIX B3 Supplementary Results for Treatment Performance

Table B3.1: COD Results for MFCs Using Biochar Electrode

	Biochar on Brewery			Biochar on Abattoir		
Cycle	1	2	3	1	2	3
Initial COD /mg/L	6895	6895	5920	4726.66	5200	5200
Final COD /mg/L	636.66	1840	2640	3483.33	4320	2960
Difference /mg/L	5364.29	4332.86	2186.67	1065.71	754.29	1493.33

Table B3.2: COD Results for MFCs Using Carbon Paper Electrode

	Carbon Paper on Brewery			Carbon Paper on Abattoir		
Cycle	1	2	3	1	2	3
Initial COD /mg/L	6895	6895	6895	4726.66	4726.66	5200
Final COD /mg/L	4400	3753	4160	1630	2960	2800
Difference /mg/L	2495	2693.14	2344.29	2654.28	1514.28	1600