THE POTENTIA FUEL CELL ANODE WITH E TRANSFER

BARANITHARAN ETHIRAJ

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Faculty of Chemical & Natural Resources Engineering
UNIVERSITY MALAYSIA PAHANG

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ABSTRACT

Palm oil mill effluent (POME) is an organic waste material produced at the oil palm mills. In its raw form, POME is highly polluting due to its high content of biological (BOD) and chemical oxygen demand (COD). In this context, treatment of wastewater using MFC (Microbial fuel cell) seems to be promising technology because it reduces operation energy requirement and shows efficient treatment too. In the present work, MFC with POME were used to study the effect of different electrode materials and to harvest high power density (PD) using controlled inoculum. Three different electrode materials such as PACF (Polyacrylonitrile carbon felt), SFCC (Single forward carbon cloth) and GR (Graphite rod) were used as anode and cathode materials for the MFC experiments. Among the raw POME and different concentrations of POME used, the PACF, SFCC with raw POME (60600 mg/L) showed the maximum power density (PD) of about 45mW/m^2 and 102.50 mW/m^2 respectively but both PACF and SFCC showed low coulombic efficiency (CE) of about 0.8 % and 2.2 % respectively as well as low COD removal efficiency of about 45 % and 54.45 % respectively. The PACF and SFCC MFC with 1:50 dilution (964 mg/L) showed higher COD removal efficiency of about 70 % and 78 % respectively and also CE of about 24% and 51% respectively but showed low PD of about 22 mW/m^2 and 28.48 mW/m^{2}respectively. While, GR with raw POME showed very low PD, CE and COD removal efficiency of about 11.238 mW/m^2, 0.2% and 28% respectively. Predominant microbes from anaerobic sludge (AS) were successfully isolated and identified as *Pseudomonas aeroginousa, Pseudomonas mendocina, Pseudomonas viridiivida, Acetinobacter schindleri, Actinobacillus capsulatus and Brevibacterium paucivorans*using BIOLOG gene III analysis. Biofilm formation on electrode surface was analyzed using Fourier transformed infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA) and field emission scanning electron microscopy (FESEM) analysis. Biofilm was characterized using PCR-DGGE (polymerase chain reaction – denaturing gradient gel electrophoresis) analysis and sequencing and identified the predominant microbes in biofilm which includes *Azospiraoryzae, Acetobacterperoxydans and Solimonasvariicoloris*.The electrochemical activities have been investigated by electrochemical impedance spectroscopy (EIS). In the final experiment, MFCs inoculated with controlled inoculum (CI) and POME as substrate. The CI was made using the microorganisms which are adapted and grown in palm oil mill effluent. CI was the mixture of fermentative and electrogenic microorganisms. It consists of electrogen (*Pseudomonas aeroginousa*) from AS and fermentative microorganisms (*Azospiraoryzae, Acetobacterperoxydans, Solimonasvariicoloris*) from biofilm since no electrogen found in biofilm. The MFC operated with CI reached the maximum power density of 107.35mW/m^2, which was two times higher as compared to MFC operated with AS as inoculum. The maximum CE of 74 % was achieved from the MFC with CI, which was 50% higher than the CE with AS. But, it showed lower COD removal efficiency of about 32%, which might be due to the absence of required fermentative microorganisms in CI to utilize POME. EIS and the simulated results showed the reduction of charge transfer resistance (R_{ct}) by 19.5% during the operation of the cell with CI. These results demonstrate that the power output of MFCs can be increased using CI.

ABSTRAK

Sisa kilang kelapa sawit atau POME adalah bahan buangan organik yang dihasilkan di kilang kelapa sawit. POME sangat tercemar dalam keadaan mentah kerana kandungan minyak/ lemak BOD dan COD yang sangat tinggi. Dalam konteks ini, rawatan sisa buangan yang menggunakan Microbial Fuel Cell (MFC) menjanjikan teknologi yang berpotensi kerana ia mengurangkan tenaga operasi dan rawatan bahan buangan yang lebih berkesan. Pada masa kini, penggunaan MFC menggunakan POMEtelah dikaji pada elektrod daripada bahan berbeza dan bagi mendapatkan power density (PD) yang tinggi inokulum terkawal telah digunakan. Tiga bahan elektrod yang berbeza seperti PACF (Polyacrylonitrile carbon felt), SFCC (Single forward carbon cloth) and GR (Graphite rod) telah digunakan sebagai anod dan katod dalam kajian MFC. Kajian antara POME yang mentah dengan POME yang berbeza kepekatan menunjukkan bahawa PACF dan SFCC pada POME mentah (60600 mg/L) mempunyai PD yang maksimum iaitu masing masingdengan 45mW/m^2 dan 102.50 mW/m^2, tetapicoulombic efficiency (CE) yang rendah iaitu 0.8% dan 2.2%, dan juga kecekapan pengurangan COD yang rendah adalah 45% dan 54.45%. PACF dan SFCC pada MFC dengan pencairan 1:50 (964 mg/L) menunjukkan kecekapan pengurangan COD yang tinggi iaitu 70% dan 78%, begitu juga dengan juga penggunaan CE mencapai 24% dan 51%, namun PD menunjukkan kuasa yang rendah iaitu 22 mW/m^2 dan 28.48 mW/m^2. GR pada POME yang mentah menunjukkan PD, CE dan kecekapan pengurangan COD yang paling rendah iaitu masing-masing dengan 11.238 mW/m2, 0.2% dan 28%. Mikrob yang dominan daripada anaerobic sludge (AS) telah berjaya diasingkan dan dikenalpasti sebagai *Pseudomonas aeroginousa,Pseudomonas mendocina, Pseudomonas viridiivida, Acetinobacter schindleri, Actinobacillus capsulatus dan Brevibacterium paucivorans* menggunakan analisis BIOLOG gen III. Pembentukan biofilm pada permukaan elektrod telah dianalisis menggunakan Fourier Transformed Infrared (FTIR) spectroscopy, Thermogravimetric Analysis (TGA) dan Field Emission Scanning Electron Microscopy (FESEM). Biofilm pula telah dianalisis menggunakan PCR-DGGE (polymerase chain reaction – denaturing gradient gel electrophoresis) termasuklah menyusunan dan mengenalpastian mikrob dominan dalam biofilm seperti *Azospira oryzae, Acetobacter peroxydans dan Solimonas variicoloris.* Aktiviti elektrokimia telah dikaji denganmenggunaka Electrochemical Impedance Spectroscopy (EIS). MFC telah disuntik dengan inokulum yang terkawal (CI) menggunakan POME sebagai substrat dalam experimen terakhir. CI telah dihasilkan menggunakan mikroorganisma yang telah diadaptasi dan dibiak dalam sisa kilang kelapa sawit. CI adalah campuran mikroorganisma yang bersifat fermentasi dan elektrogenik. Ia terdiri daripada elektrogen (*Pseudomonas aeroginousa*) dari AS dan fermentasi mikroorganisma (*Azospira oryzae, Acetobacter peroxydans, Solimonas variicoloris*) daripada biofilm disebabkan ketiadaan elektrogen dalam biofilm. Operasi MFC dengan CI mencapai kuasa kepadatan yang maksimum sebanyak 107.35mW / m2, iaitu dua kali ganda lebih tinggi berbanding MFC yang dikendalikan dengan AS sebagai inokulum. CE maksimum iaitu sebanyak 74% diperolehi daripada MFC dengan CI, iaitu 50% lebih tinggi daripada CE dengan AS. Namun, ia menunjukkan pengurangan COD yang rendah sebanyak 32%, disebabkan ketiadaan fermentasi mikroorganisma dalam CI bagi menggunakan POME. EIS dan keputusan simulasi menunjukkan pengurangan charge transfer resistance (R_{ct}) sebanyak 19.5% semasa operasi sel dengan CI. Keputusan ini menunjukkan bahawa kuasa output MFC boleh ditingkatkan dengan menggunakan CI.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

A	Ampere
I	Current
V	Voltage
P	Power
R	Resistance
v	Volume
A	Area
Ω	Ohm (resistance)

LIST OF ABBREVIATIONS

COD	Chemical oxygen demand
FESEM	Field emission scanning electron microscopy
FTIR	Fourier transformed infrared spectroscopy
TGA	Thermogravimetric analysis
EIS	Electrochemical impedance spectroscopy
MFC	Microbial fuel cell
PACF	Polyacrylonitrile carbon felt
SFCC	Single forward carbon cloth
GR	Graphite rod
PEM	Proton exchange membrane
POME	Palm oil mill effluent
SHE	Standard hydrogen electrode
CI	Controlled inoculum
AS	Anaerobic sludge
PD	Power density

CHAPTER 1

INTRODUCTION

1.1 OVERVIEW

Energy, water and environment are important commodities, which are needed for the human existence on our earth. In the advancement of our civilization these three commodities have served up as the basic resources for the finance, social and cultural development. Energy crisis in 1972 have made our community to inspect the confines in - energy resources (Meadows et al., 1972). This was the time when our society through the various institutions has organized programs intended to inspect worldwide scarcity of natural resources on our earth. It has become clear that our future society should adapt a new idea for their development, which is based on the inadequate natural resources (Afgan, 2004).

Energy needs in the world continue to rise and in an effort to support energy independence, research initiatives are focused on alternate, renewable and carbon neutral energy sources. Modern society utilizes more and more energy for industry, services, homes and transport. This is especially true for oil, which has turn into the most traded commodity, and part of economic growth is linked to its price. Nevertheless, neither oil nor any of the other fossil fuels, such as coal and natural gas, are unlimited resources (Abdul-Rahman, 2003).

The combined effect of rising demand and depleting resources calls for a close monitoring of the energy situation. Concerns about climate change and growing global demand for the finite oil and natural gas reserves are intensifying the search for alternatives to fossil fuels. According to Mike and Swadesh (2009) even though the nuclear source considered as carbon free approach in generating energy, until now there is no proper solution found for the disposal of radioactive waste. Therefore, green energy is still a preferable energy source compare to nuclear energy.

Traditionally, Malaysian energy policy (Zamzam Jaafar et al., 2003) always around four fuel strategy that is oil, natural gas, coal and hydropower. The oil reserves are anticipated to last atleast for the next fifteen years or so while the gas reserves can last for the next forty two years (Zamzam Jaafar et al., 2003). This forces the goverment to introduce the fifth fuel strategy. The Malaysian government has included renewable energy as the fifth fuel and thereby, increased the role of renewable energy as an alternative to the other sources of energy (Yusoff, 2006).

There is a growing demand in the development of sustainable and renewable energy portfolio recently. Renewable energy and alternative energy source developed in order to reduce the pollution. Renewable energy is the energy from resources that will not be deleted , such as wind, mini hydro, solar and biomass (Randhawa, 2004). However, many regions do not lend themselves well to some or all of these options.

Shortage of energy source is not the only major concern in the world today. Contaminated water or water pollution are also considered an important issue and the overall drop in water-source quality suggests the requirement of novel technologies for the treatment and recycle of the wastewaters generated. According to Shi (2002) until the middle of 1800's, water pollution was restricted to small, local areas. When the industrial revolution occurs after the middle of 18th century, the advancement of the internal combustion engine, and the petroleum-fuelled explosion of the chemical industry happened. With the fast development rate of various industries, a large amount of fresh water is used as a raw material, as a means of production which is the process water and for the cooling purposes. Many types of raw material, intermediate products and wastes are brought into the water when water passes through the industrial process. So indeed, the wastewater is an essential by product of modern industry, and it plays a key role in polluting water environment (Shi, 2002).

Improper management system of industries will cause the wastewater go directly to the river or into the runoff system of the area and become the point source of water pollution. On the initial discharge, these wastewaters can have high levels of inorganic pollutants which can be easily biodegradable, but its impact load on the ecosystems, either in Bio-chemical Oxygen Demand (BOD), Total Suspended Solids (TSS) or Chemical Oxygen Demand (COD) (Czysz et al., 1989). So, in order to overcome this environmental problem faced worldwide, strict regulations on pollution discharge have been imposed by environment protection bodies, which focus primarily on waste reduction (Chan et al., 2009).

Due to the stringent conditions on wastewater discharge worldwide, wastewater must be collected and transmitted to a treatment facility and treated to remove pollutants to a level of agreement before a municipal or industrial facility can release it (Drinan and Spellman, 2001). There are various technologies for the treatment of different type of wastewater which includes biological treatment. Many countries, beyond those considered to be developing, have waste management systems with significant improvement margins to reach worldwide state-of-the art engineering, health and safety standards. These are still characterized by a heavy dependence on land filling (both engineered and non-engineered) and diverging, but generally low levels of recycling and composting, as well as a general absence of waste-to-energy schemes and plants (Karagiannidis, 2012). Therefore, producing energy from waste has attracted researches attention recently.

Biological treatment used for wastewater treatment appears to be one of the promising technologies. According to Metcalf et al. (1991) with suitable analysis and environmental control, almost all wastewaters having biodegradable components with a BOD/COD ratio of 0.5 or higher can be treated easily by biological methods. Compared to other techniques of effluent treatment, this method has the reward of lesser treatment charges without secondary pollution (Sponza and Ulukög, 2005). Among traditional technologies, anaerobic treatment followed by aerobic biological processes are mainly used because of their advantages, such as less biomass yield and low ingredients need (Spanjers and Lier, 2006). Both aerobic and anaerobic treatments are biological treatment technologies and are applicable at the Microbial Fuel Cell (MFC). Microbial fuel cell is one of the promising technologies because it treats the wastewater and producing electricity using microbes as catalysts (Logan et al., 2005). From a chemical analysis perspective, the carbon, ammonia and other pollutants in sewage represent potential for 9.3 times higher energy to be obtained from wastewater than by currently used to treat it (Shizas and Bagley, 2004). So, this energy could be obtained from wastewater using MFC and provide energy to the wastewater treatment plant itself. Therefore, MFC could be an alternative for traditional wastewater treatment because it operates at lower temperatures and yield less biomass with simultaneous generation of bioelectricity.

POME (Palm oil mill effluent) is one of the complex substrates comprising amino acids, short fibers, organelles, nitrogenous constituents, free organic acids and a mixture of carbohydrates ranging from hemicelluloses to simple sugars etc. (Santosa, 2008). It is an organic waste material produced at the palm oil mills. Through the production of one ton crude palm oil, over two and half tonnes of POME are produced (Latif Ahmad et al., 2003). Usually, the biochemical oxygen demand (BOD) and chemical oxygen demand (COD) in the palm oil effluent are in the range of 15000 - 100000 mg/L and 10250 - 43750 mg/L respectively. Due to its acidic nature (pH 3.4 – 5.2), high values of chemical oxygen demand and biochemical oxygen demand (BOD), POME can produce significant environmental harms if released without efficient treatment (Borja et al., 1996). Currently, palm oil mills face a big challenge in achieving higher severe environmental standards imposed by environmental boards.

Malaysia is the world's second largest producer and exporter of palm oil; contributing 49.5 % of world production and 64.5 % of world exports. Despite high economic return to the country, the industry also generates large amount of wastes such as empty fruit bunch (EFB), mesocarp fibre, shell and palm oil mill effluent (POME) for every ton of fresh fruit bunches (FFB) processed in the mills. According to Wu et al. (2010), in year 2008 alone, at least 44 million tonnes of POME was produced in Malaysia and the numbers are anticipated to rise every year. With the fast expansion of palm oil industry and public awareness of environmental pollution, the industry is grateful both publicly and aesthetically to treat its wastewater prior to discharging it. Moreover, new technologies have been created and innovated in order to find an alternative way to treat POME where MFC is one of them.

As the demands of renewable energy and wastewater treatment become the hot topic worldwide, bioelectricity is considered as an additional alternative energy that could be achieved from effluent by MFC (Angenent et al., 2004).

1.2 PROBLEM STATEMENT

Over the past decades, more cost-effective feasible technological alternatives have been proposed for the POME treatment, including skimming devices, flotation, chemical coagulation, land disposal, anaerobic and aerobic biological processes (Borja et al., 1996). However, these treatment methods not only need large treatment areas and long retention times, but also are high energy-consuming (Jong et al., 2011).

Microbial fuel cell (MFC) represents a new fuel cell trend to produce electricity from a diversity of organic substrates through direct oxidation by electrochemical active microorganisms under ambient conditions (Pant et al., 2010). But MFC is still far from commercial reality due to its low power generation and low Coulombic efficiency (CE). The main factors which affects the MFC performance are substrate degradation, electrode material, type of microorganisms, rate of electron transfer from microorganisms to the anode and proton mass transfer in the liquid (Liu et al., 2005a).

Electrode is one of the main components in affecting the MFC performance. Over the past ten years, a variety of electrodes have been widely investigated for MFCs. The electrode materials such as graphite rod, graphite fiber brush, carbon cloth, carbon paper and carbon felt have been used commonly in the microbial fuel cells. Among the electrode materials, carbon felt got advantages over other materials. In order to scale up the MFC, cheap, good conduction, good chemical stability and high mechanical strength electrode material is needed.

So far, different type of microorganisms have been used and studied in MFC such as *Geobacter metallireducens* (Min et al., 2005a), *Pseudomonas aeruginosa* (Rabaey et al., 2004), *Shewanella putrefaciens* (Kim et al., 1999a) and so on. Eventhough, some pure cultures (*Geobacter metallireducens and Shewanella putrefaciens*) called as electrogens can able to transfer electrons directly and produce current more or less equal to mixed cultures, it cannot utilize mixed or complex substrates. But, most of the industrial and domestic wastewater contains complex substrates and it makes pure culture not suitable for treating wastewater using MFC.

In MFC, attachment of bacteria and biofilm formation on the electrode surface are important for the better transfer of electrons between microorganisms and electrode surface (Franks et al., 2010). Conventional theory classifies biofilm structure around includes three basic steps of development, initial attachment, maturation and detachment (Toutain et al., 2004). The EPS physically immobilize the bacteria while at the same time offer them opportunity for cell to cell contact and communication (Read et al., 2010). Furthermore, the electrochemistry of the bioanode is complex owing to changing microbial communities in the anode biofilm (Jung and Regan, 2011) and understanding this would play a part in improving the MFC operation and MFC performance.

Until now, little investigation in the inoculum has been made that are most essential for maximal current production. Usually anaerobic sludge (AS) has been used as inoculum in most of the MFC experiments but AS has not only fermentative microorganisms also contains unwanted microorganisms which could reduce the MFC performance. Anaerobic sludge may or may not contain electrogen but the activity of at least one electrogen is an absolute requirement for microbial fuel cells to effectively convert organic fuels to electricity. Even if electrogens exist in the AS but if unwanted microorganisms also present in the AS that will influence the electrogens and fermentative microorganisms which in turn reduces the performance of MFC. Fermentative bacteria consume complex organic substrates and produce intermediate products whereas electrogenic microorganisms can consume certain molecules like acetate and hydrogen directly as well as those intermediate products produced by fermentative organisms and completely oxidize it. So for the better performance of MFC, this synergistic interaction plays an important role but the presence of unwanted microbes in AS affects the synergistic interaction and reduces the MFC performance.

1.3 OBJECTIVES

- To produce electricity from POME with concurrent accomplishment of wastewater treatment.
- To evaluate the effect of different electrode materials on MFC Perfromance.
- To elucidate the effect of anode biofilm formation on power generation.
- To enhance the power generation using selected microorganisms.

1.4 SCOPE OF RESEARCH

In order to meet the outlined objective, the following scopes of research have been identified.

- To simultaneously study the treatment of palm oil mill effluent and production of electricity using microbial fuel cells (MFCs).
- Anaerobic Samples of POME treatment plant will be obtained from local palm oil industry and existing predominant microorganisms in the sample will be isolated and identified using BIOLOG.

- Different electrode materials such as PACF (Polyacrylonitrile carbon felt), SFCC (Single forward carbon cloth) and GR (Graphite rod) will be tested to study the influence of electrode materials on electron transfer in MFC

- Biofilm formed on the electrode surface will be isolated and identified using PCR, DGGE and sequence analysis and study the influence of biofilm formation on power generation.

- Controlled inoculum was prepared using isolated fermentative and electrogenic microorganisms.

- Operate the MFC with controlled inoculum (CI) to study the efficiency of CI in enhancing the electron transfer between microorganisms and anode to attain higher power density