SIMULTANEOUS POWER GENERATION AND WASTEWATER TREATMENT USING MICROBIAL FUEL CELL

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SUPERVISOR'S DECLARATION

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STUDENT'S DECLARATION

I declare that this report is the result of my own research except as cited in the references and summaries which have been duly acknowledge. The project has not been accepted for any degree and is not concurrently submitted for award of other degree.

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LIST OF ABBREVIATIONS

B

BOD Biochemical Oxygen Demand

C

CE Coulumbic Efficiency

CO Carbon Monoxide

COD Chemical Oxygen Demand

D

DMRB Dissimilatory Metal-Reducing Bacteria

DOE Department of Environment Malaysia

E

EAB Electrochemically Active Bacteria

G

GAC Granular Activated Carbon

M

MFC Microbial Fuel Cell

O

OCV Open Circuit Potential

P

PACF Polyacrylonitrile Carbon Felt

PD Power Density

PEM Proton Exchange Membrane

POME Palm Oil Mill Effluent

S

SCMFC Single Chamber Microbial Fuel Cell

SPW Starch Processing Wastewater

T

TS Total Solid

TSS Total Suspended Solid

LIST OF SYMBOLS

Symbol	Description	MKS Units
A	Area of Electrode	m^2
C	Concentration	mol/L or M
D	Diameter	Mm
d	Depth	Cm
F	Faraday's Constant	C/mol e^-
I	Current	A
I_{max}	Maximum Current	A
L	Thickness/Length	mm
P	Power	W
q	Electrical Charge	C
R	Resistance	Ω
s	Conductivity	mS/cm
T	Temperature	℃
t	Time	Hr
V	Voltage	V
V	Volume	mL
v	Working Volume of Anode	m^3
V_{An}	Volume of Liquid in Anode Compartment	mL
V_{max}	Maximum Voltage	V
X	Concentration of Biomass	mg/L
Δ_{COD}	Change in COD Concentration	mg/L

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ABSTRAK

Efluen kilang minyak sawit (POME) merupakan salah satu pencemar di Malaysia. Konvensional aerobik dan anaerobik rawatan air sisa memerlukan lebih banyak tenaga untuk beroperasi. Dalam konteks ini, rawatan air sisa menggunakan Microbial Fuel Cell seolah-olah menjadi teknologi yang menjanjikan kerana ia mengurangkan keperluan tenaga operasi dan menunjukkan rawatan yang berkesan juga. Kajian ini tertumpu kepada penjanaan kuasa serentak dan rawatan air sisa dengan menggunakan MFC. Objektif kajian ini adalah untuk mengkaji prestasi MFC dengan menggunakan karbon Polyacrylonitrile sebagai elektrod dan untuk mengkaji kesan luas permukaaan elektrod pada kecekapan coulombic dan kecekapan penyikiran Chemical Oxygen Demand (COD) untuk MFC. POME telah digunakan untuk menuai tenaga dan mengurangkan COD dari POME kompleks. Saiz yang berbeza untuk PACF elektrod telah digunakan sebagai elektrod untuk semua eksperimen. Cara penggumpulan data adalah melalui memerhati dan merekodkan voltan, arus dan kuasa yang dihasilkan oleh MFC. Hasil kajian telah dianalisis untuk mendapatkan ketumpatan kuasa yang optimum, kecekapan coulumbic dan kecekapan penyingkiran COD. Ketumpatan kuasa, ketumpatan arus dan kecekapan coulombic MFC dengan POME telah dikira. Membandingkan keputusan yang diperolehi dan dikira, MFC dengan luas permukaan (34.79cm^2) menunjukkan nilai tertinggi bagi ketumpatan kuasa maksimum kira-kira 76,2133 mW/m2, kecekapan coulumbic sebanyak 0.9561% dan kecekapan penyingkiran COD sebanyak 45.6%.

SIMULTANEOUS POWER GENERATION AND WASTEWATER TREATMENT USING MICROBIAL FUEL CELL

ABSTRACT

Palm Oil Mill Effluent (POME) is one of the major pollutants in Malaysia. Conventional aerobic and anaerobic treatment of wastewater needs more energy to operate it. In this context, treatment of wastewater using Microbial Fuel Cell seems to be promising technology because it reduces operational energy requirement and shows efficient treatment too. This research focused on simultaneous power generation and wastewater treatment by using MFC. The objectives of the study are to study the performance of MFC using Polyacrylonitrile carbon felt (PACF) as electrode and to study the effect of surface area of electrode on coulombic efficiency and Chemcial Oxygen Demand (COD) removal efficiency of MFC. POME was used to harvest energy and reduce COD from complex POME. Different size of PACF was used as electrode for all the experiments. The data collection mode was through observing and recording the voltage, current and power produced by the MFC. The findings were analyzed to obtain optimum power density, coulumbic efficiency and Chemical Oxygen Demand (COD) removal efficiency. Power density, current density and coulombic efficiency of MFC with POME were calculated. Comparing the results obtained and calculated, MFC with PACF surface area (34.79cm^2) showed the highest value for maximum power density of about 76.2133 mW/m^2, coulumbic effiency of 0.9561% and COD removal efficiency of 45.6%.

CHAPTER 1

INTRODUCTION

Microbial fuel cells (MFCs) have emerged in recent years as a promising yet challenging technology. In a MFC, microorganisms interact with electrodes using electrons, which are either removed or supplied through an electrical circuit. MFC is considered to be a promising sustainable technology to meet increasing energy needs, especially using wastewaters as substrates, which can generate electricity and accomplish wastewater treatment simultaneously, thus may offset the operational costs of wastewater treatment plant. Bacteria can be used in MFCs to generate electricity while accomplishing the biodegradation of organic matters or wastes.

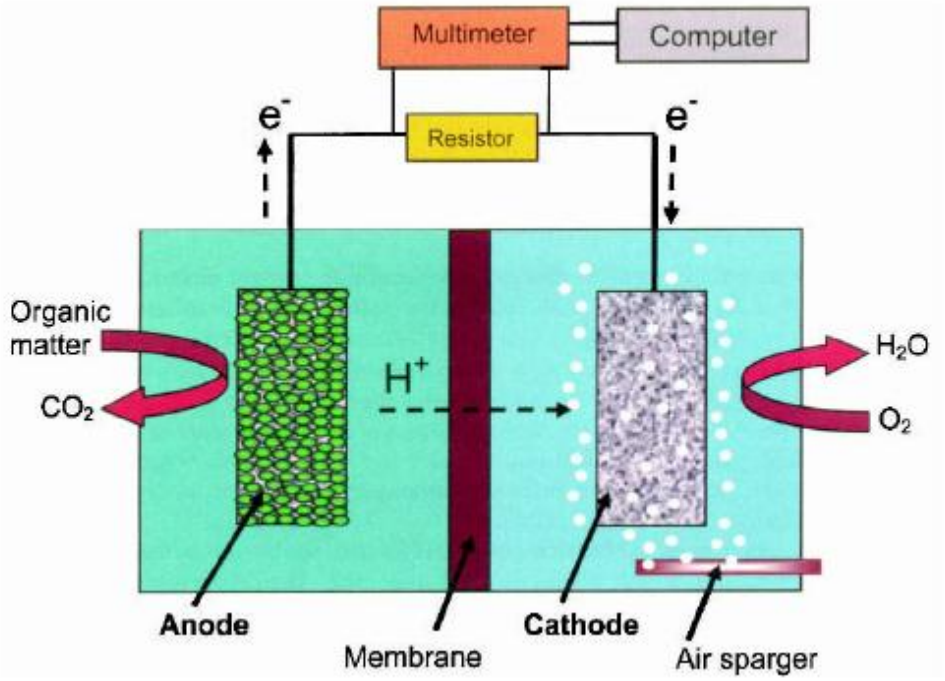

Figure 1.1 Graphical Representation of Microbial Fuel Cells (Logan, B.E. 2008.Microbial fuel cells)

Microbes in the anodic chamber of an MFC oxidize added substrates and generate electrons and protons in the process. Carbon dioxide is produced as an oxidation product. However, there is no net carbon emission because the carbon dioxide in the renewable biomass originally comes from the atmosphere in the photosynthesis process. Unlike in a direct combustion process, the electrons are absorbed by the anode and are transported to the cathode through an external circuit. After crossing a Proton Exchange Membrane (PEM) or a salt bridge, the protons enter the cathodic chamber where they combine with oxygen to form water. Microbes in the anodic chamber extract electrons and protons in the dissimilative process of oxidizing organic substrates. Electric current generation is made possible by keeping microbes separated from oxygen or any other end terminal acceptor other than the anode and this requires an anaerobic anodic chamber.

Typical electrode reactions are shown in Equation (1.1) and Equation (1.2) using acetate as an example substrate.

Anodic reaction: $CH3COO^- + 2H2O \longrightarrow microbes\ 2CO_2 + 7H^+ + 8e^-$ (1.1)

Cathodicreaction : $O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$ (1.2)

The overall reaction is the break-down of the substrate to carbon dioxide and water with a concomitant production of electricity as a by-product. Based on the electrode reaction pair above, an MFC bioreactor can generate electricity from the electron flow from the anode to cathode in the external circuit.

The first experimental evidence of bioelectricity was found in the late eighteenth century by Luigi Galvani, who observed electric response by connecting frog legs to a metallic conductor. To further explore the potential of bioelectricity, Michael C. Potter built the first MFC in 1911. In the 1980s, British researcher H. Peter Bennetto succeeded in extracting electric power from MFCs by employing pure cultures of bacteria to catalyze the oxidation of organics and utilizing artificial electron mediators to facilitate electron transfer in the anode. The number of MFCs applied to the biological treatment of wastewater increase greatly during the 1990s, especially after Logan and other researchers developed new MFCs using municipal or industrial wastewater as the substrate which greatly facilitated the technology.

At present, however, one of the bottleneck problems for the application of this methodology is the low output of power. Principally, the output power depends on the rate of substrate degradation, the rate of electron transfer from the bacteria to the

anode, the circuit resistance, the proton mass transfer in the liquid, the performance of the electrode and the external operating conditions and so on.

Electrode is the key component in deciding the performance and cost of MFC. Electrode design is the greatest challenge in making MFCs a cost-effective and scalable technology. Recently, interest in the electrode material and its configuration has steadily increased in studies for MFCs. Over the past decade, a variety of electrodes have been extensively explored for MFCs. These electrodes can be classified into two main groups, bio-electrodes (including anode and biocathode) and chemical-electrodes (more specifically, air-cathode and aqueous air-cathode), according to whether or not bacteria is used as a catalyst.

Different electrode materials vary in their physical and chemical properties (e.g., surface area, electric conductivity, and chemical stability), thus, they also vary in their impact on microbial attachment, electron transfer, electrode resistance and the rate of electrode surface reaction. Therefore, it is of great significance to select and develop suitable electrode materials to optimize and promote the performance of MFCs. Moreover, as a main component, the electrode materials determine the price of MFCs and thus influence the wastewater treatment cost. Therefore, this field has attracted ever-increasing interest and lots of efforts related to electrode preparations and designs have been made.

The attractiveness of this novel technology is related to the wide range of potential applications, including the possibility of achieving energy recovery from wastewaters. In addition MFCs have been considered for hydrogen production,

sulphide removal, and as biosensors for organic content in wastewaters. Many MFC devices utilizing specific axenic cultures have been developed, however, MFCs operated with mixed cultures show higher resistance against process disturbance, larger substrate versatility and also higher power output.

Since the first application of the two chamber design, the configuration of MFCs has been continuously optimized. Moreover, improved electrode materials and better understanding of bacterial community involved in the electrochemical reactions, have led to ever increasing performance.

The maximum current (I_{max}) generated with MFCs is still very low, being only of 0.1A, and the average power density of MFCs is about 40Wm^{-3}, when operated in batch mode and fed with a synthetic wastewater. The major obstacles for practical applications of MFCs in a wastewater treatment plant concerns difficulties mainly in the scaling-up process and the very high capital costs.

1.1 Background of Research

The use of fossil fuels, especially oil and gas, in recent years has accelerated and this triggers a global energy crisis. Renewable bio energy is viewed as one of the ways to alleviate the current global warming crisis.

It is undeniable that energy cannot be created nor destroyed. It can only convert from one form to another, for instance Microbial Fuel Cells used substrates in

wastewater to generate electricity and simultaneously the wastewater is being treated, which means the energy is converted from chemical energy to electrical energy. While the current technology is promising, none of the processes can fully extract all the energy available in wastewater. Therefore, new development and improvement of technologies are necessary to take advantage of the maximum energy available in sewage and sludge.

Significant advancements in increasing the current densities of microbial fuel cells have been made recently by modifying fuel cell architecture and materials while treating the microorganisms as a 'black box'. Substantial improvements will be required before other commonly projected uses of microbial fuel cells, such as large-scale conversion of organic wastes and biomass to electricity, or powering vehicles, mobile electronic devices, or households with suitably scaled microbial fuel cells will be possible. Additional potential engineering modifications seem promising.

The anode material and its configuration represent an important parameter in a MFC, as it influences the development of the microbial community involved in the electrochemical bio-reactions. The study tries to evaluate MFC with high anode surface area, achieved by using polyacrylonitrile carbon felt (PACF). The performance of the MFC with the PACF anode configuration was studied using a mixed microorganism culture from real wastewaters in batch and continuous mode operation.

1.2 Problem Statement

Types of electrode material can be one of the factors that affect the performance of MFC. For all the types of electrodes, their base materials must generally be of good conduction, good chemical stability, high mechanical strength, and low cost. Besides the types of electrode material, the surface area of the electrode is also considered as an important parameter in determining the performance of MFC. There is an issue arises, by increasing the surface area of electrode, the coulombic efficiency of MFC will be increased or not?

1.3 Research Objective

1. To study the performance of MFC using Polyacrylonitrile carbon felt (PACF) as electrode.
2. To study the effect of surface area of electrode on Coulombic Efficiency and COD Removal Efficiency of MFC.

`1.4 Scope of the Research Work

- The anaerobic sludge and raw Palm Oil Mill Effluent (POME) that collected from the Neram Felda Palm Oil Industry are used in MFC for the simultaneous treatment of POME as well as to generate electricity.
- Various surface areas of PACF are used in anode and cathode compartments to determine the effect of electrode surface area on the performance of MFC.
- Optimized surface area of electrode is determined through observing the maximum current and power density produced by the MFC.
- How surface area of electrode affects Coulombic Efficiency is calculated using Chemical Oxygen Demand (COD) removal and current generation data of PACF with different surface areas.

1.5 Significance of the Research

This research will be a significant endeavour in solving energy crisis in a country by reducing the dependence on the fossil fuel to generate energy. Besides, the problem of wastewater can also be solved because, the organic waste in the wastewater will be eventually consumed and converted into electric energy by microorganisms that grow and exist in the wastewater.

CHAPTER 2

LITERATURE REVIEW

2.1 Palm Oil Mill Effluent (POME)

Palm Oil Mill Effluent (POME) is a thick brownish liquid that contains high amount of total solids (40,500 mg/L), oil and grease (4000 mg/L), Chemical Oxygen Demand (COD) (50,000 mg/L), and Biochemical Oxygen Demand (BOD) (25,000 mg/L). This highly polluting effluent is becoming a major problem to environment as if it not being treated well before discharged based on standard limit for effluent discharged. Normally, POME is treated by collecting the samples from mixing ponds which act as activated sludge and being analyze using water analyzer method to obtain parameters such as BOD, COD, suspended solid, turbidity and pH (Hazlan, 2006).

2.2 Inoculum

The majority of modern microbial fuel cells rely on mixed bacterial cultures, usually sampled from natural environments like from soil or sewage sludge. These cultures are abundantly available in our environment, they consist of wide range of substrates – ranging from simple organic acids (Liu et al., 2005), to carbohydrates including complex carbohydrates like starch and cellulose, (NieBen et al., 2006; Rismani-Yazdi et al., 2007) and even to proteins (Heilmann and Logan, 2006).

2.2.1 Electrochemically Active Bacteria

According to Chang et al., 2006, Electrochemically active bacteria (EAB) is defined as bacteria that possess the ability to transfer electrons from oxidized fuel (substrate) to a working electrode without mediators, making it possible to establish mediator-less MFCs. Dissimilatory metal-reducing bacteria (DMRB), which are capable of the reduction of solid metal oxides, are known EAB species, including *Geobacter*and *Shewanella* spp. It was shown that the anode electrode in MFCs served as the electron acceptor for growth and metabolism of EAB, which are capable of current production in the absence of a mediator.

2.2.2 Substrates of Microbial Fuel Cell

There are many organic substrates that can be the possible energy sources to generate electricity using MFC. These substrates range from carbohydrates (glucose, sucrose, and etc.), volatile fatty acid (acetate, formate, and etc.), alcohols (methanol and

ethanol), amino acids, proteins and even inorganic components like sulphides (Cheng et al., 2007, Clauwaert et al., 2008c, He et al., 2005, Heilmann and Logan, 2006, Ishii et al., 2008, Liu et al., 2005b, Logan et al., 2005, Min and Logan, 2004, Rabaey et al., 2003, Rabaey et al., 2006). Due to the inertness towards alternative microbial conversions (fermentation and methanogenesis) at room temperature of acetate, it is considered as the commonly used substrate in MFCs. This results in high coulombic efficiencies of up to 98% (Rabaey et al., 2005b) and high power outputs of up to 115 $W.m^3$ (Cheng and Logan, 2007) for mixed anodophilic cultures.

2.2.2.1 Synthetic Wastewater

Synthetic or chemical wastewater with well-defined composition is also used by several researchers as it is easy to control in terms of loading strength, pH and conductivity. Venkata Mohan et al. (2008a,b) have used synthetic wastewater at different loading rates in similar MFC configurations to achieve variable performances. Several media used for bacterial growth contains significant amount of redox mediators, such as cysteine, and high strength wastewater contains reduced sulfur species, which can work as abiotic electron donor and increase power production for a short while (Aldrovandi et al., 2009) thus not representing the true performance of the system. This can be avoided by using a minimal salt medium with a single electron donor such as glucose or acetate. To check the influence of wastewater composition on the performance of MFC, Rodrigo et al. (2009) fed MFCs with two different synthetic wastewaters with the same organic pollutants (glucose and peptone) and same organic loading (315 mg/dm^3) but with a different ratio of readily/slowly biodegradable substrate. The MFC fed with slowly biodegradable

waste was more efficient in terms of electricity production probably due to the production of intermediates favouring electricity formation.

2.2.2.2 Brewery Wastewater

Wastewater from breweries has been a favorite among researchers as a substrate in MFCs, primarily because of its low strength. Besides, it is suitable for electricity generation in MFCs due to the food-derived nature of the organic matter and the lack of high concentrations of inhibitory substances (for example, ammonia in animal wastewaters) (Feng et al., 2008). Although the concentration of brewery wastewater varies, it is typically in the range of 3000–5000 mg of COD/L which is approximately 10 times more concentrated than domestic wastewater (Vijayaraghavan et al., 2006). It could also be an ideal substrate for MFCs due to its nature of high carbohydrate content and low ammonium nitrogen concentration. Beer brewery wastewater treatment using air cathode MFC was investigated by Feng et al. (2008) and a maximum Power Density (PD) of 528 mW/m^2 was achieved when 50 mM phosphate buffer was added to the wastewater. In this case the maximum power produced by brewery wastewater was lower than that achieved using domestic wastewater, when both wastewaters were compared at similar strengths. This might be due to difference in conductivities of two wastewaters. Diluting the brewery wastewater with deionized water decreased the solution conductivity from 3.23 mS/cm to 0.12 mS/cm. Recently, Wen et al. (2009) using a model based on polarization curve for the MFC, reported that the most important factors which influenced the performance of the MFC with brewery wastewater were reaction kinetic loss and mass transport loss (both were 0.248 V when current density was 1.79 A/m^2). These can be avoided by increasing the

concentration of brewery wastewater and by increasing the reaction temperature and using a rough electrode to provide for more reaction sites.

2.2.2.3 Starch processing Wastewater

Starch processing wastewater (SPW) contains a relatively high content of carbohydrates (2300–3500 mg/L), sugars (0.65–1.18%), protein (0.12–0.15%) and starch (1500–2600 mg/L), representing an important energy-rich resource, which can be potentially converted to a wide variety of useful products (Jin et al., 1998). SPW was used as a fuel to enrich a microbial consortium generating electricity and current generation (0.044 mA/cm^2) was coupled toa fall in COD from over 1700 mg/L to 50 mg/L in 6 weeks (Kimet al., 2004). Lu et al. (2009) operated a MFC with SPW containing4900 mg/L of COD over four cycles and obtained a maximum voltage output and power density of 490.8 mV and 239.4 mW/m^2 in the third cycle. However, the CE was only 7%. They attributed this low CE to oxygen diffusion to the anode compartment resulting in oxidization of other electron acceptors, biomass production and fermentation.

2.2.2.4 Dye Wastewater

Azo dyes constitute the largest chemical class of synthetic dyes and are extensively present in effluent from dye-manufacturing industries and textile industries. Their removal from these effluents before discharge is of paramount importance as the intense color of these dyes leads to severe environmental problems such as

obstruction of light and oxygen transfer into water which is detrimental to aquatic life (Pant et al., 2008). Besides, several of these dyes are also toxic in nature. Very recently, efforts have been made to utilize these dyes as a substrate in MFC leading to color removal from such dye-containing wastewaters as well as generating electricity. Sun et al. (2009) reported accelerated decolorization of active brilliant red X-3B (ABRX3), a model azo dye, in a MFC when glucose and confectionary wastewater were used as co-substrates. Though higher dye concentrations (even up to 1500 mg/L) did not inhibit their decolorization; however, electricity generation from glucose was affected by higher concentrations of ABRX3 (>300 mg/L). This was attributed to the competition between azo dye and the anode for electrons from carbon sources. Thus, simultaneous treatment of azo dye-containing wastewater and readily biodegradable organic matter-containing wastewater could be achieved by mixing two kinds of wastewater in the MFCs, with the advantage of saving both cost and energy, however, the system still requires considerable improvements in terms of finding appropriate bacterial community that is capable of utilizing a mixture of dyes and other simple carbon sources in order to make MFCs a realistic solution for this kind of wastewater.

2.2.2.5 Inorganic and Other Substrates

Apart from these above mentioned substrates, some other substrates have also been explored. Electricity generation with anodic sulfide oxidation was reported (Rabaey et al., 2006) with a potential different of39 mW/L. Huang and Logan (2008) reported the effectiveness of electricity production with paper recycling plant wastewater using MFC and obtained a maximum PD of 672 mW/m^2 after amending the wastewater with phosphate buffer. Luo et al. (2009) reported the degradation of phenol and current generation in MFC. The power generation using phenol as the sole substrate

was lower than that of glucose and the CE was less than 10% indicating a substantial loss. The large amount of wastewater produced in integrated biorefineries is also a potential source of energy (Kaparaju et al., 2009). Recently the use of MFCs to remove the fermentation inhibitors in cellulosic biorefineries including furfural, 5-hydroxymethylfurfural, vanillic acid, 4-hydroxybenzaldehyde and 4-hydroxyacetophenone while simultaneously producing electricity was demonstrated (Borole et al., 2009). A combination of a carbon monoxide (CO) fermenter and MFC as an anaerobic continuous process was also reported recently (Kim and Chang, 2009). The CO fermenter was enriched to produce acetate which was fed to a MFC to generate electricity. Though the conversion yield was quite low, it proved that syn-gas (mainly CO) can be converted to electricity through microbial process. 1,2-Dichloro ethane degradation by anodophilic bacteria enriched in MFCs was reported by Pham et al. (2009). Further, removal of sulfate and thiosulfate in a single- chamber MFC inoculated with Desulfovibriodesulfuricans was investigated (Zhao et al., 2009) and a 0.115 mA/cm^{2}maximum current production was observed.

2.3 Discovery of Microbial Fuel Cell

The first MFC was invented and built by Michael C. Potter in 1911. He demonstrated a current flow between two electrodes emerged in a bacterial culture and in sterile medium. However his work was not to receive any major coverage. In 1931, Barnet Cohen created a number of microbial half fuel cells that connected in series which produced over 35V and 2 mA of current. He was successfully drew the attention of the public. More work on the subject was studied by DelDuca et al. who managed to use hydrogen produced by the fermentation of glucose by *Clostridium butyricum* as

the reactant at the anode of a hydrogen and air fuel cell. Unfortunately it was found that the cell his created has unreliable owing due to the unstable nature of hydrogen production by the micro-organisms although the cell functioned. In 1970s, the MFC issue of DelDuca et al. was resolved by Suzuki. He also continued the current design concept of MFC and started to understand how MFCs function. This idea was picked up and studied in more detail by MJ Allen and then later by H. Peter Bennetto both from King's College London. The potential and possible methods for the generation of electricity of MFC were discovered by Bennetto. He started his work in 1980s by studying the operation of a MFC as to generate electricity for the developing countries.

2.4 Conventional Microbial Fuel Cell

The Conventional MFC consists of biological anode and abiotic cathode. The abiotic cathode usually requires a catalyst or an electron mediator to achieve high electron transfer, increasing the cost and lowering the operational sustainability. (Zhen and Angenent, 2006).There are two chambers in a conventional MFC- anode and cathode chambers that are separated by a Proton Exchange Membrane (PEM). The anode side contains electrochemically-active microorganisms whereas the cathode is abiotic. Therefore, it is a half biological system. The microorganisms act as the biocatalyst to motivate the degradation of organic wastes to produce electrons. These electrons will be traveled to the cathode side via an electric circuit. The electrons then flow through an electrical circuit with a load or a resistor to the cathode. The potential difference (Volt) between the anode and the cathode, together with the flow of electrons (Ampere) results in the generation of electrical power (Watt). The protons flow

through the proton or cation exchange membrane to the cathode. These electrons then will enter the second chamber- cathode. The presence of free electrons on the cathode will initiate the reduction of oxygen to produce water. (Benetto, 1990 as cited in Application of Bacterial Biocathodes in Microbial Fuel Cell)

2.5 Electron Transfer Mechanisms

In MFCs, the bacterial transfer of electrons from the substrates to electrodes is mainly through three ways as shown in Figure 2.1. The mechanism of electron transfer may be of direct transfer, indirect electron transfer or by mediator-driven MFC.

2.5.1 Direct Electron Transfer

There are several microoraganisms *(Eg. Shewanellaputrefaciens, Geobactersulferreducens, G. metallireducens, and Rhodoferaxferrireducens)*that transfer electrons from inside the cell to extracellular acceptors via c-type cytochromes, biofilms and highly conductive pili (nanowires) (Derek R, 2008). These microorganisms have high Coulombic Efficiency (The amount of electrons recovered as current versus the maximum recovery from the substrate) (Logan, B.E., and Regan, J.M., 2006; Balat, M. 2009). And can form biofilms on the anode surface that act as electron acceptors and transfer electrons directly to the anode resulting in the production of more energy (Chaudhuri and Lovley, 2003;Kim et al., 2002).

2.5.2 Indirect Electron Transfer

In this mechanism, electrons from microbial carriers are transported onto the electrode surface either by a microorganism's (*Shewanellaoneidensis, Geothrixferementans)* own mediator which in turn facilitate extracellular electron transfer or by added mediators. The MFCs that use mediators as electron shuttles are called mediator MFCs. Mediators provide a platform for the microorganisms to generate electrochemically active reduced products. The reduced form of the mediator is cell permeable, accept electrons from the electron carrier and transfer them onto the electrode surface (Lovley, 2006). Usually neutral red, thionine, methylene blue, anthraquinone-2, 6-disulfonate, phenazines and iron chelates are added to the reactor as redox mediators (Du et al., 2007). Mediators are required in MFCs that use *Proteus vulgaris,Escherichia coli, Streptococcus lactis,* and *Pseudomonas* species as these bacteria cannot transfer electrons outside the cell. To be effective, the mediator should be able to penetrate the cell membranes easily, able to grab the electrons from the electron carriers of the electron transport chains, should increase electron transfer from the metabolite, stable during long periods of redox cycling and non-toxic to microbes (Du et al., 2007; Ieropoulos et al., 2005; Osman et al., 2010).

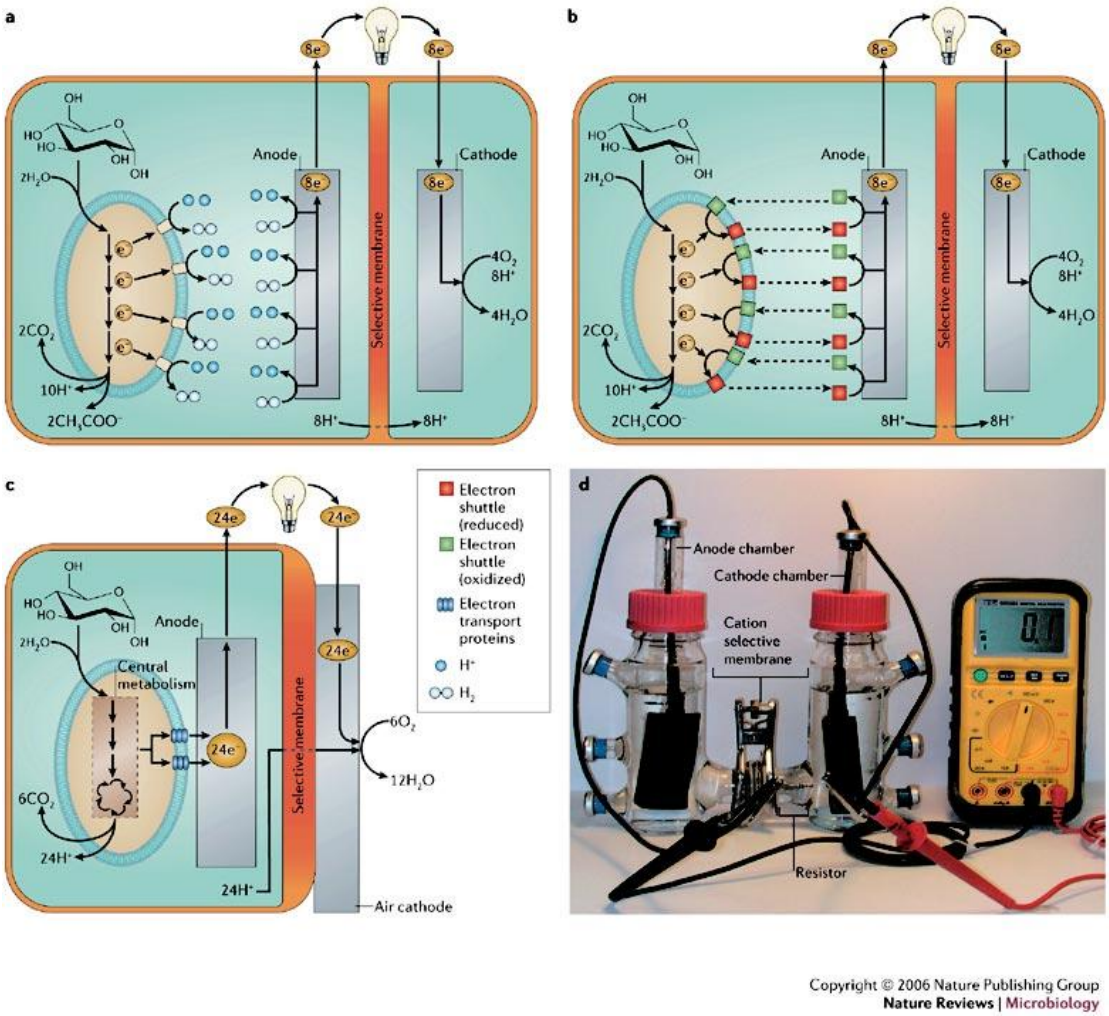

Figure 2.1 Electron Transfer Mechanism

2.5.3 Mediator-Driven Microbial Fuel Cell

An electron-shuttling mediator accepts electrons from reduced cell constituents and abiotically transfers the electrons to the anode. The reoxidized mediator can then undergo repeated cycles of reduction and oxidation. In most instances, the cells that have been used in such fuel cells only incompletely oxidize their organic fuels. (Lovley, 2006)

2.6 Electrode Materials in Microbial Fuel Cell

The electrode materials in MFC have some general characters and also its self-characteristic. For all the types of electrodes, their base materials must generally be of good conduction, good chemical stability, high mechanical strength, and low cost. Carbon materials and non-corrosive metals, which can basically meet the general requirements above, are currently the most-widely used base materials like carbon paper, graphite plate, carbon cloth, carbon mesh, granular graphite, granular activated carbon, carbon felt, reticulated vitrified carbon, carbon brush and stainless steel mesh. The selection of electrode material affects the performance of MFCs.

Various materials have been investigated as electrodes to increase the performance and power output of the MFCs. For anode, carbon cloth, carbon felt, graphite felt, carbon mesh and graphite fiber brush are frequently used due to their stability, high electric conductivity and large surface area (Logan, 2010; Logan and Regan, 2006). For cathodes, platinum (Pt), platinum black, activated carbon (AC), graphite based cathodes and biocathodes are used (Chen et al., 2008; Du et al., 2007). Though platinum coated electrodes are more efficient and superior in power production due to higher catalytic activity with oxygen than other electrodes, they are not cost effective (Logan, 2010; Oh et al., 2004) Alternate catalysts for platinum include ferric iron, manganese oxides, iron and cobalt based compounds. Ferricyanide ($K_3(Fe(CN)_6$) is frequently used as an electron acceptor in the MFCs due to its good performance and low over-potential (Logan and Regan, 2006). Aelterman et al. (2008) compared graphite and carbon felt, and 2 and 5 mm graphite granules, and found that the graphite felt electrode yielded the highest maximum power output, amounting to up to 386W/m^3 in the total anode compartment. Li et al. (2010) reported that a

membrane-less MFC, using GAC (granular activated carbon) as the electrode, had a power density 2.5 times higher than an MFC that used carbon cloth

Common materials in laboratory MFCs include a large variety of carbon materials and several metal materials, which vary greatly in configuration and surface area. The configuration and performance of these commonly used anode materials are summarized in Table 1. Photos of these materials were shown in Figure 1. It is known that type and concentration of bacteria on anodes is able to significantly affect power density (or current density) in MFCs. Thus the inoculation sources were also summarized in Table 1. It is shown that mixed culture, including activated sludge, domestic wastewater and preacclimated bacteria from an active MFC (originally inoculated with activated sludge or domestic wastewater), were most common used inoculums in studies for anode materials.

The anode material and its configuration represent an important parameter in an MFC, for it influences the development of the microbial community involved in the electrochemical reactions. In particular, a three-dimensional anode would allow a greater surface area for microbial attachment and therefore improve anode potential. Graphite granules have been widely used as both anode and cathode material. Several other type of three-dimensional anodes have been previously tested such as reticulate vitreous carbon, granular activated carbon, carbon foam and graphite brush electrodes. In general the power production has shown to increase with higher surface area materials

2.6.1 Carbonaceous Anode

Carbonaceous materials are the most widely used materials for MFC anodes because of their good biocompatibility, good chemical stability, high conductivity, and relatively low cost. In terms of configuration, carbon-based electrodes can be divided into a plane structure, a packed structure, and a brush structure. The carbonaceous electrodes are discussed in detail in this section based on this classification.

2.6.1.1 Plane Structure

In the laboratory, carbon paper, graphite plates or sheets, and carbon cloth are the most common materials for plain electrodes (Min and Logan, 2004; Sun et al., 2010). Carbon paper is very thin and relatively stiff but slightly brittle. Graphite plates or sheets have higher strength than carbon paper. Roughened graphite electrodes have been reported to produce a higher power density than flat graphite electrodes (Heijne et al., 2008). These two materials have a compact structure and a relatively smooth surface, both of which facilitate the quantitative measurement of biomass per unit of surface area. However, their low specific area and high cost inhibit the application of these electrodes in large-scale MFCs.

In comparison with carbon sheets, carbon cloth is more flexible and much more porous, allowing more surface area for bacterial growth. However, it is prohibitively expensive to use for MFCs (ca. $\$1000/m^2$) (Zhang et al., 2010). An inexpensive carbon mesh material ($\$10–40/m^2$) was examined by Wang et al. (2009) as a substantially less expensive alternative to carbon paper and carbon cloth; results showed that the carbon mesh exhibited a slightly higher power density than carbon cloth after both materials were treated with ammonia gas. Besides the plain materials

described above, some rarely used fibrous materials, such as graphite foil, carbon fiber veil, and activated carbon cloth, have also been reported and comparatively evaluated for sulfide electrochemical oxidation in the anode of MFCs (Zhao et al., 2008). The results showed that the activated carbon cloth achieved the best sulphide removal and power generation due to its high specific surface and adsorption capacity.

Graphite or carbon felt is another fiber fabric that is much thicker than the materials described above. Its loose texture confers more space for bacterial growth than carbon cloth and graphite sheets, but the growth of bacteria is more likely to be restricted by the mass transfer of substrate and products on its inner surface. In order to increase the available surface area for bacteria, the felt is cut into cubes and placed into an anode chamber. Graphite foam is yet another porous carbon-based material with a definite thickness, but it is seldom used in MFCs. Chaudhuri and Lovley (2003) compared the performance of graphite rod, felt, and foam based on the surface area of the resulting electrode. Similar currents and biomasses were obtained from graphite rod and felt electrodes, and the graphite foam electrode produced 2.4 times more current density and 2.7 times more cell density than the graphite rod one.

2.6.1.2 Packed Structure

To increase the surface area available to bacteria, the use of carbon-based electrodes in packing forms for MFCs anode is becoming increasingly common (Aelterman et al., 2008; Di Lorenzo et al., 2010; Li et al., 2010; Rabaey et al., 2005). Similar to the biological filter, the anode chamber of the MFC can be filled with granular or irregularly shaped packing. However, the granular packing material, such as granular graphite, must be conductive. Graphite rods are usually used to collect electrons in

laboratory-scale MFCs. Having a high specific area is the main advantage of this configuration. The specific area of granular graphite (1.5−5.5 mm diameter) used in MFCs was estimated to be between 817 and 2,720 m^2/m^3 (Rabaey et al., 2005). In order to make the complete bed conductive, the granules must be tightly packed next to each other, although dead zones for current collection may still exist after long term running (Logan, 2007). In addition, the porosities of the packed electrode are relatively low (only ranged from 30 to 50% for granular media), and thus, potential clogging after long-term running is another problem (Rabaey et al., 2009). The use of granular graphite as an anode material in packed bed MFCs was first reported by Rabaey et al. (2005). Granular activated carbon (GAC) and small cubes of graphite or carbon felt can also be used as materials for packing bed MFCs. Aelterman et al. (2008) compared graphite and carbon felt, and 2 and 5 mm graphite granules, and found that the graphite felt electrode yielded the highest maximum power output, amounting to up to $386W/m^3$ in the total anode compartment. Li et al. (2010) reported that a membrane-less MFC, using GAC as the electrode, had a power density 2.5 times higher than an MFC that used carbon cloth. They thus inferred that the high surface area of GAC significantly improves bacterial adhesion and electron transfer from bacteria to the GAC surfaces.

2.6.1.3 Brush Structure

The graphite brush anode is an ideal electrode that achieves high surface area, high porosities, and efficient current collection. The use of a brush anode was first reported by Logan et al. (2007). In their studies, the brushes were made of carbon fibers cut to a set length and wound into a twisted core consisting of two conductive but noncorrosive titanium wires. Two brush sizes were used in this study: the smaller

brush, about 2.5 cm in diameter and 2.5 cm long, had an estimated surface area of 18,200 m^2/m^3-brush's volume and 95% porosity, while the larger brush, about 5 cm in diameter and 7 cm long, produced 7,170 m^2/m^3-brush's volume and 98% porosity. The cube MFCs containing the smaller brush reached a maximum power density of 2,400 mW/m^2 (normalized to the cathode projected surface area), and a maximum columbic efficiency (CE) of 60%. Bottle MFCs with the larger brush anode produced a maximum power density of 1,430 mW/m^2 compared to a 600 mW/m^2 plain carbon paper anode. The performance of brushes with different masses of fibers were also tested, but the lack of a clear trend in power per mass loading suggested that the clumping of fibers was a problem that hindered bacterial access to the fiber surfaces, as well as the diffusion of substrate into the brush interior (Logan, 2007).

2.6.1.4 Metal and Metal Oxide Anode

Metal materials are much more conductive than carbon materials, but they are not widely applicable as carbon materials in MFCs. Many metals were ruled out because of the non-corrosive requirement for anode materials. So far, only stainless steel and titanium have qualified as relative common base materials for anodes.

Generally, the smooth surface of metals does not facilitate the adhesion of bacteria. Some non-corrosive materials, such as stainless steel, fail to achieve higher power densities compared with carbon materials. Dumas et al. (2007) tested the suitability of a stainless steel plate as both the anode and biocathode electrodes in an MFC, and found that the power density (23 mW/m^2) was limited by the anode. In another study, Dumas et al. (2008a) found that the stainless steel anode was less

efficient than the graphite one. In contrast, Erable and Bergel (2009) found that the stainless steel grid anode produced much higher current densities than plain graphite ones when a constant potential (-0.1 V vs. the saturated calomel electrode) was applied to them. These results, however, may be reversed when current densities are normalized to the electrode surface. Titanium is another commonly used metal material for MFC anodes. As mentioned above, titanium, such as titanium wires in a graphite brush, is regularly used as a current collector. terHeijne et al. (2008) compared titanium and graphite in terms of their suitability as an anode in MFCs. Their results showed that the anode performance decreased in the following order: roughened graphite >Pt-coated titanium > flat graphite > uncoated titanium. No current was observed for the uncoated titanium anode. For the three other materials, the specific surface area and biomass activity were important variables in explaining the differences in current density between them.

Gold anodes have also been used in several studies (Crittenden et al., 2006; Richter et al., 2008). Richter et al. (2008) found that *Geobactersulfurreducens* could grow on gold anodes, producing currents nearly as effectively as in graphite anodes.

Table 2.1 Anode Materials, Configuration, Inoculation Source and Power Generation Performance in MFC (Retrieved from Review Paper of Recent progress in electrodes for microbial fuel cells by Wei J.C., Liang P., & Huang X.)

Electrode Materials		**Configuration**	**Electrode Size**	**Inoculation source**	**Reactor configuration**	**Maximum power or current density**	**Reference**
Carbon	Carbon paper	Plane	2.5cm x 4.5cm, 22.5cm^2 total	Primary clarifier overflow	Two-bottle, air cathode	600mW/m^2 (anode area)	Logan et al. (2007)
Carbon	Carbon cloth	Plane	7cm^2 in projected area	Preacclimated bacteria from an active MFC	Two-bottle, air cathode	46 W/m^3 (anode chamber volume)	Zhang et al. (2009b)
Carbon	Graphite plate	Plane	1.92 cm^2	*Shewanellaoneidensis (MR-1)*	Two Chamber, air-cathode	3290 mW/m^2 (anode area)	Dewan et al. (2008)
Carbon	Graphite plate	Plane	155 cm^2	*Shewanellaoneidensis* (MR-1)	Two Chamber, air-cathode	1410 mW/m^2 (anode area)	Dewan et al. (2008)
Carbon	Carbon mesh	Plane	7 cm^2 in projected area	Preacclimated bacteria from an active MFC	Preacclimated bacteria from an active MFC	893 mW/m^2 (anode area), 45 mW/m^2 (anode chamber volume)	Wang et al. (2009)

Table 2.1 Continued

Carbon	Activated carbon cloth	Plane	1.5 cm^2 in projected area	*D. desulfuricans*strain Essex 6 (for sulfate removal)	Single chamber, air-cathode MFCs	0.51 mW/cm^2 (geometric electrode area)	Zhao et al. (2008)
Carbon	Granular graphite	Packed	Granular diameters: 1.5~5 mm; anode chamber: 390 mL	Preacclimated bacteria from an active MFC	Tubular MFC, catholyte: $K_3Fe(CN)_6$	90 W/m^3 (net anodic chamber volume)	Rabaey et al. (2005)
Carbon	Graphite felt	Packed	Anode chamber: 156mL	Preacclimated bacteria from an active MFC	Two chamber MFC, catholyte: $K_3Fe(CN)_6$	386 W/m^3 (anode chamber volume)	Aelterman et al. (2008)
Carbon	Carbon felt	Packed	Anode chamber: 156mL	Preacclimated bacteria from an active MFC	Two chamber MFC, catholyte: $K_3Fe(CN)_6$	356 W/m^3 (anode chamber volume)	Aelterman et al. (2008)

Table 2.1 Continued

Carbon	Granular activated carbon	Packed	Anode chamber: 450 mL, wet volume: 250 mL	Domestic wastewater	Single chamber cylindrical MFC, air-cathode	5 W/m^3 (volume of anode chamber)	Jiang and Li (2009)
Carbon	Reticulated vitreous carbon	Packed	Anode volume: 190 mL; anode surface area: 97 cm^2	Anaerobic sludge from a anerobic bioreactor treating brewery wastewater	Two chamber cylindrical MFC: $K_3Fe(CN)_6$ catholyte	170 mW/m^2 (anode surface area)	He et al. (2005)
Carbon	Carbon brush	Brush	4 cm long by 3cm in diameter	Preacclimated bacteria from an active MFC	Single chamber cube air-cathode MFC, batch-fed	2400 mW/m^2 (cathode area), or 73 W/m^3	Logan et al. (2007)

Table 2.1 Continued

Metal	Stainless steel plate	Plane	20 x 30 cm, total surface area 0.12 m^2	Marine sediments	Artificial marine MFC	23 mW/m^2 (anode surface area)	Dumas et al. (2007)
Metal	Pt-coated titanium	Plane	Projected area: 22 cm^2	Preacclimated bacteria from active MFC	Two chamber (plexiglass plates with flow channels)	Unreported	TerHeijne et al. (2008)

Table 2.2 Anode Materials, Advantages and Disadvantages of Different Electrode Materials in MFC

Electrode Materials	Advantages	Disadvantages	Literature
Carbon Cloth	Flexible and much more porous, allowing more surface area for bacterial growth	Clogging. Dead microbes often fill these pores and reduce the effective surface area of the electrode. It is prohibitively expensive to use for MFCs (ca.$1000/m2) (Zhang et al., 2010)	S. Ishii, K. Watanabe, S. Yabuki, B.E. Logan, Y. Sekiguchi, Appl. Environ. Microbiol. 74 (2008) 7348–7355. Wei J.C., Peng L., & Xia H. (2011). Recent Progress in Electrodes for Microbial Fuel Cells
Carbon Paper	Easy to connect wiring	Lack of durability, fragile	J.R. Kim, S.H. Jung, J.M. Regan, B.E. Logan, Bioresour. Technol. 98 (2007) 2568–2577.
Graphite Rod	Good electrical conductivity and chemical stability, relatively cheap, and easy to get	Difficult to increase the surface area for microorganism adsorption, low porosity	H. Liu, S.A. Cheng, B.E. Logan, Environ. Sci. Technol. 39 (2005) 5488–5493.
Graphite Fiber Brush	Higher specific surface areas, easy to produce	Clogging	Y. Ahn, B.E. Logan, Bioresour. Technol. 101 (2010) 469–475.
Carbon Felt	Large aperture	Large resistance	H.J. Kim, H.S. Park, M.S. Hyun, I.S. Chang, M. Kim, B.H. Kim, Enzyme Microbial Technol. 30 (2002) 145–152.
Reticulated Vitreous Carbon (RVC)	Good electrical conductivity and plasticity	Large resistance, fragile	Z. He, S.D. Minteer, L.T. Angenent, Environ. Sci. Technol. 39 (2005) 5262–5267.

Table 2.2 Continued

Carbon Nanotubes (CNTs)	Large specific surface area High mechanical strength and ductility Excellent stability and conductivity	High cost of CNTs manufacture, which was reported to be $80–100 Clogging The fabrication of CNTs is complex and expensive, which also limits their large-scale commercial production	K. Donaldson, R. Aitken, L. Tran, V. Stone, R. Duffin, G. Forrest, A. Alexander, Toxicol. Sci. 92 (2006) 5–22. V.K.K. Upadhyayula, V. Gadhamshetty, Biotechnol. Adv. 28 (2010) 802–816. A.M.K. Esawi, M.M. Farag, Mater. Des. 28 (2007) 2394–2401. L.M. Sherman, Plast. Technol. (2007) 1–7. V.N. Popov, Mater. Sci. Eng. R 43 (2004) 61–102.
Carbon Mesh	Inexpensive	Unstable and inconsistent results in long term performance when treating wastewater	Sarah H., Fang Z., and Logan B. E. (2011). Performance of Two Different Types of Anodes in Membrane Electrode Assembly Microbial Fuel Cells for Power Generation from Domestic Wastewater.

Table 2.2 Continued

Graphite Felt	Inexpensive Easy maintenance for the electrode exchange	Lower current efficiency compared to the gas-diffusion electrode	Masao S., Tetsuro K., Keiichi O., and Nobuo Y. (2000)Water-repellency Effect of Graphite Felt used for Trickle-bed Cathode to Electrochemically Produce Hydrogen Peroxide Through Reduction of Oxygen.
Stainless Steel	Corrosion-resistance	Low power density production	Peter R.G., Mark E.N., and Clare E.R.(n.d.).Fundamentals of Benthic MFC: Theory, Development and Application.
Granular graphite	Large specific surface area to decrease the activation losses at the bacteria	Dead zones for current collection may still exist after long term running Potential clogging after long-term running due to low porosities of the packed electrode	Rabaey K., Lissens G., and Verstraete W. (n.d.) MFC: Performance and Perspective Wei J.C., Peng L., & Xia H. (2011). Recent Progress in Electrodes for Microbial Fuel Cells

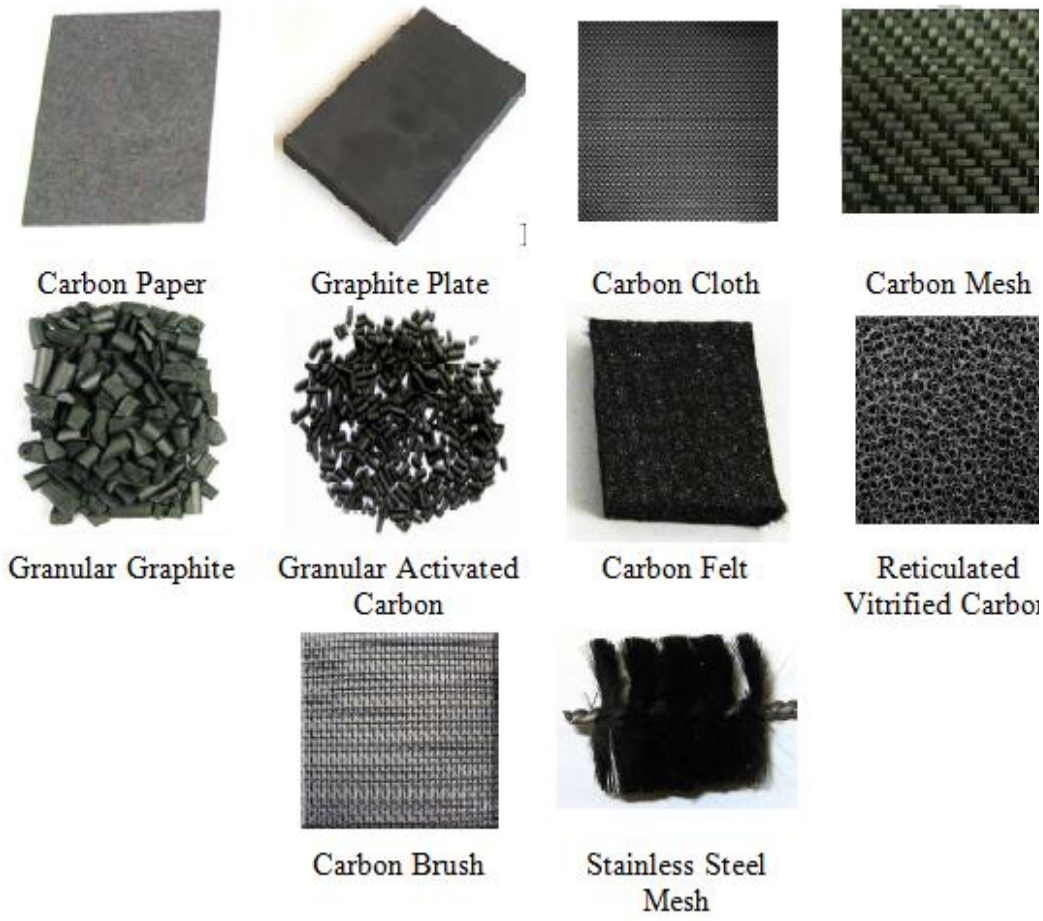

Figure 2.2 Electrode Materials Used for MFC

2.7 Effect of Increasing Anode Surface Area on the Performance of a Single Chamber Microbial Fuel Cell

According to Lorenzo et. al. (2010) experimental work, the effect of increasing anode surface area to reactor volume ratios on the performance of a single chamber microbial fuel cell (SCMFC) was evaluated. The increase in anode surface area was achieved by using packed beds of irregular graphite granules with a mean size of 0.3 cm. Three different granule bed depths were in particular considered, 0.3, 1, and 3 cm, whilst a graphite plate anode was used as a one-dimensional point of comparison. A preliminary model of the current distribution in the packed bed electrode was also applied to the MFC, in which the effective utilization of the electrode was correlated to its specific area, electrode thickness, solution conductivity and slope of the polarization curve.

In this research, the SCMFC used three thicknesses of granules: 0.3, 1 and 3 cm bed depth. This gave total anode volumes of approximately 3.75, 12.5 and 37.5cm^3, respectively. The anode cross-sectional area was 12.5cm^2 whilst the total anode surface area increased with the pellet layer thickness, and was calculated by approximating the area of a single pellet with the surface of a sphere having an average diameter of 0.4cm and by multiplying the surface of one pellet into the total number of pellets introduced in the reactor. The estimated total anode surface areas, with this assumption, were 90cm^2 for a 0.3cm layer of pellets; 499cm^2 in the case of a 1cm layer and 1247cm^2 in the case of a 3cm layer (calculations are based on the actual number of granules used).

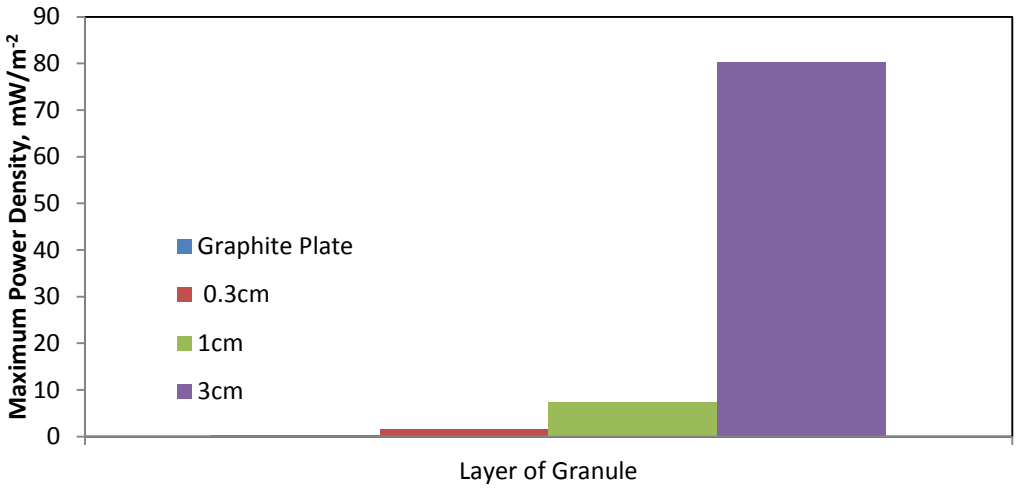

Figure 2.3 Effect of Layer of Granules on Maximum Power Density (mW/m^2)

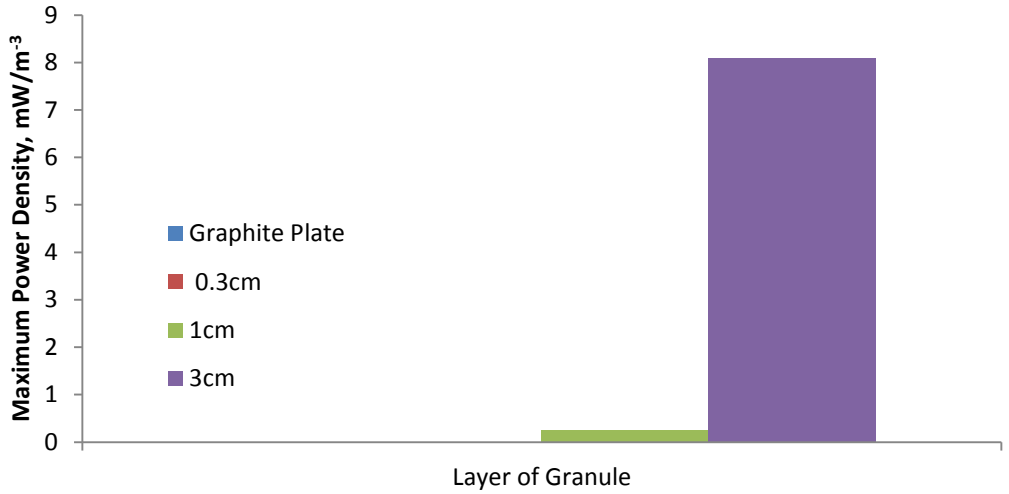

Figure 2.4 Effect of Layer of Granules on Maximum Power Density (mW/m^3)

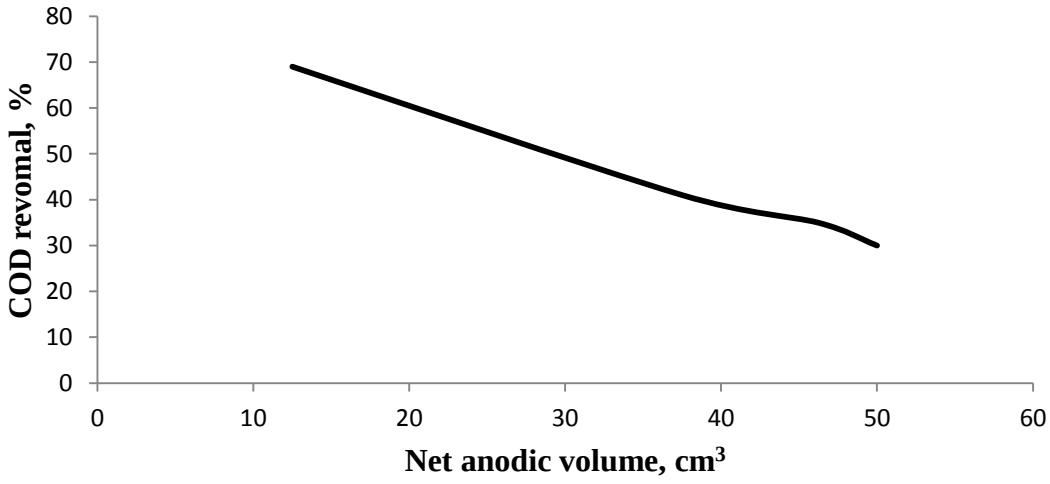

Figure 2.5 Effect of Net Anodic Volume on COD Removal

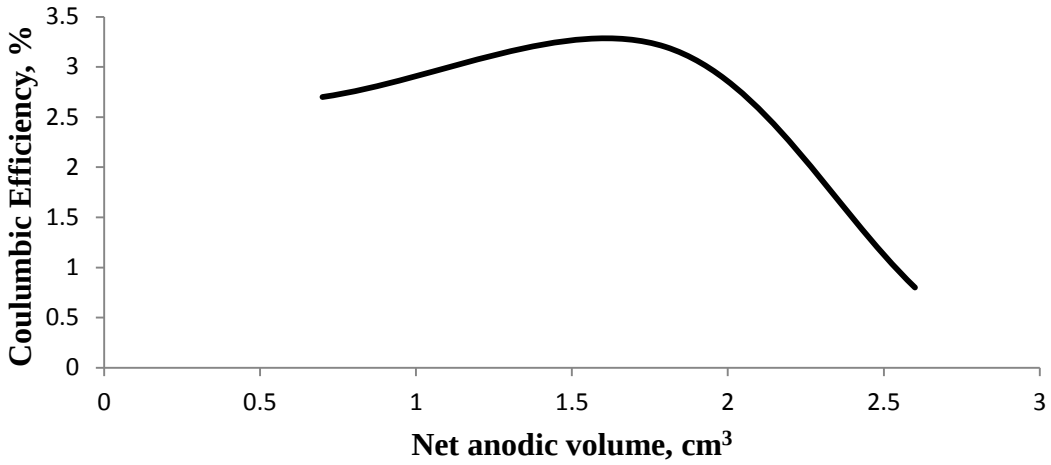

Figure 2.6 Effect of Net Anodic Volume on Coulumbic Efficiency

From the results obtained, the graphite plate anode and graphite granules anodes in layers of 0.3 and 1 cm, the differences in the internal resistances produced were minor: 128Ω, for graphite plate and 0.3cm layer, and 104 Ω for 1 cm layer of pellets. On the other hand, with a 3cm layer configuration the internal resistance decreased to 5Ω, due to the much shorter distance between anode and cathode.

The wastewater treatment performance improved with the thickness of the anode bed depth. The reactors with a 3cm layer of granules in fact, led to 79% of COD removal, nearly 3 times higher than with the graphite plate anode. This is the consequence of an enhanced area for the development of biofilm involved in the COD biodegradation. The higher anode surface area and the reduced internal resistance increased the Coulombic efficiency: switching from graphite plate to 3 cm graphite granules led to a Coulombic efficiency approximately 37 times higher.

Among the four anode configurations analyzed in this work, the 3 cm layer of graphite granule anode resulted in the best reactor performance, both from an

electrochemical (current, power output and Coulombic efficiency) and a wastewater treatment efficiency (COD removal) point of view.

2.8 Performance of Two-Chamber Microbial Fuel Cell in Different Anode and Cathode Electrode Sizes

According to the study of Li et al. (2011), Power generation in microbial fuel cell (MFC) at different cathode electrode surface area was examined in two chambered system with sodium acetate as carbon sources. The anode and cathode used was made of graphite. Two MFC equips with different anode electrode surface areas (A_{An}) of 66 cm^2 and 14 cm^2 were used. Once the MFC demonstrated a repeatable cycle of power generation, the different cathode surface area (A_{cat} was 336 cm^2, 66 cm^2, and 14 cm^2) was used, making the ratio of anode and cathode areas was 1:1(A_{An}=A_{cat}=14 cm^2, MFC1), 1:5 (A_{An}=14 cm^2, A_{cat}=66 cm^2, MFC2), 1:24(A_{An}=14 cm^2, A_{cat}=336 cm^2, MFC3), 5:1 (A_{An}=66 cm^2, A_{cat}=14 cm^2, MFC4) , 1:1 (A_{An}=A_{cat}=66 cm^2, MFC5), 1:5 (A_{An}=66 cm^2, A_{cat}=336 cm^2, MFC6), respectively. Titanium wire was used for the connection of the external circuit. All MFC were operated in room temperature. The anode and cathode compartments were filled with the same with phosphate buffer solution (12.8 g L^{-1} Na_2HPO_4, 3 g L^{-1} KH_2PO_4), and the anode compartment was filled with sodium acetate (4g L^{-1}). The sludge from river mud was used as inoculums in the anode compartment of the MFC. Potassium ferricyanide (50 mmol L^{-1}) was used as the electron acceptor in the cathode.

As for the result, when the anode was fixed at 66 cm^2, increasing the cathode size from 14 to 66 cm^2, the maximum power density increased from 3.63 W/m^3 to 4.62 W/m^3, and further increasing the cathode size to 336 cm^2 increased the maximum power density by 83% (6.65 W/m^3). When the anode was fixed at 14 cm^2, increasing the cathode size from 14 to 336 cm^2, the maximum power density increased from 2.56 W/m^3 to 3.29 W/m^3, resulted in a 28 % improvement in cell power density. This result is consistent with other studies; they found that increasing the cathode surface area relative to that of the anode area consistently increased power output, and showing that the power output was proportional to cathode surface area when the PEM is of a sufficient size for the system. And higher power density was obtained when higher anode electrode surface area of 66 cm^2 was used. Previous studies indicated that increasing the anode surface area could enhance bacteria adhesion, electron and power density.

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Research Design

The study intends to develop a Microbial Fuel Cell (MFC) with different surface areas of electrode. The objective of this experiment is to find the effect of surface area of electrode on the power density produced in MFC. Thus, this study was started with the preparation of inoculum, anodic and cathodic materials. After preparing that, the MFC was constructed. This research was partially based its finding through both quantitative and qualitative research methods because this permits a flexible and iterative approach. During data gathering the choice and design of methods were constantly modified because it will try to find and build theories that will explain the relationship of one variable with another variable through qualitative elements in research. Figure 3.1 shows the overall process of the experiment.

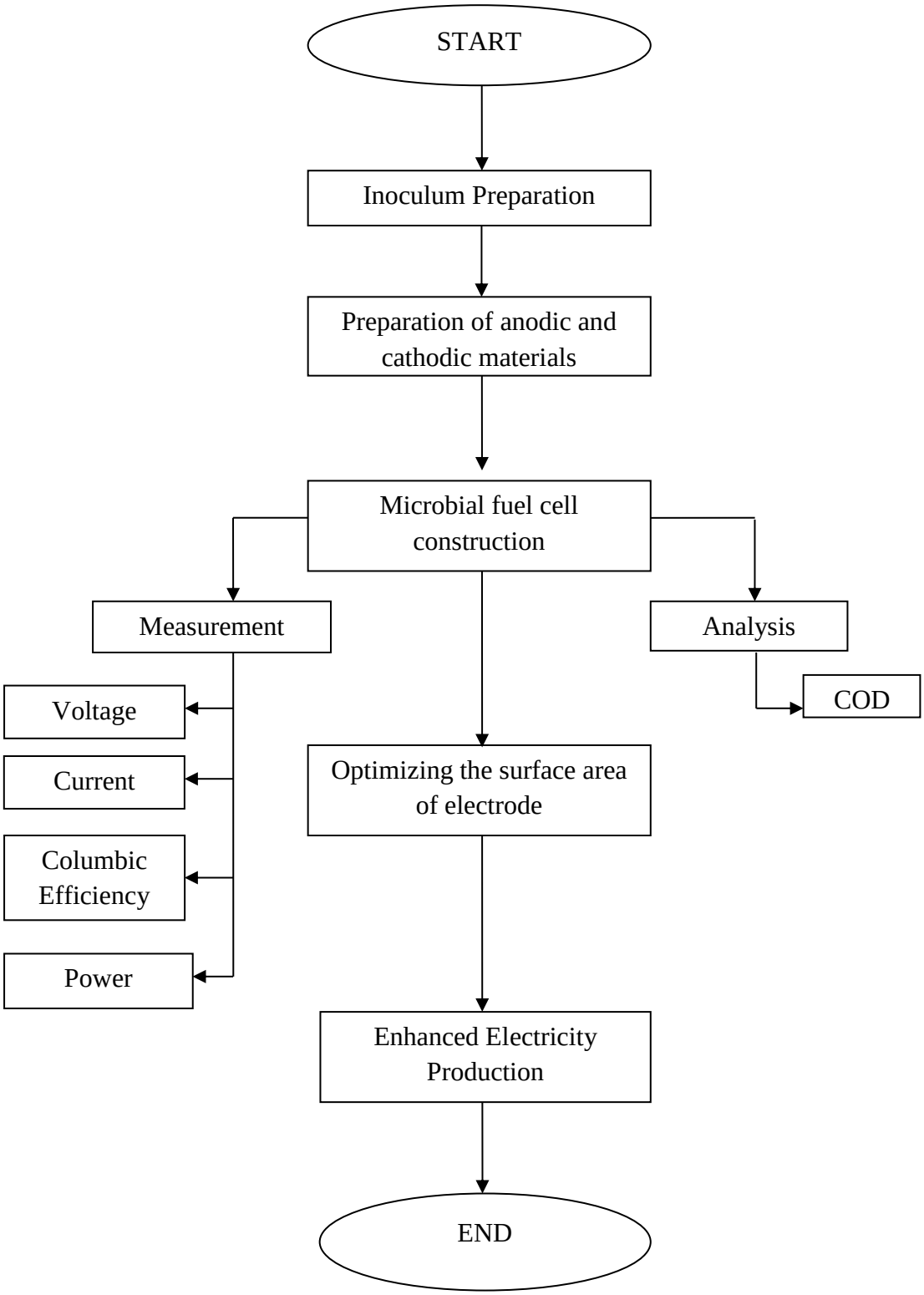

Figure 3.1 Flow Diagram of Overall Process of MFC

3.2. Sampling of Raw Palm Oil Mill Effluent (POME) and Anaerobic sludge

The raw POME and anaerobic sludge samples were collected from Neram Felda palm oil industry, Kuantan. The Raw POME was collected before it discharge into the collection pond or mixing pond and the *temperature* of *raw POME* at the discharge point was around 80 ℃ to 90 ℃. Anaerobic sludge was obtained from bottom sampling port of anaerobic treatment plant. The cooperation from the palm oil mill and the people in-charge, Mr.Zuhan leaded to smooth sampling frequency and time. POME samples was collected and stored at 4 ℃ in refrigerator.

3.3 Characterization of Raw Palm Oil Mill Effluent

The characteristic of the raw POME, such as pH, oil and grease, biochemical oxygen demand (BOD), chemical oxygen demand (COD), total solids (TS), total suspended solids (TSS), ammoniacal nitrogen (Am-N), and nitrate nitrogen ($N - NO_3^-$) were determined according to the Standard Methods for the Examination of Water and Wastewater (APHA, 2000). The characteristics of raw POME were illustrated in the range of minimum and maximum detected concentrations. The characteristics of the POME were compared to the given data as in Table 3.1

Table 3.1 Characteristics of POME and Its Respective Standard Discharge Limit by the Malaysian Department of the Environment

PARAMETERS	CONCENTRATION mg/L	STANDARD LIMIT mg/L
pH	4.7	5-9
Oil and grease	4000	50
BOD	25000	100
COD	50000	-
Total Solids	40500	-
Total Suspended Solids	18000	400
Total nitrogen	750	150

(Retrieved from *Study On Mechanical Pretreatment Process Of Palm Oilmill Effluent (POME),* Hazira, 2006)

3.4 Development of MFC with Different Surface Areas of Polyacrylonitrile Carbon Felt (PACF) as Electrode

3.4.1 Inoculum Preparation

The anaerobic sludge (50ml) and raw POME (450ml) were added into anode by using measuring cylinder and beaker.

3.4.2 Microbial Fuel Cell (MFC) Construction

The MFC consisted anaerobic sludge mixed with raw POME in anode and Potassium Permanganate ($KMnO_4$) in cathode for MFC using $KMnO_4$ as electron receiver which is separated by a Proton Exchange Membrane (PEM) (Nafion 117,DuPont Co., USA) was prepared. The PACF washed several times and membrane was pre-treated by boiling in H_2SO_4 and de-ionized water for 2 hours, and then stored in water prior

to be used. Each compartment of MFC consists of PACF electrode as anode and cathode. Both anode and cathode were connected to variable resistance box and multimeter to measure the voltage and current produced. The experiment was conducted for 15 days as to observe the changes of current and voltage produced by the MFC. The MFC was operated in ambient temperature from 25 to 28℃. The concentration of anaerobic sludge and raw POME used in anode was remained constant throughout the entire experiment.

3.4.3 Optimizing the Surface Area of Electrodes

In order to improve the electrode performance, the surface area of electrode was optimized. The meaning of optimize here is to modify the surface area of electrode as to achieve production of maximum voltage, current and coulumbic efficiency for MFC. Accomplishing this objective will minimize the electrode-skin interface impedance which influences the electrode electrical performance. After constructing the MFC, the current and voltage produced by the MFC were observed and recorded for 15 days. Each experiment was conducted for 15 days and repeated with different surface area. By comparing the results of maximum current and voltage produced for each experiment, the optimized surface area of electrode was determined. Among the three trials, the MFC that produced the maximum current and voltage is considered as optimized electrode surface area for the MFC.

3.5 Measurement and Analysis

3.5.1 Voltage, Current, Coulumbic Effiency and Power Density Measurement

3.5.1.1 Fluke 189 Digital Multimeter

Figure 3.2: Fluke 189 Digital Multimeter

The voltage and current produced by the MFC were measured and stored using multimeter and the data was retrieved from the multimeter using Fluke view forms software. Maximum current production from the MFC was observed and obtained through the polarization and power density curve. This polarization and power density curve were generated in the MFC when external resistance on the system was changed from 50-200kΩ. Before starting each impedance measurement the MFC was prepolarized for at least 15 min at the measuring potential provided by the potentiostat to reach steady state conditions. Power density (Pv, W/m^3) normalized by volume and power density normalized by surface area (P_A, W/m^2) obtained were measured using Equation (3.1), (3.2) and (3.3).

$$P = VI \tag{3.1}$$

$$P_{An} = \frac{V^2}{A_{An}\, R} \tag{3.2}$$

$$P_v = \frac{V^2}{vR} \quad (3.3)$$

Where A = area of anode electrode (m^2), P = power (W), V = the potential (v), v = Working volume of anode (m^3), R = external resistance (Ω) and I = current (A).

3.5.2 Data Analysis

3.5.2.1 COD Removal Efficiency

The COD of the anode effluent is determined using COD Digestion Reactor (0 - 1500-mg/L range) and measured using a Spectrophotometer, HACH DR/2400@DR/2800 as instructed by the lab instructor. As to perform the COD analysis, the COD reactor was preheated to T=150 ℃. 2.00 mL of anode effluent for each experiment was added to the COD Digestion Reagent Vial by using clean volumetric pipette. This was the Prepared Sample (1:25 and 1:50 dilution with de-ionized water). Afterward, 2.00 mL of de-ionized water was added to the vial. This was the Blank. The vials were capped tightly and followed by rinsing them with de-ionized water, then wiped with a clean paper towel. The vials were inverted gently several times to mix before placing them in the preheated COD Reactor for t =2 hours. The vials were cooled to 120 ℃ or less. Each vial was inverted several times while still warm. Next, the vials were placed into a rack and cooled to room temperature. HACH Programs was initiated. The outside of the vials were cleaned with a damp towel followed by a dry one to remove fingerprints or other marks. 16-mm adapter was installed. The Blank was placed into the adapter. The display shown: 0 mg/L COD. When the timer beeps, the Prepared Sample was placed into the

adapter. The results of COD for Prepared Sample were displayed in mg/L COD. The COD removal efficiency was calculated using Equation (3.4)

$$\text{COD removal efficiency} = \frac{\text{Initial COD concentration} - \text{Final COD concentration}}{\text{Final COD concentration}} \quad (3.4)$$

3.5.2.2 Coulombic Efficiency

The CE for complex substrates can be calculated for a fed batch system (*Logan,* 2008) as Equation (3.5)

$$\text{Coulombic Efficiency} = \frac{8 \int_0^{tb} I dt}{F \; V_{An} \Delta_{COD}} \quad (3.5)$$

Where Δ_{COD} = Change in COD concentration, *I*= current, *dt* = change in time, V_{An}= volume of liquid in anode compartment, *F*= Faraday's constant (96485 C/mol e^-).Where 8 is a constant, based on M_{O2} = 32 for the molecular weight of O_2 and b = 4 for the number of electrons exchanged per mole of oxygen.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Performance of MFC with POME

Palm oil mill effluent was collected and characterized as shown in Table 4.1. The predominant microorganisms present in the anaerobic sludge were identified using BIOLOG gene III test (Biolog Inc., United States). The performance of MFC treatment was evaluated using wastewater treatment efficiency by comparing before and after treatment values of wastewater parameters as shown in Table 4.1

Table 4.1 Efficiency of MFC Treatment with PACF

Parameters	Before MFC treatment	After MFC treatment with PACF	Removal % (MFC with PACF)
COD (mg/l)	53000mg/L	288400mg/L	45.58%
BOD (mg/l)	24000mg/L	13200mg/L	45%
Total solids (mg/l)	24050mg/L	9986mg/L	58.47%
Total suspended solids (mg/l)	10040mg/L	2920mg/L	70.91%
Ammoniacal nitrogen (mg/l)	23 mg/L	10mg/L	56.52%
Nitrate nitrogen (mg/l)	160 mg/L	78mg/L	51.25%
Total dissolved solids (mg/l)	12900mg/L	5320mg/L	58.75%

However, when comparing the results for after MFC treatment with PACF and the discharge limit shows in Table 4.2. It can be concluded that the POME is still not suitable to directly discharge into the river and it needs further treatment before being discharged into the river. Table 4.2 shows the discharge permits based on the Environmental Quality Act 1974 which were outlined by the Department of Environment Malaysia (DOE). Standard A is an effluent that is going to be released on the upper stream of a river, which will flow to a Drinking Water Treatment Plant. Standard B however is an effluent that is going to be released on the downstream of a river, which is no Drinking Treatment Plant available at the downstream of the river.

Table 4.2 Discharge Limit

	Parameters	Units	Standards	
			A	B
1	Temperature	^{0}C	< 40.0	< 40.0
2	pH	pH	6.0 – 9.0	5.5 – 9.0
3	BOD_5 at 20 ^{o}C	mg/L	< 20.0	< 50.0
4	COD	mg/L	< 50	< 100
5	Suspended Solids	mg/L	< 50	< 100

4.2 Continuous Current Generation

The continuous current generation in the batch mode for three different PACF surface areas of MFC were fluctuating and increasing with the time up to 15 days as shown in Figure 4.1, 4.2 and 4.3. The figures also show that the increased surface area of electrode (PACF) increases the current generation in MFC. The stabilized current produced that can be observed from the figures fall in the range of 2-7 days which indicating the formation of exoelectrogenic biofilms by the microbes.

There was an obvious similarity between these three figures: the pattern of the curve which is fluctuating and increasing with the increasing of time. However, at the end of 15 days of conducting these three different PACF surface areas of MFC, the maximum current generated for each MFC was different compared to another. The MFC with PACF surface area (34.79cm^2) has the highest current generation,

1519.8μA, followed by MFC with PACF surface area (29.11cm^2), 1419.3μA, and MFC with PACF surface area (27.69cm^2), 1337.3μA. Among the three surface areas of PACF electrode configurations analysed by this work, the MFC with PACF surface area (34.79cm^2) resulted in the best reactor performance from continuous current generation point of view.

At the end of 15th day for three experiments, we noticed that the current produced is still in the trend of increasing instead of dropping and it is getting higher for the larger surface area of PAFC electrode MFC. This indicates that the performance of the MFC was improved and the activity of exoelectrogenic biofilm on the anode was not inhibited but improved.

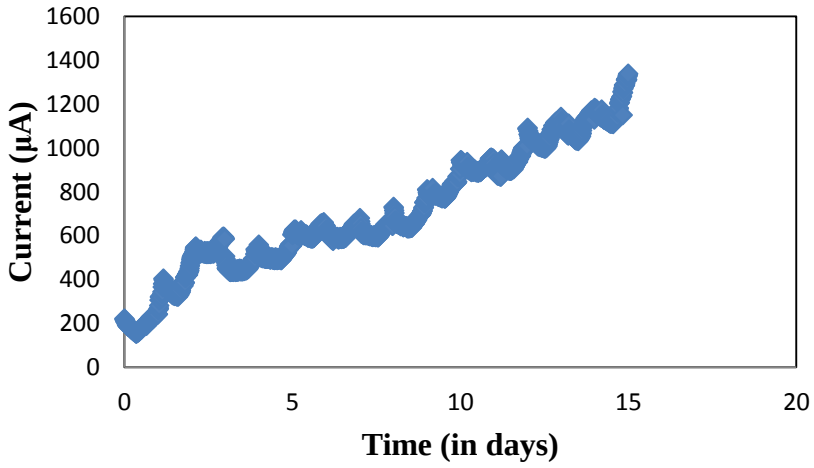

Figure 4.1 Current versus Time for MFC with PACF Surface Area (27.69cm^2)

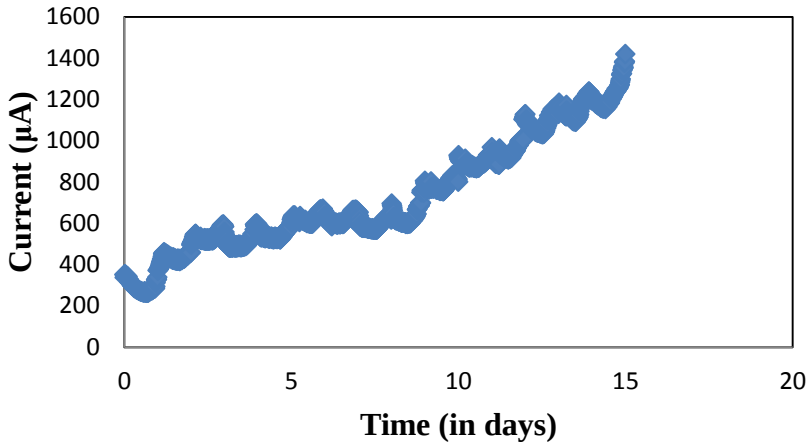

Figure 4.2 Current versus Time for MFC with PACF Surface Area (29.11cm^2)

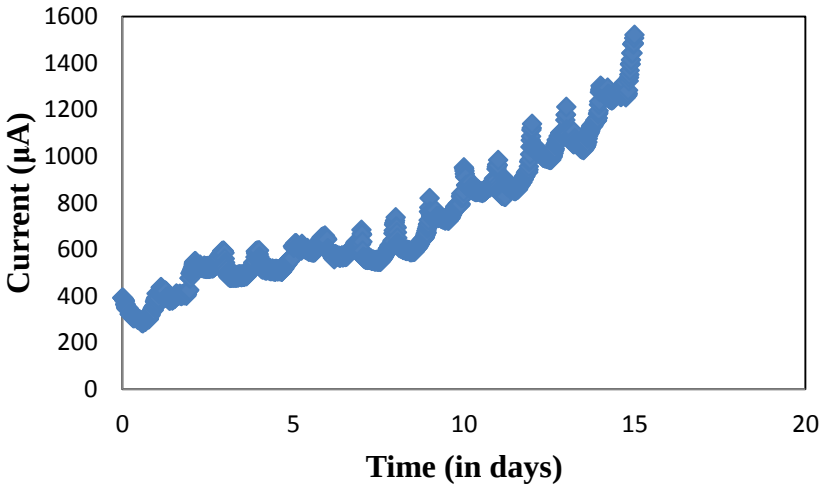

Figure 4.3 Current versus Time for MFC with PACF Surface Area (34.79cm^2)

4.3 Polarization and Power Density

A polarization curve is used to characterize current as a function of voltage. By changing the circuit external resistance (load) we can obtain a new voltage and hence a new current at that resistance.

Polarization and power density curves were obtained for MFC with PACF as anode and cathode at different surface areas. The open circuit potential (OCV) was

higher in the case of PACF with surface area (34.79cm^2) than PACF with surface area (29.11cm^2) and PACF with surface area (27.69cm^2). During the generation of polarization curves, the values of voltage versus current were recorded for MFC with different PACF surface areas as shown in Figure 4.4 and 4.5. The polarization curve obtained exhibited a gradual drop in voltage resulting in arc shape occurrences in power density curves. The power density was increased with the current density by increasing the resistance and reached a maximum point then dropped to a minimum value.

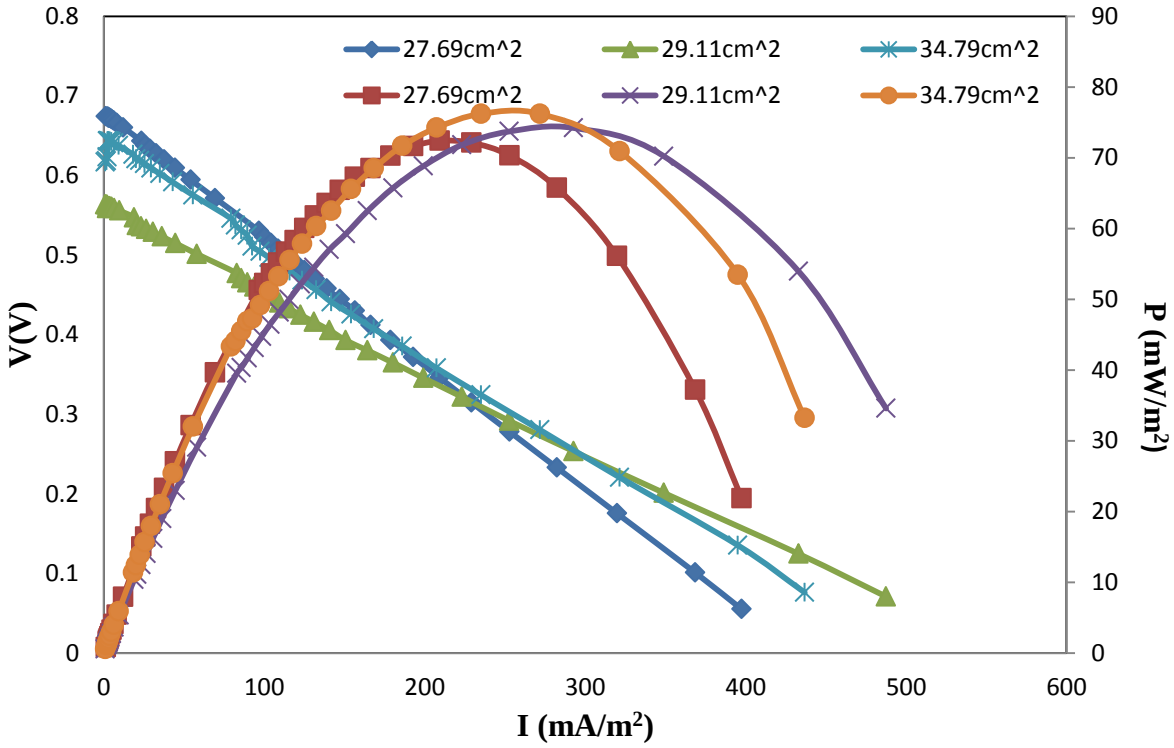

Figure 4.4 Voltage and Power Density generated as a Function of Current at Different PACF Surface Areas of MFC

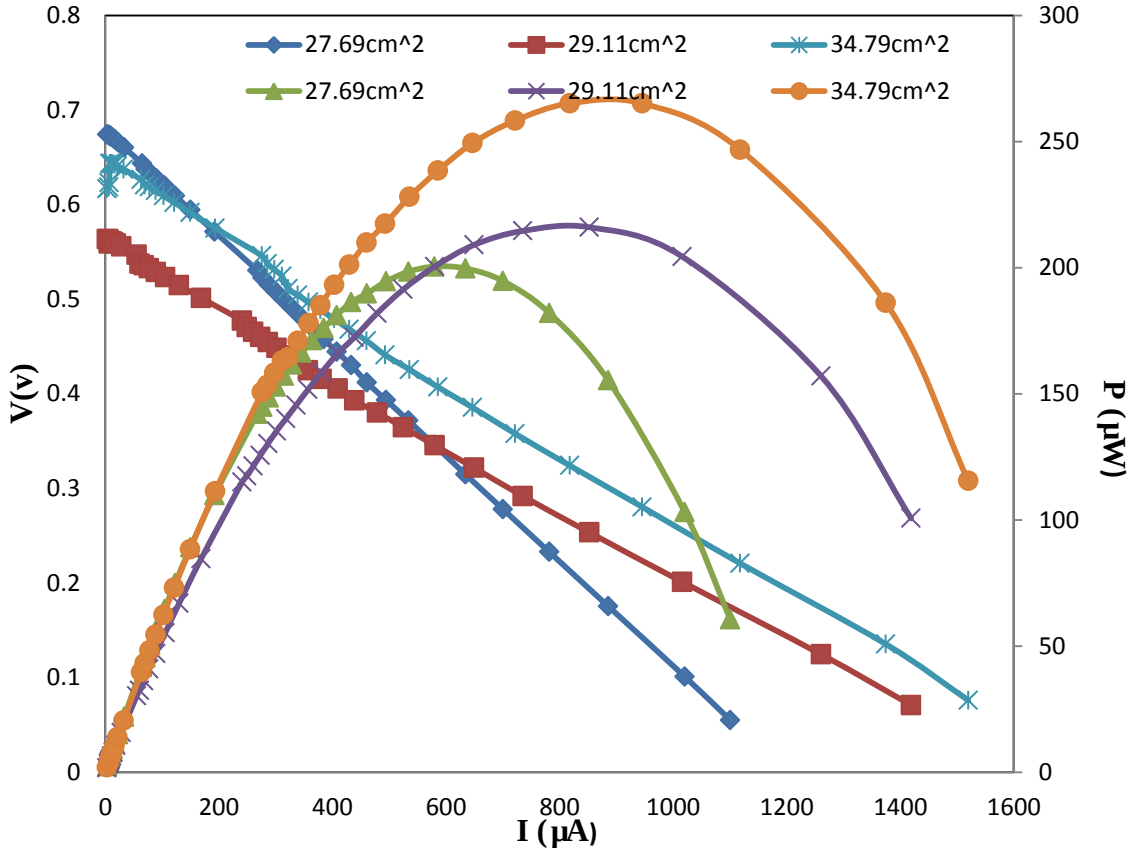

Figure 4.5 Voltage and Power Density generated as a Function of Current at Different PACF Surface Areas of MFC

As shown in Figure 4.5, the power generation in the batch mode included three phases: ascending phase, stationary phase and declining phase (Min et al., 2005). In order to make the MFC more applicable, the stationary phase should be as long as possible which can be achieved by reducing the internal resistance of the MFC (LI et al., 2008). This could be accomplished by increasing the active surface area of the cathode and/or by adding a biocatalyst.

MFC with PACF surface areas (27.69cm^2, 29.11cm^2 and 34.79cm^2) produced maximum power densities of about 72.3944mW/m^2, 74.2094 mW/m^2 and76.2133mW/m^2 and respectively. The maximum current densities obtained were 397.5442mA/m^2,487.5644 mA/m^2 and 436.8497mA/m^2 for MFC with PACF surface

areas (27.69cm^2, 29.11cm^2 and 34.79cm^2). MFC with larger surface area of PACF (34.79cm^2) produced much higher power.

This result is consistent with other similar studies; they found that increasing the anode surface area relative to that of the cathode area consistently increased power output, and showing that the power output was proportional to anode and cathode surface area when the PEM is of a sufficient size for the system (Oh et al., 2004)

Besides, these results indicated that increasing the surface area of PACF (electrode) could enhance bacteria adhesion, hence, more biofilms can be formed by the bacteria on the PACF surface that act as electron acceptors and transfer more electrons directly to the anode resulting in the higher power and more energy production. We can observe from both of the figures that when reaching the maximum power for three MFC with different PACF surface areas, the corresponded voltage from the polarization curve is small, this can be explained by the factor of increasing of current and ohmic resistance.

There are several factors which affects the power generation of MFC. The highly viscous nature of POME clogged the electrode surface which reduces the mass transfer rate thus it affects electricity generation. MFC with POME forms a thick biofilm on the electrode surface which interrupts the electron transfer from microbes to the electrode surface and it could be a reason for low power density produced by MFC with complex POME compare to MFC with simple substrates. Further factors such as longer electrode spacing which decreases the proton transfer rate and equal anode and cathode surface area limits the power generation.

4.4 Effect of PACF Surface Area on Coulombic Efficiency

As shown in the Figure 4.6, this figure depicts the coulombic efficiency of MFC varies with different surface area of PACF. As can be seen that coulombic efficiency increases with increased surface area of PACF and among the these different surface area of PACF, MFC with PACF surface area (34.79cm^2) showed higher coulombic efficiency, 0.9561% than other MFC with PACF surface area (27.69cm^2, 0.6073% and 29.11cm^2, 0.7263%). Nevertheless, these values are substantially lower than 83 and 97% reported by others using pure cultures and aqueous cathodes (Bond et al., 2003). The most likely reason for a low coulombic efficiency is the loss of substrate due to diffusion of oxygen through the Nafion membrane, although other factors may contribute to reduced efficiencies as well.

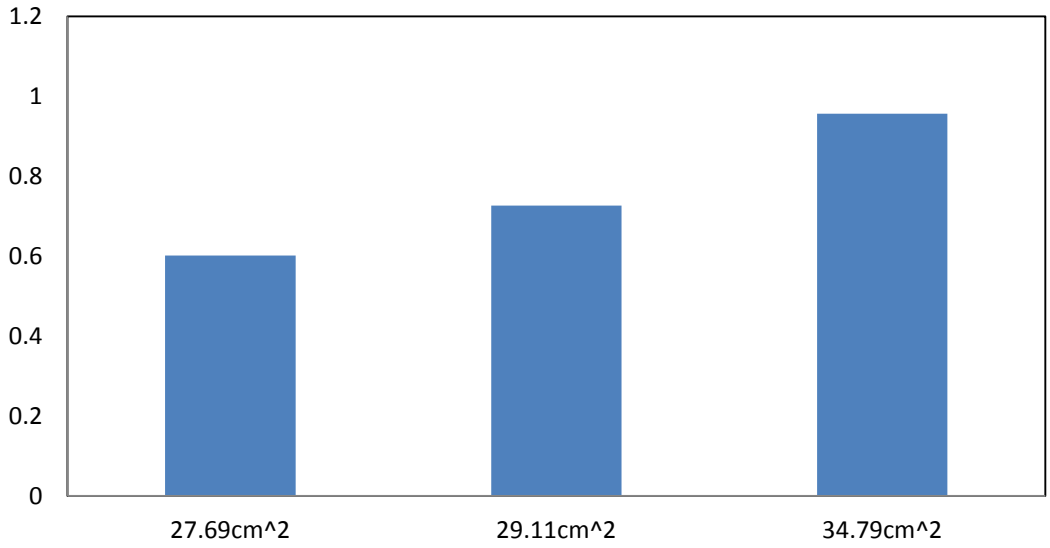

Figure 4.6 Relationship between MFC with Different PACF Surface Areas and Coulombic Efficiency

Coulumbic efficiency describes how much of the electrons can be abstracted from the electron-rich substrates via the electrodes (Aelterman et al., 2006). This indicates that, to achieve high coulumbic efficiency, the surface area of the electrode must be large enough for the microbes to adhere and produce more biofilms in order to transfer more electrons to the electrode. However, even with large surface area of electrode used, the coulombic efficiency may still be very low due to the reason of low rate of electron abstraction (Tender et al., 2002).

In mixed community biofilms with complex nutrient sources, Coulombic efficiency may be dramatically reduced due to alternative metabolism, such as methanogenesis or aerobic respiration (Lovley et al., 2008). Large surface area of electrode has higher chances for microorganisms like electricigen to adhere and hence produce biofilms on the electrode. Electricity production with electricigens has a number of advantages. One of great significances is the high coulumbic efficiency that results from these microorganisms being able to completely oxidize organic substrates in POME to carbon dioxide with PACF electrode serving as the sole electron acceptor (Judy et al., 2008).

The predominant microorganisms present in the anaerobic sludge such as *Pseudomonas mendocina, Pseudomonas viridiivida, Acetinobacterschindleri, Actinobacilluscapsulatus* and *Brevibacteriumpaucivorans* can be the potential microbes that are operationally stable and yield high coulumbic efficiency. These are all bio-electrochemically active and can form a biofilm on the anode surface and transfer electrons directly by conductance through the membrane. When they are

used, the anode acts as the final electron acceptor in the dissimilatory respiratory chain of the microbes in the biofilm. Biofilms forming on a cathode surface may also play an important role in electron transfer between the microbes and the electrodes which might help in yielding high coulumbic efficiency (Chaudhuri et al., 2003).

4.5 Effect of PACF Surface Area on COD Removal Efficiency

The COD removals of the palm mill wastewater in the MFC system over time are shown in Figure 4.7. The figure showed that COD removal efficiency increases with increased PACF surface area of MFC.As time increased, the efficiency increased and reached a peak and followed by decreasing until approximately of 41.5%, 43.6% and45.6% for MFC with PACF surface area (27.69cm^2, 29.11cm^2 and 34.79cm^2) respectively after 15days. It also shows that MFC with PACF surface area (34.79cm^2) has acquired higher COD removal efficiency than other MFC with PACF surface areas (27.69cm^2 and 29.11cm^2). The decreasing of COD removal efficiency is probably due to the reason of decreasing of number of microbes. As the time increases, the organic substrate which is considered as the food supply of the microbes had started to become limiting, this situation indicates that the microbes which unable to obtain food will start dying.

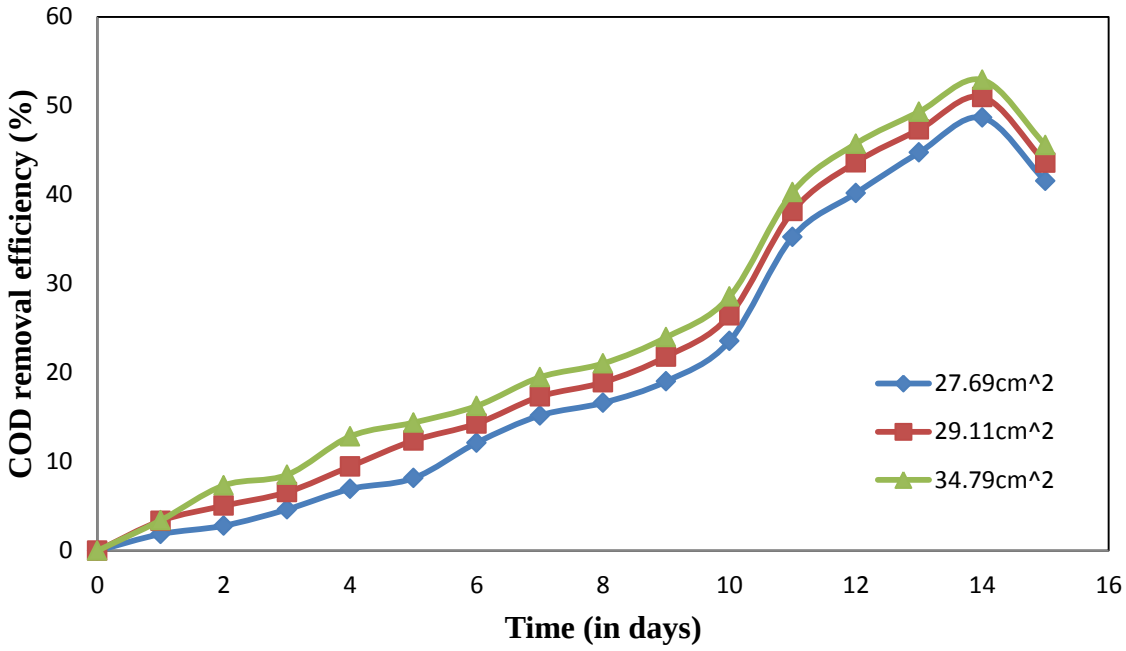

Figure 4.7 Profile of COD Removal Efficiency of MFC with Different PACF Surface Areas

Table 4.3 Performance Comparison on MFC with Different PACF Surface Areas

Type of Electrode	Surface Area of Electrode (cm^2)	Maximum Current (µA)	Maximum Power Density (mW/m^2)	Coulumbic Efficiency (%)	COD Removal Efficiency (%)
PACF	27.69	1337.3	72.3944	0.6073	41.5
PACF	29.11	1419.3	74.2094	0.7263	43.6
PACF	34.79	1519.8	76.2133	0.9561	45.6

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

In this study, Polyacrylonitrile carbon felt, a type of electrode material in MFC was used to treat palm oil mill effluent (POME) whilst generating electricity. The highest COD removal efficiency of approximately 45.6% was achieved in the MFC system with PACF surface area (34.79cm^2). The power generation capability of an MFC which achieved maximum and minimum power densities of 76.2133mW/m^2 and 72.3944mW/m^{2}forMFC with PACF surface area (34.79cm^2) and (27.69cm^2) respectively. Maximum and minimum Coulumbic efficiency of about 0.9561% and 0.6073% was achieved for MFC with PACF surface area (34.79cm^2) and (27.69cm^2) respectively. These results indicated that the surface area of electrode has significant effect on the performance of MFC. The larger the surface area of electrode, the better

the performance of MFC can be achieved. Therefore, we can conclude that MFC with larger surface area of electrode can effectively increase the performance of MFC as well as COD removal efficiency in wastewater treatment.

5.2 Recommendations

The purpose of this research is to study the effect of using different PACF surface areas on the performance of MFC as well as COD removal efficiency in wastewater treatment. For the future research, some recommendations below might become useful in order to achieve more excellent result:

i) Study on other electrode materials with different surface areas like Carbon Cloth, Granular Graphite, Granular Active Carbon and etc. that can affect the performance of MFC.

ii) The duration for each experiment conducted can be extended more than 15 days as to observe more precise and accurate results.

iii) Study the influence of different microbial community on wastewater treatment and bioenergy generation, the effects of various fuels, in particular complex fuels, on microbial population structures and their electricity generation abilities.

iv) Carry out in-depth exploration of external and internal resistance of MFC and a detailed investigation of ohmic, kinetic and mass transfer properties as to improve the performance of MFC.

v) Use different types of membranes as Proton Exchange Membrane (PEM), for instance, bipolar membrane, glass wool, nano-porous filter and etc. to replace Nafion membrane as to study how the types of membranes as PEM can affect the performance of MFC.

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