BIOELECTRICITY GENERATION FROM MIXTURE OF PALM OIL MILL EFFLUENT AND WET PALM OIL SLUDGE BY USING GRAPHITE ROD AS ELECTRODE IN MICROBIAL FUEL CELL

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NURUL IZYAN BINTI ISMAIL

Thesis submitted in fulfillment of the requirements
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ABSTRAK

Dwi Sel fuel mikrob (SFM) telah dibina untuk mengkaji potensi efluen kilang kelapa sawit (EKKS) sebagai substrat dan enap cemar minyak sawit basah (ECMSB) sebagai bahan tambahan untuk menjana elektrik. Pelbagai jumlah dos iaitu 0 mg/L, 2mg/L, 4 mg/L dan 6 mg/L ECMSB telah ditambah untuk dicampur dengan EKKS. Tempoh operasi SFM ialah 20 hari iaitu 5 hari bagi setiap dos. Rod grafit digunakan sebagai elektrod sepanjang operasi SFM. Operasi SFM menggunakan campuran daripada EKKS dengan dos 4 mg/L ECMSB menunjukkan kuasa maksimum iaitu 9.17 x 10-6W. Kuasa maksimum yang dicapai pada hari kedua operasi SFM. Faktor-faktor yang mempengaruhi prestasi MFC telah ditentukan. Jumlah pepejal terampai (JPT), permintaan oksigen kimia (POK) dan pH menunjukkan kesan terhadap prestasi SFM. Peratusan tertinggi penyingkiran POK ialah 21% yang menunjukkan keberkesanan SFM. Parameter operasi iaitu ECMSB sebagai aditif dan masa operasi telah dikenalpasti dalam kajian ini. 4 mg/L dos ECMSB sebagai bahan tambahan dalam SFM menunjukkan penghasilan kuasa tertinggi sepanjang operasi. Penghasilan kuasa tertinggi untuk setiap 0 mg/L, 2mg/L, 4 mg/L dan 6 mg/L dos telah dicapai pada hari kedua operasi. Hasilnya menunjukkan bahawa SFM berjaya menunjukkan potensi penjanaan elektrik daripada campuran EKKS dan ECMSB menggunakan grafit sebagai elektrod. Selain itu, parameter operasi, JPT, POK dan pH menunjukkan pengaruh yang besar dalam prestasi SFM.

ABSTRACT

A dual chamber microbial fuel cell (MFC) was constructed to study the potential of palm oil mill effluent (POME) as substrate and wet palm oil sludge (WPOS) as additive to generate electricity. Various amount of dosage which is 0 mg/L, 2mg/L, 4 mg/L and 6 mg/L of WPOS was added to mix with the POME. The duration of MFC operation was 20 days which 5 days for each dosage of WPOS. Graphite rod was used as electrode throughout the MFC operation. The MFC operation using mixture from POME with 4 mg/L dosage of WPOS show a maximum power which is 9.17 x 10^{-6}W. The maximum power achieved in second day of MFC operation. The factors that effecting the performance of MFC was determined. Total suspended solid (TSS), chemical oxygen demand (COD) and pH showed the effect towards the MFC performance. The highest percent of COD removal was 21% which indicate the effectiveness of MFC. Operating parameter which is WPOS as additive and operational time was identified in this study. 4 mg/L dosage of WPOS as additive in MFC showed the highest power production throughout the operation. The high power for each 0 mg/L, 2mg/L, 4 mg/L and 6 mg/L was achieved in second day of their operation. The result indicates that MFC succeeded show the potential of electricity generation from the mixture of POME an WPOS using graphite as electrode. Besides that, operating parameter, TSS, COD and pH indicate the great influence in MFC performance.

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LIST OF SYMBOLS

°C	Celsius

LIST OF ABBREVIATIONS

COD	Chemical Oxygen Demand
EFB	Empty fruit branches
MFC	Microbial Fuel Cell
POME	Palm Oil Mill Effluent
POS	Palm Oil Sludge
PKS	Palm kernel shells
PEM	Proton exchange membrane
TSS	Total Suspended Solid
WPOS	Wet Palm Oil Sludge

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Oil palm agriculture began in West Africa, where oil palm trees were originally interplanted with other annual and perennial crops in traditional agricultural production systems. It is believed to have been domesticated in Nigeria approximately 5,000 years ago. Production was primarily for subsistence or regional trade. By the early 1970s, monocrop oil palm plantations had grown significantly in Malaysia and Indonesia, and by 2000, these two countries accounted for slightly more than half of the world's total plantation area, while Nigeria accounted for slightly more than 30% (Singh Nee Nigam & Pandey, 2009). Indonesia, Malaysia, and Thailand have been the world’s leading producers of palm oil. Most of the palm oil mills produce a lot of waste from extracting palm fruit oil. Over 115 million tons of palm oil mill effluent or known as POME, is produced in the SEA region each year. However, POME considered as industrial wastewater that is 100 times more harmful than municipal sewage (Show et al., 2021).

In order to address growing environmental concerns, it is desirable to treat industrial effluents efficiently and sustainably in order to ensure their safe disposal into the environment (Show et al., 2021). Although biological treatment is the most often used approach in Malaysia, other methods such as physicochemical and membrane filtering are investigated. Improving POME treatment procedures and generating environmentally friendly, renewable energy can help clean up the environment (Hassan, 2014). Besides treating the POME, other alternative is used to address this issue which producing energy in line with the energy demand in Malaysia.

The availability and supply of fossil fuels in Malaysia has a direct impact on the country’s economic growth. There was still a heavy reliance on oil and natural gas in the country's industrial and transportation sectors. Furthermore, the industrial sector's rapid rise has resulted in an increase in energy demand (Mushtaq et al., 2013). Hence, the dependency on fossil fuels must be decreased. Providing sufficient, economical, and environmentally friendly electricity is a modern necessity. For an upper middle-income country such as Malaysia, it is critical to harness a secure, dependable electrical supply to fuel economic growth, protect the environment, and maintain price competitiveness (Jaye et al., 2016). Significant effort is being made to explore alternate means of generating electricity. The development of new energy generation from renewable resources that does not result in net carbon dioxide emissions is highly sought. In recent years, academic researchers have shown substantial interest in a technology called microbial fuel cells (MFCs) that converts the energy held in chemical bonds in organic compounds to electrical energy via catalytic reactions by microorganisms (Du et al., 2007)

A conventional MFC is divided into anode and cathode compartments by a cationic membrane or known as proton exchange membrane (PEM). In the anode compartment, microbes digest organic compound like glucose, which serves as an electron donor. Electrons and protons are generated during the metabolism of these organic compounds. Following that, electrons are transported to the anode surface. The electrons migrate from the anode to the cathode via the electrical circuit, whereas the protons flow through the electrolyte and then the PEM (Chaturvedi & Verma, 2016). However, there is limitation in this application. The limits of MFC's widespread use as an alternative energy source are its limited power output and high operating costs for commercial applications. Besides that, the amount of energy generated by MFC is dependent on a variety of factors, including the catalyst, design, substrate, type of membrane, and temperature. Among these elements, the MFC membrane has been called the most crucial component of the entire system, as it is separating the cathode and anode.

The membrane must allow protons to pass from the anode to the cathode while preventing the passage of other materials such as oxygen and substrates (Ghasemi et al., 2015).

1.2 Problem Statement

Malaysia has been one of the world's largest producers and exporters of palm oil products in recent decades. The number of palm oil mills is quickly expanding each year, resulting in an increase in the amount of fresh fruit bunch waste or effluent discharge. However, POME is considered as one of the Malaysia's significant environmental contaminants. POME's suspended solid and nutrient content may be able to sustain algae growth (Kamyab et al., 2018). POME discharges without proper treatment have a detrimental effect on the environment. As a result, the Malaysian government enacted the Environmental Quality Act 2009, which establishes the standard effluent discharge limit. Although biological treatment is the most often used approach in Malaysia, other methods such as physicochemical and membrane filtering are investigated. Improving POME treatment procedures and generating environmentally friendly, renewable energy can help clean up the environment (Hassan, 2014). Therefore, many technologies have been introduced to solve the issues. One of the technologies is microbial fuel cell.

Microbial fuel cell technology is a new field of alternative renewable energy production that also provides the environmental bioremediation opportunities (Javed et al., 2018). In recent years, microbial fuel cell becomes one of a technology that producing the electricity by using electrons derived that come from the biochemical reactions. The bacteria from the substrate will be catalysed. This technology able to generate electricity through the bioelectrochemical process. POME is one of the substrates that commonly used in microbial fuel cell. It isconsidered as polluted wastewater. The untreated POME discharge will give a negative effect to the environment due to their high in chemical oxygen demand (COD) and biochemical oxygen demand (BOD). Besides that, POME consists of phosphorus and concentration of organic nitrogen that significantly higher (Kamyab et al., 2018). Hence, it is vital to investigate performance of the untreated POME sludge and palm oil sludge as substrate in the microbial fuel cell in order to generate the electricity. Due to their high potential to be used as substrate to generate the electricity by using the microbial fuel cell.

Previous studies show that the power produced from the microbial fuel cell is still low and not achieved the target (Moqsud et al., 2013). Therefore, it is important to design and develop the electrochemical reactor/cell by varying in terms of electrode's arrangement and type of the electrode's material. There are many types of electrodes can be used as cathode and anode such as graphite, graphite felt, carbon paper, carbon-cloth, Pt, Pt black, reticulated vitreous carbon (RVC). Different activation polarization will be show based on the different using of anode electrode material. By choosing the good materials, the performance of the microbial fuel cell will be increasing and might be different. In the other hand, there are also various types of electrodes that can be used as cathode in the microbial fuel cell such as Graphite, graphite felt, carbon paper, carbon-cloth, Pt, Pt black, RVC, Glass, polycarbonate, Plexiglas (Du et al., 2007). All these materials are suitable to be used as electrode in microbial fuel cell to enhance the performance of the microbial fuel cell. Thus, the generation of bioelectricity from the microbial fuel cell can be identified by varying them.

Besides that, the microbial fuel cell generates limited voltage and current which from the unit cells and thus their practical applicability was limit (Kim et al., 2020). This issue has led to the performance of the microbial fuel cell and thus the reduction of the electricity generation. In addition, there are many factors that can affect the performance of MFC and the important factors including substrate, electron transfer, material of the membrane and the condition of the operating which are temperature, salinity and pH and the design of the MFC (Aghababaie et al., 2015). Hence the operating parameters including operational time, inter-electrode distance and pH on the electrochemical process are crucial to be investigated to determine the effect of parameters to the MFC.

1.3 Objective of Study

The main objective of this study is to generate bioelectricity from in microbial fuel cell (MFC). Meanwhile the specific objectives are:

- To investigate influence of the circuit on the power, voltage, and current output from MFC by using graphite rod as electrode
- To determine effect of various essential factors on the performance of microbial fuel cell such as electrode materials, total suspended solid, chemical oxygen demand, pH and operating parameter, which is WPOS as additive and operational time

1.4 Scope of Study

This study is focus on generation of electricity from POME and wet palm oil sludge by using graphite rod in MFC. POME and WPOS which has the potential for the generation of electricity have been chosen as a substrate in MFC. Both samples have been acquired from Kilang Sawit Lepar Hilir 3 and stored in cold room with -4°C temperature. MFC were fabricated using an octagon water tank with 1.6 litre of volume.

Next, the performance of POME and WPOS to generate electricity in MFC was investigated. Voltage and current and was determined by using digital multimeter. Meanwhile the power produce was determined by using formula Ohm’s Law in this study. The effect of operating parameter was investigated. The parameters included operational time and dosage of WPOS. The operation of MFC was applied in 20 days which 5 days for each different amount of dosage. Besides that, the water quality of the POME and WPOS on the MFC process was analysed before and after MFC operation. Chemical oxygen demand (COD), total suspended solid (TSS) and pH are the parameter that have been analysed for the water quality.

CHAPTER 2

LITERATURE REVIEW

2.1 Review of Palm Oil

2.1.1 Malaysia Palm Oil Industry

The oil palm sector is well-known in Malaysia, where plantations can be found practically everywhere. Malaysia began cultivating oil palm about a century ago. Malaysia's economic growth is based on the palm oil sector. Malaysia is unquestionably a critical supply of this product. In 2008 until 2011, the world's estimated palm oil production was 42.9, 45.3, 45.9, and 49.9 million tonnes, respectively. These amounts are significant in comparison to 1980, when only 4.8 million tonnes of palm oil were produced worldwide (Awalludin et al., 2015).

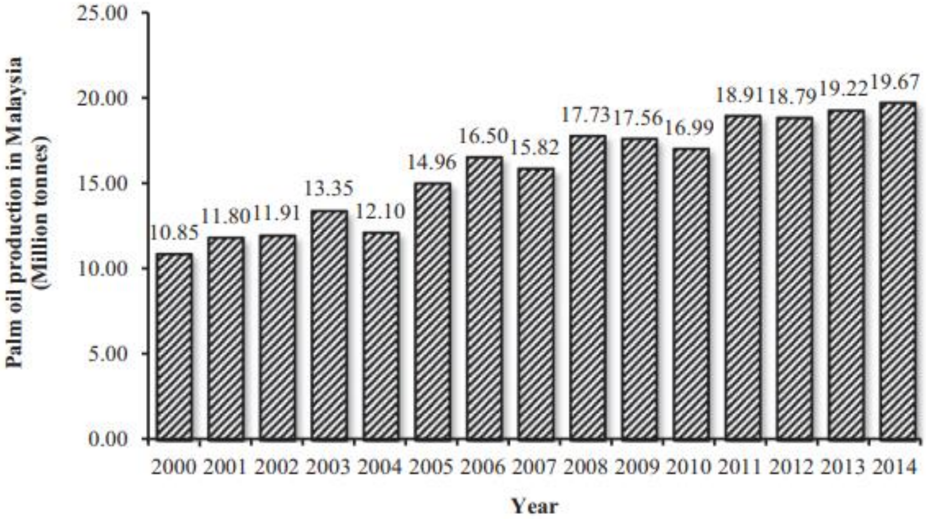

Figure 2.1 Palm oil production in Malaysia (Awalludin et al., 2015)

The figure 2.1 presents the amount of palm oil produced in Malaysia from 2000 to 2014. Malaysia grew their palm oil production overall, despite several years of reduction in total palm oil production in comparison to previous years. Malaysia exports most of its palm oil to the People's Republic of China (PRC). In 2011, Malaysia exported 3.98 million tonnes of its total 11.78 million tonnes of palm oil to the PRC (Awalludin et al., 2015). Malaysia is estimated to have 454 palm oil mills (POMs) operating in 2017. The palm oil industry has become a significant contributor to Malaysia's gross domestic product (GDP), with an estimated RM 80 billion in 2018, accounting for up to 8.7 percent of GDP (Tan & Lim, 2019).

2.1.2 Waste Generation in Palm Oil Industry

The industry of palm oil generates a large amount of agro-industrial waste, both solid and liquid. Oil palm plantations were estimated to generate more than 295 million tonnes of waste annually on a global scale. Malaysia and Indonesia, the world's top palm oil producers, are generate over 230 million dry tonnes of oil palm solid biomass waste in 2020. Approximately 75% of waste which is biomass waste generated by cultivation of oil palm where it often left rotten for the purpose of recovery of nutrient and mulching in plantation. Meanwhile the remaining 25% produced by oil palm milling and can be used to generate energy by the process of direct combustion (Ong et al., 2021).

Oil palm is Malaysia’s most important product which has changed the economy and agriculture in the country. Oil palm mills known to have many benefits. However, it also gives impact on the environment which input and output of the activities. A lot of water and energy used by crude palm oil mills in the production process which is the input side. For the output side, there is a lot of solid waste, wastewater and air pollution produce from the process. There may be empty fruit branches (EFB), Palm kernel shells (PKS) and mesocarp fruit fibres (MF) in the solid waste. The liquid waste is formed during the wet extraction of palm oil in a decanter. This liquid waste is referred to as palm oil mill effluent (POME), along with wastes from the cooling water and steriliser (Abdullah & Sulaim, 2013).

POME has known for being a significant source of water contamination. POME's acidic, viscous, and polluting characteristics can seriously contaminate water and disrupt aquatic ecosystems if released without proper treatment, as well as the livelihoods of towns downstream that rely on rivers such as the Kinabatangan River for water. The potential for pollution enhances the POME complexity treatment, necessitating consideration of economic, ecological, and sustainability factors during the treatment decision-making process. The management of POME is a source of contention in the palm oil business, as the procedure is detrimental to the industry, but it mandated by regulatory standards. Besides that, carbon footprint also has contribute in POME basic operation because of waste management, energy use in facilities, retrieval of FBB and transportation (Tan & Lim, 2019).

However, there are numerous uses or applications of palm oil fruits, and their processed wastes can be found in a variety of sectors, including pastries, confectioneries, pharmaceuticals, and dietary supplements. The question over whether to consume palm oil is perpetually contentious among researchers and experts. Additionally, it was suggested that contributors to heart-related disease may be a result of the bad diet typically adopted in western countries with reduced vegetable oil consumption. Besides that, palm oil is widely used in non-foods applications, accounting for approximately 20% of total palm oil consumption (Kaniapan et al., 2021).

2.2 Properties of Wastes

2.2.1 Properties of Palm Oil Mill Effluent

Palm oil mill effluent (POME) is a thick, dark brown waste product that comes from the process of making palm oil. POME is mostly water (about 95%), residual oil (about 4%), and solid materials (about 1%) (Ong et al., 2021). The primary process that contributes to POME production is the discharge of water from the FFB sterilising stage, slurry from the pressed oil clarifying stage, and wastewater from the hydro-cyclone unit (Poh et al., 2020). The primary source of POME is palm oil clarifying process wastewater, which accounts for 60% of the POME created. The wastewater discharged during FFB sterilisation and separation of kernel shell hydro-cyclone accounts for approximately 36% and 4%, respectively, of the total quantity of POME generated during the oil mill process (Kaniapan et al., 2021).

POME contains nutrients such as phosphorus, nitrogen, magnesium, potassium and calcium. All these nutrients are important for the growth of plant. Additionally, POME has a high melting point, a pH of less than 7 and rich in organic compounds (Lokman et al., 2021). POME is indeed a mixture of wastewater from wet crude palm oil milling that contains of steriliser condensate or fruit bunch steam sterilisation, clarification wastewater which is oil recovery from wet sludge cake, and hydro cyclone wastewater which is water-aided kernel-shell separation in decreasing polluting strength and volumetric ratio is 15:9:1 (Cheng et al., 2021).

Proper treatments are required for POME before it can be disposed due to its noxious and eutrophic properties which is high viscosity, and the colour is dense brownish. Besides that, the discharge temperature is high which the range from 80°C until 90°C. POME also relatively high in biological oxygen demand (BOD) which about 25,000 mg/L. Besides that, the chemical oxygen demand in POME is high which up to 54,000 mg/L. The content of oil and grease is about 8000 mg/L and 44,000 mg/L was found for total suspended reading (TSS). POME characteristics are batch, facility, and processing time dependent, and may vary according to maturity of fruit and type, as well as the technology of the treatment (Tan & Lim, 2019).

2.2.2 Properties of Wet Palm Oil Sludge

Palm oil sludge (POS) is a semi-solid by-product of acidification, anaerobic treatment, and aerobic treatment of palm oil mill effluent (POME). Due to the huge amount of POME which is 800 dm^3 of POME per tonne of FFB were created during oil extraction and cleaning procedures, significant amounts of POS are formed in mills located across Malaysia. Untreated POS, PKS, and EFB disposal can have a negative impact on the environment (Lee et al., 2017).

Due to insufficient utilisation of the vast amount of waste generated, the palm plantation now disposes of the majority of POS waste. The sludge has an undesirable odour and adds to land contamination, which has an indirect effect on public health and the environment. Thus, turning POS to a value-added substance may be a viable method of mitigating environmental impacts (Iberahim et al., 2019).

2.3 Microbial Fuel Cell (MFC)

2.3.1 Basic Principle of MFC

A microbial fuel cell (MFC) consists of an anode, a cathode, and an electrolyte (s). An ion exchange membrane may or may not be used to separate the anodic and cathodic chambers (IEM). In the anodic chamber, live bacteria with biofilm formation or state of planktonic will oxidise substrates and create electrons, protons, and other metabolites as end products. The anode collects the electrons generated by the bacteria and directs them to the cathode via an external load. On the other side, the protons either percolate through the IEM or just diffuse to the cathode, where they are reduced by the arriving of electrons, completing the circuit. Electric current is generated when electrons travel through an external load. Water is created as a by-product of the protons being reduced in the oxygen presence at the anode, making the process environment friendly (Das, 2017). Figure 2.2 illustrate the basic principle in MFC.

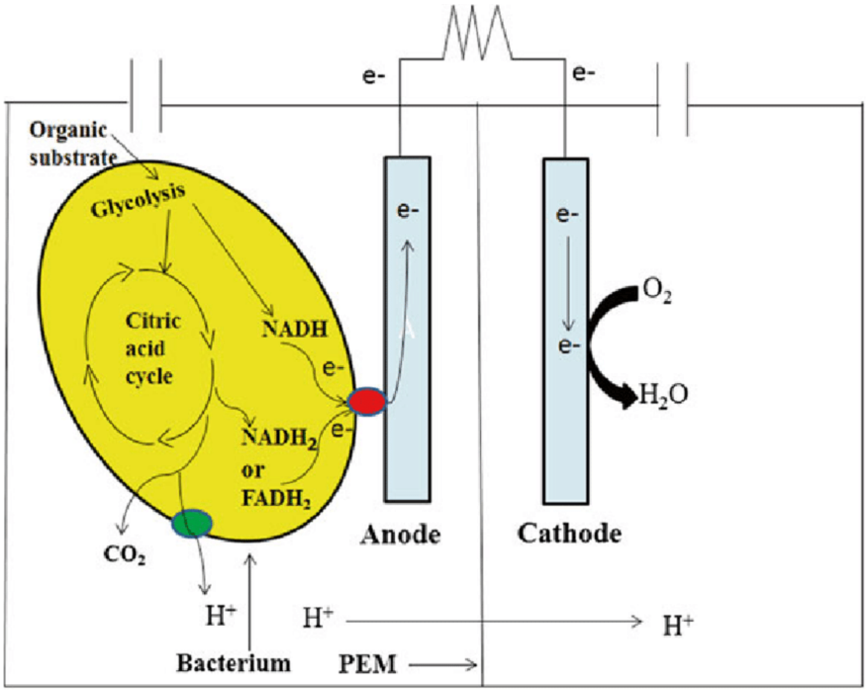

Figure 2.2 Basic principle of MFC (Kalia, 2016)

2.3.2 Dual Chambered MFC

There are various types of microbial fuel cell (MFC). Dual chambered MFC is one of them. These type of MFC consists of two chamber which are anodic and cathodic chamber (Uddin et al., 2019). A dual chambered MFC utilizes an ion exchange membrane or separator to connect the two chamber where will mediates it for the proton transfer process (Das, 2017). Oxidization of substrate by the microbe will occur in the anode chamber. Besides that, propagating both electrons and protons are occurred in the process. Then, the proton will be penetrating to the cathode through the proton exchange membrane. Meanwhile the external wire will let the electrons flow from the cathode to anode and thus completed the process and cycle in dual chambered MFC (Uddin et al., 2019).

There is difference between dual chambered MFC and single chamber MFC. These dual chambered MFC is operated in a water-cathode mode. Meanwhile, the single-chamber MFC will operate in air-cathode mode. The performance of the cathode in dual chambered MFC can be enhance by practicing several ways including pH controlling, minimize the flow rate, remove the pure oxygen and electron mediator’s addition. Therefore, the performance of dual chambered MFC can be improved (Flimban, S.G.A., Ismail, I.M.I., Kim, T., Oh, 2019). Due to the cathode design, commercialization of the dual chamber MFC system has proven more difficult than that of the single chamber MFC system. The cathode part of a two-compartment MFC contains a liquid oxidant such as ferricyanide (K3(CN)6) that serves as the final electron acceptor (Technologiae, 2017). Figure 2.3 illustrate the structure of dual chamber MFC

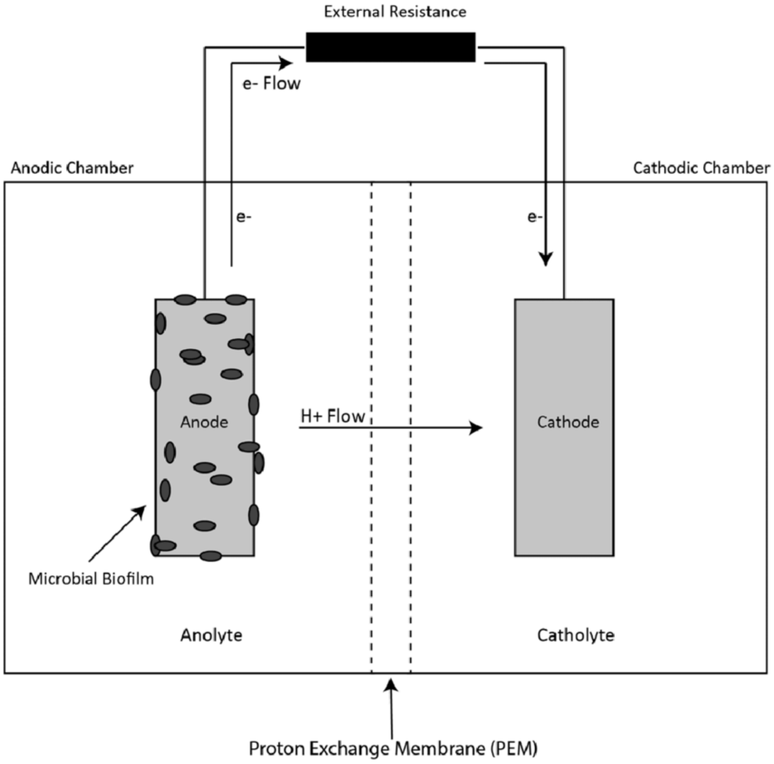

Figure 2.3 Structure of dual chamber MFC (Breheny et al., 2019)

2.4 Components of MFC

2.4.1 Electrode Materials

Microbial fuel cell performance enhancement is very crucial and thus the power generation can be increase. The power output from the MFC is related to components MFC performance. Hence, election of the materials which is more innovative must be developed in order to achieve the maximum power generation in MFC. High power generation can be achieved by choosing the components in terms of material of the anode, material of the cathode, surface of the electrode, spacing of the electrode, configuration, and concentration of the substrate (Mustakeem, 2015).

In efficient MFC work, there are two crucial things which are the cost of the electrode and their performance. Hence, the investigation regarding to configuration and the electrode materials has been carried out in recent years. The energy losses might be occurred due the electrode material which by the high internal resistance. Besides that, operation time is very important (Hamed et al., 2020). Besides that, the electrode material must consist of high conductivity, be stable in chemical and economically viable. To support microbial development and long-term function, the electrode should be biocompatible. Additionally, the MFC electrode should have a large enough surface area to support the bacterial microflora growth. In order to generate a high-power output, electrode must be a good conductor. hence, the electron can transfer efficiently from bacterial microflora (Javed et al., 2018).

Nowadays, various form of carbon has been applied as anode and cathode in the construction of MFC. Carbon based materials known as well-defined surface area.For instance, brush anode able to maintain the electrochemically active microorganisms which in the surface due to their large surface area. Thus, the electricity generation could be increase (Nam et al., 2017). Various form of carbon has been applied as anode and cathode in the construction of MFC as shown in figure 2.4

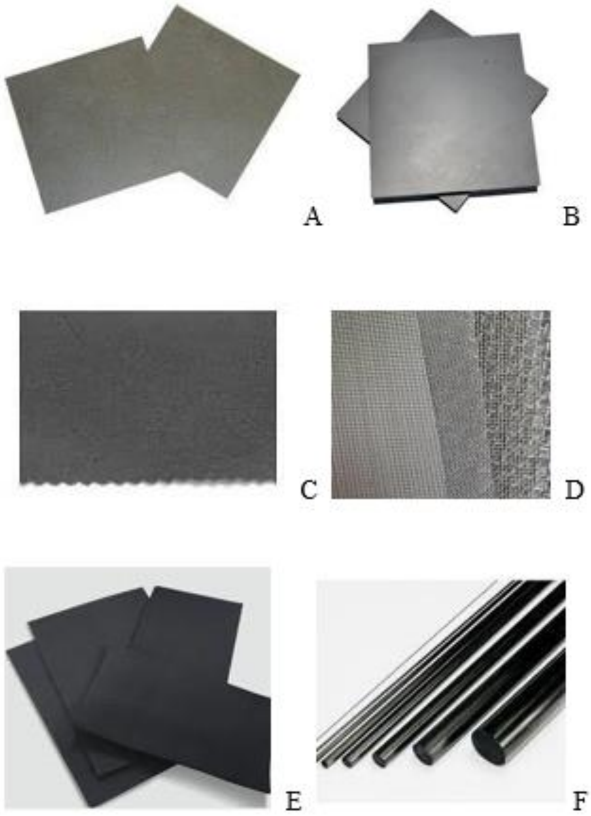

Figure 2.4 Types of electrode materials used in MFC: (A) carbon paper; (B) graphite plate; (C) carbon cloth; (D) stainless steel mesh; (E) graphite felt; (F) carbon rod

2.4.2 Separator

There are many factors that influence the power generation in MFC which are catalyst, concentration of the substrate, configuration, temperature, and membrane types. The membrane of MFC, which separates cathode and anode has been called the most crucial part in the MFC among all these factors. The function of the membrane is to allow the protons to pass from anode to the cathode. Meanwhile, the other materials such as oxygen and substrates are denied for the transfer process. When the oxygen penetrates to the part of anode, the process efficiency which in the anode aerobic, power density and treatment of the wastewater will be decreasing. Likewise, the penetration of media which to the cathode. This process will affect the efficiency of the microorganism COD removal due to the power out declination (Ghasemi et al., 2015).

Membrane technology is at the core of MFC design and has a direct impact on process performance. It is critical to choose an appropriate membrane that accounts for oxygen diffusion, substrate loss, and internal resistance. In MFCs, proton exchange membranes (PEM) have been commonly used. PEMs' high proton conductivity facilitates transfer of proton from anode to the cathode, while their hydrophobic coating prevents water leakage. However, it contributing in high cost of MFC systems and lowers power output via internal resistances (Technologiae, 2017). Hence, it is crucial to find another alternative to replace the PEM such as using filter paper or salt bridge as separator.

2.5 Utilization of Substrate in MFCs

Organic substrates are critical in operation of MFC because the rate of substrate conversion influences the amount of energy generated. The waste material's properties, concentrations, and composition will determine the viability of economic and efficiency of organic waste conversion to bioenergy. MFCs can be used to generate energy on a wide variety of substrates, which between pure or simple compounds to complex range. The pure substrates utilization has proved advantageous for researchers interested in several fundamental features of MFC operation (Technologiae, 2017).

Simple substrates such like acetate and glucose have been extensively studied and demonstrated a high-power production. Meanwhile, complex substrate including starch wastewater, swine wastewater and domestic wastewater domestic wastewater have also been extensively studied. However, it demonstrated a low power density. The digestion for microbes is hard when using a complex substrate. Thus, power output obtained is often lower than simple substrates. One of the complex substrate is POME (Baranitharan et al., 2013).

2.6 Factors Effect of Performance in MFC

2.6.1 Total Suspended Solid

The presence of total suspended solid (TSS) are frequently found in the wastewater. TSS is one of the operating parameters that will affect the performance of MFC. The presence of TSS in MFC will affect the generation of power density and current density. The biodegradable function in MFC might be decrease due to the presence of TSS. The degradation of organic matter by the bacteria are related with the films where it was grown on the suspended solid particles surface. However, the decreasing of biodegradable function will lead to the increasing of internal resistance in the system. The higher the internal resistance, the lower power generation. Thus, the performance of the MFC will be decrease too (Ismail & Radeef, 2019).

2.6.2 Chemical Oxygen Demand

Chemical oxygen demand (COD) will affect the performance of the MFC. When the concentration of COD increase, the power density recorded decrease. The lower power output occurs due to the dependency of anodic reaction with the characteristic of the substrate and the availability of carbon in the anode chamber of MFC. The factors will be limit by the colloidal particles if there are colloidal particles happens in the substrate. Besides that, the internal resistance will increase and thus decreasing thepower density. The higher the internal resistance, the lower the power output. The generation of power density in MFC could be decrease due to the high COD (López Velarde Santos et al., 2017).

Additionally, the deficiency of carbon sources availability due to high COD in anodic chamber will hinder the production of power. In anodic chamber, characteristics of the substrate and amount of carbon presence are affecting the anodic reactions. As a result, the power produce is less when the substrate consists of colloidal particles. The ability to produce electricity in MFC based on the activity of the bacteria or reduction oxidation reaction which the electron and protons will be generated as well as electron acceptor. Anode potential and electrolyte by using the substrate will affect the power generation. If there are a lot of colloidal particles in the electrolyte solution, the transfer of electron and proton could be diminished (López Velarde Santos et al., 2017).

2.6.3 pH

The suitable pH for the bacteria to growth is to be around a neutral pH. In order to get the higher generation of the electricity, the value of pH must be about 7.5 or above (Aghababaie et al., 2015). The anode potential is increasing during the decreasing of the pH and thus voltage production is low and same with the current where it will be smaller. If thereis enhancement in pH, the output of voltage and current will be high due to the negative anode potential production. Hence, the pH will be low when the current discharge is high. Thus, electrochemical performance in MFC is decreasing and will affect the performance of MFC (Zhang et al., 2011).

2.6.4 Operating Parameter

In the anode compartment of the double chambered MFC, indigenous microorganisms from the anaerobic WPOS were allowed to proliferate facultatively. After operating the MFC, the anode was removed, and it was discovered that biofilm was growing on the anodic electrode. Given that the separated bacteria were able to grow and live in the MFC environment, there is a significant chance that the prospective electro-active bacteria are able to create electricity by utilising the abundant substrate in POME (M. H. Nor et al., 2015). In the previous studies (M. H. Nor et al., 2015), the results indicated that the power density remained relatively steady throughout the MFC operation, with a progressive decline near the end of operation. This is because the anaerobic WPOS contains a variety of microorganisms that consumed the available organic waste from POME, hence generating continuous energy.

2.7 Characteristic of MFC Performance Evaluation

In MFC performance measured, voltage is one of the key parameters that must be identify. The performance of the MFC is influence by the power produce under the constant voltage. Power is depending on two things which are voltage (V) and current (I). The amount of energy can be determinedby using this equation.

$$\text{Power output (W)} = \text{Voltage (V) x Current (A)} \qquad 2.1$$

CHAPTER 3

METHODOLOGY

3.1 Introduction

Methodology is a technique for determining the outcome of a specific research project. This chapter will describe the method to design and develop the microbial fuel cell as well as demonstrate the procedure and instruments used to provide. In this chapter, sample collection is well described. Kilang Lepar Hilir 3 was selected as location to collect the sample. POME was collected from first pit of effluent before entering the cooling pond to reduce temperature. WPOS choose as additive to enhance biological activity. All the sample collected was stored in cold room with -4°C temperature. An octagon (1.6 litre) water tank with plexiglass material was used and designed as MFC. A flowchart was used to show the flow of the study as shown in Figure 3.1

3.2 Methodology Flowchart

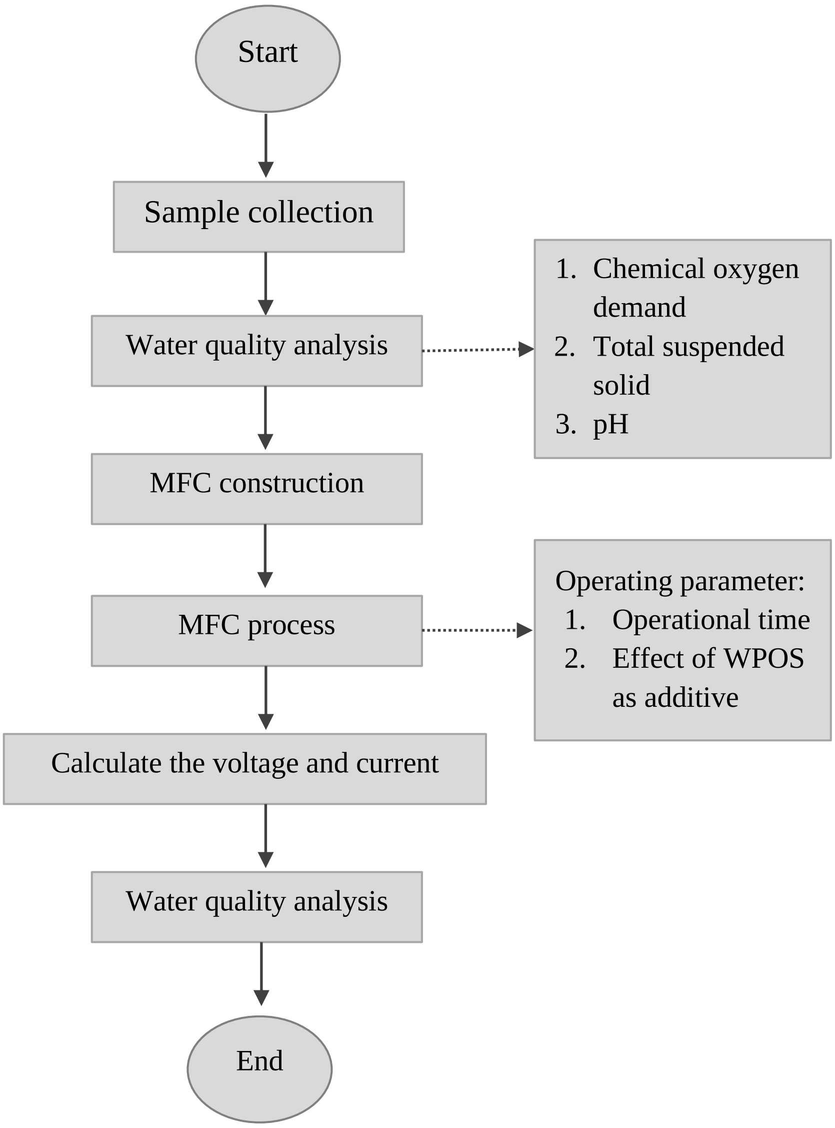

Figure 3.1 A flowchart of study's process

3.3 Sample Preparation

The wastewater that has been chosen as substrate in this study were palm oil mill effluent (POME) and wet palm oil sludge. The location for the sample collection is from the effluent at Kilang Sawit Lepar Hilir 3, Gambang, Kuantan, Pahang. POME will be taken from the first pit of effluent which is the first stage before cooling pond where not been treated yet as shown in figure 3.2. Meanwhile for WPOS, the sample will be collected at the final stage. Then, both POME and WPOS will be stored in cold room with -4°C temperature. 300ml sample of POME are prepared for MFC. Meanwhile, WPOS will be acted as additive where 0, g/L, 2mg/L, 4 mg/L and 6 mg/L dosage of WPOS added in MFC for each 5 days.

Figure 3.2 Sample collection from first pit of POME effluent

3.4 Water Quality Analysis for Effect of Performance

3.4.1 Measurement of TSS

Apparatus that will be used in TSS is glass fiber, filter paper, aluminium evaporating dish and oven as shown in figure 3.3

Figure 3.3 Apparatus used in TSS analysis

The procedure of TSS is stated as below:

1. Filter disks was placed into apparatus of filtration. Vacuum was applied. Filter then was wet by a deionized water with small volume.
2. After that, the filter was placed in aluminium evaporating dish and oven was set to 104 ± 1°C for 1 hour.
3. Filters was removed from oven after 1 hour. The filters were cooled in desiccator for 20 minutes. Then, each filter was weighed by using analytical balance.
4. Then, filtration apparatus was set up again. Sample was shake vigorously. 100 ml sample was measured and poured into filter. Graduated cylinder was rinsed with

three 20 ml volume of deionized water and after filtration was completed, continued to suction for three minutes.

5. After that, filter was placed for 1 hour into oven with 104 ± 1°C temperature. After 1 hour, filter was removed from oven and placed in desiccator.
6. Each of filter was weighed by using analytical balance. TSS was calculated as described below

$$\text{Total Suspended Solid (TSS)} = \frac{(A - B)}{V} \tag{3.1}$$

Where: A = mass of filter + dried residue (mg)

B = mass of filter (mg), and

V = volume of sample filtered (L)

3.4.2 Measurement of COD

Apparatus that will be used in COD is vial, pipet and DRB 200 reactor. Figure 3.4 show COD process

Figure 3.4 Apparatus used in COD analysis

The procedure of COD is stated as below:

1. The power of DRB200 Reactor was set to on and preheated to 150°C for 1 hours
2. Then, sample was prepared. Cap from the vial was removed. The vial was hold at 45-degree angle. 2 ml of sample was added into vial using pipet.
3. After sample preparation, the blank was prepared. Cap of second vial was removed and hold at 45-degrees angle. 2 ml of deionized water was added in vial using pipet.
4. The vials were closed tightly. Then, vials were rinsed with water and clean paper used to clean it. The vials were inverted gently to mix by holding the vials cap.
5. Then, vials were put in preheated DRB200 reactor and vials were heated for 2 hours. After 2 hours, vials were let to cool for 20 minutes and inverted several times. Then, vials were placed in tube rack to cools down.
6. After that, 435 COD HR program was started. Blank sample cell was cleaned and inserted into cell holder. Then, ZERO was pushed and 0 or 0.0 mg/L COD was showed.
7. Finally, prepared sample cell was cleaned and were inserted into cell holder. READ was pushed and the results was showed in mg/L COD.

3.4.3 Measurement of pH

The acidity of water was measured by using pH Meter as shown in figure 3.5

Figure 3.5 Apparatus used in pH analysis

The procedure of pH is stated as below:

1. The electrode tip was rinsed in deionized water
2. Then, electrode tip was placed in a beaker with sample. Read button was pressed and wait until the reading on the display stop
3. Finally, result of pH and temperature was recorded

3.5 MFC Construction

Dual chambered MFC were designed using an octagon water tank with Plexiglass material. The volume of the water tank is 1.6 L. The tank will be divided into two side of chamber which the first chamber will consists of anode electrode. On the other chamber, cathode will be used as electrode. Both chambers are using graphite rod as electrode with 1 cm diameter and 10 cm length. Anode and cathode electrode are connected by using a copper wire. Digital multimeter are used to measure the reading of voltage and current. Figure 3.6 illustrate the design and set up of MFC.

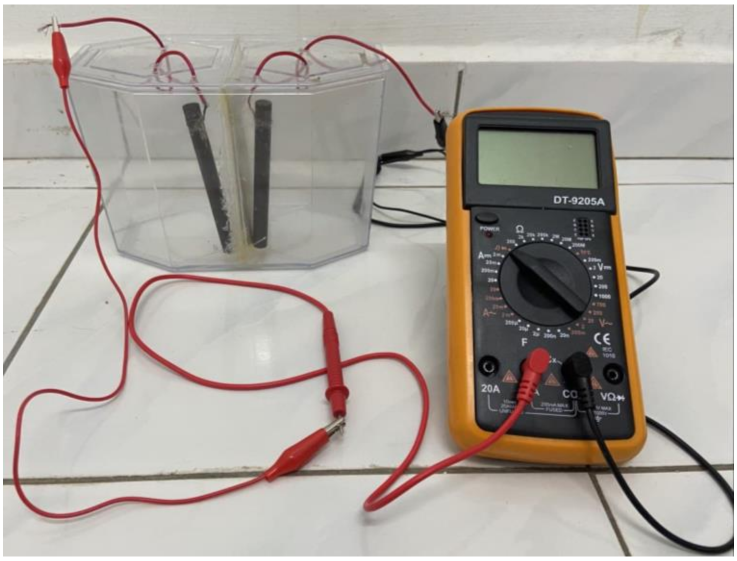

Figure 3.6 Design and set up of MFC

Both anode and cathode chamber are separated by separator. Filter papers are used as separator in MFC to avoid from mixing of sample and water in both chambers. Dimension of the filter is 8.5 cm in length and 11 cm in height. Filter papers are soaked with salt water for 24 hours before it placed in the middle of MFC. Figure 3.7 illustrate the modification of filter paper in MFC.

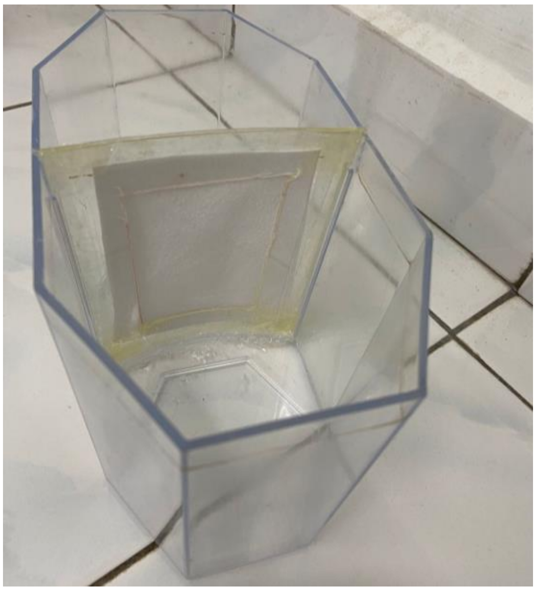

Figure 3.7 Modification of filter paper in MFC

3.6 Electrochemical Process in MFC

The basic set up for the microbial fuel cells consists of several material which are two electrodes anode and cathode, separator and external connection between the electrodes and the fuel cell. Anodic chamber is where the sample will be place. Microbes are used to oxidize the substrate which is the mixture of POME and wet palm oil sludge. Then, the microorganisms will release the electron and transfer from anode to cathode through the external wire which is the copper wire. For completing the reaction, the proton will be transport to the cathode across the separator for every electron conducted.

3.7 Acquisition of Power Generation Data

MFC are monitored for 20 days which 5 days each for different dosage. Current and voltage generate from MFC are measured by using a digital multimeter for 7 hours in a day. The power output (P) of the cells is calculated by using the Ohm’s Law as described below:

$$\text{Power output (W)} = \text{Voltage (V) x Current (A)} \qquad 3.2$$

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

The research’s aim is to generate bioelectricity from the POME in MFC by using graphite rod as electrode. In this chapter, the results and the outcome of the analysis are discussed. The first part included the bioelectricity production which is voltage, current and power by using graphite rod as electrode. The amount of WPOS added which is 0 mg/L, 2 mg/L, 4 mg/L and 6 mg/L in POME which effect to the bioelectricity production are discussed. The second part included the effect of various essential factors on the performance of MFC. The effect of operating parameter such as WPOS as additive and operational time are discussed. Water quality analysis, which is TSS, COD and pH are shown in this part.

4.2 Electricity Generation Analysis

4.2.1 Voltage, Current and Power Generation

The voltage and current over the time which is 5 days for each different dosage of WPOS were recorded by using digital multimeter. Figure 4.1 illustrates the voltage variation over time for different dosage of WPOS throughout the MFCs test.

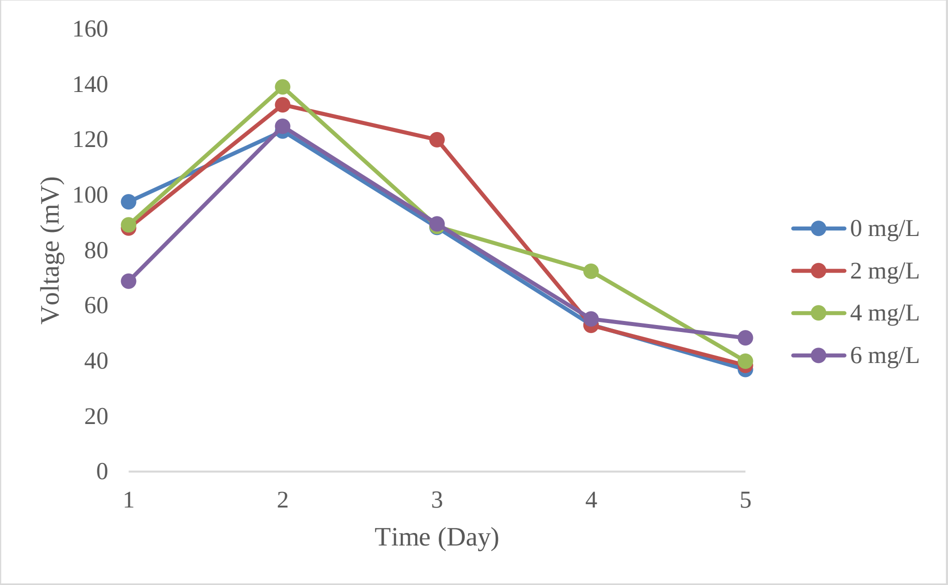

Figure 4.1 Voltage variation over time for different dosage of WPOS throughout the MFCs test

The voltage of each dosage of WPOS is increasing in day 2 and start to drop-in day 3. The peak value of the voltage for different dosage of WPOS was reached in second day. The highest voltage was achieved is 139 mV. The voltage where there is no additive added in POME show the good start compared to other POME with additive added. Same goes to the current generate in MFC. The current is increasing until the second day and decreased gradually with elapsed time as shown in figure 4.2.

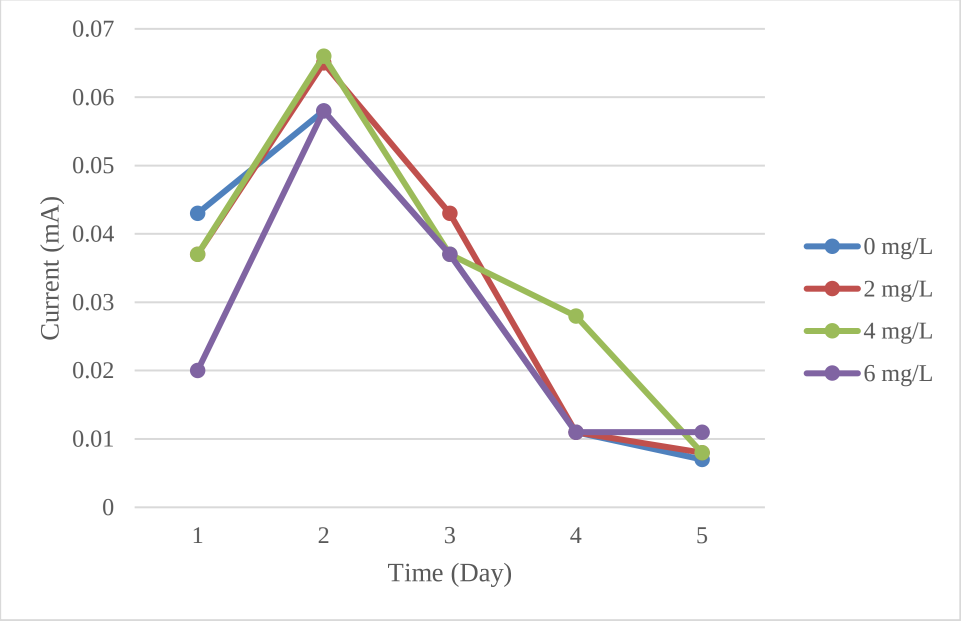

Figure 4.2 Current variation over time for different dosage of WPOS throughout the MFCs test

Raw POME generated more electricity and current at the start, which shows the microorganisms were already active when they were first added to the water. However, the higher current of MFCs is obtained with 4 mg/L dosage WPOS added which is 0.066 mA. Figure 4.3 illustrate the power variation over time throughout the MFCs test.

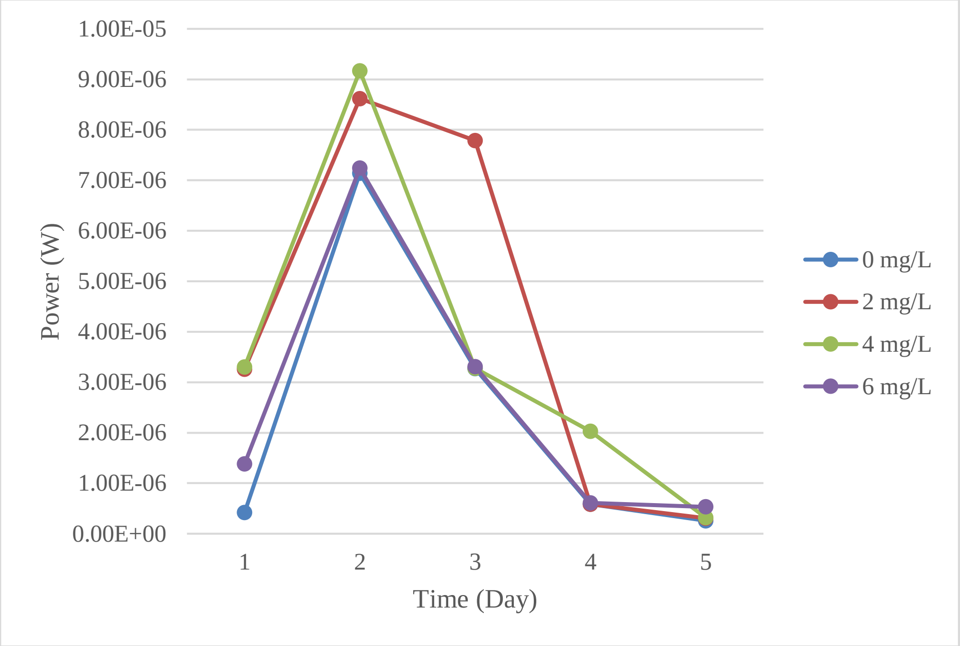

Figure 4.3 Power variation over time for different dosage of WPOS throughout the MFCs test

The initial power generation showed significantly higher in the second day. The highest power generation achieved is 9.17 x 10^{-6} W. It shows the presence of more biological activity at the beginning of the process. However, the figure shows all the power generation started to decrease on the third day of the process. POME may clog on the surface of the electrode due to their highly viscous nature, where it will slow down the rate of mass transfer. Thus, the electricity generation were affected. In addition, the presence of a membrane which create higher internal resistance may be the reason of lower power generation in MFC (M. H. M. Nor et al., 2015). Based on the result obtain, it shows that the power generation achieved is low which is 9.17 x 10^{-6} W. Previous studies (Baranitharan et al., 2013) demonstrated a low power density by using complex substrate such as POME and WPOS. The digestion for microbes is hard when using a complex substrate compared to simple substrate. Thus, power output obtained is often lower than simple substrates.

4.3 Effect of Electrode on Operational System

Graphite rod has chosen as electrode for anode and cathode chamber in MFC. Graphite used due to their high electrical conductivity, chemical stability, biocompatibility and cheap (Mustakeem, 2015). The power generation in MFC using graphite rod is proven by achieving the maximum power, 9.17×10^{-6} W. It can be achieved due to their high electrical conductivity where it helps to speed up the electrons flow and show less resistance. According to Ohm's Law, current is inversely proportional to resistance where the resistance will reduce when the material is highly electrically conductive (Asim Ali Yaqoob & Umar, 2021). The electron transfer increase with the increasing of electricity production. Thus, the power is achieved highly on the second day for each dosage of WPOS. In addition, graphite rod act as anode electrode where it is biocompatible. The electrode is biocompatible with the growth of microbial in anode chamber. Thus, the electrons generated increased. The energy will loss if the anode material not compatible as graphite due to their absence of microbes which compatibility healthy (Asim Ali Yaqoob & Umar, 2021).

4.4 Factors Effecting Performance of MFC

There are several parameters that have been identified which can affect the performance of MFC. TSS, COD and pH are the parameters that have been considered in this study. The parameter was evaluated by comparing the initial and final reading for different dosage which is 0 mg/L, 2 mg/L, 4 mg/L and 6 mg/L of each parameter within 20 days.

4.4.1 Total Suspended Solid

Total suspended solid (TSS) is one of the factors effecting the performance of MFC. The reading of the initial TSS and final reading for each different dosage of WPOS have been identified. Table 4.1 illustrate the TSS analysis evaluated based on different dosage of WPOS. The parameter was evaluated by comparing the initial and final reading for different dosage of each parameter.

Table 4.1 TSS analysis evaluated based on different dosage of WPOS before and after MFC operation

Parameter	Initial	0 mg/L	2 mg/L	4 mg/L	6 mg/L
TSS (mg/L)	4800	4470	950	1473	810

It shows the TSS for each dosage of WPOS is decreasing from the initial which is 4800 mg/L. The high amount of TSS may disrupt the power generation in MFC. TSS may lead the bacteria to less able to break down the organic matter, which could disrupt the process due to the increasing of internal resistance. The bacteria that break down the organic matter are usually found on the surface of suspended solids particles (Ismail & Radeef, 2019). The high internal resistance on voltage source may affect the ability of the current supply. Hence, the amount of TSS must reduce to decrease the disruption in order to generate the electricity in MFC.

4.4.2 Chemical oxygen demand

Chemical oxygen demand (COD) is another parameter that have been considered which can affect the performance of MFC in this study. The reading of the initial COD and final reading for each different dosage of WPOS have been identified. The COD analysis was evaluated by comparing the initial and final reading for different dosage of each parameter as shown in table 4.2

Table 4.2 COD analysis evaluated based on different dosage of WPOS before and after MFC operation

Parameter	Initial	0 mg/L	2 mg/L	4 mg/L	6 mg/L
COD (mg/L)	669	531	539	569	586

Table 4.2 depicts the final COD of each WPOS are decreased compared to the initial reading. The initial COD show the highest reading which is 669 mg/L. The 6 mg/L dosage show a slight decrease of COD compared to other dosage. However, the final readings of each dosage indicate it still high although there is a slight decline. Hence, the electricity production could be affected in MFC as shown in figure 3. The power production not high and start to drop after day 2. This is due to the electrolyte solution in the MFC was already saturated. Besides that, the deficiency of carbon sources availability due to high COD in anodic chamber will hinder the production of power. In anodic chamber, characteristics of the substrate and amount of carbon presence are affecting the anodic reactions. As a result, the power produce is less when the substrate consists of colloidal particles. The ability to produce electricity in MFC based on the activity of the bacteria or reduction oxidation reaction which the electron and protons will be generated as well as electron acceptor. Anode potential and electrolyte by using the substrate will affect the power generation. If there are a lot of colloidal particles in the electrolyte solution, the transfer of electron and proton could be diminished (López Velarde Santos et al., 2017). However, the MFC indicate that the removal of COD can be done. Table 4.3 show the percentage of COD removed for different dosage of WPOS before and after MFC operation.

Table 4.3 Percentage of COD removed for different dosage of WPOS before and after MFC operation

WPOS dosage (mg/L)	**Initial COD (mg/L)**	**Final COD (mg/L)**	**COD removal (%)**
0	669	531	21
2	669	539	19
4	669	569	15
6	669	586	12

Table 4.3 shows the result of COD removal before and after MFC operation. The maximum COD removal in MFC is 21%. It indicates MFC able to remove the COD which can lead to the pollution if discharged without treated. The removal of COD in MFC show that the oxidation of the anodic chamber is done through the direct anodic oxidation. There is presence of microorganism in consumption of organic matter (López Velarde Santos et al., 2017). Therefore, the using of MFC prove it can remove the COD in POME and WPOS in the operation.

4.4.3 pH

Other factors that can affect the performance of MFC is pH. The pH of the POME and additive of WPOS have been analysed before and after the operation of MFC as shown in table 4.4

Table 4.4 TSS analysis evaluated based on different dosage of WPOS before and after MFC operation

Parameter	**Initial**	**0 mg/L**	**2 mg/L**	**4 mg/L**	**6 mg/L**
pH	4.71	4.68	4.63	4.22	4.32

Table 4.4 depicts pH of each dosage of WPOS is decreasing from the initial reading. However, the reduction of pH is not too much where it still in acidic condition. The acidic pH might affect the performance of MFC where the power production will decrease. For the growth of bacteria, neutral pH is the optimum pH. However, in some wastewater, the pH level is very low. POME is one of the wastewaters that show the lower pH where the initial pH is 4.71 before MFC operation. This condition will lead the MFC to work inadequately. The slightly alkaline anodic pH which is around 7.5 considered as the suitable pH for the electricity generation (Aghababaie et al., 2015). The result shows the pH of each dosage are slightly decreased with the lowest pH is 4.22. The decreasing of the pH has affected the power generation in MFC as shown in figure 3 where the power achieved is 3.19 x 10^{-7} W was low compared to 6 mg/L with 4.32 at

the end of MFC operation. Low pH can make the anodic biofilm less active and slow down the growth. Meanwhile for microbes to metabolize, grow and attach to anode, neutral environment should be considered. The microbe’s diversity was restricted with pH 4 and 5 which is under the acid conditions. The lower pH will affect the anodic microbe’s abundance. Thus, the electricity generation in MFC decreased (Zhang et al., 2011).

4.4.4 Operating Parameter

4.4.4.1 Effect of WPOS as Additive

Various dosage of WPOS have been added in anode chamber to stimulating the biological activity. The results of power using POME and mix with the WPOS in MFC was recorded in 5 days. Generally, the generation of electricity increasing and reached its peak on the second day after which is decreased gradually. For the next 3 days the power continued to drop. Maximum current achieved was 0.66 mA while the maximum power achieved was 9.17 x 10^{-6} W. The highest current was achieved with 4 mg/L of dosage added. This is due to the fact that WPOS consists a lot of different types of microorganisms in it and by that the electricity was provide continuously (M. H. M. Nor et al., 2015). It shows the high-power generation compared to the POME without WPOS. This proves that electricity generation is better with the presence of WPOS in anodic chamber of MFC. However, the WPOS with 6 mg/L show the low power generation compared to the 4 mg/L of WPOS. This may happen due to the biofilm that grows on the surface of electrode after 15 days of operation. The thick biofilm form may interrupt the movement of electron where it might stop the electrons moving from microbes to the electrode surface. Thus, reduce the electricity generation (Baranitharan et al., 2013).

4.4.4.2 Operational Time

The operational time for MFC to generate the electricity has been evaluated for 20 days where 5 days needed for each different dosage of WPOS, 0 mg/L, 2 mg/L, 4 mg/L and 6 mg/L. Each different dosage shows the same trend of electricity production where the peaks of power achieved is on the second days of MFC operation. The power starting to drop gradually elapsed time on third day of operation. However, on the last day of the operation, the current production for each dosage of WPOS still can be seen although it is not high as the second day. It indicates that the bacteria are still active at the beginning of the operation and start to slow down on third day. The bacteria are crucial in order to oxidize the available organic matter where the electron and proton will be produced. It will derive the energy by transferring electrons to terminal electron acceptor which is oxygen in cathode chamber (Song et al., 2019). Thus, the electricity can be generated continuously in MFC.

CHAPTER 5

CONCLUSION

5.1 Introduction

The main objective of this study is to generate bioelectricity from mixture of POME and WPOS using graphite rod as electrode in MFC. In this chapter, the generation of bioelectricity in MFC is concluded. POME have been used as substrate in MFC and WPOS as additive to enhance the growth of the microbes. Several dosages which are 0 mg/L, 2 mg/L, 4 mg/L and 6 mg/L have been used to identify the effectiveness of WPOS as additive in MFC. Graphite rod have been used as electrode in MFC due to their high electrical conductivity, chemical stability, biocompatibility and cheap. The operation of MFC are about 20 days where each different dosage operates for 5 days. Several factors that effecting performance of MFC including electrode type, TSS, COD and pH have been determined in this study. The analysis of TSS, COD and pH have been evaluated before and after MFC operation with different dosage of WPOS.

5.2 Conclusion

In this study, the mixture of POME and WPOS have been successfully generating electricity in microbial fuel cell by using graphite rod as electrode. Electricity generation from mixture of POME and WPOS with 4 mg/L dosage has shown significantly higher than other dosage of WPOS. The highest power generation achieved is 9.17×10^{-6} W. The result show that the power generation in MFC is increasing until the second day and decreased gradually with elapsed time. The peak power has been achieved on second day of operation for each dosage of WPOS. The result show that biological activity of the microbes is active until second day and start to slow down on the third day until end of operation. This may occur due to several factors including the facts that POME may clog on the surface of the electrode due to their highly viscous nature, where it will slow down the rate of mass transfer. However, the power generation has been achieved due to the correct selection of electrode which is graphite rod. This electrode helps to speed up the electrons flow and show less resistance due to their high electrical conductivity. The electrons generated increased due to electrode characteristic which is biocompatible. It will affect the performance of MFC due to the energy losses if the anode material not compatible. In addition, WPOS show the effectiveness as additive to enhance power generation in MFC. There are several parameters can affect the performance of MFC which is TSS, COD and pH. The parameter was evaluated by comparing the initial and final reading for different dosage. This study show that the parameters can affect the performance of MFC. The high amount of TSS may disrupt the power generation in MFC. Besides that, the deficiency of carbon sources availability due to high COD in anodic chamber will hinder the production of power. However, MFC shows that the removal of COD successfully done with the highest percent of removal is 21%. Next, the acidic pH might affect the performance of MFC where the power production will decrease. In conclusion, MFC are able to generate electricity from mixture of POME and WPOS although the power production is still low. Various improvement can be done to enhance the efficiency of MFC. Thus, the optimum power can be achieved.

5.3 Recommendation

The power produce from MFC in this study is still unsatisfactory. The potential as source of renewable energy must improve by increasing the efficiency of MFC. Hence the dependency on non-renewable energy can be diminish. For future studies, several recommendations should be considered to increase the power generation in MFC. Firstly, the use of food or agriculture waste is suggested as a substrate in MFC. Besides that, mediator such as neutral red and potassium ferricyanide can be added to help electron that produce by microorganisms to be transferred to electrode. Thus, electricity generated can be enhanced in MFC. Finally, the modification should be done by developing an advanced anodes to increase the anode electrode conductivity such as metal oxides or graphene derivatives. Electrochemical performance in MFC can be enhance by using those as anode electrode.

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APPENDICES

Appendix A: Wet Palm Oil sludge collection at Kilang Lepar Hilir 3

Appendix B: Measure of voltage in MFCs process