INVESTIGATION ON THE PERFORMANCE OF INNOVATIVE POWDERED ACTIVATED CARBON HYBRID MICROBIAL FUEL CELL IN TREATING PALM OIL MILL EFFLUENT

LIM PING FENG

UNIVERSITI TUNKU ABDUL RAHMAN

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LIM PING FENG

A project submitted in partial fulfillment of the requirements for the award of Bachelor of Engineering (Hons) Environmental Engineering

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DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

Signature : ________________

Name : LIM PING FENG

ID No. : 11AGB03537

Date : ________________

APPROVAL FOR SUBMISSION

I certify that this project entitled **"INVESTIGATION ON THE PERFORMANCE OF INNOVATIVE POWDERED ACTIVATED CARBON HYBRID MICROBIAL FUEL CELL"** was prepared by **LIM PING FENG** has met the required standard for submission on partial fulfillment of the requirements for the award of Bachelor of Engineering (Hons) Environmental Engineering at Universiti Tunku Abdul Rahman.

Approved by,

Signature : _________________, __________________

Supervisor : Dr. Ng Choon Aun & Dr. Mohammed J. K. Bashir

Date : _________________

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ABSTRACT

Performance of nine 0.5L MFCs with and without PAC and cultivated at different SRTs with different feed concentrations were studied and compared for their effects on wastewater treatment, biogas and power productions. The best MFC could remove the COD from the POME up to 64.4%. This study also shows that biogas could be better produced by the MFCs which were fed with relatively higher feed concentration compared to the MFCs fed with relatively lower feed concentration. However, it was found that the power production for the MFCs fed with relatively lower feed concentration had better power density production compared to the MFCs fed with the relatively higher feed concentration. In addition, all the MFC cultivated at longer SRTs with PAC could perform better in terms of biogas production, COD removal and power production.

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LIST OF SYMBOLS / ABBREVIATIONS

BAC	Biological activated carbon
BOD	Biological oxygen demand
COD	Chemical oxygen demand
HRT	Hydraulic retention time
MFC	Microbial fuel cell
MLSS	Mix liquor suspended solids
MLVSS	Mix liquor volatile suspended solids
PAC	Powdered activated carbon
PEM	Proton exchange membrane
SRT	Sludge retention time
TSS	Total suspended solids
VSS	Volatile suspended solids
V	Voltage
I	Current
P	Power density
R	Resistance

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CHAPTER 1

INTRODUCTION

1.1 Background

It is an advantage for a community to be able to treat its wastewater in an economical way. After years of research, the activated sludge process outshines as the most commonly conventional biological wastewater treatment used around the world. The fundamental principle behind all activated sludge processes is that microorganisms grow and feed on organic contaminants in wastewater, form particles that clump together. These particles are then allowed to settle to the bottom of the tank meanwhile the supernatant flows on for further treatment. The activated sludge process was initially developed in the early 1900s in England but the actual widespread of the technology was after 1940s (Noah, 2003). Since then, numbers of research and development have been done to the activated sludge process for the sake of improving the methods. However, oxygen supply by the aeration for activated sludge treatment process accounts the largest portion of the total energy consumption, range from about 45% to 75% of the whole treatment plant energy expenditure (Liu, et al., 2011). Besides, activated sludge process also produces large amount of excess sludge which required an appropriate treatment and disposal and eventually increases the operational cost (Aelterman, et al., 2006). Hence, people are looking for alternatives that can provide a solution to these problems which conventional wastewater treatment faces.

As the coal and petroleum is depleting which leads the global energy price to increase in recent times, anaerobic digestion (AD) has come under the spotlight to be the new generation of wastewater treatment technology. Anaerobic digestion is a biological process where the bacteria break down the organic matter in an environment with little or absence of oxygen. The microbial reactions can generate biogas which mainly is methane gas which later converts into electricity. This waste-to-energy approach is considered to be effective and sustainable, but nevertheless the AD have to be operated at relatively high temperature which in turn requires heat input and eventually increases the energy cost. According to Zhen, Fei and Zheng (2013), the conversion of biogas to electricity requires a converter to perform the conversion job which in the end contributes to the capital cost of treatment plant.

Researches had been done to improve the AD technology and that’s how the idea of microbial fuel cells (MFCs) born. MFCs are now emerging as a potential and sustainable wastewater treatment technology. MFCs are a new technology that uses bacteria to oxidize various organic or inorganic compounds and generates electricity. Gaviria (2011) stated that MFCs can direct generate electricity without any conversion steps required. MFCs also able to operate efficiently at ambient temperature or even low temperature, thus no additional heat input required for MFCs. Furthermore, MFCs able to run under anaerobic condition, therefore no additional energy required to provide oxygen into the chamber. Similarly to AD, the microorganisms activities in MFCs also able to produce the biogas and can be convert into electrical energy. However, such renewable and sustainable technology is still in the development stage, challenges such as high strength wastewater and acclimatization of microorganisms in MFCs have become the top priority in research worldwide.

A gradual progress has taken place in the direction of integrating adsorptive and biological processes in the field of water and wastewater treatment. In this regard, powdered activated carbon (PAC) is renowned by its capability of combining the merits of adsorption and biological removal in a same reactor (Cecen, 2011). The establishment of biological activity with the PAC will develop into biological activated carbon (BAC) and it will promote the attachment of microorganisms and formation of biofilm. The addition of PAC into wastewater can enhance the absorption and degradation of the organic matter and nutrient of substrate (Boonyungyuen and wichitsathian, 2014). However, the dosage of PAC has to be added just right according to the volume of wastewater treated. Lack of PAC replenishment or too low concentration of PAC may lead to membrane fouling. On the contrary, high dosage of PAC could reduce membrane fouling but may increase the cost too (Torretta, et al., 2013).

1.2 Problem Statements

Microbial fuel cells (MFCs) are considered as new source of energy where it can directly use bacterial metabolism to generate electrical current, but the application of MFCs is not bound to energy area only. MFCs can be a solution for the untreated waste as it can remove the organic and inorganic compound available by oxidation. The biogas produced can be collected and further converted into electrical energy. However, the power generated by MFCs is relatively low and this has become the limiting factor of the widespread of MFCs. Due to the promise of sustainable energy generation from organic wastes, thousand of researches have been done in this technology. The drawback of the MFCs can be due to the type of the electrode, distance of the electrode, design of MFCs, oxygen supply, external circuit resistance, pH and temperature. Besides that, studies are also done on the type of substrate used in MFCs, concentration of the substrate and amount of wastewater in relation to power generation. Yet, there is no ideal solution which can fully utilize the MFCs performance.

Sludge retention time (SRT) is considered as one the most important parameters in determining the performance of MFCs. The power generation is highly depends on the microbes behaviour and the growth of anaerobic bacteria can be improved by the increment of SRT. Long operating SRT is usually needed for better microbial growth and degrades biodegradable organic pollutants. On the other hand, short operating SRT can cause biodegradation to be incomplete and washout of microbes from the system faster than they grow. Thus, an optimum operating SRT is required to find out in order to improve the MFCs performance.

Even though there are many research have been done on the effect of SRT on the power generation efficiency of MFCs, the optimum operating SRT to obtain the biggest power production is yet to be investigated. Therefore, the aim of this study is to focus on the optimum operating SRT and the effect of different wastewater concentrations on the performance of powdered activated carbon (PAC) hybrid microbial fuel cell (MFC).

1.3 Aims and Objectives

The objectives of the thesis are shown as following:

i. To study the effects of different Sludge Retention Time (SRT) on the electrical power generation, amount of biogas produced and organic removal efficiency of powdered activated carbon (PAC) hybrid microbial fuel cell (MFC).
ii. To investigate the effects of different concentration of wastewater feed on the electrical power generation, amount of biogas produced and organic removal efficiency of powdered activated carbon (PAC) hybrid microbial fuel cell (MFC).

CHAPTER 2

LITERATURE REVIEW

2.1 Palm Oil Mill Effluent (POME)

The expansion of palm oil industry in Malaysia has been phenomenal. The growth in palm oil demand has boosted the national economy and more research and development (R&D) efforts were put in this area of field. According to a statement made by Oil World in 2013, in the last 20 years, the total production of 17 oils and fats have doubled and palm oil has account for 30% of world production of all oils and fats in 2013/14 as shown in Figure 2.1. Palm oil emerges as the largest, in terms of production as a result of increase in palm oil demand. With the increase in palm oil demand, many lands were opened up for palm oil cultivation, thus increase in hectarage of oil palm as shown in Table 2.1. Hence, Malaysia becomes one of the largest palm oil exporters and producer in the worlds where it accounts 46% of world exports and 37% of world production in 2011. While the palm oil industry has been known for its benefit towards economic growth and development, it also made an impact to the environment due to the production of large quantities of by-product from the oil extraction process (Parveen, et al., 2010).

Palm Oil Mill Effluent (POME) is the by-products generated from the oil extraction process of palm oil from the fresh fruit brunch (FFB) in palm oil mill. Due to its acidic nature, with pH range in 3.4-5.2 and extreme high concentration of chemical oxygen demand (COD) with value range in 15,000-100,000mg/L as illustrated in Table 2.2, the POME is prohibited to be discharged into the environment directly without being treated (Jong, et al., 2011). In year 1978, the enactment of the Environmental Quality Regulations detailing POME discharge standards as shown in Table 2.3 have compel this industry to oblige by law. Tons of efforts and commitment were contributed to work out an environmentally and economically sound treatment technologies that can reach the common goal pollution abatement. Finally, three most commonly used systems were adopted for the POME treatment and these three were the ponding system, open tank digester with extended aeration system, and the closed anaerobic digester system (MPOB, 2012). However, these three conventional treatment systems are not sustainable, not only because it required large treatment areas and long retention times, but also consume very high energy, which in return indicates cost ineffective. Therefore, an alternative treatment shall be looked into in which it can meet the discharge standard criteria meanwhile reduce the cost of POME treatment.

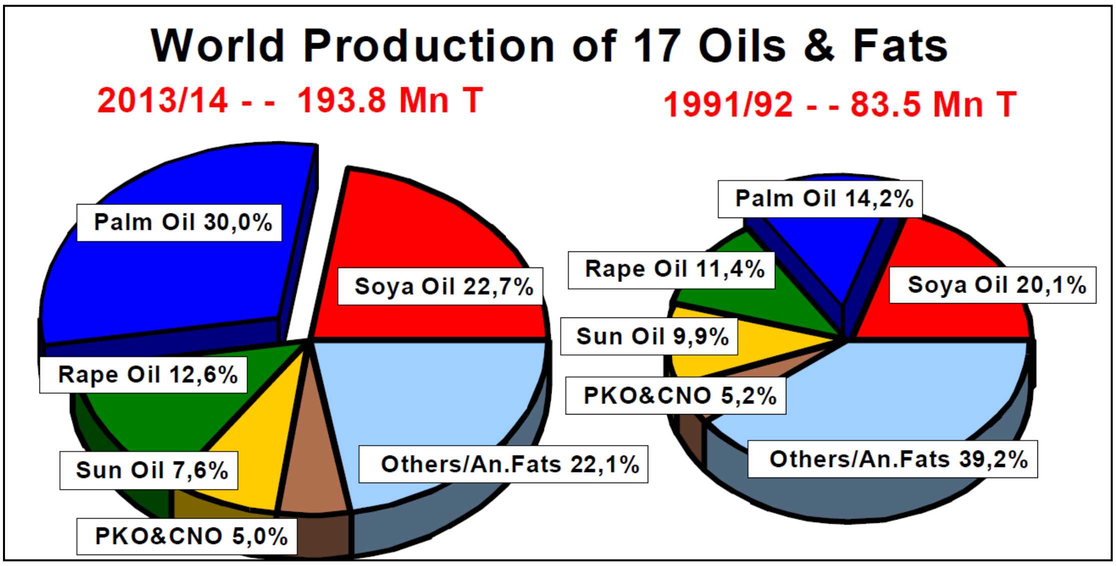

Figure 2.1: World production of 17 oils and fats (Oil World, 2013).

Table 2.1: Hectarage of oil palm in Malaysia (MPOB, 2012).

Hectarage of oil palm in Malaysia	
Year	**Hectarage**
1990	2094028
1995	2540087
2000	3376664
2005	4051374
2010	4853766
2011	5000109

Table 2.2: Characteristics of POME (MPOB, 2012).

Parameter	Mean	Range
pH	4.2	3.4 - 5.2
Biological Oxygen Demand	25000	10250 – 43750
Chemical Oxygen Demand	51000	15000 – 100000
Total Solids	40000	11500 – 79000
Suspended Solids	18000	5000 – 54000
Volatile Solids	34000	9000 – 72000
Oil and Grease	6000	130 – 18000
Ammoniacal Nitrogen	35	4 – 80
Total Nitrogen	750	180 - 1400

Table 2.3: POME discharge standards (MPOB, 2012).

Parameter	Discharge Limit
pH	5 - 9
Biological Oxygen Demand	100
Chemical Oxygen Demand	-
Total Solids	-
Suspended Solids	400
Oil and Grease	50
Ammoniacal Nitrogen	100
Total Nitrogen	-
Temperature (℃)	45

2.2 MFC

The recent innovation in the field of microbial fuel cell (MFC) has taken the spotlight and provides a potential microbial environmental technology to generate energy whilst treating the organic wastewaters at the same time. MFC is a bioreactor which can harness the power by converts the chemical energy into electrical energy through catalytic reactions of microorganisms under anaerobic conditions. The production of electrical energy using the MFC is considered to be one of the most efficient (Hao Yu et al., 2007; Salgado, 2009) and carbon neutral energy sources technology (Lovely, 2006). According to Logan (2010), MFCs can produce power densities as much as $1 kW/m^3$ of reactor volume ideally.

Basically a MFC design consists of an anode, cathode, a proton exchange membrane (PEM) and external electrical circuit as shown in Figure 2.2 (Pham et al., 2006). The bacterial community in the anode compartment oxidizes the organic substrates to produce carbon dioxide, electrons and protons through biological process (Rabaey and Verstraete, 2005). These electrons produced were later being transferred to the anode and reached the cathode compartment via an external electrical circuit, as a result the electric current produced with flow of electrons (Salgado, 2009). The electrical energy was measured using a voltmeter or ammeter connected to the external circuit. Subsequently, the proton produced at anode compartment would diffuse through the PEM to the cathode compartment and combine with the electrons and oxygen molecule to form water. Generally the anode compartment is kept under anaerobic conditions as oxygen will inhibits the electricity generation whereas the cathode is provided with oxygen (Logan, 2009; Rahimnejad Mostafa, 2009). The equation below illustrates the redox reaction process occurring in the MFCs in the case of a glucose fed system (Pham et al., 2006).

Anode: $C_6H_{12}O_6 + 6H_2O \longrightarrow 6CO_2 + 24H^+ + 24e^-$

Cathode: $24H^+ + 24e^- + 6O_2 \longrightarrow 12H_2O$

$$\mathbf{C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O + \text{Electrical energy}}$$

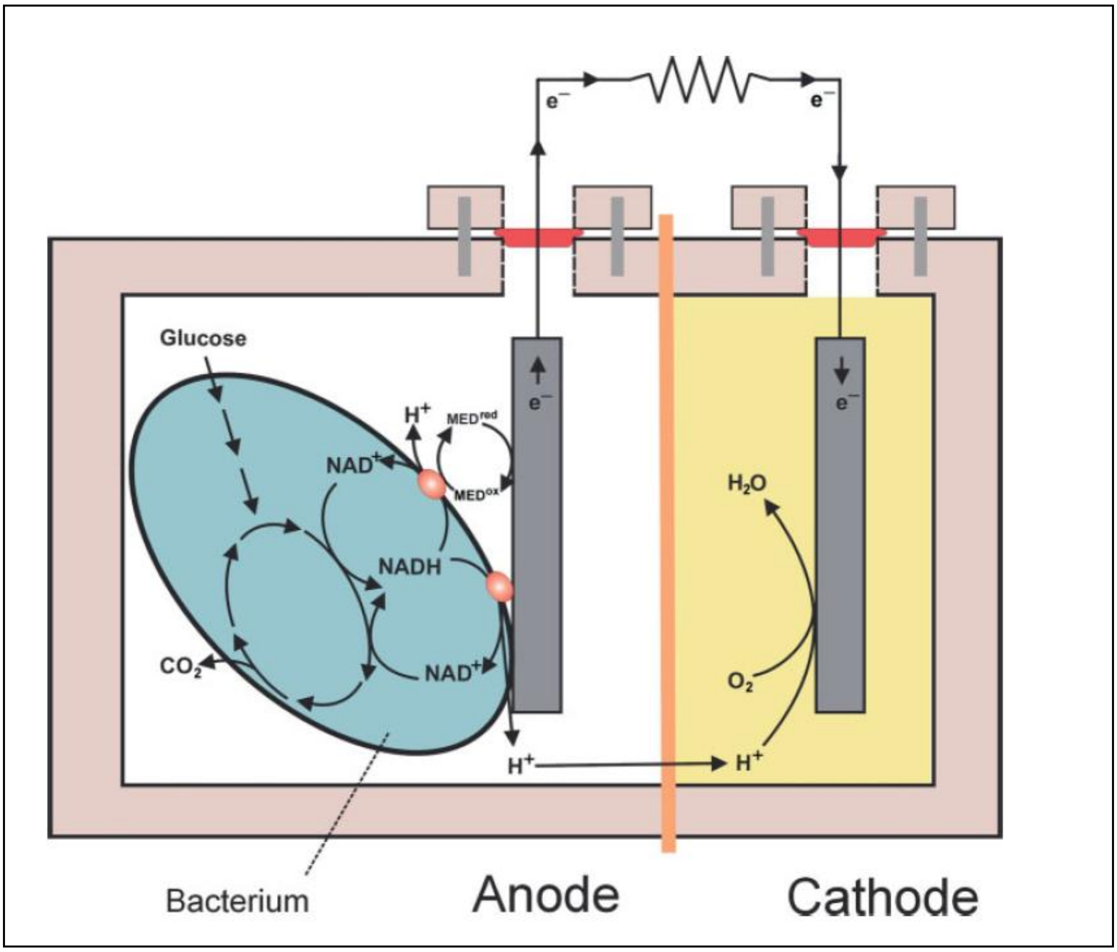

Figure 2.2: Graphical Microbial Fuel Cell (Pham et al., 2006).

The depletion in fossil fuel and environment effect has lead people to seek for more sustainable, cost effective, environmentally friendly and reliable energy source. The capability of MFC to harness energy from various wastewater sources including industrial, domestic and synthetic wastewater has gained wide research interest. Years of study and research have resulted in the development of several types and methods MFC configuration. While the potency of MFC has been widely studied and explored, there are still ample of limitation in the system such as low electricity generation, the difficulty of storing biogas and others which needed to be improved upon the MFC technology (Oji, Opara and Oduola, 2012).

2.2.1 Type of MFC

The idea of MFC has been delivered since long time ago, thus there are many types of MFC can be found around the world. However, MFCs are most commonly being differentiated into six types, which are single chamber MFC, dual chamber MFC, mediator MFC, mediator-less MFC, membrane MFC and membrane-less MFC.

I. Single chamber MFC

The design of single chamber MFC is simpler and efficient by placing the anode and cathode into one compartment. The cathode is bounded directly on the Proton Exchange Membrane (PEM). One side of the cathode is face air while the other side faces the solution in the chamber. This design can omit the aeration as oxygen in air can transfer to the cathode (Pandey, Mishra and Agrawal, 2011).

II. Dual chamber MFC

The MFC consists of two chambers separated by material that can transfer the protons between the two compartments. It is usually being built in a "H" shape, whereby two compartment been connected by a proton exchange membrane (PEM) such as Nafion or Ultrex or a simple salt bridge. The main reason of the membrane is allows protons to pass between chambers but not substrate or electron acceptor from the cathode chamber especially oxygen (Pandey, Mishra and Agrawal, 2011). The anode compartment is usually in anaerobic condition whereas oxygen will to provide in the cathode compartment. Hence, oxygen should not diffuse into anode chamber and disturb the bio-activity in anode chamber. Logan (2006) stated that rate of oxygen diffuse into anode chamber without a PEM is 2.7 % higher than a dual chamber using a PEM. Besides that, it also produces little power due to the high internal resistance.

III. Mediator MFC

A mediator is a compound which helps the bacteria that inactive for transfer the electron. Synthetic or natural mediator compounds such as Thionine,, humic acid, neutral red, methylene bluemethyl viologen, hydroxyl naphtoquinone and etc are redox intermediates (Mansoorian, 2014). The mediator used in the earlier development of the MFC has been found to be toxic to microorganism and thus reduce the efficiency of MFC. Therefore, this type of MFC is seldom being adopted nowadays.

IV. Mediator-less MFC

A mediator-less MFC is a type of MFC that does not required any mediator to transfer electrons to the electrode. The mediator-less MFC uses aodophiles to form layer of biofilm on the anode surface to act as an end terminal electron acceptor in anaerobic condition. The need not use of mediator has put mediator-less MFC to be more commercial potential as compared to mediator MFC (Surajit and Neelam, 2010).

V. Membrane MFC

Membrane acts as a physical separator of anode chamber and cathode chamber no matter in single chamber or dual chamber. PEM is the preferable physical separator to be used in MFC as it has high conductivity to proton. Cations will be allowed to transfer from anodic compartment to cathodic compartment. But, the membrane is prone to fouling. Biofilms will be formed easily on the PEM surface and caused fouling to membrane (Chae et al., 2008). New PEM replacement needs high cost which leads to the decreasing use of membrane MFC.

VI. Membrane-less MFC

Membrane functions as an electrolyte that plays as an electric insulator and let proton transfer through in MFC. But the proton transfers through membrane can be a rate limiting factor typically with membrane fouling which due to the suspended solids and soluble pollutant in wastewater treatment process (Ghangrekar, n.d.). Therefore the function of membrane-less MFC is offseting the cost of the membrane and the membrane maintenance. However, the absence of membrane will increase the oxygen transfer into the anode chamber, which is responsible for energy recoveries and low electron, as a result cause membrane-less MFC inefficient (Kim, 2007).

Table 2.4: Types of microbial fuel cell, COD removal rate and power density.

Types of MFC	COD removal rate (%)	Power density (mW/m^2)	Reference
Membrane-less	75.9	30	Wang, H. et al., 2013
Single chamber	-	173	Pandey, B. K. et al., 2011
Dual chamber	-	0.8	Rakesh, et al.,2014
Mediator-less & membrane	90.46	621.13	Mansoorian, H. J. et al., 2014
Membrane-less & single chamber	-	0.15	Liu, H.et al., 2008
Single chamber & air cathode	-	676	Zhang, X. et al., 2013
Single chamber & membrane	92.5	1460	Ren, L. et al., 2014
Membrane-less	-	85.3	Du, Z. et al., 2008
Single chamber & mediator	-	19	Nimje, V. R., 2012
Dual chamber	-	600	Kim, M. H., 2009
Membrane-less	-	37.4	Zhu, F., 2011
Single chamber	88%	133	Li, Z. L., 2007

2.3 Biogas production

Biogas particularly methane gas can be produced through anaerobic digestion process. The degradation of anaerobic digestion process occurs in four stages which are hydrolysis, acidification, acetogenesis and methanogenesis. In the first stage, anaerobic bacteria will use enzymes to decompose organic substances such as protein, carbohydrates and fats into smaller molecular compounds. Then in second stage, acid forming bacteria will continue decompose the molecular compound into organic acids, carbon dioxide, hydrogen sulphide and ammonia. Acetate, carbon dioxide and hydrogen will be formed in the acetogenesis stage by acid bacteria. Last stage the methanogenic bacteria will produce methane, carbon dioxide and water.

In anaerobic digestion, the complex organic substance in POME is being degraded to form methane gas mostly. This implies that the methane gas produced can be converted into electrical energy to reduce the plant total energy cost. As Malaysia is one of the largest exporter and producer of plam oil in the world, the amount of POME produced is also approximately very huge quantity. Hence, according to the number of POME provided by Malaysia Palm Oil Board (MPOB) generated in 2011, the biomethane production is estimated to reach 578,693 tonnes and is equivalent to 3,214,958MWh of electricity generated (Chin, 2013). Every year, a typical household in Malaysia consumed an average of 4387kWh electricity and the estimated of power generated is expected to be able to support 700,000 households in Malaysia (Mahlia and Chan, 2011).

Table 2.5: Estimated methane gas production from POME based on the Crude Palm Oil production of Malaysia in 2011 (Chin, 2013).

Parameter	Unit	Value
CPO production	Tonnes	18,911,520
POME generated	m^3	56,734,560
COD level in POME	mg/L	51,000
CH_4 produced	Tonnes	578,693
Electricity generated	MWh	3,214,958

Even though the microbial activities are the same for all amaerobic digestion processes, each plant is different from another and different parameters should be input in design considerations. Several factors that can affect the production of biogas must be taken into consideration. Some of these factors are the types of wastewater to be treated, volume capacity, temperature, wastewater strength, types of bacteria available, pH and etc (WtERT, 2009).

2.4 MFC wastewater treatment

MFC is well known for its bio-electrochemical systems. Besides than electrical production, MFC also has shown promising performance on the organic removal efficiency. Recently there are many researches done on the biological oxidation of pure carbon sources such as glucose, acetate, and lactate in MFC processes. Moreover, wastewater from domestic and industrial were reported to be treated using

MFC. From this, it shows that MFC can be a promising alternative technology to be applied on different waste flows containing biodegradable organics as a growth medium. The main advantage is the chance to mineralize the organic matter in the wastewater into water and carbon dioxide, subsequently reduce the chemical oxygen demand (COD) in the wastewater.

Table 2.6: COD removal rate and power density of different wastewater.

Types of wastewater	COD concentration (mg/L)	COD removal rate (%)	Power density (mW/m^2)	Reference
Synthetic	446	90.86	6.73	Ghangrekar, M. M. et al., n.d.
Synthetic	3000	75.90	30	Wang, H. et al., 2013
Sucrose based synthetic	1000	25.00	127	Kubota, K. et al., 2010
Dairy industry	3620	90.46	621.13	Mansoorian, H. J. et al., 2014
POME	60600	70.00	45	Baranitharan, E. et al., 2013
Glucose based synthetic	1124	88.00	133	Li, Z. L., 2007
Domestic	210	92.50	1460	Ren, L. et al., 2014

Literature review above shows various type of wastewater like synthetic wastewater, dairy industry wastewater, POME and domestic were being used in MFC as nutrient medium. Based on the result obtained, the COD removal efficiency is considered good as mostly were able to reduce more than 70% of COD. Furthermore, MFC's performance not limited to COD removal only, it also able to remove others parameters such as biological oxygen demand (BOD), total solids, total suspended solids, ammoniacal nitrogen, nitrate nitrogen and total dissolved solids (Baranitharan, Maksudur and Prasad, 2013). The application of MFC is very wide and the treatment efficiency of MFC can be evaluated based on many different characteristics in the wastewater used. However, electricity production and COD removal rate are the major concern throughout this project.

2.5 Factors affecting MFC performance

There are several factors which may affect the overall MFC performance in terms of electricity production and wastewater treatment efficiency. The factors are mainly categorized into two aspects which are the design of MFC and the operation condition of MFC. The design of MFC such as the type of electrode, distance between anode and cathode, anode surface area, PEM fouling were further to be studied. Meanwhile the operation condition of MFC such as the temperature, pH, SRT, HRT, wastewater concentration, F/M ratio and types of bacteria were studied as well.

2.5.1Design of MFC

I. Type of electrode

The types of electrode materials are vital to the performance of MFC. For a MFC, power generation and overall performance are closely related to the electrode used. For all types of electrodes, their base materials must always be of good conduction, chemical resistant, high mechanical strength, and low cost (Wei, Liang and Huang, 2011). The most common electrode used for anode was carbon cloth, carbon felt, graphite felt, carbon mesh and graphite fiber because of their stability, high electricity conductivity and large surface area (Logan, 2010; Logan and Regan, 2006). Whereas for cathode, electrodes such as platinum, platinum black, activated carbon, graphite and biocathode are in favor (Chen et al., 2008; Du et al., 2007). Bio-electrode is a new finding where it functions as a conductor, a carrier of bacteria, and some special surface characteristics of electrode materials that promote to high bio-catalytic activity.

II. Anode surface area

The anode surface characteristic is one of the deciding factors that affect the bacterial attachment and electrical connections between bacteria and the electrode surface. Larger anode surface area can improve the power output as it provides much more space to hold the bacterial population per unit area. In return, more bio-electro activity occurs and leads to more electron transfer and power production (Scott, et al., 2007). In MFC, the formation of a biofilm on the anode surface due to the bacterial attachment is important for the efficient biological transfer of electrons between microbes and anode (Baranitharan, et al., 2014).

Table 2.7: Power density of different electrode material and size.

Electrode Materials	Size (cm^2)	Maximum power density (mW/m^2)	References
Carbon paper	22.5	600	Logan, B. et al., 2007
Graphite plate	192	3290	Dewan, A. et al., 2008
Graphite plate	155	1410	Dewan, A. et al., 2008
Carbon mesh	7	893	Wang, X. et al., 2009
Carbon cloth	7	766	Cheng, S. A. et al., 2007
Carbon brush	7	2400	Logan, B. et al., 2007

III. Distance between anode and cathode

The electricity production is affected by the spacing between the anode and cathode. It was reported that the power density increased with decrease in the distance between the electrodes (Ghangrekar and Shinde, 2006). It is believes that the shorter electrode distance can substantially reduce the resistance and thus increase the power generation (Santoro, et al., 2011). This suggests that the distance of electrodes in MFC should be built as close as possible to enhance the power production. However, extremely small distance between the electrodes would not likely increase the power density but decrease in power density due to oxygen cross over and affect the bio-chemical activity at anode (Cheng and Logan, 2011). Therefore, further studies shall be done to find out the optimum distance of electrodes in relation to other design factors such as the electrode material, substrate used, types of cathode, etc.

IV. Proton Exchange Membrane (PEM) fouling

The power output is highly depended on the proton transfer from anode to cathode through the PEM. The fouling of PEM will deteriorate the performance of MFC in terms of electricity production. It was found that fouling of PEM can induce reduction of ion exchange capacity, conductivity and diffusion coefficients of protons. Fouling can also reduce the efficiency and increase the operating and cost of replacing a new membrane. The fouling layer attached on PEM is proven consisted of microorganisms encased in extracellular polymers and inorganic salt precipitations (Xu, et al., 2012).

From a physiochemical point of view, membrane fouling can be influenced by biotic and abiotic factors. Biotic factors are related to microorganisms with size of 0.1-15micrometer are totally retained on the membrane surface. Such kind of microorganisms may have hydrophobic surface which causing them to adhere to the hydrophobic membranes and eventually form a biofilm (Nomura et al., 2007). Abiotic factors such as temperature, total suspended solid (TSS) concentration and sludge retention time (SRT) also have big impact on fouling. High temperature can reduce the particle size which leads to small and denser structure that blocked the membrane’s pores (Lin et al., 2009; Masse et al., 2006). Besides that, high concentration of TSS can also cause sudden and rapid membrane fouling (Ho and Sung, 2009).

2.5.2 Operation condition

I. Temperature

Temperature is a vital parameter that affects the performance of MFC in terms of COD removal and electricity production. Bacteria reactions can be varied over different range of temperature and is depend on the tolerance of the bacteria. Generally, the rise in temperature can boost the anaerobic microbial electro-activity to produce more electricity (Gonzalez et al., 2013). According to Behera et al., (2011), higher temperature can reduce the internal resistance of MFC and thus increase the electrical power generation. Bacteria of thermophilic types usually get very active during high temperature but if the temperature is extremely high, it will destroy the bacteria especially damage of nucleic acid part of bacteria. In an experimental setup, a water bath is needed to maintain the high temperature of MFC and this required extra operation cost. Therefore normally MFC will be conducted under the ambient or room temperature.

Table 2.8: Effect of temperature over the power production in MFC (Gonzalez, et al., 2013).

Temperature (℃)	Voltage (mV)	Power density (mW/m^2)
20	111	0.73
25	112	0.75
30	117	0.82
35	119	0.88
40	133	1.01

II. pH

The value of pH in MFC plays a significant role on the activity of bacteria in terms of COD removal rate and electrical energy production. The optimal range of pH best for the methane-producing bacteria is observed to be in the range of 6.3 – 7.8. Apparently, any pH values lower than 5.5 are suitable for acidogenic bacteria to live. Within this condition, the organic removal rate is expected to decrease as compared to neutral and alkaline conditions and only hydrogen production would be the dominant mechanism. Due to low removal rate, lesser electrons will be produced and lead to lower electricity generation (Marashi and Kariminia, 2015). The highest current can be obtained in MFC during the pH value range 7 – 8 (Gil et al., 2003). Based on Figure 2.3, pH value at neutral or slightly alkaline condition is a favorable environment for the growth of electrogenic bacteria which leads to higher power production.

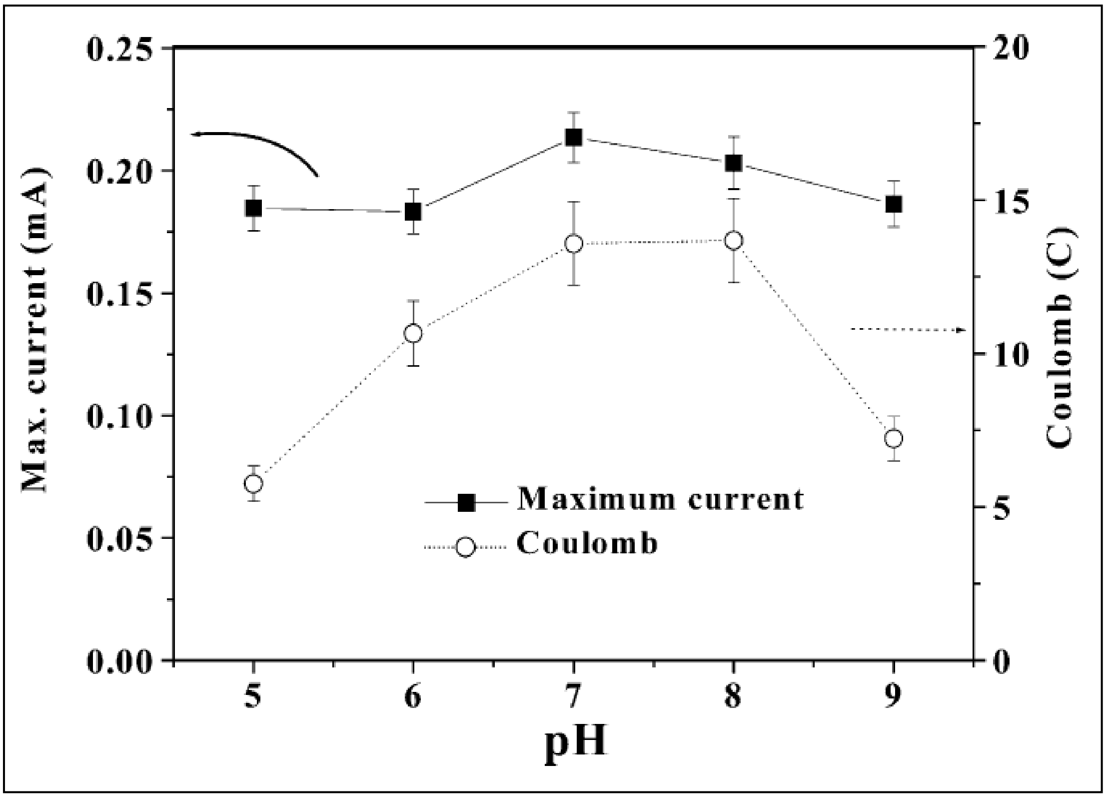

Figure 2.3: Effects of pH on the performance of MFC (Gil et al., 2003).

III. Sludge Retention Time (SRT)

Sludge retention time (SRT) is a crucial operating factor that has an effect on the performance of MFC in terms of microbial growth, power production and organic removal rate. SRT is defined as the time of sludge remains in the system by dividing the total volume of the discharge per unit time. Long SRT could provide a conducive condition to increase in sludge concentration and thus biomass loading, which facilitates the anaerobic process to be more efficient

(Huang, Gui and Qian, 2001). Low operating SRT could lead to incomplete microbial growth and high possibility of microbes wash out from the system faster than they grow. Review on the Table 2.9, it is proven that higher SRT has higher removal efficiency and thus produce better quality of effluent. Although high SRT shows good removal efficiency, but the relationship of SRT and treatment efficiency is highly affected by other operating parameters and feed wastewater characteristics (Lin et al., 2013).

Microbial growth can be influenced by the operating SRT in a biological treatment. It is an important criterion to be used in MFC operation. The active and fertile electrochemical microbes would form layer of biofilm on the anode electrode surface and more organic matter will be degraded which eventually contribute to more electricity production. According to Khan et al (2014), formation of biofilm enriched with electrochemically active bacteria on the electrode surface required sufficient retention time, which then the charge transfer resistance will be reduced and resulted in increase of power generation.

Table 2.9: Influent and effluent quality at different SRT (Aida et al., 2014).

Parameter mg/L	SRT 30 days		SRT 15 days		SRT 4 days	
	Influent	Effluent	Influent	Effluent	Influent	Effluent
COD	1300	63 (95%)	1267	86 (93%)	1496	105 (92%)
BOD_5	538	35 (93%)	760	53 (93%)	897	79 (90%)
TSS	52	6.6 (99%)	74	9.3 (99%)	87	11 (99%)
NH_3-N	50	1.1 (98%)	65	1.4 (98%)	51	7.8 (84%)
PO_4^{3-}	10	1.9 (81%)	12.3	2.5 (79%)	9	2.8 (68%)

IV. Hydraulic Retention Time (HRT)

In wastewater treatment process, hydraulic retention time HR is one of the most significant parameters that affects the design and operation of treating facilities. HRT is defined as the length of time that a soluble compound stays in a bioreactor. HRT is the volume of reactor tank divided by the discharge flow rate. It is noted that high HRT is suitable to be applied on high concentration of COD and BOD wastewater (aida et al., 2014). Higher HRT usually results in better removal efficiency due to longer time for microbe to grow and form biofilm with organic pollutant. Hence, increase in HRT leads to increase in organic removal efficiency. However, power production is unlike the trend of organic removal rate. In fact, You et al. (2006) stated that high HRT will produce unstable voltage output whereas short HRT can obtaine a very stable voltage output. In addition, power density was observed to be decreasing when HRT is increase (Liu et al., 2004). Further studies regarding the relationship between HRT and the power production in MFC should be done in order to have more power production with optimize operating HRT.

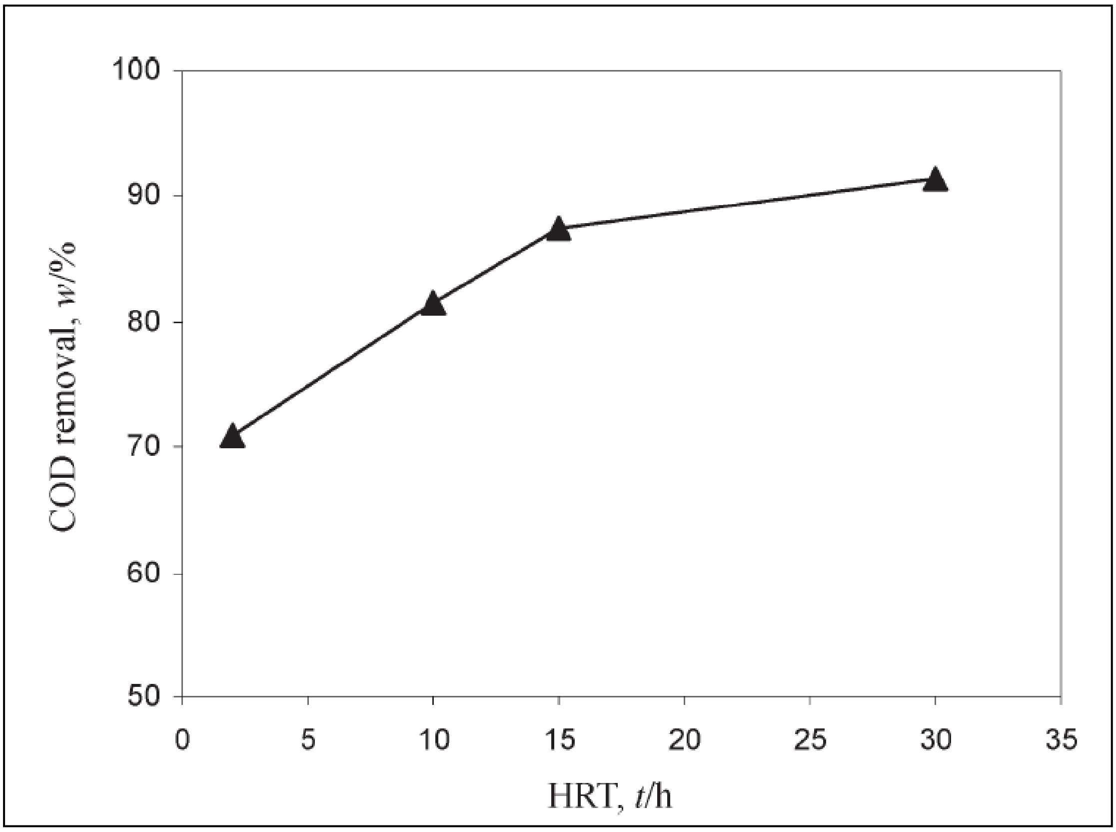

Figure 2.4: Effect of HRT on different parameter removal rate.

Finally, it is important that to ensure the MFC is operated under a steady-state conditions. The influence of HRT under a unsteady-state condition is unverified. To achieve a steady-state MFC does not depend only on the extent of operation time but also on the adaption of sludge to the wastewater components. Industrial wastewaters usually recommend using higher HRT for degradation of complex compounds and longer biomass adaption periods.

V. Wastewater concentration

Wastewater concentration is a very important factor to be considered for the design of MFC. Concentration of organic and inorganic composition in wastewater can affect the process performance of the MFC whereby the power production is higher in shorter period when fed with higher concentration of substrate (Kim et al., 2007). Concentration of composition such the sulfate and ferric (III) can affect the power production directly due to the nature of compound itself as an electrolyte to carry more electrons to anode (Kubota et al., 2010). MFC which is fed with POME with higher COD content could obtain much more power density due to more availability of electrons. However, most of the substrates will be converted into fermentation product by fermentative bacteria and it is difficult to be metabolized by the microorganisms, which lead to lower COD removal efficiency in RAW POME as shown in Figure 2.5.

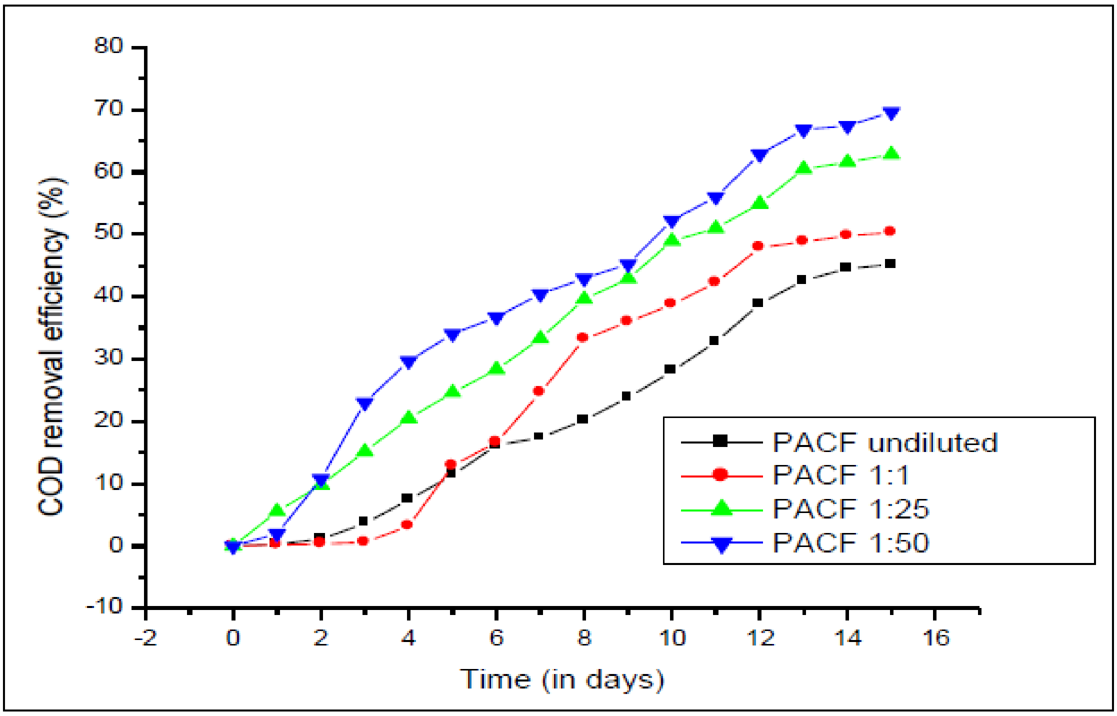

Figure 2.5: COD removal efficiency of PACF MFC at different dilutions of raw POME with time (Baranitharan, Maksudur and Prasad, 2013).

VI. Type of bacteria

There are many types of bacterial communities that have the ability to oxidize organic matters or ability to transfer electrons to anode. This kind of bacterial which can oxidize organic compounds and transfer electrons to anode is very much needed in MFCs. Bacteria such as the iron-reducing Shewanella and Geobacter bacteria, Klebsiella pneumonia, Rhodopseudomonas palustris, and Dessulfobulbus propionicus are showing great potential to be used in MFCs. Those iron reducing bacteria had been discovered that they can span their outer membrane for direct electrons transfer to the external metals such as iron and manganese. Then the attachment of those bacteria on electrodes can easily transfer the electrons to the anode while oxygen is being reduced in the cathode compartment (Pandey, Mishra and Agrawal, 2011). A mixed culture bacteria is reported to have higher resistance for process disturbances, substrate consumption and higher power output (Rabaey and Verstraete, 2005).

Table 2.10: Maximum power density using different bacteria culture.

Bacteria Culture	Reactor type	Fuel used	Power density mW/m^2	References
Mix	Single chamber	Glucose	766	Cheng et al., 2006
Mix	Single chamber	Domestic wastewater	464	Cheng et al., 2006
Mix	Upflow	Sucrose	560	Bond and Lovely, 2003
Pure	Single chamber	Glucose	355.5	Bond and Lovely, 2003
Mix	Dual chamber	Acetate	480	Cheng et al., 2006
Pure	Double chamber	Glucose	33.4	Bond and Lovely, 2003

2.6 Powdered Activated Carbon (PAC)

Powdered activated carbon has strong adsorption ability. Many studies had been done regarding the impact of PAC addition and it has shown positive result especially in biological treatment system. The addition of PAC is known for its ability to enhance the biological treatment efficiency, refractory organic compounds and heavy metal removal rate and enhance the nitrification by improving the activity of nitrifiers in anaerobic treatment (Aghamohammadi et al., 2007). PAC could transform into 'biological activated carbon' (BAC) when added into activated sludge and improve the pollutant removal due to its simultaneous processes of adsorption and biodegradation (Liu et al., 2005; Cecen et al., 2003). The MFC performance improved greatly as the PAC particle increases the area bacteria attached to it. When the amount of attached bacteria is increasing, the electrons transfer rate increase too and thus increase the power output.

There is a reduction of membrane fouling when PAC is added into MFC which equipped with PEM. Few researches have proven that the addition of PAC to sludge can contribute to membrane fouling reduction. The PAC particles able to adsorp the foulants and form a bigger sludge floc. It is reported that PAC has scouring effect that can remove the deposited foulants on the membrane surface

(Park et al., 200). However, frequent PAC replenishment is necessary in order to have better fouling control and the amount of PAC replenish is depending on the SRT used (Torretta et al., 2013).

CHAPTER 3

METHODOLOGY

The research purposes for this study were to investigate the effects of different SRTs and concentration of wastewater feed on the performance of MFCs in terms of electrical power generation, amount of biogas produced and organic removal efficiency with addition of PAC.

3.1 Materials

3.1.1 Microbial Culture

A total of five liter of anaerobic activated sludge was obtained from a local Palm Oil Mill where located in Air Kuning. The 5L culture of specific microorganisms with anaerobic activated sludge has taken up to 3 months to achieve stabilize state before being distributed into 9 MFCs. Each MFC is designed to accommodate total volume of 500ml. The culture was fed with POME along with PAC replenishment continuously until the culture obtains stabilization state.

3.1.2 Powdered Activated Carbon (PAC)

One gram per liter of powdered activated carbon (PAC) was added into each of the MFC. The PAC used throughout the project is extra pure charcoal powdered activated carbon obtained from GENE Chem. The specification of the PAC was shown in following table 3.1.

Table 3.1: Specification of PAC used in the study.

Composition	Value
pH	4.5 – 7.5
Soluble matter in ethanol	0.2%
Soluble matter in hydrochloric acid	0.2%
Residue on ignition (as SO_4)	3.0%
Chloride (Cl)	0.10%
Sulfur compounds (as SO_4)	0.15%
Iron (Fe)	0.10%
Zinc (Zn)	0.10%
Heavy metals (as Pb)	0.01%

3.2 Experimental Setup and Operation

Nine 0.5L MFCs as per Table 3.2 were set up. All MFCs were added with 1g/L of PAC except A-30 (Without PAC). A-series of MFCs (A-30, A-50, A-70 and A-∞) were fed with high concentration of POME (34,127mg/L COD) while B-series MFCs (B-30, B-50, B-70 and B-∞) were fed with low concentration POME (23,769mg/L COD). All the MFCs were cultivated at ambient temperature and their pH is maintained at 7-8.

Table 3.2: Information on the MFCs involved in the study.

<table>
<tr><th>Name of MFC</th><th>Working volume (L)</th><th>Type of MLSS</th><th>SRT (days)</th><th>Feed concentration (mg/L)</th></tr>
<tr><td>A-30 (without PAC)</td><td rowspan="9">0.5</td><td>Anaerobic activated sludge</td><td>30</td><td rowspan="5">34,127</td></tr>
<tr><td>A-30</td><td rowspan="8">Anaerobic activated sludge + PAC</td><td>30</td></tr>
<tr><td>A-50</td><td>50</td></tr>
<tr><td>A-70</td><td>70</td></tr>
<tr><td>A-∞</td><td>∞</td></tr>
<tr><td>B-30</td><td>30</td><td rowspan="4">23,769</td></tr>
<tr><td>B-50</td><td>50</td></tr>
<tr><td>B-70</td><td>70</td></tr>
<tr><td>B-∞</td><td>∞</td></tr>
</table>

3.2.1 Air Cathode Preparation

Carbon cloth was used as the anode and cathode materials. The carbon cloth used for submerged anode is 0% wet proofed while for the cathode layer is 30% wet proofed. A mixture of 0.7g fine carbon powder (USP Grade), 9.1ml of deionized water, 21.5ml of Triton X-100 surfactant was mixed together for 1 hour. Then, one gram of Polytetrafluoroethylene (PTFE) was added into the mixed solution and continued the mixing for another 30 minutes. Later, the solution was placed in the ultrasonicator bath for 15 minutes. This sonication process was followed by mixing process for another 5 minutes. The 15 minutes sonication process and 5 minutes mixing process were repeated one more time. Next, 2.75g of fine carbon powdered was added into the mixed solution and mixed for another 1 hour. The mixed solution would become slurry. The slurry (20% wt solid) is then prepared to be applied on the water facing side of cathode carbon cloth using silkscreen technique. The cathode water facing side coated with this slurry would develop into carbon based layer (CBL). The coated cathode carbon cloth was then heated between two hot plates for 30 minutes at 280 ℃ using furnace. The cathode carbon cloth was continued being heated at 343 ℃ for another 2.5 hours before it is done. Besides that, air facing side of cathode was coated with PTFE solution. Subsequently, the cathode was air dried for 10 minutes before being heated at 350 ℃ for 15 minutes. The method of preparing air facing side cathode was repeated another three times before it is ready to be used in MFC. The completed air facing cathode layer was as shown in Figure 3.1.

Figure 3.1: The air facing cathode layer.

3.2.2 MFC Design

The 9 MFCs were designed and constructed to be a single chamber and air cathode microbial fuel cell. The material used to build the MFCs were PVC pipes as shown in Figure 3.2. Unlike the dual chamber MFC, air cathode MFC by means that one side of the cathode layer was exposed to the open air and the other side was facing with the wastewater. The MFCs used in this study were operated in batch mode in order to determine the electrical and biogas production whilst using POME as the substrate for the anaerobic activated sludge.

Figure 3.2: The experimental design setup.

The overall design of the MFC was as shown in Figure 3.3. Four valves were constructed on top of each MFC whereby one valve is design for desludge purpose, the other is for discharge supernatant purpose, one for biogas collection purpose while the last one is connected to a nitrogen filled gas bag. Both anode and cathode layer were connected with a copper wire as electron conductor before being connected to resistor and multimeter to complete a circuit.

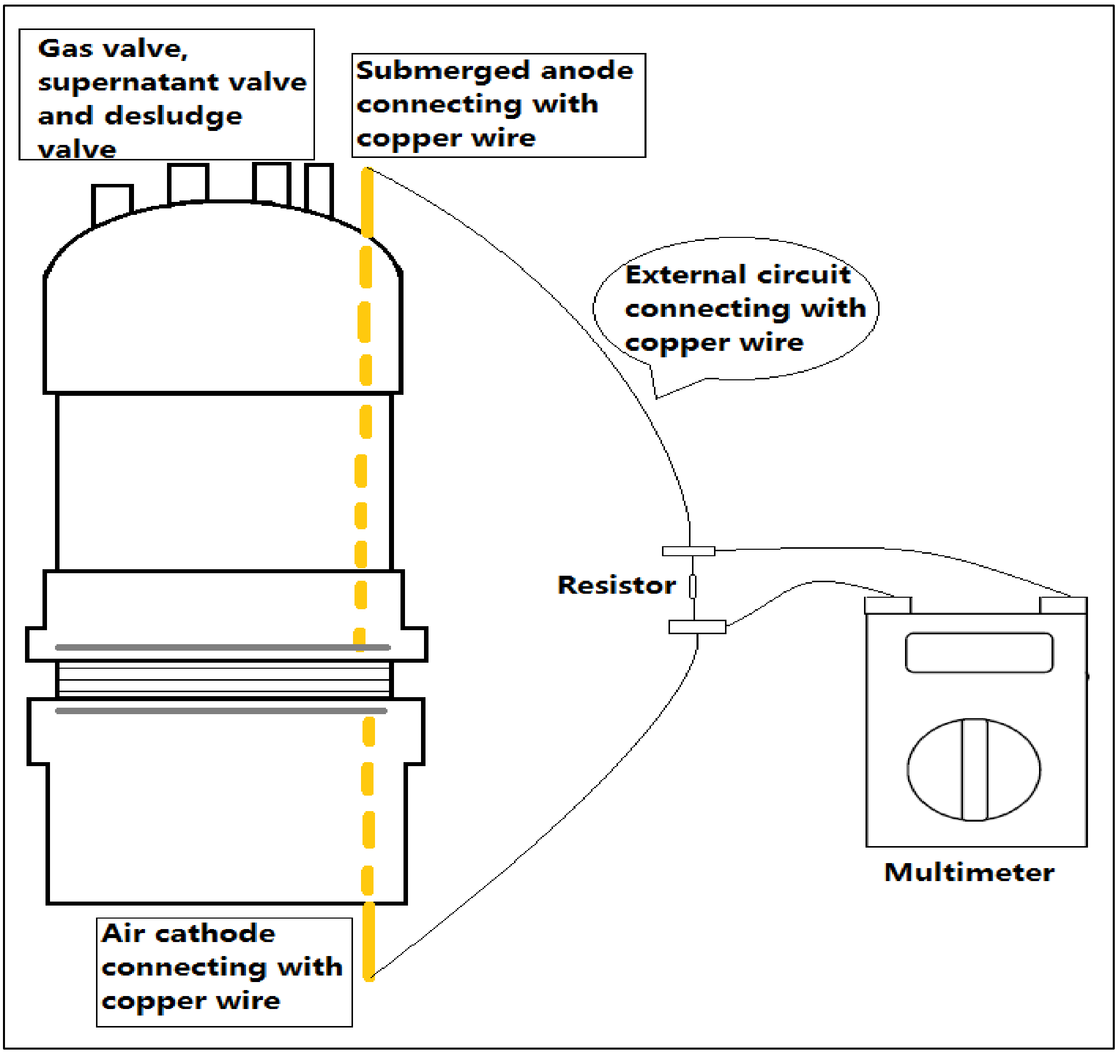

Figure 3.3: The schematic diagram of MFC.

3.2.3 Investigation of the Effects of Different Operating Sludge Retention Times (SRTs) and Concentrations of Wastewater Feed to the MFCs

MFCs were fed daily with POME wastewater. Two different types of concentration of POME were prepared and fed to the MFCs as per Table 3.3. Relatively higher concentration POME contained of 34,127mg/L COD whereas relatively lower concentration POME contained of 23,769mg/L COD. There are nine MFCs operated at different SRTs were setup. The SRTs used in this study were 30, 50, 70 and ∞

(pseudo infinite) days. Each SRT was used by 2 MFCs except for SRT 30 day which consists of three MFCs using it. The total working volume of each MFC is 0.5L. In addition, the hydraulic retention time (HRT) was fixed at 4 days for this study. Therefore, the total amount of discharge including supernatant and sludge is 125ml for each MFC. Each respective SRT would have different amount of desludge where SRT 30 desludges 17ml, SRT 50 desludges 10ml and SRT 70 desludge 7ml. SRT pseudo infinite would not carried out desludge process, it only discharges supernatant daily. Meanwhile, PAC needed to be replenished daily during feed in. The amount of PAC replenished is based onto the SRTs used. PAC replenishment for SRT 30 is 0.333g, SRT 50 is 0.02g and SRT 70 is 0.014g. SRT pseudo infinite would have no PAC replenishment after initially added with 1g of PAC during cultivation stage.

Table 3.3: Amount of daily desludge, feed and PAC replenishment.

Name of MFC	SRT (days)	Feed concentration (mg/L)	Desludge (ml)	Supernatant discharge (ml)	Feed in POME + water (ml)	PAC replenishment (g)
A-30 (without PAC)	30	34,127	17	108	100 + 25	NA
A-30	30		17	108		0.333
A-50	50		10	115		0.02
A-70	70		7	118		0.014
A-∞	∞		NA	125		NA
B-30	30	23,769	17	108		0.333
B-50	50		10	115		0.02
B-70	70		7	118		0.014
B-∞	∞		NA	125		NA

3.3 Analytical Methods

3.3.1 Total Suspended Solid (TSS) and Volatile Suspended Solid (VSS)

According to the 2540D Total Suspended Solids and 2540E Volatile Solids stated in Standard Methods, 21st Edition, the TSS and VSS of anaerobic activated sludge were determined. A filter paper was placed in a gooch crucible heated at 550 ℃ for 15 minutes in muffle furnace. Then, the crucible was weighed using an analytical balance after store and cool down in desiccators. 1ml of sample was applied on the filter paper. Suction flask was used to remove all traces of water. Next, the samples were dried in an oven at 105 ℃ for 2 hours. The samples were then put cooled in desiccators before weighing. Subsequently, the samples were further ignited at 550 ℃ for 15 minutes in muffle furnace. The samples were again put cooled in desiccators before weighing. The TSS and VSS were determined using following formula:

$$TSS = \frac{(B-A)\times 1000}{sample\ volume, ml} \tag{3.1}$$

$$VSS = \frac{(B-C)\times 1000}{sample\ volume, ml} \tag{3.2}$$

Where

TSS = total suspended solids, g/L
VSS = volatile suspended solids, g/L
A = weight of crucible + filter paper, g
B = weight of crucible + filter paper + sample after heated in oven, g
C = weight of crucible + filter paper + sample after ignited in furnace, g

3.3.2 Chemical Oxygen Demand (COD)

The COD of initial influent (POME) and final effluent (supernatant) was determined using the 5220 D Closed Reflux Colorimetric Standard Method as stated in Standard Method, 21st Edition. The supernatant collected from MFCs was centrifuged at 3000rpm for 45 minutes using Beckman Coulter Allegra 6 Centrifuge to separate the supernatant and suspended solids present in the sample. The COD reactor (HACH-DRB 200) was preheated to 150 ℃ before using it. Then, 2ml of samples was added into the vial (HACH HR+) ranging from 0-15000 mg/L and inverted gently for several times to mix. The vials were later put in the preheated COD reactor to heat for 2 hours at 150 ℃. After 2 hours heated, the samples were put cool before using the UV/VIS spectrophotometer (HACH DR 6000) to analyze the COD value of each sample. The COD removal rate of MFCs was calculated using the following formula:

$$\boldsymbol{COD\ removal\ rate} = \frac{\boldsymbol{Initial\ COD - Final\ COD}}{\boldsymbol{Initial\ COD}} \times \mathbf{100}\% \quad (3.3)$$

3.3.3 Electrical Power Production

A 100Ω external resistor was connected to the anode and cathode. The electricity of MFCs was measured daily using a multimeter. The voltage of each MFC was measured in millivolt (mV). By applying the Ohm's law, current (I) could be calculated.

$$\boldsymbol{v} = \boldsymbol{IR} \quad (3.4)$$

Where

$\boldsymbol{v}$ = voltage, V
I = current, A
R = external resistance, Ω

The power production of MFCs was calculated in terms of volumetric power density. The equation of volumetric used as follow:

$$\boldsymbol{P} = \frac{\boldsymbol{v}^2}{\boldsymbol{RV}} \quad (3.5)$$

Where

P = volumetric power density, W/m^3
$\boldsymbol{v}$ = voltage, V
R = external resistance, Ω
V = volume of anode chamber, m^3

The polarization curve was able to be plotted by connecting to different ohmic resistors (1Ω - 1000Ω) and voltage was measured at different external resistance. The gradient of linear curve for the graph of voltage against current is the internal resistance of MFCs. The equation of internal resistance used is as follow:

$$R_{int} = \frac{\Delta v}{\Delta I} \quad (3.6)$$

Where

R_{int} = internal resistance, Ω

Δv = the difference in voltage, V

ΔI = the difference in current, A

3.3.4 Biogas Production

The biogas collection was carried out by using water displacement method as shown in Figure 3.4. The amount of biogas produced was taken by measuring the height difference of water displaced using a 250ml measuring cylinder. The volume of biogas produced is the deduction of final reading to initial reading.

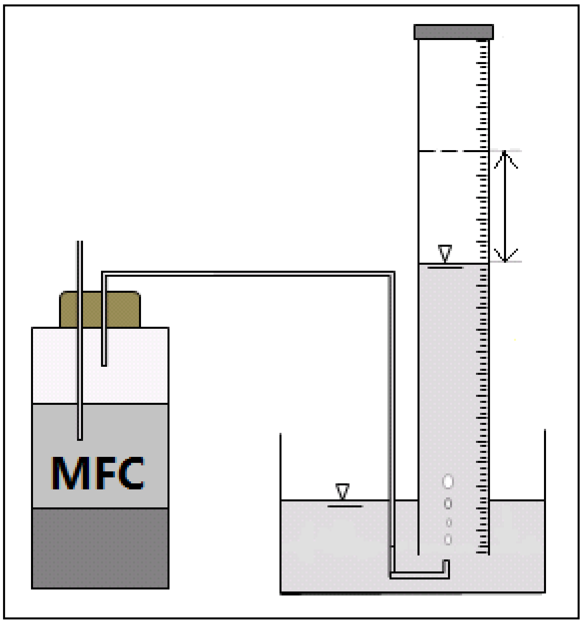

Figure 3.4: Schematic diagram of biogas collection using water displacement method.

3.3.5 pH Measurement

The pH of the anaerobic activated sludge was necessary to be maintained at pH range 7 -8 to create a favorable environment for bacteria to grow. The pH of each MFC was measured once a week to monitor the pH condition within MFCs. The pH meter (Hanna HI 2550) was used to determine the pH of MFC. Calibration was done each time before measured the pH of MFCs to avoid unwanted error. The pH electrode was rinsed with distilled water each time before testing the pH to avoid any unwanted error.

CHAPTER 4

RESULTS AND DISCUSSIONS

This chapter discusses about the performances of powdered activated carbon (PAC) hybrid microbial fuel cells (MFCs) at different sludge retention times (SRTs) and feed concentrations. The overall performances were determined in terms of organic pollutant removal efficiency, power generation and biogas production. In this study, there are total nine MFCs constructed at different operating parameters. The nine MFCs i) with and without PAC addition, ii) with different SRTs, and iii) with different feed concentrations had been cultivating for two months, their performance were assessed mainly in terms of organic removal rate, biogas and electricity production rates.

The organic pollutant removal efficiency, power and biogas production of different MFCs were found to be affected by SRT, substrate concentration and the presence of additive. The pH of each MFC was maintained in the range of 7.12 to 7.37 throughout the study. This indicated that the organic acids produced were effectively metabolized and created a favorable environment for the methanogenic and electrogenic bacteria to grow (Gil et al, 2003). Hydraulic retention time (HRT) was fixed at 4 days whereas the F/M ratio was set at the range of 0.5-1.0 to prevent any influence on the performance. The operating condition for each MFC is shown in Table 4.1.

Table 4.1: Operating conditions of MFCs.

Parameter	A-30 (Without PAC)	A-30	A-50	A-70	A-∞	B-30	B-50	B-70	B-∞
Temperature, °C	Ambient	Ambient	Ambient	Ambient	Ambient	Ambient	Ambient	Ambient	Ambient
PAC dosage, g L^{-1}	0	1	1	1	1	1	1	1	1
HRT, d	4	4	4	4	4	4	4	4	4
SRT, d	30	30	50	70	∞	30	50	70	∞
Feed COD, g L^{-1}	34.1 ± 1.0					23.7 ± 1.0			
F/M ratio	0.5 - 1.0	0.5 - 1.0	0.5 - 1.0	0.5 - 1.0	0.5 - 1.0	0.5 - 1.0	0.5 - 1.0	0.5 - 1.0	0.5 - 1.0
pH	7.12 ± 0.18	7.22 ± 0.20	7.25 ± 0.15	7.35 ± 0.23	7.37 ± 0.23	7.18 ± 0.12	7.31 ± 0.15	7.30 ± 0.20	7.26 ± 0.18

4.1 The Effects of with and without PAC Addition on the Treatment performance of MFCs

Two MFCs were built to find out the effects of with and without PAC addition on the treatment performance of MFCs. The two MFCs were namely A-30 (without PAC) and A-30 with addition of 1g/L PAC. MFC added with PAC was required to replenish each time after daily desludging process in order to maintain the PAC concentration and freshness. The performance of MFCs added with and without PAC was investigated and the results were shown in Table 4.2.

Table 4.2: Treatment performance of MFCs added with and without PAC.

Parameter	A-30 (Without PAC)	A-30
Temperature, °C	Ambient	Ambient
PAC dosage, g L^{-1}	0	1
HRT, d	4	4
SRT, d	30	30
Feed COD, g L^{-1}	34.1 ± 1.0	
Supernatant COD, g L^{-1}	19.0 ± 3.0	14.6 ± 1.5
COD removal efficiency, %	44.27 ± 8.72	57.31 ± 4.54
MLSS, g L^{-1}	13.17 ± 1.10	16.70 ± 3.10
MLVSS, g L^{-1}	11.70 ± 1.36	14.23 ± 3.27
F/M ratio	0.5 - 1.0	0.5 - 1.0
pH	7.12 ± 0.18	7.22 ± 0.20
Average biogas yield, mL hr^{-1}	30.07 ± 3.19	37.04 ± 3.88
Average voltage, mV	6.98	35.62
Average power density, mW m^{-3}	2.53	72.51

4.1.1 The Effects of PAC addition on Organic pollutant removal efficiency

The organic pollutant removal efficiencies of MFCs with and without PAC addition were as per Table 4.2. The organic pollutant removal rate was measured in terms of COD removal rate. With the addition of PAC, the COD removal rate was relatively higher than MFC without PAC. The MFC with PAC could achieve 57.31% of organic pollutant removal rate, which is 12.86% more than MFC without PAC. The addition of PAC into the MFC also showed significant difference in the biomass growth rate through the comparison of A-30 (Without PAC) and A-30 in terms of MLSS and MLVSS. It was found that the biomass in MFC added with PAC able to build up more effectively as compared to MFC without PAC.

It is proven that PAC could enhance the MFCs performance. This was because PAC is famous for its strong adsorption characteristics and able to produce better effluent quality through adsorption of the fine pollutants. The addition of PAC with activated sludge of MFCs would develop into biological activated carbon (BAC), thus promote the attachment of microorganisms and biofilm formation on the anode surface (Ng et al, 2010; Cecen et al, 2011; Ng et al, 2013). The BAC would encourage the simultaneous process of adsorption and biodegradation of organic pollutants, eventually improve the performance of MFCs. However, PAC has to be replenished after being desludged in order to maintain the PAC dosage in each MFC except for MFC without PAC.

4.1.2 The Effects of PAC addition on Power generation

The power production of MFCs with and without PAC addition was measured daily for 600 hours. The results were as per Figure 4.1. The MFC added with 1g/L of PAC showed better performance in terms of power density as compared to MFC without PAC addition. In Figure 4.1, the highest power density obtained by the MFC added with PAC was 345.85mW/m ^{3} whereas only 19.85mW/m ^{3} of power density obtained by MFC without the PAC addition. As per Table 4.2, the average voltage and power density of MFC with PAC showed huge difference compared with MFC without PAC addition. From Figure 4.1, the sudden drop in power density at 528 hour can be deduced that the biofilm which formed on the electrode surface had detached at that moment and it required time to build up new biofilm. Thus the gradually increasing in power density after the sudden drop verified that a new biofilm is formed to replace the detached layer (Ieropoulos, Winfield and Greenman, 2010).

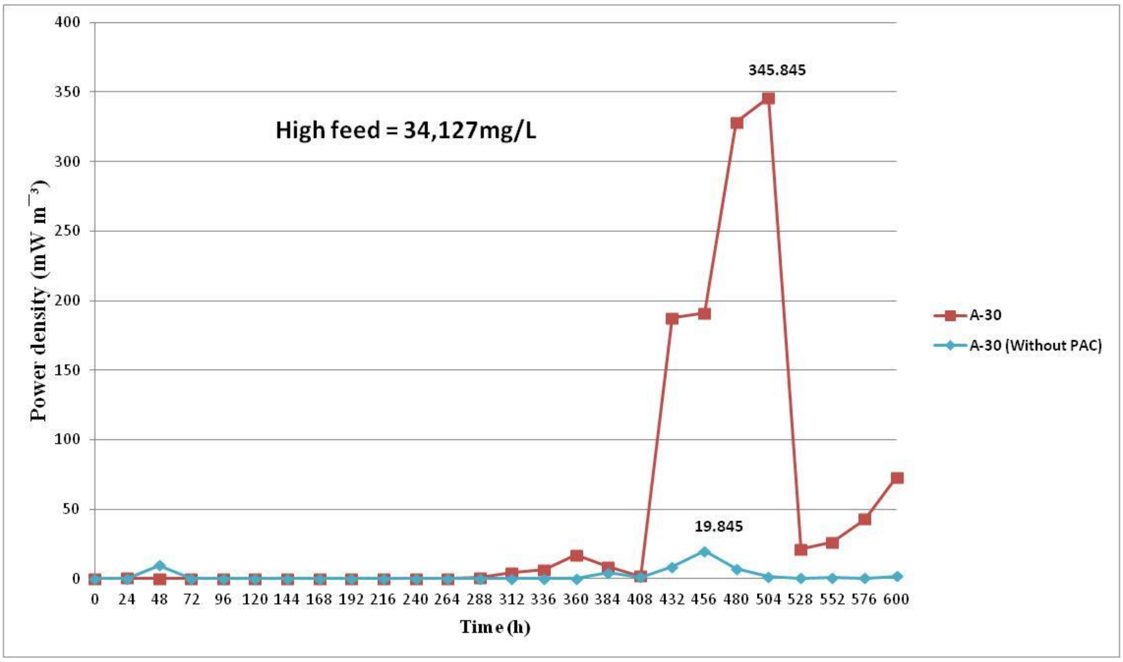

Figure 4.1: Power density over 600 hours for MFCs added with and without PAC.

4.1.3 The Effects of PAC addition on Biogas production

The MFC added with 1g/L of PAC showed better performance in terms of biogas productions as compared to MFC without PAC addition. From Figure 4.2, the total volume of biogas collected after about 26 days from MFC with PAC could reach 940ml, which is 22.4% higher than MFC without PAC addition. This indicated that PAC could enhance the biological treatment ability by degrading the complex organic substances in POME into methane gas.

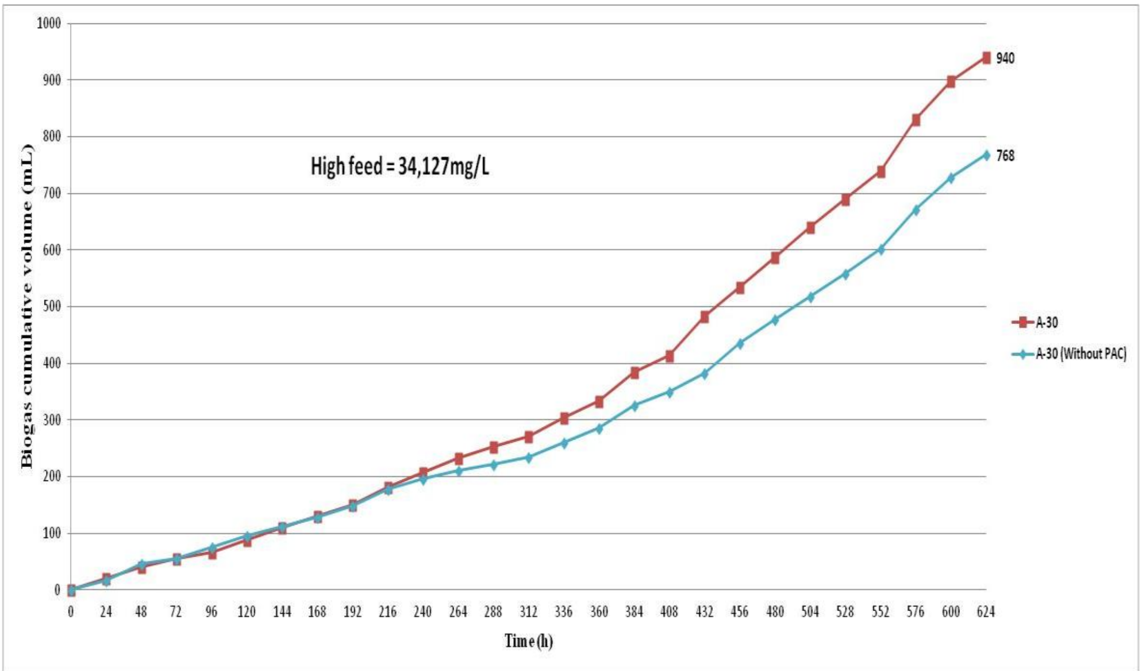

Figure 4.2: Biogas cumulative volumes over 624 hours for MFCs added with and without PAC.

4.2 The Treatment Performance of MFCs controlled at different SRTs

Four MFCs were built to find out the effects of different SRTs on the treatment performance of MFCs. The four MFCs added with 1g/L of PAC were namely A-30, A-50, A-70 and A-∞. MFCs added with PAC (A-30, A-50 and A-70) were required to replenish according to the amount of desludge at different SRTs while MFC with pseudo infinite could omitted the PAC replenishment process as it doesn't need to desuldge daily. The performance of MFCs controlled at different SRTs was investigated and the results were shown in following Table 4.3.

Table 4.3: Treatment performance of MFCs with different SRTs.

Parameter	A-30	A-50	A-70	A-∞
Feed COD, g L^{-1}	34.1 ± 1.0			
Supernatant COD, g L^{-1}	14.6 ± 1.5	13.6 ± 1.4	12.1 ± 1.1	14.8 ± 1.8
COD removal efficiency, %	57.31 ± 4.54	60.13 ± 4.07	64.40 ± 3.24	56.75 ± 5.18
MLSS, g L^{-1}	16.70 ± 3.10	17.66 ± 2.26	18.63 ± 1.22	15.77 ± 1.33
MLVSS, g L^{-1}	14.23 ± 3.27	15.05 ± 2.30	15.87 ± 0.73	13.27 ± 1.56
pH	7.22 ± 0.20	7.25 ± 0.15	7.35 ± 0.23	7.37 ± 0.23
Average biogas yield, mL hr^{-1}	37.04 ± 3.88	39.37 ± 3.98	41.48 ± 4.31	34.52 ± 3.30
Average voltage, mV	35.62	66.2	105.96	6.26
Average power density, mW m^{-3}	72.51	146.91	279.73	1.32

4.2.1 The Organic pollutant removal rate of MFCs controlled at different SRTs

Based on Table 4.3, it shows that the total COD removal efficiencies of MFCs were increased along with prolonged SRT. The highest COD removal efficiency up to 64.4% was obtained by MFC (A-70) with the SRT of 70 days and 34.1g/L of POME feed concentration, followed by A-50 with 60.13%, A-30 with 57.31%. This proved that the prolonged of SRT could promote microbial growth especially the anaerobic activated sludge with PAC and thus enhance the biodegradation of organic pollutants. MFC with pseudo infinite performed the least with only 56.75%. This may be because there was no daily desludge process and PAC replenishment which led to aged microbes lost its degradation and adsorption ability. The growth rate of biomass could be also proven by the concentrations of MLSS and MLVSS of MFCs. The mix liquor volatile suspended solids indicated the excess built up of biomass in MFCs with prolonging the SRTs. A-70 had the highest MLVSS (15.87g/L) as compared to others.

4.2.2 The Power generation of MFCs controlled at different SRTs

The power generation over 600 hours for the MFCs were measured and calculated as per Figure 4.3. Based on Figure 4.3, the highest power density was achieved by A-70 at 666.125mW/m³, followed by A-50 and A-30at 407.2658mW/m³ and 345.845mW/m³ repectively. Table 4.3 shows the same trend. The average power density obtained by A-70 is the highest at 279.73mW/m³. It was found that higher power density could be achieved with longer SRT. Prolonged SRT provided sufficient retention time for the enrichment and forming process of anaerobic electrogenic bacteria on the anode surface. On the other hand, shorter SRT MFCs such as A-30 and A-50 showed lower average power density output due to higher daily desludging process. SRT 30 days and SRT 50 days required daily sludge removal of 25mL and 15mL respectively whereas SRT 70 days only desludged for about 10mL daily. The shorter retention time limited the bacteria growth and biodegradation has resulted in lower power density production. MFCs operated in SRT of pseudo infinite days showed the lowest average power density production among all MFCs. Pseudo infinite SRT indicated that no daily sludge removal but only daily removal of supernatant. This may caused aged anaerobic activated sludge and aged BAC to lose their ability to biodegrade and adsorption of pollutants, eventually led to biofilm fouling of electrodes. The biofilm fouling layer would increase the internal resistance and reduced the electron transfer, which resulted in low power production (Li et al, 2013).

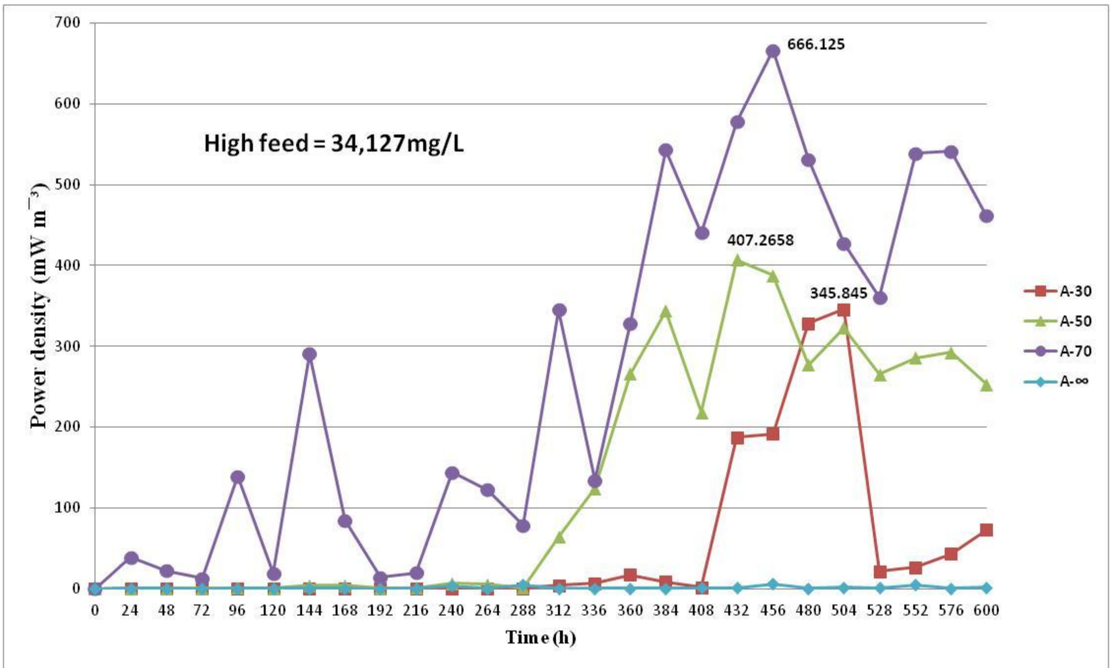

Figure 4.3: Power density over 600 hours for four high concentration feed MFCs with different SRTs.

4.2.3 The Biogas production of MFCs controlled at different SRTs

SRT is also a crucial parameter in determining the biogas production as the microbial growth is closely related to the biogas production. With the pH and temperature is maintained at a favorable condition, the methanogenic bacteria growth could be enhanced by prolonging the sludge retention time. Therefore, the biogas production was increased as the SRT is prolonged as illustrated in Figure 4.4. MFCs with the SRT of pseudo infinite showed the lowest biogas production. It is believed that the less impressive performance of the MFCs cultivated at pseudo infinite is due to the number of aged methanogenic bacteria in them is increasing faster than the young methanogenic bacteria growth due to absence of daily desludging process. As a result, BAC would slowly losing its adsorption capacity and its mesopores filled with products of dead microbial cells, which then led to reduction in microbial activity (Sirotkin et al., 200; Ng et al, 2010; Ng et al, 2013) and resulted lower biogas production .

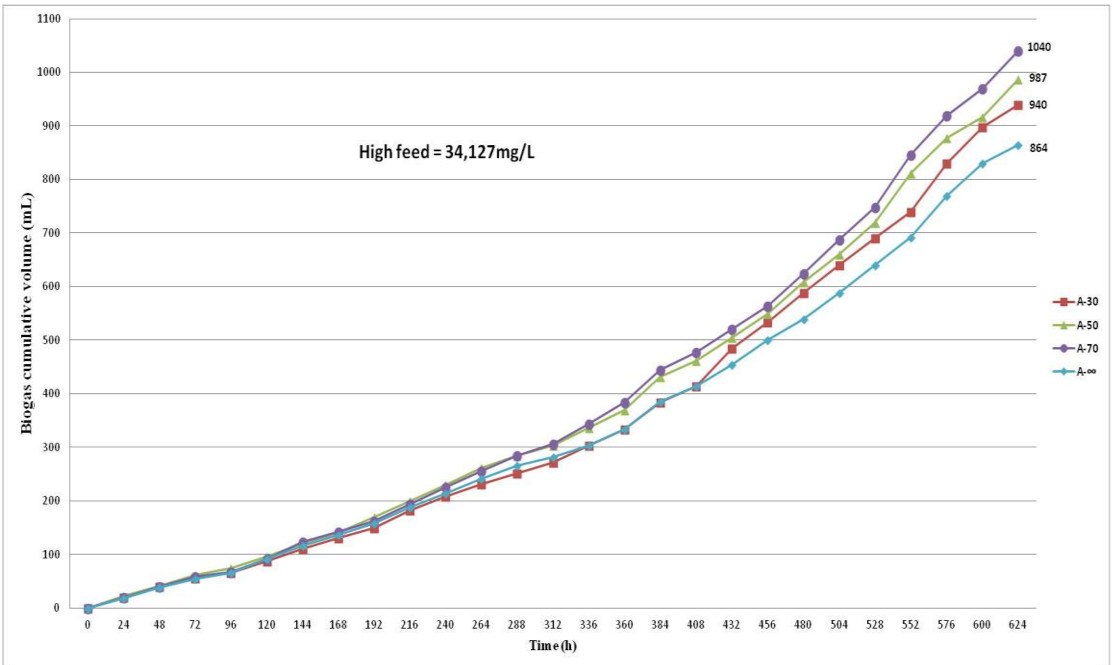

Figure 4.4: Biogas cumulative volumes over 624 hours for four high concentration feed MFCs with different SRTs.

4.3 The Effects of Feed Concentration on the performance of MFCs

Another four MFCs were built to find out the effects of different feed concentration on the treatment performance of MFCs. These four MFCs added with 1g/L of PAC were namely B-30, B-50, B-70 and B-∞. Four PAC hybrid MFCs (A-30, A-50, A-70 and A-∞) were fed with relatively higher feed concentration (34,127mg/L) while another four PAC hybrid MFCs (B-30, B-50, B-70 and B-∞) were fed with relatively lower feed concentration (23,769mg/L). The performance of MFCs fed with different feed concentrations was investigated and the results were shown in following Table 4.4.

Table 4.4: Treatment performance of MFCs fed with different feed concentrations at different SRTs.

Parameter	A-30	A-50	A-70	A-∞	B-30	B-50	B-70	B-∞
Feed COD, g L^{-1}	34.1 ± 1.0				23.7 ± 1.0			
Supernatant COD, g L^{-1}	14.6 ± 1.5	13.6 ± 1.4	12.1 ± 1.1	14.8 ± 1.8	13.0 ± 1.7	12.5 ± 1.6	10.8 ± 1.1	15.8 ± 1.7
COD removal efficiency, %	57.31 ± 4.54	60.13 ± 4.07	64.40 ± 3.24	56.75 ± 5.18	45.49 ± 7.45	47.42 ± 6.54	54.74 ± 4.80	33.63 ± 7.28
MLSS, g L^{-1}	16.70 ± 3.10	17.66 ± 2.26	18.63 ± 1.22	15.77 ± 1.33	11.03 ± 2.98	13.77 ± 1.83	15.77 ± 2.81	14.07 ± 2.13
MLVSS, g L^{-1}	14.23 ± 3.27	15.05 ± 2.30	15.87 ± 0.73	13.27 ± 1.56	9.50 ± 3.00	11.90 ± 2.05	13.43 ± 2.40	11.87 ± 2.13
pH	7.22 ± 0.20	7.25 ± 0.15	7.35 ± 0.23	7.37 ± 0.23	7.18 ± 0.12	7.31 ± 0.15	7.30 ± 0.20	7.26 ± 0.18
Average biogas yield, mL hr^{-1}	37.04 ± 3.88	39.37 ± 3.98	41.48 ± 4.31	34.52 ± 3.30	26.26 ± 2.23	27.41 ± 2.32	27.59 ± 2.30	22.44 ± 1.98
Average voltage, mV	35.62	66.2	105.96	6.26	130.31	148.93	161.61	1.16
Average power density, mW m^{-3}	72.51	146.91	279.73	1.32	366.16	487.69	558.58	0.05

4.3.1 The Effects of Feed Concentration on Organic pollutant removal rate

The microbial growth was also being affected by the POME feed concentration. The reduction in feed concentration from 34.1g/L (high concentration) to 23.7g/L (low concentration) has led to the reduction of MLSS and MLVSS. The COD removal efficiency showed the same trend as the reduction of MLSS and MLVSS. The highest COD removal rate could achieve by MFC fed with relatively lower POME concentration (B-70) is about 54.74%, which is lower than any of the MFCs fed with relatively higher POME concentration. This may be due to deficiency of organic substrate as carbon source for microbes. Hence, the removal efficiency of the MFCs fed with lower feed concentration is lower as compared to the MFCs fed with higher feed concentration.

4.3.2 The Effects of Feed Concentration on Power generation

The feed concentration could also affect the power density production. MFCs fed with high concentration of POME were only able to produce highest power density of 666.125mW/m ^{3} as shown in Figure 4.3 while MFCs fed with low feed concentration could produce highest power density of 691.92mW/m ^{3} as per Figure 4.5. However, the sudden increase of the high power density as per Figure 4.5 was due to sudden increase in quantity of POME feed.

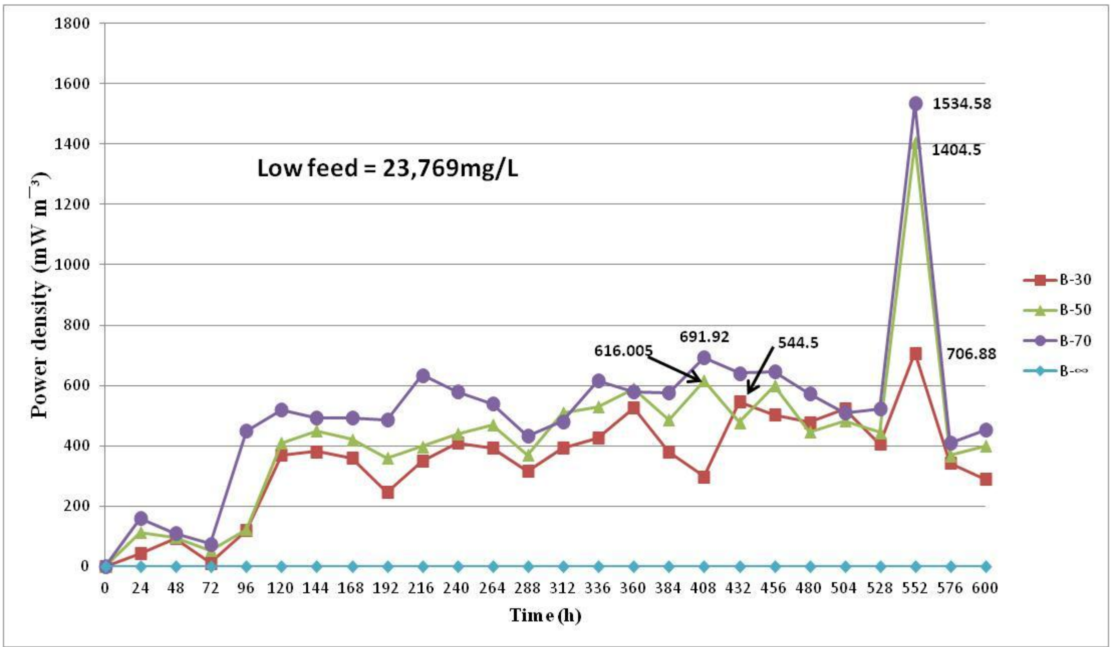

Figure 4.5: Power density over 600 hours for four low concentration feed MFCs with different SRTs.

The low in power production for high substrate concentration as per Figure 4.6 could be because most of the organics in the high concentration substrate were converted into fermentation products subsequently caused most of the electrons unavailable for power production, therefore the substrates are difficult to metabolize completely could be the reason for low power generation (Baranitharan, Maksudur and Prasad, 2013). Besides, there is another possibility which was mainly due to internal resistance in MFCs. From Figure 4.7 and Figure 4.8, the gradient of the linear curve is the internal resistance, Rint= $\Delta V/\Delta I$ and Figure 4.7 showed that high concentration of feed would have higher internal resistance and hence generate lower power density (Logan et al, 2006). MFCs fed with high substrate concentration also increased the time needed to reach constant open circuit voltage (OCV). For instance A-70 required 456 hours to achieve the peak voltage while B-70 only needed 408 hours. The trends are as shown in Figure 4.6. This is mainly attributed to the substrate inhibition effect. High concentration of substrate is more likely to have this effect where some of the substrates would inhibit the activity of microbes in biodegradation process. Inhibited microorganisms would lose its capability to continuously consume the carbon sources available in the substrate solution and as a result the constant OCV was achieved earlier at lower power output (Ghoreyshi et al, 2011). The power output of the MFCs as per Figure 4.3 is lower than that of the MFCs as per Figure 4.5.

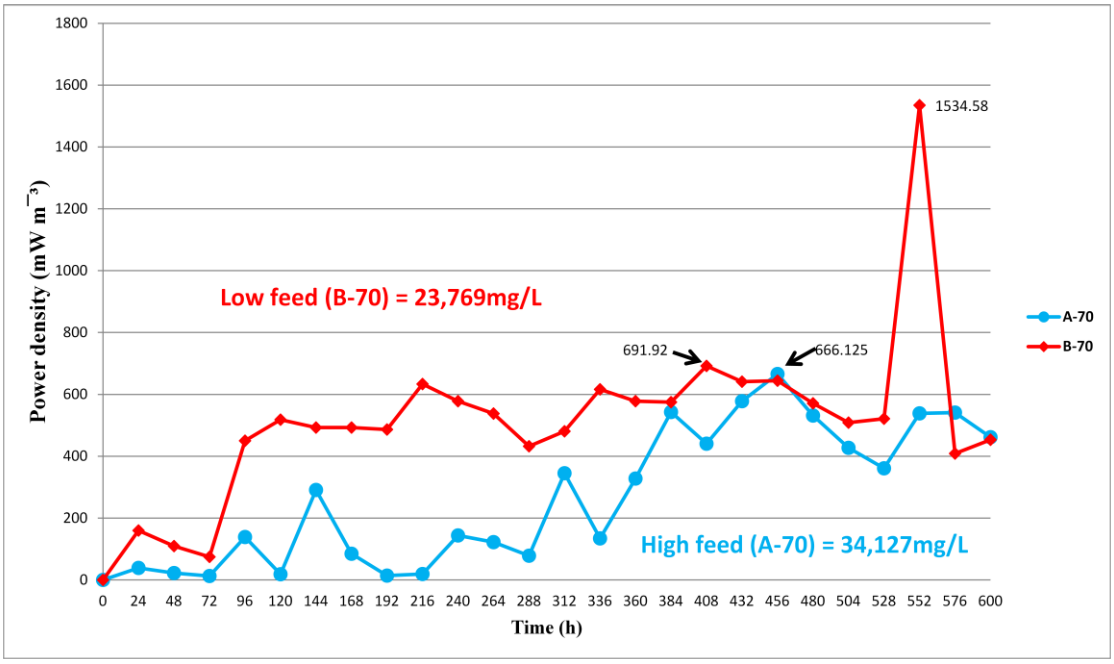

Figure 4.6: Comparison of power density over 600 hours for two different concentration feed MFCs at SRT 70.

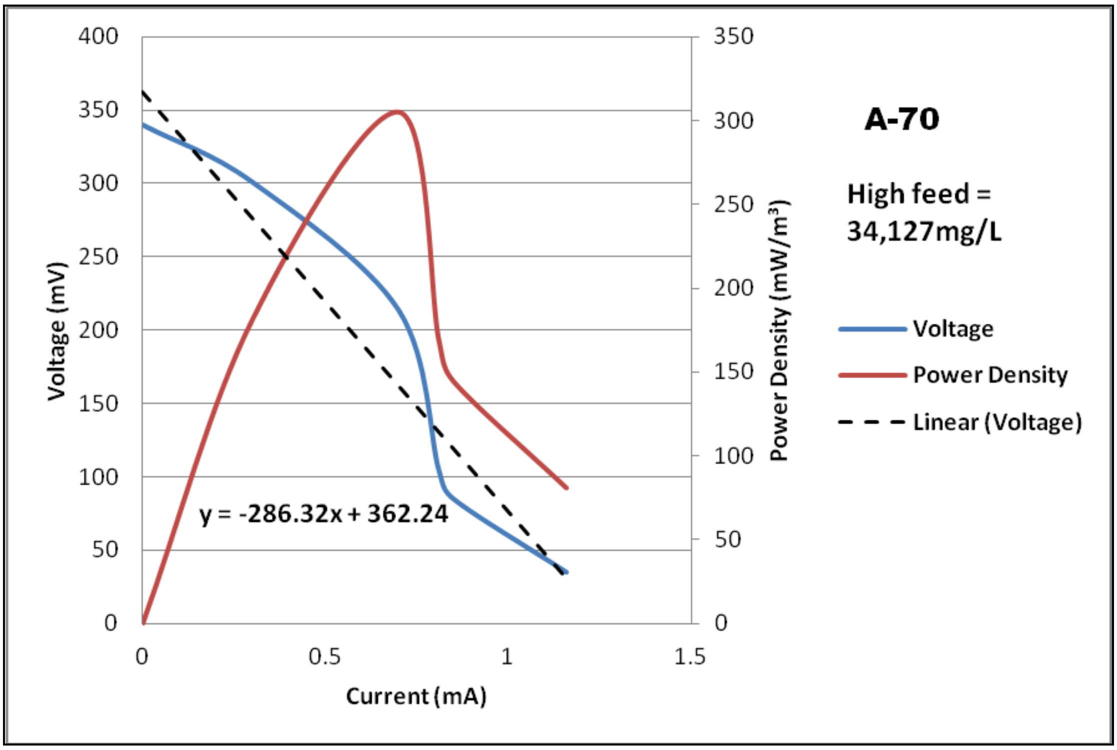

Figure 4.7: Polarization curve for SRT 70 days and high concentration feed MFC.

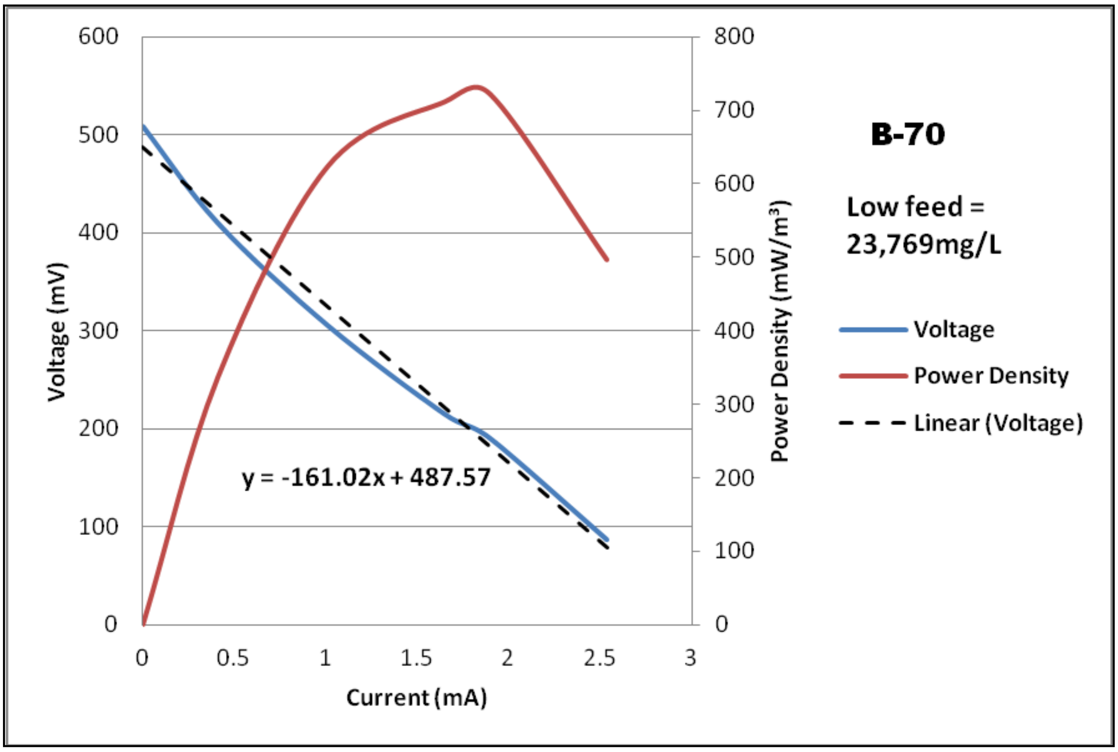

Figure 4.8: Polarization curve for SRT 70 days and low concentration feed MFC.

4.3.3 The Effects of Feed Concentration on Biogas production

High concentration of feed provides larger volume of organic matter, which is favorable for biogas production (Miyamoto et al, 2015). By comparison between Figure 4.4 and Figure 4.9, MFCs fed with high concentration of POME could obtain relatively higher biogas production. From Figure 4.10, the total volume of biogas which could be collected by A-70 is 1040mL over 624 hours whereas the MFCs fed with low concentration POME could only obtain total volume of biogas at 703mL by B-70. The biogas production was improved up to 47.94% for the A-70 compared to B-70.

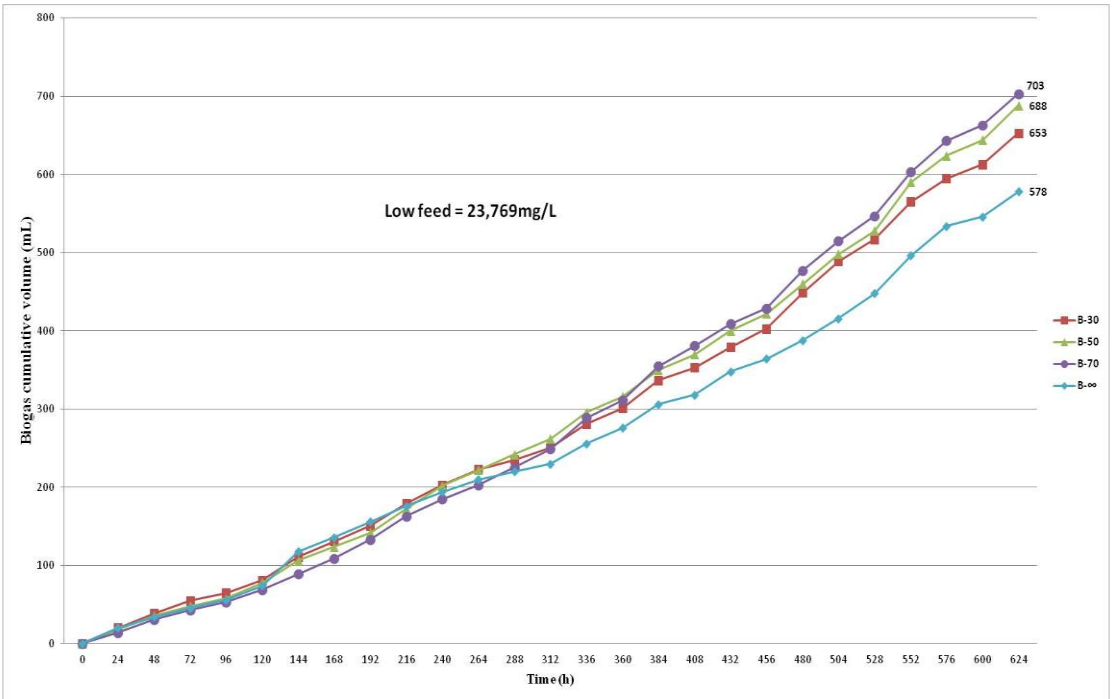

Figure 4.9: Biogas cumulative volumes over 624 hours for four low concentration feed MFCs.

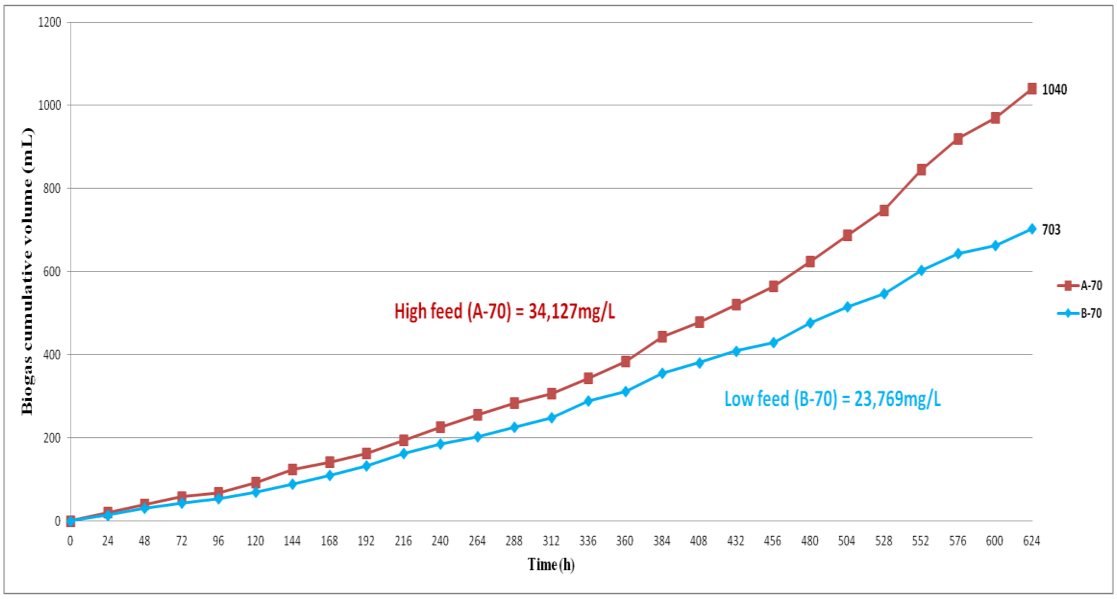

Figure 4.10: Comparison of biogas cumulative volumes over 624 hours for two different concentration feed MFCs at SRT 70.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The treatment performance of MFCs with PAC addition cultivated at SRT 70 days and fed with relatively higher feed concentration was the best MFC among others in terms of biogas production and COD removal efficiency. The addition of PAC, sludge retention time and feed concentration has been found to be the primary factor affecting the treatment performance in terms of biogas production and COD removal. Notable improvement in biogas production and COD removal under longer SRT and high feed concentration could be due to better microbial growth. The treatment performance of MFCs with PAC addition in terms of power density production is best for MFC cultivated at SRT 70 days but fed with relatively lower feed concentration. Power density of the MFC could improve significantly with longer SRT but with relatively low feed concentration. This could be due to the MFC has lower internal resistance and most of the carbon sources available in the relatively low concentration POME solution could be biodegraded more complete. This would help the MFC to produce higher voltage.

5.2 Recommendations

The addition of powdered activated carbon, sludge retention times and feed concentrations could improve the microbial fuel cell performances in terms of organic pollutant removal, electricity and biogas production. However, the results achieved in this study are yet to be the ideal outcomes for MFCs, there are still consisting of numerous ways could be done to bring out the best of MFCs. Some advance recommendations for this research are offered as shown below:

i. It is recommended to cultivate specific electrogenic type bacteria namely Shewanella Oneidensis bacteria in microbial fuel cell to enhance the electricity generation.
ii. The culture of inoculums shall be analyzed under Scanning Electron Microscopy (SEM) to examine the behavior of bacterial growth at electrode.
iii. The effects of MFCs cathode surface area should be investigated. Further study is needed to find out the optimum surface area ratio of cathode to anode.
iv. The materials used to prepare the cathode carbon based layer should be study to find another alternative materials and methods to produce a better cathode electrode of MFC.
v. It is recommended to incorporate a stirrer into a MFC to ensure well mixing. Stirring operation shall be halt for a certain time period to provide time for settlements of suspended solids and supernatant discharge. Stirring speed shall be control at minimal to avoid biofilms wipe out.

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APPENDICES

APPENDIX A: Analytical laboratory instrument

Figure A1: Muffle furnace

Figure A2: Oven

Figure A3: pH meter

Figure A4: UV-Vis Spectrophotometer

Figure A5: Analytical balance

Figure A6: COD reactor

APPENDIX B: Figures

Figure B1: Deposition layer found on the anode surface of MFC.

Figure B2: Deposition layer found on the air cathode surface of MFC.