APPLICATION OF AIR-CATHODE MICROBIAL FUEL CELL TO INDUSTRIAL WASTEWATER

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APPLICATION OF AIR-CATHODE MICROBIAL FUEL CELL TO INDUSTRIAL WASTEWATER

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CHAPTER I

INTRODUCTION

It is a widely known fact that in this energy-demand increasing world, the traditional fossil fuel cannot indefinitely sustain global industrialization and economic growth as in past centuries. Finding other alternatives that could be clean and renewable such as wind power, solar energy seems to fit energy trends in the future. Currently on a global scale, energy use is 13.5TW/yr, while the United States consumption rate is 3.34 TW [1]. That means the US itself used 25% of the energy produced whereas it has only 5% of the world's population. Moreover the cost of wastewater treatment has increased over the years and is expected to reach as high as $2 trillion in the US in the next twenty years [2]. Nowadays almost 4%-5% of electricity production is utilized in related water infrastructure activities such as water distribution, water treatment and wastewater treatment. Because of costs for wastewater aeration, sludge treatment and wastewater pumping, wastewater treatment plants alone consume 1.5% of the above power production. However, the biodegradable matter contained in the wastewater has so much energy, solutions to recover it rather than use energy to remove it should be sought [3]. At a conventional wastewater treatment plant in Toronto, Canada, it was estimated that there was 9.3 times as much energy in the wastewater than was used to treat the

wastewater [4]. So finding a method that can recover the unused energy from wastewater and meanwhile treat the wastewater seems an ideal solution for the current energy dilemma. The Microbial Fuel Cell (MFC) concept originated in the early 1990s, and compare with other fuel cell. An MFC is just a process that treating the wastewater in a reactor and has electricity as the major product. In other words, the MFC is considered a rechargeable battery by replacing wastewater every fixed interval. The electrons produced from bacteria metabolism are captured by the reactor alone with the chemical oxygen demand being reduced by this process. Compared to conventional treatment processes, it can yield less sludge production because of its anaerobic reaction principle. According to Kabey, for an aerobic treatment process, the observed growth yield is 0.4g biomass formed per gram of organic substrate consumed whereas an anaerobic treatment process produces 0.077g sludge [5]. The operating cost could be considerably reduced because of the less and simplified sludge treatment process. Contrary to the traditional fossil fuel, MFC product-electricity is clean, renewable and zero-polluting. The large-scale application for MFC could not arouse any concern about green-house gas emission. Moreover, methane as another minor product in the reactor could be used as a component in the biofuel. Besides the above outlined advantages, MFC is indeed provide a novel method in the wastewater treatment.

Objective

The thesis objectives mainly include two aspects: compare two different kinds of high strength industrial wastewater's power production efficiency and COD removal efficiency; and investigating the relationship between the air-cathode area and maximum

voltage produced. The two wastewaters used in the work are a candy-manufacture wastewater, composed predominantly of simple sugars and a thin-stillage wastewater. In the first objective, the only variable is the wastewater itself where all other parameters remain in same. The reactor used in the experiment is called an air-cathode fuel cell, and contains a cathode coated with PTFE on the air side to prevent oxygen diffusion. The COD removal efficiency, power density and columbic efficiency are the major three factors that need to be examined in order to make a comparison between the two wastewaters used in this work. The other objective of this work deals with changing the fuel cell air-cathode area, using the same initial COD wastewater to allow discuss of the relationship between the air-cathode area and the time needed to obtain the maximum power output. The above procedures were conducted approximately at 25 degree (room temperature). Based on what details obtained from the above two objectives, recommendations on how to improve the reactor performance will be given by the end of thesis.

CHAPTER II

Literature Review

Types of biofuel cell

From its definition, the fuel cell is a device that converts chemical energy from a fuel into the electricity through a chemical reaction with oxygen or another oxidizing agent. Hereby the biofuel cell uses living organisms to produce electricity. Based on different forms of intermediate substance, Microbial Fuel Cells and Enzymatic Biofuel Cells are the major biofuel cells. The microbial fuel cell directly uses the bacteria present in the system to produce electricity. The enzymatic fuel cell uses the enzymes responsible for the production of electrochemical active species to produce electricity[42].

Enzymatic biofuel cell

The enzymatic biofuel cell is a type of fuel cell which uses biocatalysts to convert chemical energy into electrical energy [42]. Enzymes are used to catalytically oxidize the fuel at the anode and reduce the ensuing oxidant at the cathode. The specificity of the enzyme reactions at the anode and cathode electrodes of an enzymatic fuel cell eliminates the need for other components required for conventional fuel cells such as membrane.

Although it has the above advantages, it still cannot be commercialized because of its price and sensitivity, also it needs special ways for their stabilization and utilization [42].

Microbial Fuel Cell

There are three major types of Microbial Fuel Cells: sediment biofuel cell, photoautotrophic biofuel cell and heterotrophic biofuel cell.

- Sediment biofuel cell

  In a sediment biofuel cell, energy is harvested from marine sediment. The MFC is placed between the marine sediment and seawater interface. The oxidizable carbon compounds and other components present in sediments on ocean floors and similar environments produce power in conjuction with oxygen reduction at the cathode in the overlying water [6]. The decomposition of carbon compounds result in the reduction of oxygen at the surface and reduction of nitrate, iron and manganese in the underlying centimeters. As each oxidant is reduced and different chemicals are formed at different depths, a voltage drop of 0.75V is observed within a few centimeters of the sediment column [7]. This is the basic idea for how a sediment fuel cell works. Currently, this type of fuel cell is leading largely used by US Navy.

- Photoautotrophic biofuel cell

  Photosynthesis is a process in which light energy is converted into chemical energy by using chlorophyll in photosynthetic organisms such as green plants, algae and even some photosynthetic bacteria. The photoautotrophic biofuel cell is

a model that converts this chemical energy into electricity. Cyanobacteria are used to oxidize water to produce electrons that pass to the anode to produce electricity [8].

3. Heterotrophic microbial fuel cell

This kind of microbial fuel cell is what will be used in the experiment. It is also the most common type of microbial fuel cell. Glucose, protein and nutrients could provide the energy source in the reactor [43].

Development of Microbial Fuel Cell

As early as 1790, the bioelectric phenomenon was noticed by Luigi Galvani when twitching of an isolated frog leg was observed as a brief electrical discharge was passed through it, and the term bioelectricity was created [9]. However, the first observation that bacteria can produce electrical current was in 1911 by Potter . After that, very few practical advances were made until the 1970s. Between 1970 and 1980, the oil crisis provided a perfect opportunity for biological fuel cell advance. The biological fuel cell powered by rice husks, a source of lignocelluloses, which upon fermentation yields many useful enzymes, produced 40mA of current at 6V [10]. In the 1990s, because the fuel cell concept has been largely advocated by the government, a growing number of researchers began to study MFC. However, the experiments required the use of a chemical mediator or electron shuttles which could carry electrons from inside the cell to exogenous electrodes, until Kim discovered the mediator does not necessarily need to be added [3]. So the mediator-less microbial fuel cell gained more attention among researchers after Kim's discoveries. In 2004, Logan and his group members discovered continuous electricity production from domestic wastewater and organic substrates in a flat plate microbial fuel cell [11]. His group also tried to use the different reactor configurations to facilitate power production. For instance, in 2004 they tried to use an air-cathode single chamber microbial fuel cell to acquire power production [12]. Other researchers like Liu and Cheng got power production from acetate or butyrate using a single chamber microbial fuel cell in 2005 [13]. Kim (2007) also discussed power generation using different cation, anion and ultrafiltration membranes in the microbial fuel cell [14]. Later the microbial fuel cells were used for more practical applications.

Mehanna and Saito used a microbial fuel cell to reduce salinity of a feedwater prior to entering a reverse osmosis system [15]. He and his group members discussed electricity production coupled to ammonia removal in a microbial fuel cell [16].

Basic components of a Microbial Fuel Cell

Typically, a microbial fuel cell consists of two electrodes, anode and cathode, bacteria and substrate.

Respiration of bacteria

ATP (Adenosine TriPhosphate) serves as the main energy molecule that can be obtained through respiration. There are two types of respiration, aerobic and anaerobic. The difference between these two terms is whether or not the oxygen participates in the whole process. For instance, some organisms use oxygen to produce carbon dioxide and water. This is called aerobic respiration while other organisms including some microbes, bacteria and fungi, respire without oxygen participation. This process is known as an anaerobic process. The electrons released from organic matter are donated to NAD^+, the NADH can be created by accepting one hydrogen ion. Then NADH donates these electrons to a molecule of lower potential. The difference of these two potentials is captured by ATP. The principle operation of the microbial fuel cell is to capture electrons from the respiratory chain to the electrode. There are three common ways to transfer electrons from bacteria's metabolic activity: external mediators, directly by bacterial transfer, or extra cellular electron transfer [17]. Before 1999, experiments were conducted using chemical mediators or electron shuttles that could carry electrons

from inside the cell to exogenous electrodes. Kim in 1999 recognized that the mediator does not necessarily have to be added in the reactor. Bacteria have been known to transfer electrons to a surface via two mechanism: electron shuttling via self-produced mediators (such as pycocyanin and related compounds produced by Pseudomonas Aeruginosa) and nanowires produced by both Geobacter and Shewanella species [18]. In 1911, Potter found that yeast Saccharomyces cerevisaae and bacteria such as Bacillus Coli could produce a voltage resulting in electricity generation. Since then, diverse chemicals such as neutral red, thionin, potassium ferricyanide have been added to the reaction in order to facilitate the shuttling of electrons from inside cell to the outside of the cell. In 1999, Kim firstly demonstrated electricity production by a bacterium in the absence of an exogenous mediator. Kim and his group researchers observed current generation from Shewanella putrefacians in a reactor designed to be a lactate biosensor. Although the power output is quite low, no external exogenous mediators were added [19]. Since then, the concept of mediator-less exoelectrogens were created by researchers. In this thesis, all of reactors used in the experiment are mediator-less microbial fuel cells.

Principles of microbial fuel cell

A typical schematic of an MFC consists of two chambers, one anode and the other cathode. They are located in the two chambers. The anode chamber should be anaerobic because oxygen in the anode chamber will inhibit electricity generation. So the bacteria in the anode should be isolated from oxygen. Usually the two chambers were formed by using one proton exchange membrane. The anode chamber is a place where bacteria

grow and the cathode chamber is the place that electrons react with the catholyte. The cathode should be exposed to the air or sparged with air to allow enough oxygen for reaction [37]. Figure 2.1 below is a schematic for a two-chamber MFC:

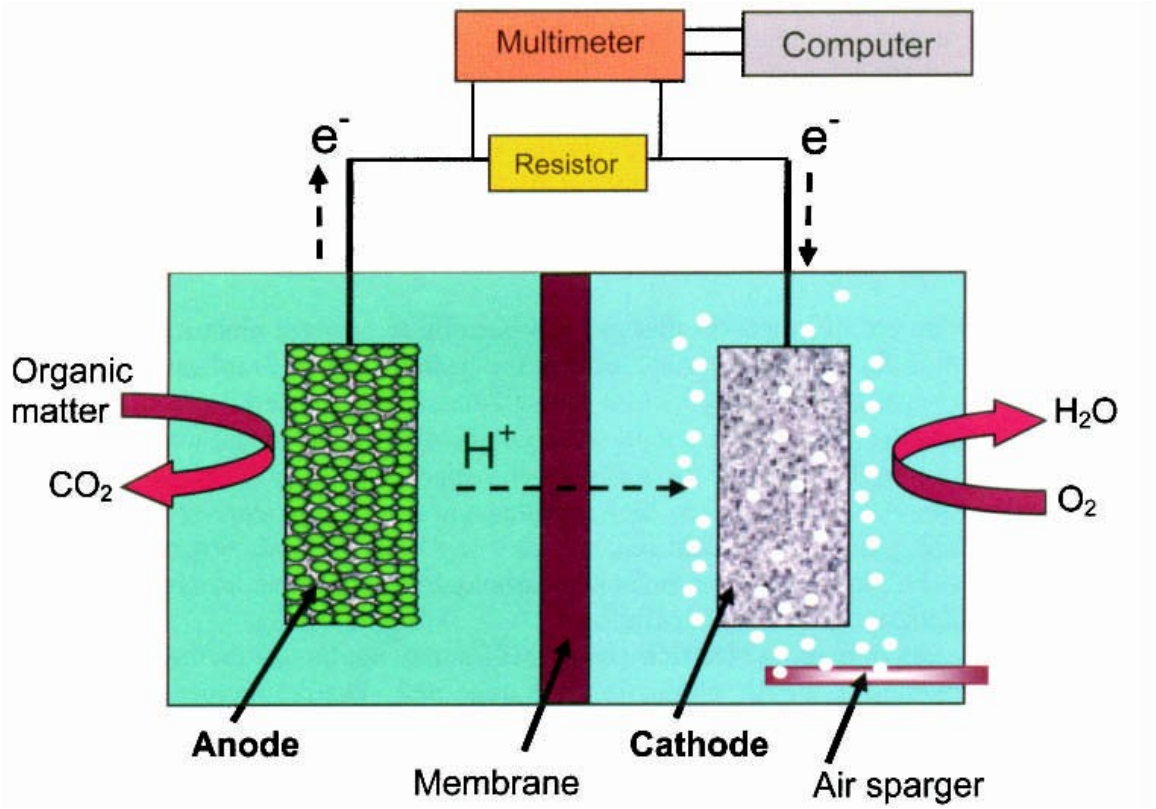


Figure 2.1 Schematic of the basic components of a microbial fuel cell [3].

As mentioned above, the bacteria live on the anode part; their metabolism can produce the electrons to the anode and protons to the solution. The two chambers are separated by a membrane- usually a proton exchange membrane. The electrons released will inhabit the anode and then transferred to the cathode through an external wire. The released protons are transferred through the proton exchange membrane, so if the cathode could provide enough oxygen, the final product in the cathode is water. The

potential difference between the anode and cathode could generate current for the external circuit. Usually a data acquisition system was connected parallel to the resistor in the circuit to monitor its voltage change.

Reaction of Microbial Fuel Cell

In a typical microbial fuel cell, a series of complex chemical reactions occur. For example, at the anode, the substrate undergoes enzymatic oxidation. The NAD^+ is reduced to NADH [20]. The following equations expresses this reaction.

Enzymatic Oxidation:

$C_n(H_2O)_m + NAD^+$ ------- $CO_2 + H^+ + NADH$

$NADH + Mediator_{ox}$ ------ $NAD^+ + H^+ + Mediator_{re}$

$Mediator_{re}$ ------ $Mediator_{ox} + ne^-$

The following Figure 2.2 can illustrate the above process:

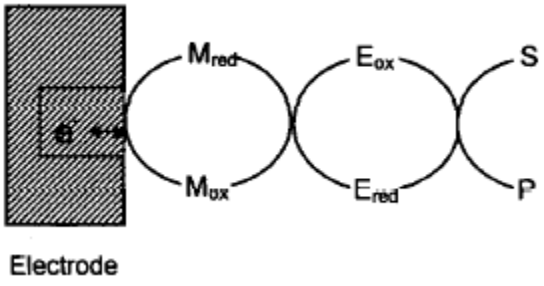


Figure 2.2 Scheme of Bioelectrocatalysis [21]

S: substrate , P: Products, E_{ox} and E_{red} : oxidized and reduced forms of enzymes, M_{red} and M_{ox}: reduced and oxidized forms of mediator

Above is the reaction that occurs at the anode, the following reaction usually happens at the cathode:

$4H^+ + O_2 + 4e^-$ ---- $2H_2O$

So from this equation, oxygen is a necessary part for the cathode.

Thus the microbial fuel cell requires two redox couples. The first couples involves the reduction of an electron mediator by the bacterial oxidative metabolism. The second couples the oxidation of the electron acceptor on the cathode surface, where oxygen is electron acceptor and water is final product in the cathode [22].

Maximum voltage generated by a microbial fuel cell

Usually the theoretical maximum voltage can be reached when the electron is replaced at the NAD^+ level. [23]

For instance, the transfer of 2 electrons from NADH to oxygen,

$½ O_2 + 2H^+ + 2e^-$ ------ H_2O $\quad E^0 = 0.815V$

$NAD^+ + H^+ + 2e^-$ ------ NADH $\quad E^0 = -0.315V$

Final equation would be :

$½ O_2 + NADH + H^+$------ $H_2O + NAD^+$ $\quad E^0 = 1.13V$

From the above equation the theoretically maximum voltage this MFC could reach is 1.13 V. From the electron chain, the reduced mediator sends the captured electrons to the anode, the mediators become oxidized and again captures electrons and sends it to the anode [24]. By this process, as the substrate or food in the wastewater samples are consumed by bacteria, the electrons will be consistently released and wastewater's COD will be reduced until there is no more food could be consumed.

Factors related to MFC performance

There is a series of factors that could affect MFC performance. Generally speaking, there are three major aspects including MFC configuration, MFC material and bacteria and wastewater. For instance, the presence or absence of a membrane could affect the power production because membranes can increase internal resistance considerably [37]. Also the electrode spacing determines the system resistance, usually the closer electrode space, the lower the system resistance. Moreover, the electrode material also can affect power production. For example, carbon paper and carbon cloth could have different effects on the anode. Also, the cathode material and catalyst could affect power production [44]. The ion strength of wastewater could also affect what is maximum value and how long the maximum voltage will last. So the above factors could affect power output.

How to optimize the MFC performance:

For the anode, performance could be optimized biologically and electrochemically [25]. For instance, the different types of biocatalysts and oxidation pathway of organic substrate could be used. Also, the anode material and geometry could be adjusted to be optimum. For the cathode, increased proton transfer to the cathode and increased consumption of oxygen could optimize the cathode performance [26, 27, 28, 29].

The application of MFC to industrial wastewater

From 2005, researchers began to apply the microbial fuel cell to treat diverse kinds of wastewater including domestic wastewater and industrial wastewater. In 2005, Oh successfully tried a microbial fuel cell to treat a food processing wastewater to acquire hydrogen and bioenergy [30]. A considerably amount of hydrogen production was achieved by using cereal wastewater, a maximum of 81mW/m^2 and a final COD< 30mg/l (Removal efficiency 95%) was recorded using a two-chambered microbial fuel cell. This result suggests that it is possible to treat industrial wastewater using a microbial fuel cell to get hydrogen and bioenergy. Also in 2005, Min and Kim tested swine wastewater in a microbial fuel cell [31]. This is a new method to treat animal wastewater. Both single-chambered and two-chambered microbial fuel cells were tested in their experiment. The maximum power density of 45mW/m^2 was achieved using a two-chambered reactor, while 261 mW/m^2 power density was recorded when reactor changed to a single chamber air-cathode fuel cell. Also in this experiment, the power density of swine wastewater is 79% higher than domestic wastewater because of its higher organic matter content. In 2006, Heilmann explored the possibility of treating protein-rich wastewater using a single chamber microbial fuel cell [32]. A meat packing wastewater that has 1420 mg/l COD produced 80mW/m^2, BOD removal efficiency and TOC removal efficiency were greater than 86%. This experiment shows that microbial fuel cells also could be applied to treat protein rich wastewater. In 2008, Huang tested the utilization of an MFC to treat paper recycling wastewater [33]. Through a 500-hr run the maximum power density reached 501mW/m^2. The coulombic efficiency was 16± 2 % and the efficiency of SCOD removal was 73±1% . Additionally in 2009, several researchers from Newcastle University examined the possibility of energy from algae

using a microbial fuel cell [34]. Chlorella and Ulva lactuca were examined in single chamber MFC as a powder. A power density of 0.98W/m^2 was obtained from C.Vulgaris and 0.76W/m^2 was obtained from U.lactuca. In this thesis, the wastewater used included thin-stillage from one brewery industry and the other sugar wastewater from one candy manufacture plant.

Other applications of MFC

As a growing number of researchers and laboratories work on MFC development, the diverse functions of MFC could be applied to several aspects. For instance, He from University of Wisconsin-Milwaukee and his group members examined the bio-electrochemical removal of nitrogen using MFC. In 2009, He and his co-workers tested electricity production coupled to ammonium in the microbial fuel cell [35]. The final result was that peak current increased with increasing ammonium addition, this shows ammonium's role is either directly as an anodic fuel or indirectly as a substrate for nitrifiers to provide carbon source for heterotrophs.

More and more researchers are using microbial fuel cells to desalinate seawater and brackish water. In 2011, Jacobson examined using a microbial desalination cell to study the biodesalination effect and power production [36].

Their findings showed that the TDS removal efficiency was mainly relate to electricity production even though other factors like water osmosis also affect TDS reduction efficiency. The microbial desalination cell could generate power that could reduce the energy required by a RO system. In their experiment, the results show that MDC could

supply 58.1% (salt solution) and 16.5% (artificial seawater) of the energy required by the RO system.

Another application of MFC is one of its modifications, the MEC- Microbial Electrolysis Cell, produces hydrogen as its product, while the MFC produced electricity as its product. Because hydrogen was produced, oxygen is absolutely prohibited in the cathode chamber. Like the MFC, the anode part of MEC also needs bacteria participation. The proton and electrons are released by bacteria as their metabolism products. When the MEC is applied to produce hydrogen, usually an external voltage should be added to the system because 0.41 volts are needed to form H_2 from acetate, however sometimes the external added volts remains about 0.2 because bacteria itself could provide 0.2~0.3V to the system. The whole process is anaerobic and hydrogen is the desired product, as such oxygen is absolutely absent. Until the additional volts were put into the system, the hydrogen production process could not occur spontaneously. The MEC could provide a novel method to obtain renewable and clean biofuel [45] .

Current Problems of MFC

The biggest problem facing, MFC is how to scale the operation. Although more and more research is being conducted, their processes remain at the laboratory level. How to develop large-scale applications to wastewater treatment plants and high-COD industrial effluents is still big problem.

Another problem that MFC faces is cost. So far, the prevalent catalyst used in the reactor is platinum that is fairly precious and expensive. How to find an alternative that is cheap and efficient is another problem that needs to be overcome.

CHAPTER III

Materials and Methods

In this chapter, the materials and methods will be introduced. In brief, the configuaration is a typical air-cathode single chamber reactor with the PTFE coated on the cathode chamber air-surface in case of water escape. The materials are mainly purchased from FuelCellEarth company (Massachusseutt). These two parts will be discussed in more details in the following paragraph.

PART A: Materials

Configuration of MFC

In this experiment, all reactors needed were single-chamber air cathode microbial fuel cells. The plastic cylindrical chamber contains two electrodes placed on opposite sides. Each chamber size is 4 cm long and 3 cm in diameter with total volume of 32 ml (including the neck). The anode material is Toray carbon paper (FuelCellEarth, MA) with a diameter of 4 cm. The carbon paper used in the anode is without any wet-proofing. The cathode material, also from (FuelCellEarth LLC, MA), contains 10% Pt on the carbon paper as the catalyst. The platinum load rate on the carbon paper is 0.5mg/cm^2. As mentioned before, in case of evaporation of water through the cathode, the air side of cathode was coated with a polytetrafluroethylene (PTFE) solution (50 % weight).

The cathode was dried at room temperature for 10 minutes and then heated for 10 minutes at 380^{o}C in an oven.

The PTFE solution was applied at the rate of 3mg/cm^{2} per layer. The following Figure (3.1) is a schematic diagram of the air-cathode microbial fuel cell. The Proton Exchange Membrane was made of Nafion 117 (DuPont). Figure 3.2 is a photograph of the air-cathode Microbial Fuel Cell that used in these experiments.

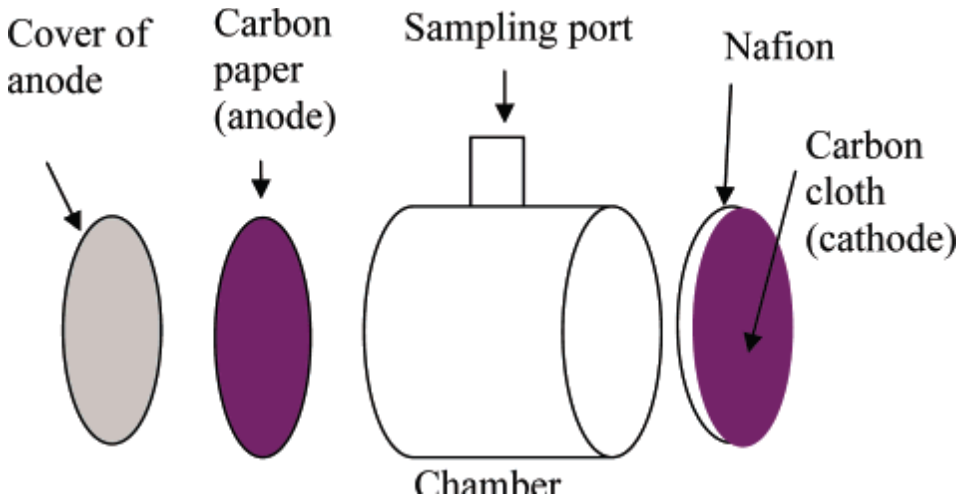


Figure 3.1 Schematic of Air-cathode Microbial Fuel Cell [37]

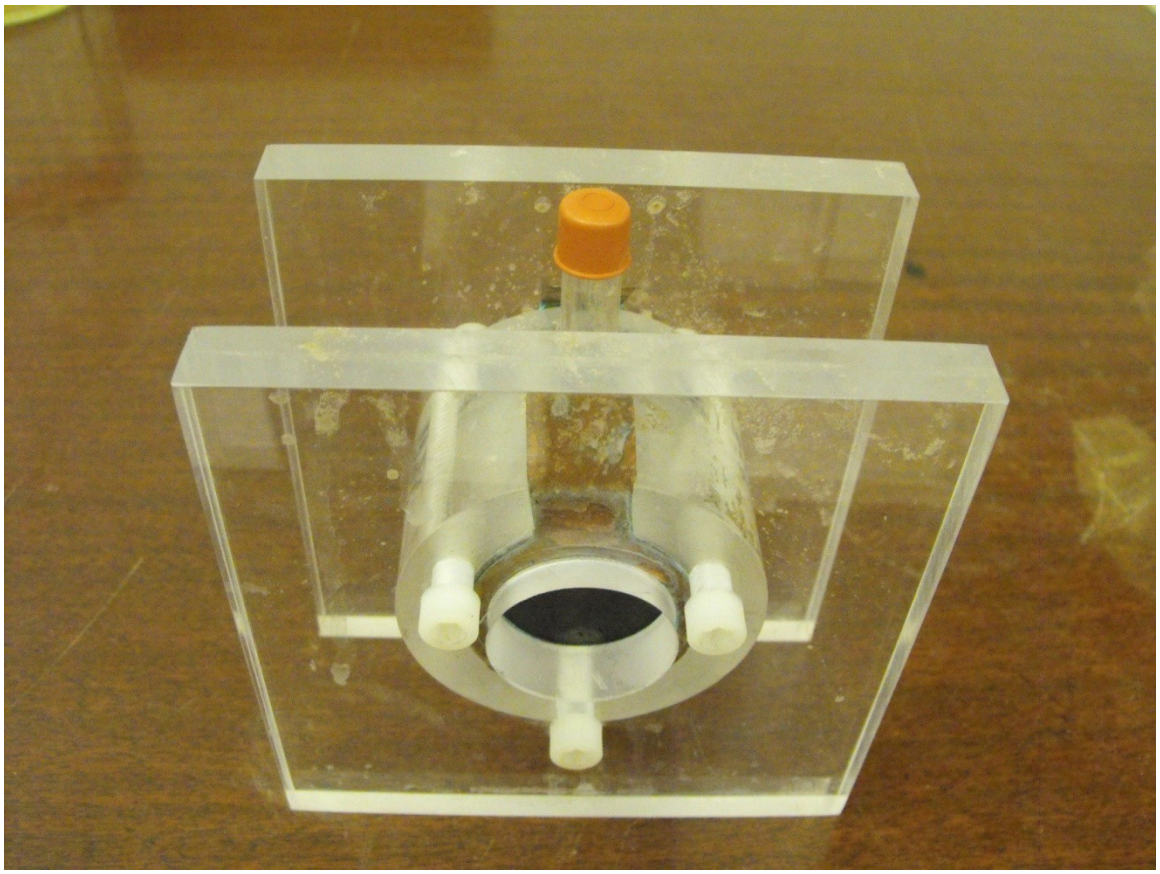


Figure 3.2 Design of Microbial Fuel Cell with air cathode

Instruments

A data acquisition board (DAQ-LabJack, U12) was used to aid with data collection. The details of how to connect the DAQ to the computer system is given in the user's guide [38]. Usually the external features include a USB connector, DB25 digital I/O connector, status LED and 30 screw terminals. Labjack U12 has eight screw terminals for analog input signals. The measurement range is +/- 10 volts for the Labjack U12. The ground signal is noted here as GND. The following figure shows a typical singled-ended connection measuring the voltage of a battery.

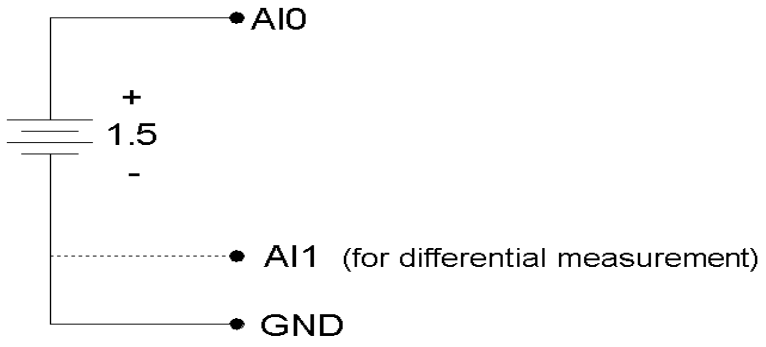


Figure 3.3 Single-ended measurement

A photograph of the data-acquisition board LabJack U12 is shown below:

Note: in the picture the AI on the left side was used for data input, here AI means analog input, the data acquisition board has total eight inputs. Usually AI connected with anode part of MFC, GND means ground to connect with cathode part of MFC.

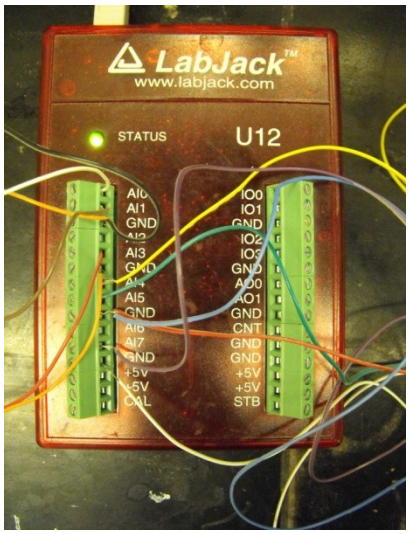


Figure 3.4 Labjack U12

Microorganism and Wastewater:

All of experiments were run in batch operation mode and contain three phases: inoculation, acclimation and operation. The inoculation is a process that allows living organisms mainly bacteria to inhabit the electrode surface. The whole inoculation process needs one week until a biofilm is formed on the electrode. The wastewater samples used in the reactor were obtained from the anaerobic digestor, Stillwater Wastewater Treatment Plant. Stock solution 1 which contained domestic wastewater, nutrient medium and phosphate buffer solution was used in the inoculation period. Stock solution 1 was replaced every day for one week. After the biofilm has been grown, the reactor was acclimated to a low-COD wastewater once daily for two days. The purpose of acclimation is mainly as a transition phase between inoculation and actual operation. Stock solution 2 was made of nutrient medium, phosphate buffer and either thin-stillage or sugar wastewater that has a controlled COD of around 2000 mg/l. The final phase, named operation, used thin-stillage or sugar wastewater to run the reactor. The intial COD of thin-stillage and sugar wastewater reached 107,612 mg/l and 39,068 mg/l respectively. The wastewater COD used in the operation phase were sample diluted

1000 mg/l, 2000 mg/l and 3000 mg/l.

The reason for selecting these two wastewaters was that the sugar wastewater contained predominantly carbohydrate as food source for bacteria and the thin-stillage contains mostly protein, which is also an indispensable ingredient for microorganism. All of the experiments are conducted at room temperature.

Glassware:

List of the various glassware used in the experiment is shown below:

- General laboratory glassware such as test tubes, pipette, calibrated cylinder
- 5ml plastic syringe
- Rubber septum
- BOD testing bottle
- Standard COD testing tube (HACH company, CO)

Reagents:

All solutions utilized in the experiments were made using reagent grade chemicals. As a matter of convenience, stock solution 1, 2 and 3 were made of several base solutions such as mineral base , nutrient base, buffer base and diluted wastewater.

Candy manufacture wastewater and thin-stillage wastewater:

The wastewater samples analyzed in the experiment were from a candy manufacturer and a brewery plant. The wastewaters were usually diluted with deionize water to obtain the required COD for the individual experiments.

Buffer base:

Potassium phosphate monobasic(K_2HPO_4) and potassium phosphate dibasic(KH_2PO_4) were used as reagents to make the buffer solution. The dry weight of KH_2PO_4 and K_2HPO_4 were 6.8 gram and 8.709 gram per liter respectively. The final concentration of phosphate buffer solution is 100 mM as P to maintain the solution in the reactor around pH 7.

Mineral base:

Mineral base was prepared by adding the following reagents to 800ml of distilled water and then diluting to 1L [39].

Table 3.1 Constituent of mineral base

$CoCl_2$. $6H_2O$ [Sigma Aldrich MO]	0.25g
$FeCl_2$. $4H_2O$ [Fisher Scientific, NJ]	2.00g
$MnCl_2.4H_2O$ [Sigma Aldrich, MO]	0.05g
H_3BO_3 [Fisher Scientific, NJ]	0.025g
$ZnCl_2$ [Fisher Scientific, NJ]	0.025g
$NaNO_3.2H_2O$ [Sigma Aldrich, MO]	0.005g
$NiCl_2.2H_2O$ [Fisher Scientific, NJ]	0.025g
Na_2SeO_4 [Fisher Scientific, NJ]	0.025g
$CuCl_2$ [Sigma Aldrich, MO]	0.005g

Nutrient Base:

The nutrient base was prepared by adding the following reagents to 800ml of distilled

water and then diluting to 1L.

Table 3.2 Constituent of nutrient base

KH_2PO_4 [Hach, CO]	135g
K_2HPO_4 [Fisher Scientific, NJ]	175g
NH_4Cl [Fisher Scientific, NJ]	53g
Na_2SO_4 [Fisher Scientific, NJ]	15g

Stock Solution:

Stock solution 1 (Inoculation period):

This stock solution was prepared by thoroughly mixing all of following:

- 13ml of 100mM of phosphate buffer (buffer base)
- 4ml of each of the mineral and nutrient solutions (mineral & nutrients base)
- 130ml of domestic wastewater

Stock solution 2 (Acclimation period, COD around 2000 mg/l):

This stock solution was prepared by thoroughly mixing all of following:

- 13 ml of 100 mM of phosphate buffer
- 4 ml of each of the mineral and nutrient solution
- 1.9 g of sucrose to 50 ml distilled water or 1.86 ml thin-stillage into 50 ml distilled water

Stock solution 3 (actual operation, COD 1000 mg/l, 2000 mg/l and 3000 mg/l)

A 100ml stock solution was prepared by thoroughly mixing all of following:

a) Sugar wastewater, required COD 1000 mg/l

- 40 ml of 100 mM of phosphate buffer

- 4 ml of each of mineral and nutrient solution
- 2.56 ml of sugar wastewater into 50 ml distilled water

b) Sugar wastewater, required COD 2000 mg/l

- 40 ml of 100 mM of phosphate buffer
- 4 ml of each mineral and nutrient solution
- 5.12 ml of sugar wastewater into 50 ml distilled water

c) Sugar wastewater, required COD 3000 mg/l

- 40 ml of 100 mM of phosphate buffer
- 4 ml of each mineral and nutrient solution
- 7.68 ml of sugar wastewater into 50 ml distilled water

d) Thin-stillage wastewater, required COD 1000 mg/l

- 40 ml of 100 mM of phosphate buffer
- 4 ml of each mineral and nutrient solution
- 0.93 ml of thin-stillage into 50 ml distilled water

e) Thin-stillage wastewater, required COD 2000 mg/l

- 40 ml of 100 mM of phosphate buffer
- 4 ml of each mineral and nutrient solution
- 1.86 ml of thin-stillage into 50 ml distilled water

f) Thin-stillage wastewater, required COD 3000 mg/l

- 40 ml of 100 mM of phosphate buffer
- 4 ml of each mineral and nutrient solution
- 2.79 ml thin-stillage into 50 ml distilled water

Part B: Methods

In this part, the general steps will be presented detailed and except for the step 3, all of the steps are same.

Step 1: Testing initial COD and BOD using stardard HACH method.

Step 2: The bacteria sample from Stillwater Wastewater Treatment Plant, it was kept at room temperature, around 20^{o}C.

Step 3: Constructing air-cathode microbial fuel cell (in the first scenario, all of the six

reactors have same cathode air-contact diameter 3cm; whereas in the second scenario, reactors have cathode air-contact diameters of 2cm, 3cm and 4cm, respectively). The cathode was covered by polytetrafluroethylene solution in 3 layers at a loading rate 3mg/cm^2 per layer and dried completetly. Then examined for leaks.

Step 4: Inoculate the reactor using stock solution 1 everyday for one week to allow biofilm grown on the anode surface.

Step 5: Acclimate the reactor using stock solution 2 to let microorganisms get used to living environment and connect reactor with the resistor by using a data acquisition board to monitor voltage change on the resistor.

Step 6: After the reactor can supply a consistent voltage to the circuit, inject target solution (1000 mg/l, 2000 mg/l and 3000 mg/l) into the reactor to run the experiment.

Step 7: Using Hach standard method (Reactor Digestion) to testing residual COD for examined water.

Note: Here from step 4, all of operations for reactor and bacteria should use nitrogen gas to maintain anaerobic environment because the electron-generating bacteria are anaerobes. If the reactor contains aerobic environment, the electron-generating bacteria will shut down for working.

Determination of samples COD and BOD

The COD of samples were determined by using a spectrometer (Hach DR/5000). After heating for 2hr by using a standard COD digestor at 25^{o}C, 2 ml of the digested sample are injected into a COD testing tube that has measuring range of 20 mg/l-1500 mg/l. Biochemical oxygen demand is another parameter that was examined before using

wastewater samples. The 5-day and ultimate BOD were tested in the experiment. 300ml incubation bottles with caps were used in the experiment, the reason for using caps on the bottle is as a double check to limit outside oxygen diffusion into the bottle. All of BOD testing bottles were incubated at $20^{o}C$ and in the dark to limit photosynthetic production of DO [40] . Because thin-stillage wastewater contains a significant amount of protein content, the ultimate BOD was also examined besides the BOD_5. 21 days BOD test value was considered as BOD_u, if the DO value drops below 1mg/l within this 21 days, artificial aeration was provided to the samples to reestablish a new DO value remains around 7.00 mg/l. The BOD_5 was calculated by using equation 3.1
Finally oxygen uptake amount was calculated by equation 3.2 .

$$BOD_5\ mg/l = (D_1 - D_2)/P \qquad \text{(Equation 3.1)}$$

Where: D_1: DO of diluted sample immediately after preparation

D_2: DO of diluted sample after 5d incubation at $20^{o}C$

P: decimal volumetric fraction of sample used, dilution ratio

$$BOD_t\ mg/l = UBOD(1 - e^{-kt}) \qquad \text{(Equation 3.2)}$$

Where: UBOD: ultimate BOD

BOD_t: oxygen uptake measured at time t, mg/l

k: first-order oxygen uptake rate.

Determination of Voltage, Current and Power

There are three parameters that need to be discussed in detail in the result and discussion section. Power density, coulombic efficiency and COD removal efficiency. The first two parameters concern electricity production.

Figure3.5 shows how to connect resistor with the Microbial Fuel Cell in the circuit.

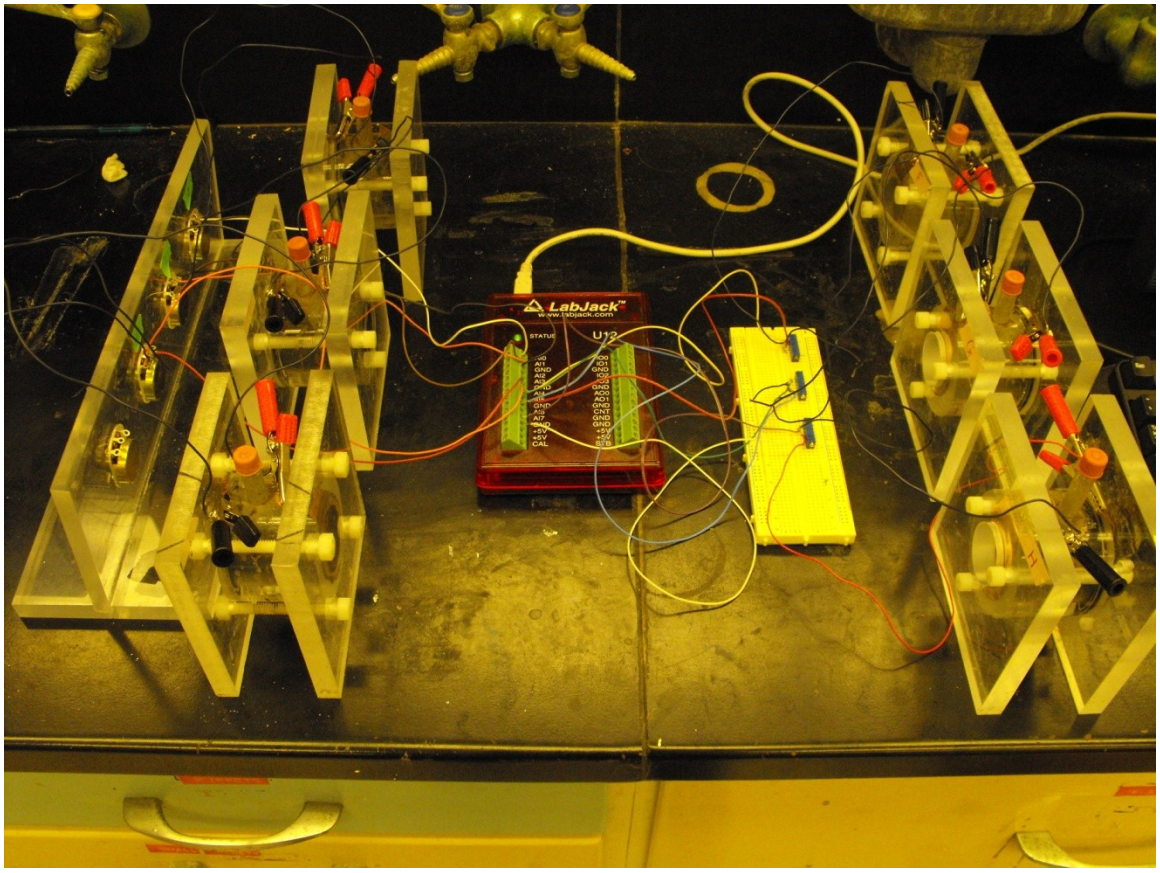


Figure 3.5 Picture for whole circuit, including MFC, resistor and LabJack U12

Voltage was measured using a multimeter (Radioshack LCD NO.22-182 auto range multimeter) and the data acquisition system board (Labjack, U12) and was used to calculate the power according to:

$P=UI/A$ (equation 3.3)

Where I is current(ampere), U is voltage(volt) and A is cathode area that contact with air($cm^{2)}$. Power was normalized by the cross-sectional area of the cathode (7.065 sq cm). If the power was not normalized by the cross-sectional area of cathode, it is hard to compare power production between different reactors that have different cathode area.

Coulombic efficiency:

Coulombic efficiency is a unitless value. By definition, Coulombic efficiency is a parameter that can reflect what percentage of electrons have been recovered from the wastewater to the theoretical amount of coulombs that can be produced from wastewater. The following equations show how to calculate coulombic efficiency [41]

$CE=(C_p/C_t) * 100\ \%$ (Equation 3.4)

Where C_p is the total coulombs calculated by integrating the current over time

C_p = [average current (A)] * [time(s)] (Equation 3.5)

C_t is the theoretical amount of coulombs that can be produced from sugar wastewater and thin-stillage wastewater

$$C_t = \frac{96485(C/mol\ e^-) * \Delta COD(\ gO_2/L) * Volume(L) * 4(mol\ e^-/\ O_2)}{32\ (g\ O_2/\ mol\ O_2)}$$ (equation 3.6)

Where, 96485 C/mol-electrons is the Faraday's constant and 4 moles of electrons are produced for one mole of oxygen. ΔCOD is the difference between inlet and outlet COD and 32g O_2/ molO_2 is molecular weight of 1 mole oxygen.

CHAPTER IV

RESULT AND DISCUSSION

BOD and COD result:

Before the experiment proceeded, some basic parameters such as COD, BOD and phosphorus, nitrogen were examined. The Table 4.1 shows BOD and COD results for the two industrial wastewaters.

Table 4.1: COD for thin-stillage, sugar wastewater sample

Dilution ratio	1:100	1:120	1:150	1:180	1:200	Ave.
Thin-stillage (mg/l)	95360	103152	139140l	99288	101120	107612
Sugar (mg/l)	40360	41472	40740	34848	37920	39068

Hach method (Reactor Digestion) was meaning to determine the wastewater initial COD. The test's working range is from 20 mg/l-1500 mg/l. The raw data for the COD measurements are in Appendix A.

After determination of the COD for these two industrial wastewaters, total nitrogen and phosphorus were also needed to be examined in order to decide the need for external nutrients. The Table 4.2 is the results for phosphorus and nitrogen content of the wastewaters.

Table 4.2: Phosphorus and nitrogen content in the wastewaters

Dilution ratio		1:120	1:150	1:180	1:200	Ave.
Thin-stillage	Phosphorus mg/l	1626	1850	1470	1430	1594
Sugar	Phosphorus mg/l	165	158	201	246	174
Thin-stillage	Nitrogen mg/l	2496	3165	3618	4080	3040
Sugar	Nitrogen mg/l	Not Detectable	Not Detectable	Not Detectable	Not Detectable	Not Detectable

Here the nitrogen result for sugar wastewater is not available because of its low level nitrogen. The raw data for Phosphorus testing data is in the Appendix B.

BOD testing results:

In order to get a better analysis, three types of methods were applied to testing BOD.

The first time, the wastewater was diluted with distilled water to achieve required dilution ratio.

Here the wastewater used was just thin-stillage because the sugar wastewater did not contain enough nutrients .

The second time the wastewater was diluted with BOD nutrient water to achieve desired concentrated sample. The BOD nutrient water and sludge were used as diluted water in the final time. In the first time, the thin stillage was constantly measured for 21 days to get ultimate BOD. Aeration will apply to keep DO at around 7.00 if the DO dropped below 1.0 mg/l. The wastewater sample with BOD nutrient water was measured for 11 days. The wastewater sample with BOD nutrient and sludge also tested with 21 days to get ultimate BOD. The following table shows results of BOD tests:

Table 4.3A: BOD testing resulst for thin-stillage wastewater

Thin-stillage	BOD_5	BOD_u	k
1:10000	44200mg/l	109800mg/l	
1:12000	61560mg/l	158760mg/l	
1:20000	49600mg/l	151600mg/l	
Average.	51786mg/l	140053mg/l	0.092/day (testing 21 days)
1:10000(BOD WATER)	65200mg/l	78900mg/l	
1:12000(BOD WATER)	62640mg/l	76680mg/l	
1:20000(BOD WATER)	63800mg/l	79200mg/l	
Average.	63880mg/l	78260mg/l	0.34/day (testing 11 days)
1:10000(BOD+ Digestor Sludge)	99700mg/l	222500mg/l	
1:12000(BOD+ Digestor Sludge)	108240mg/l	234360mg/l	
1:20000(BOD+ Digestor Sludge)	140000mg/l	332800mg/l	
Average.	115980mg/l	263220mg/l	0.1162/day (testing 21 days)

From the above data, it is obvious that k value for the BOD nutrient water plus sludge is higher than thin-stillage alone. It is reasonable because external bacteria were added into

the water and more nutrients and more bacteria will increase oxygen demanding amount. Here, there is not much discussion about thin-stillage with BOD nutrient alone because it lasted only 11days.

Table 4.3B: BOD testing result in sugar wastewater sample

Sugar	BOD_5	BOD_u	k
1:10000 (BOD Water)	33400 mg/l	43600mg/l	
1:12000 (BOD Water)	35400 mg/l	42600 mg/l	
1:20000 (BOD Water)	43400 mg/l	49400 mg/l	
Average.	37400mg/l	45200 mg/l	0.35/day (11 days)
1:10000 (BOD+Sludge)	59900 mg/l	140900 mg/l	
1:12000 (BOD+Sludge)	67920 mg/l	168240 mg/l	
1:20000 (BOD+Sludge)	101600 mg/l	261200 mg/l	
Average.	76473 mg/l	190113 mg/l	0.103/day(21 days)

From above tables, it is easy to conclude that sugar wastewater contains organic matter that almost all could be biodegraded, because BOD_u (45200mg/l) equals to COD (39068mg/l) even though theoretically COD should larger than BOD_u . It is reasonable because sugar manufacture wastewater containsugar substance that could be consumed by bacteria as food. However, for thin-stillage sample, the data reflects almost 72% of organic matter could be biodegraded because the BOD_u (78260mg/l) is almost 72% of COD (107612mg/l). That means although initial COD of thin-stillage is much higher than for the sugar waste, part of organic substances in the wastewater sample are not easily biodegraded.

Determination of internal resistance

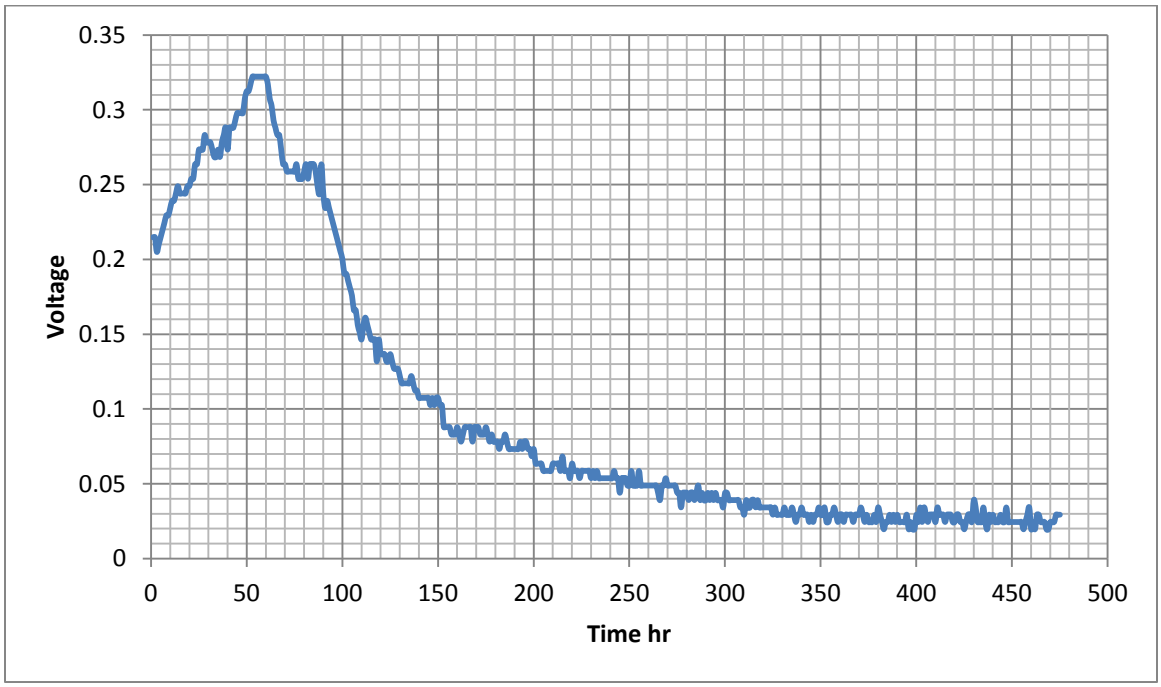
Reactor internal resistance is a big factor that can affect power output. Over the years, the

internal resistance has casted problem for researchers. Changing the MFC configuration seems the most likely method to reduce internal resistance. According to the equation, $P_{output}= [U/ (R_{internal}+R_{external})]^2 * R_{external}$, Here this is the maximum voltage that the reactor can reached, so when the first-order derivative of P_{output} equal to zero, the second-order derivative of $P_{output}<0$, and the reactor should be outputting power at the most efficient rate. The calculated results shows that when the condition is $R_{internal} = R_{external}$, the reactor has achieve its optimum point. Here, because of the inability to determine the cyclic voltammetry curve, the external resistors used are uniformly 1000 ohm.

Trial 1

In this trial, sugar samples that had COD of 3000 mg/l, 4000mg/l and 5000mg/l were tested. Figure 4.1 below shows that power peak happened at 53th hour.

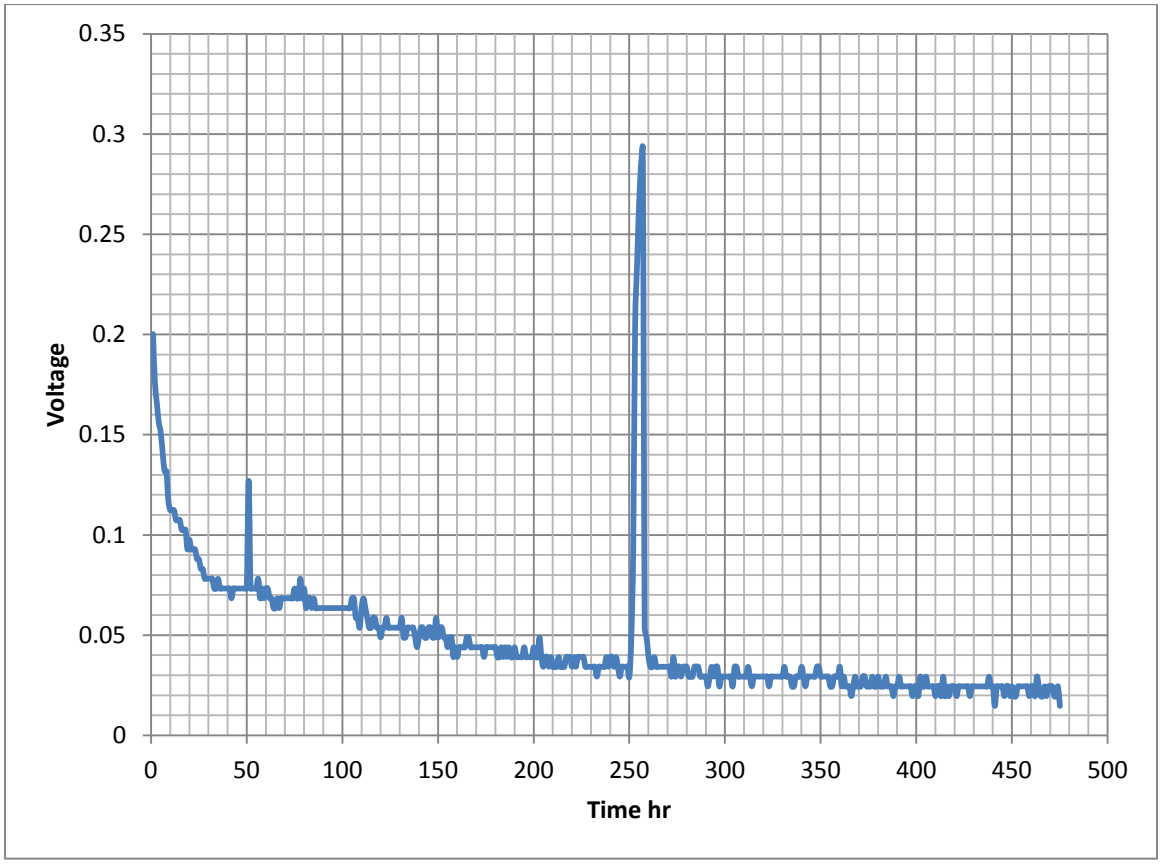
Figure 4.1: Power production for sugar samples with COD 3000mg/l



From the above figure, the whole process was monitored for 480 hours until the voltage fall below 0.03V. The voltage was generated immediately after the sugar samples

was injected into the reactor. The voltage started with 0.214844 V and reached a peak voltage of 0.322266 V at 53th hour and it lasted 8 hrs. The external resistance in the circuit was 1000 ohm, the total coulombs discharged in the system was 172C, so the final COD removal efficiency in this reactor was 62.87%, the coulomb efficiency is 22.67% and power density was 0.147 W/M^2 . The detailed calculation all provided in the Appendix D.

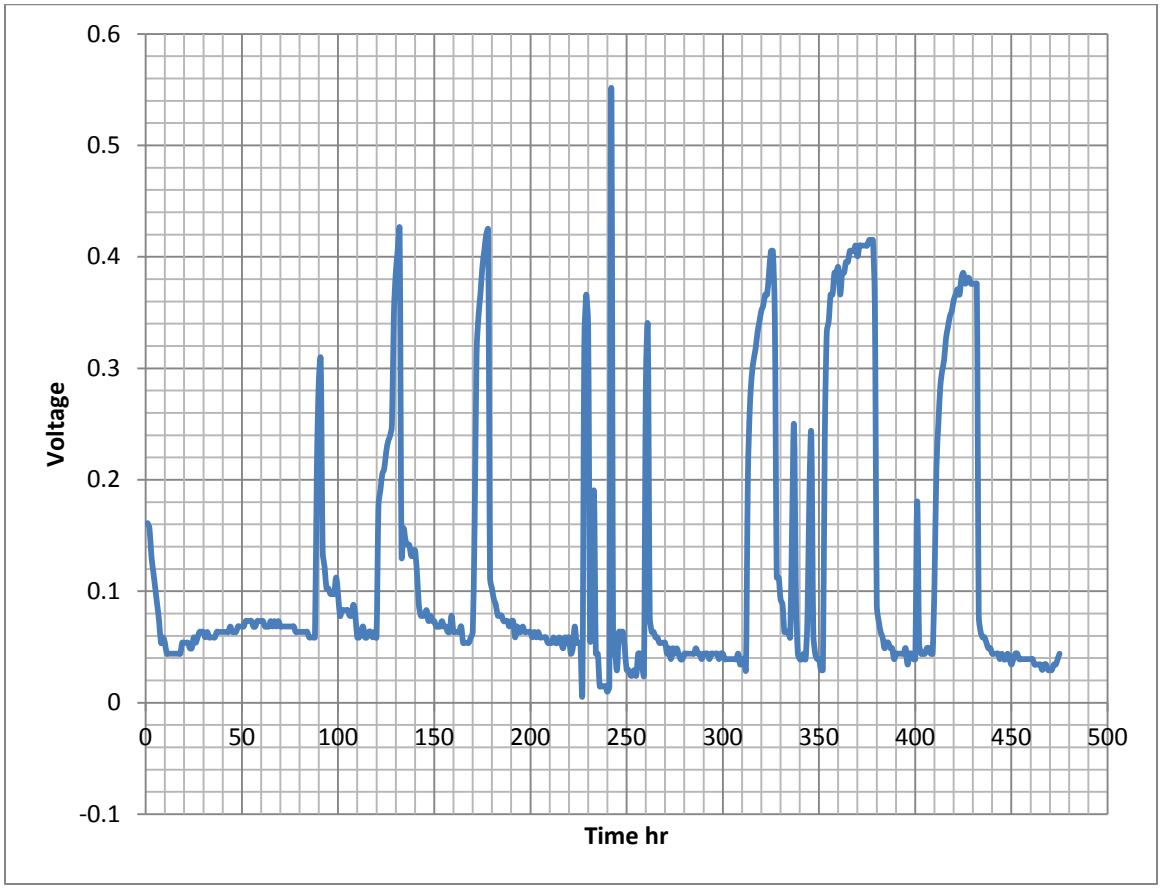
Figure 4.2: Power production for sugar sample with COD 4000mg/l



From the Figure 4.2, the power production was also monitored for 480 hours. The voltage kept dropping after the wastewater sample was injected into the reactor. The only

voltage increase occurred at approximately 253th hour and lasted 5 hours. The maximum voltage 0.29 V was collected at 257th hour. The external resistance were 1000 ohm and COD removal efficiency reached 25.7 %, average voltage and current are 0.047 V and 0.00005 A respectively. A Coulomb efficiency of 19.5% was obtained. The maximum power production was 8.583 *10^{-5} W and the power density was 0.121 W/m^2 (Normalized to anode surface area). The calculating method used here are the same in Appendix D.

Figure 4.3: Power production for sugar sample with COD 5000mg/l



From Figure 4.3, it can be seen that the voltage was monitored for 480 hrs. During the whole process, the voltage production experienced several fluctuations. The maximum voltage occurred at the 242th hour but lasted only 1 hr. The external resistance was 1000

ohm, COD removal efficiency reached 43.60%, average voltage for the whole run was 0.11748 V, the average current was 0.00012 ampere, the coulomb efficiency was 23.34%, maximum power production was 0.0003W and power density was 0.43 W/m^2 (Normalized to the anode surface area). The calculating method used here is the same as Appendix D.

Table 4.4: Summary of electrical production of 3 reactors

Reactor	External Resistance	Peak Voltage	Ave. Voltage	Ave.Current	Coulomb Efficiency	Power Density
Sugar 3000	1000 ohm	0.322V	0.099V	0.000099A	22.67%	0.147 W/m^2
Sugar 4000	1000 ohm	0.299V	0.047V	0.000047A	19.5%	0.121 W/m^2
Sugar 5000	1000 ohm	0.55V	0.117V	0.000117A	23.34%	0.43 W/m^2

Table 4.5: Summary of COD removal of 3 reactors

Reactor	Inlet COD mg/l	Outlet COD mg/l	Removal efficiency
Sugar 3000	3135	1164	62.87%
Sugar 4000	4205	3124	25.7%
Sugar 5000	5170	2916	43.60%

Summary of trial 1:

From the above three graphs, it is obvious to conclude that not all of the reactors had successful start-ups. Contrary to Figure 4.2 and 4.3, the first reactor that contained COD of 3000 mg/l sugar wastewater sample gives the most reasonable curve. The reason why in this second reactor there was a sudden voltage increase from 253th hour is unknown, possible reason maybe circuit connection is not good, in another word the circuit become open circuit at that time. Again, the reason why in Figure 4.3 there were so many "zigzag curves" maybe because of the unstable bacteria activity. From this trial, the result shows

that biofilm that attached on the electrode surface was not robust enough. Also, the water loss problem in reactor (with a COD of 4000mg/l) and (with a COD of 5000mg/l) was more serious than reactor (with a COD of 3000mg/l), so the reactor (with a COD of 3000mg/l) has a more ideal anaerobic environment than other two reactors because the air can enter into reactor easily based on the phenomenon of the water loss. This maybe another reason why figure 4.1 shows a more reasonable curve than Figure 4.2 and 4.3. In order to eliminate the above mentioned problem, in the following trial experiment, wood-clamps and nitrogen gas were used on the reactors to control the anaerobic environment inside reactor and oxygen diffusion velocity to the anode chamber. The reactor would be sandwiched after applying wood clamps and nitrogen gas will be used to flush reactor to eliminate reactor's oxygen.

Trial 2

In this trial, the wastewater used in the reactors involved one set of sugar wastewater samples and one set of thin-stillage wastewater samples. Each set contained three samples that had various inlet CODs at approximately 1000mg/l, 2000 mg/l and 3000 mg/l. The reason for picking these two waste waters is because in the sugar wastewater sample the major constituent is sugar that easily get biodegraded whereas protein is the main constituent in the thin-stillage wastewater sample. In this trial, #7, #8 and #9 reactors contains sugar samples that have COD 1000mg/l, 2000mg/l and 3000mg/l respectively. #10, #11 and #12 reactor contains thin-stillage samples that COD value at1000mg/l, 2000mg/l and 3000 mg/l respectively.

Table 4.6 Open Circuit Voltage(OCV) during inoculation period

	#7	#8	#9	#10	#11	#12
Day1	N/A	N/A	N/A	N/A	N/A	N/A
Day2	N/A	N/A	N/A	N/A	N/A	N/A
Day3	0.19V	0.207V	0.194V	0.212V	0.125V	0.235V
Day4	0.198V	0.230V	0.191V	0.214V	0.122V	0.238V
Day5	0.177V	0.198V	0.206V	0.210V	0.119V	0.226V
Day6	0.176V	0.190V	0.196V	0.211V	0.114V	0.218V
Day7	0.170V	0.185V	0.179V	0.197V	0.115V	0.216V

Table 4.7 COD removal efficiency of these reactors

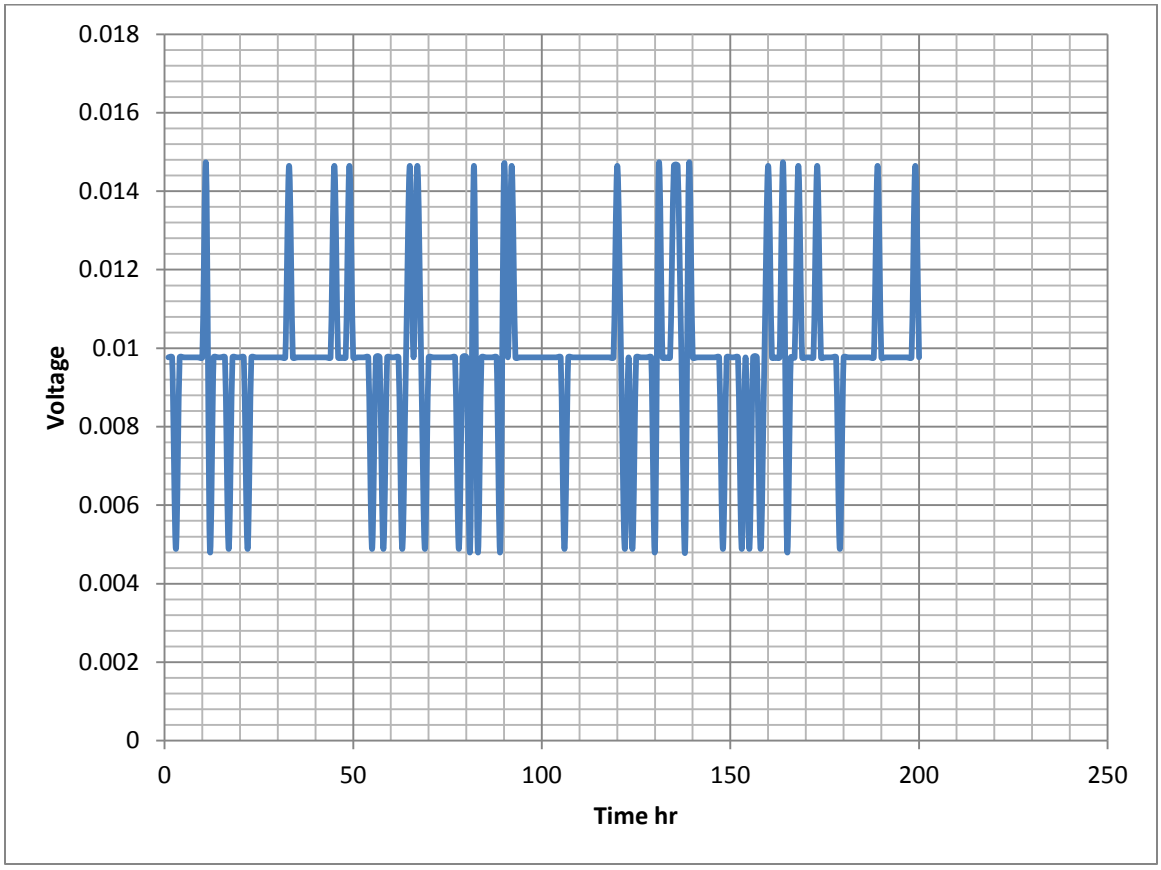
Reactor #	Inlet COD	Outlet COD	Removal Efficiency
#7	1250 mg/l	368 mg/l	70.56 %
#8	2170 mg/l	430 mg/l	80.18 %
#9	3500 mg/l	680 mg/l	80.57 %
#10	1160 mg/l	1130 mg/l	2.6 %
#11	1470 mg/l	784 mg/l	46.67 %
#12	2990 mg/l	2528 mg/l	15.45 %

Summary of Table 4.6 & 4.7 finding:

From Table 4.6, the Open Circuit Voltage remained relatively stable even though it had slightly drop from Day 5. Contrary to the other reactors, reactor 11 retained low OCV from the beginning. The reason for this low OCV here is unclear. Through the 7 day inoculation period, the biofilm been developed on the electrode surface because of the stable OCV. A possible reason may involve the oxygen diffusion through contecting area between air-cathode and reactor even though the wood clamps was used in this trial to hold the reactor closed. Another minor reason maybe the nutrients aand carbon source were used up in the reactor although the solution was changed daily in the reactor. In this trial, the #7, 8 and 9 reactors were run using sugar samples and #10, 11, 12 reactor using

thin-stillage as the substrate. From the Table 4.7, based on the COD removal efficiency, it is easily to conclude that the sugar wastewater samples are much more easily biodegraded than thin-stillage because of the simpler constituents in the sugar wastewater samples.

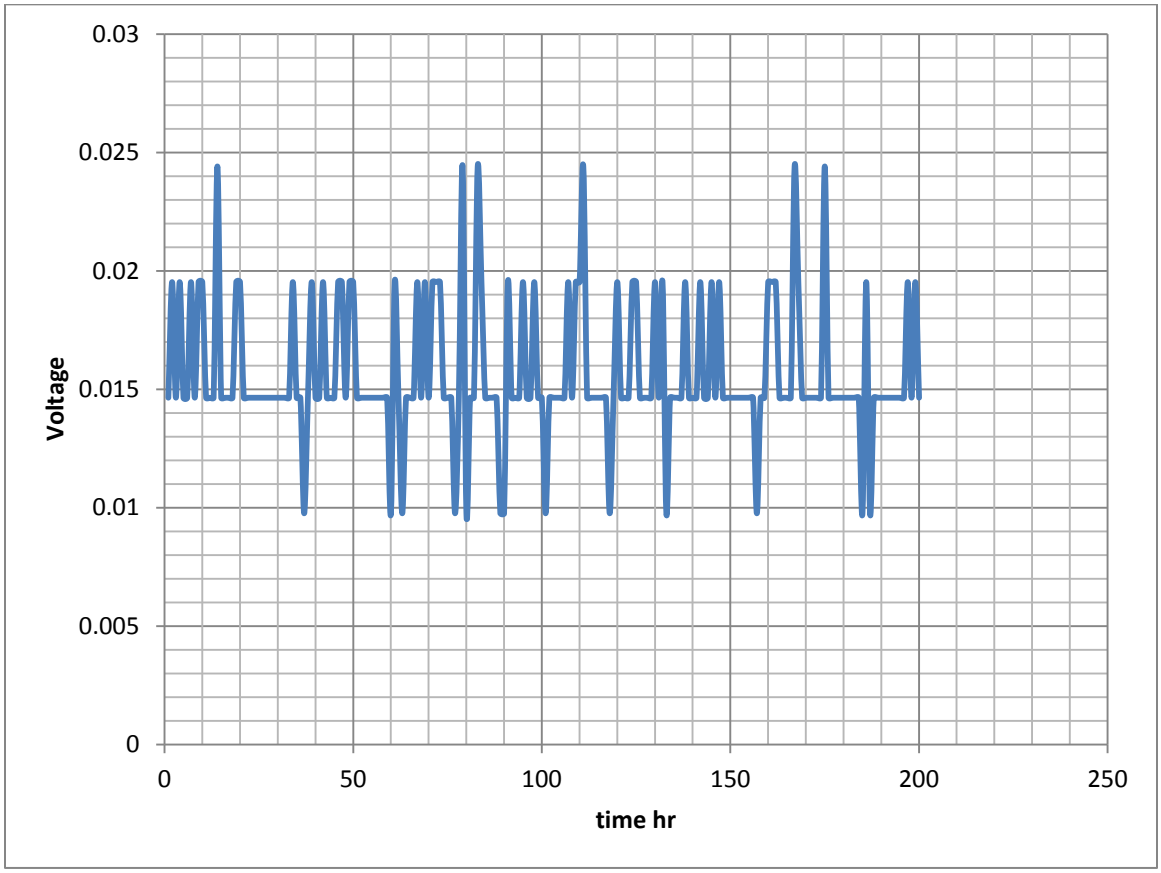
Figure 4.4 Power production for #7 reactor with sugar sample



From Figure 4.4, the voltage generation remained low range even though the COD removal efficiency reached 70%. The reactor was monitored through 200 hrs, Maximum

voltage reached 0.014648 at several time points. The external resistance was 1000Ω and average voltage was 0.0097V. The current produced in this run was $9.7*10^{-6}$A Coulombic efficiency in this run reached 2.1% and maximum power density was $3.04*10^{-4}$ W/m^2.

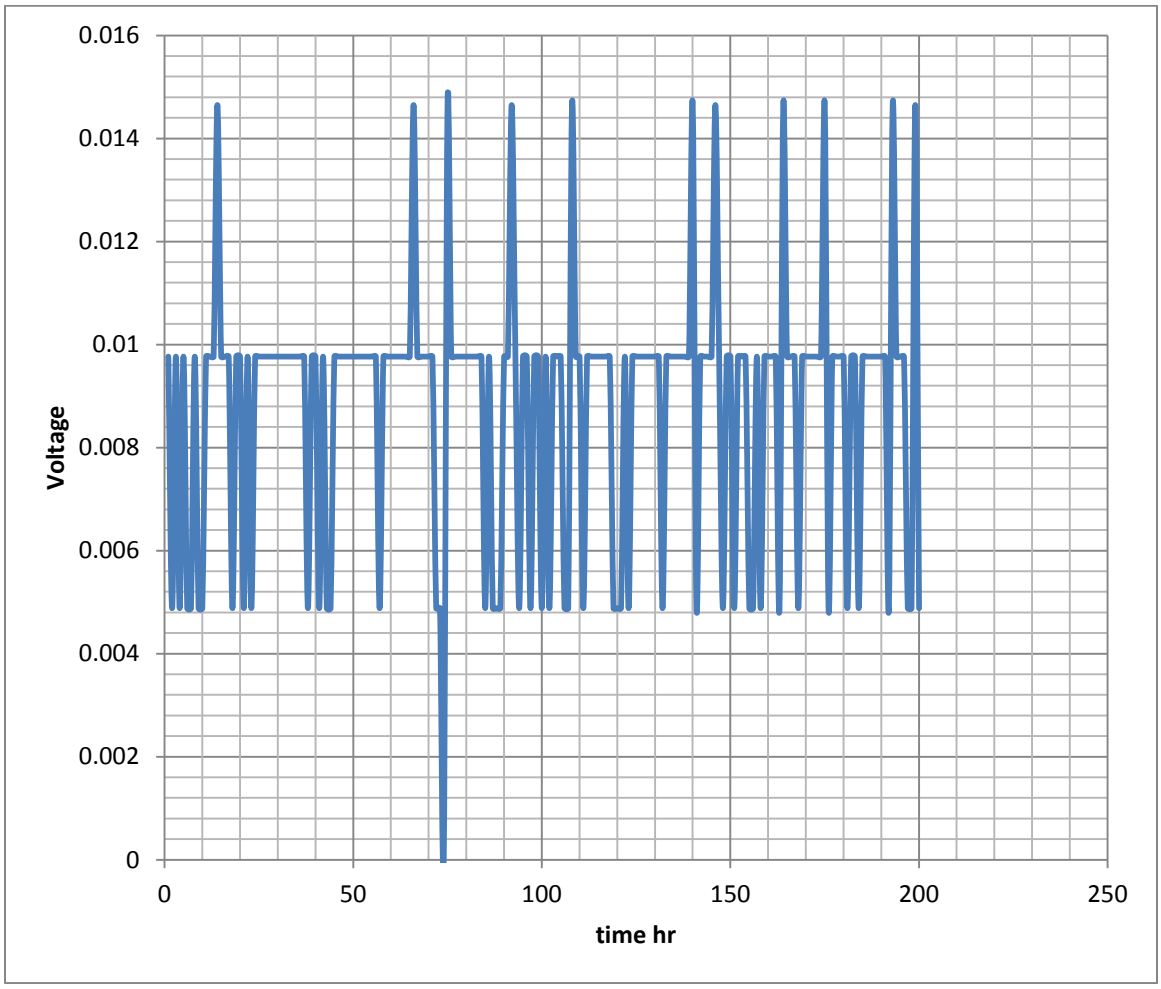
Figure 4.5 Power production for #8 reactor with sugar sample



From Figure 4.5, the reactor was run also for 200hr and the voltage generation was monitored using a data acquisitor. Through this run, the COD removal efficiency reached

80.18%. The maximum voltage produced reached 0.024414V and it happened five times during the whole cycle. The external resistor was 1000Ω and maximum power density reached $8.4366*10^{-4}$ W/m^2. The average voltage was 0.016V and average current was $1.6*10^{-5}$ A. Based on the above results, the coulomb efficiency was 1.7% for reactor #8.

Figure 4.6 Power production for #9 reactor with sugar sample

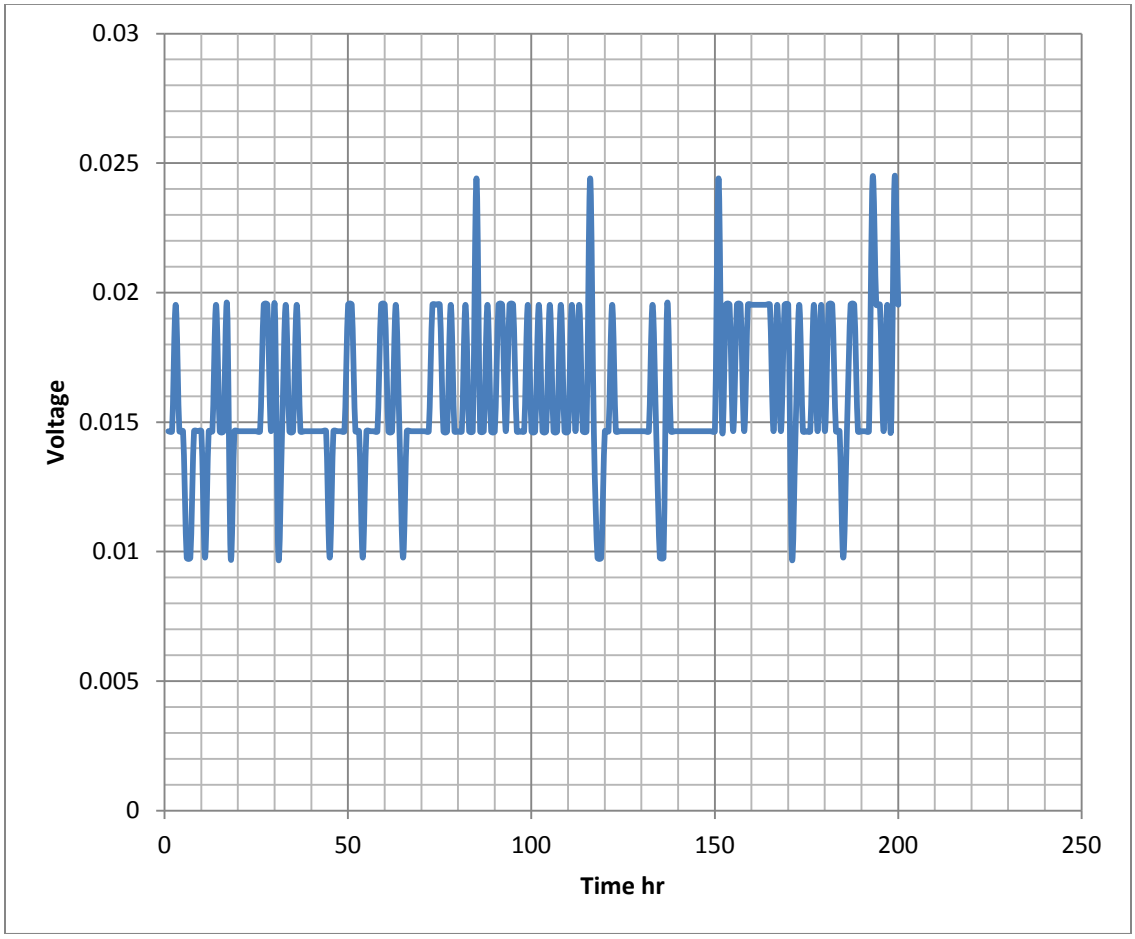


As shown in Figure 4.6, the reactor was run for 200 hr and the final COD removal efficiency reached 80.57%. The maximum voltage generation was 0.015V and external

resistor was 1000Ω and the maximum power density was 3.04* 10^{-4} W/m^2. The average voltage generated in this cycle was 0.0088V and average current is 8.8* 10^{-6} A.

Based on the above result, the coulomb efficiency reached 0.585% in reactor 9.

Figure 4.7 Power production for #10 reactor with thin-stillage sample



Reactor #10 was run for totally 200hr in Figure 4.7 and the COD removal efficiency reached only 2.6%. The maximum voltage generation reached 0.024V, the external resistor was 1000Ω and the maximum power density reached 8.44 * 10^{-4} W/m^2. The

average voltage generation was 0.016V and average current generation is $1.6*10^{-5}$ A. Based on the above results, the coulomb efficiency reached 49.57% in #10 reactor.

Figure 4.8 Power generation for #11 reactor with thin-stillage sample

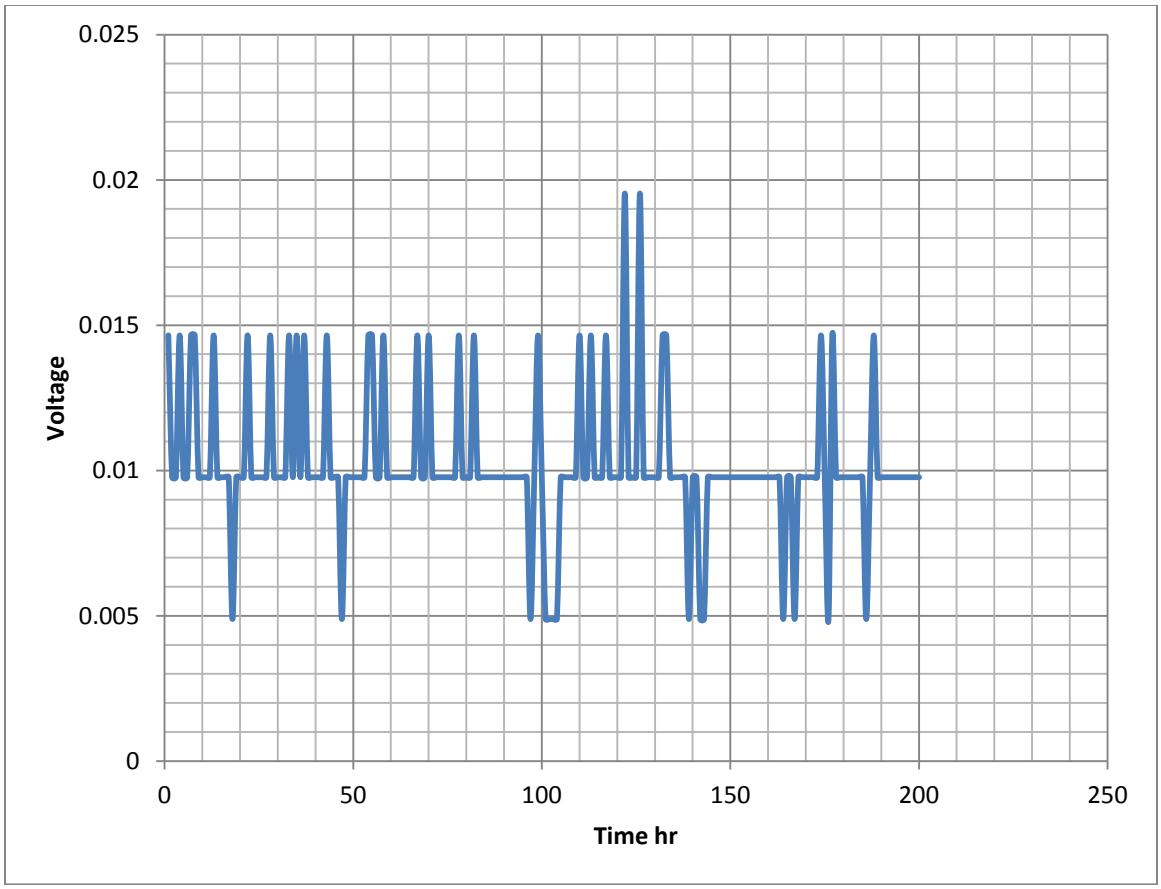
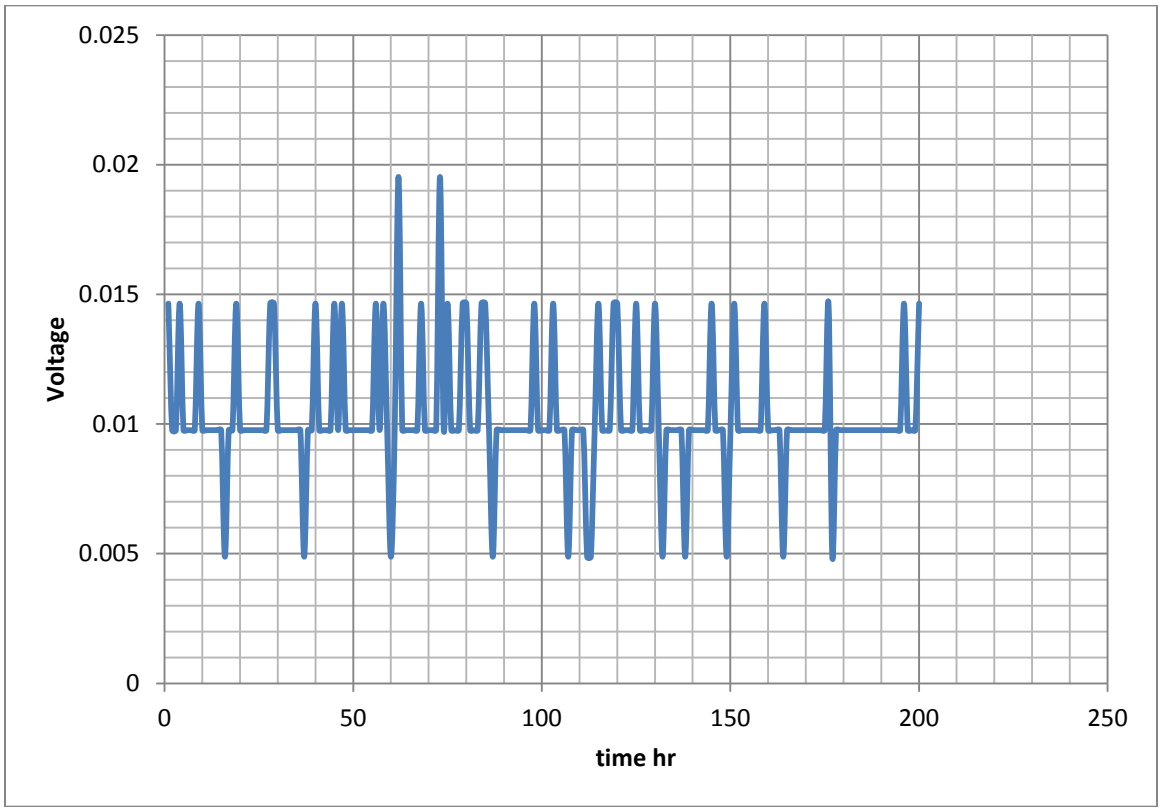


Figure 4.8 showed the reactor was run 200hr and the COD removal efficiency reached 46.67%. The maximum voltage generation was 0.02V. The external ressistor was 1000Ω and maximum power density was $5.399*10^{-4}$ W/m^2. The average voltage generation was 0.01V and average current is $1.0*10^{-5}$A. Based on above result, the

coulomb efficiency reached 1.38% for the #11 reactor.

Figure 4.9 Power production for #12 reactor with thin-stillage sample



From Figure 4.9, it can be seen that the reactor was run 200hr and the COD removal efficiency reached 15.45%. The maximum power generation was 0.02V and maximum power density reaches $5.399 * 10^{-4}$ W/m^2. The external resistor was 1000Ω. The average voltage generation was 0.01V and average current was $1.0*10^{-5}$A. Based on the above results, the coulomb efficiency reached 2.08% for #12 reactor.

Table 4.8 Power generation of trial 2

Reactor	External Resistance	Peak Voltage	Ave. Voltage	Ave. Current	CE	Power Density
#7	1000Ω	0.015	0.0097	$9.70*10^{-6}$	2.1%	$3.04*10^{-4}$
#8	1000Ω	0.024	0.0157	$1.57*10^{-5}$	1.7%	$8.44*10^{-4}$
#9	1000Ω	0.015	0.0088	$8.8*10^{-6}$	0.585%	$3.04*10^{-4}$
#10	1000Ω	0.024	0.0160	$1.60*10^{-5}$	49.57%	$8.44*10^{-4}$
#11	1000Ω	0.020	0.0101	$1.01*10^{-5}$	1.38%	$5.40*10^{-4}$
#12	1000Ω	0.020	0.0103	$1.03*10^{-5}$	2.08%	$5.40*10^{-4}$

Summary of trial 2:

In this trial, wood clamps were used to help control oxygen diffusion and water loss they helped reduce but did not eliminate them. From table 4.6, the open circuit voltage remained relatively stable indicated that biofilm had already grow on the anode surface, it is assumed that for low voltage production in this trial was mainly because the biofilm on the electrode surface was not robust enough. From these six reactors, the maximum OCV was 0.235V in reactor 12. There are several potential reasons for the low open circuit voltage, including the nutrient and carbon source were used up in the reactor and the daily changing of inoculums resulted in some electricity generating bacteria falling from the electrode surface.

From Table 4.7, it is obvious that sugar samples are more easily biodegraded than thin-stillage samples because of sugar constituents. From the table 4.8, the power production was not as good as expected. Actually, the empty reactor also has voltage difference because the internal potential developed in the reactor between electrodes. This value varies between 4.8-6.2mv. Based on table 4.8 results, the reactor generate power even though it was low. Based on above, the one-time inoculation procedure was adopted and the open circuit voltage was measured daily for one week in the next trial.

Trial 3

In this trial, only three reactors were used and only one kind of wastewater---candy manufacture wastewater . The basic idea in this trial is that using various air-cathode surface areas would impact the maximum power production and time consumption relationship. Based on the above idea, only one kind wastewater with the constant inlet COD was used for these three reactors. Here only one-time injection was used during the inoculation period in case of biofilm falling by adopting changing inoculums daily method. In this trial, all of three reactors have sugar sample that has inlet COD level at around 2000mg/l. The #13, #14 and #15 reactors have air-cathode surface diameter as 2cm, 3cm and 4cm respectively.

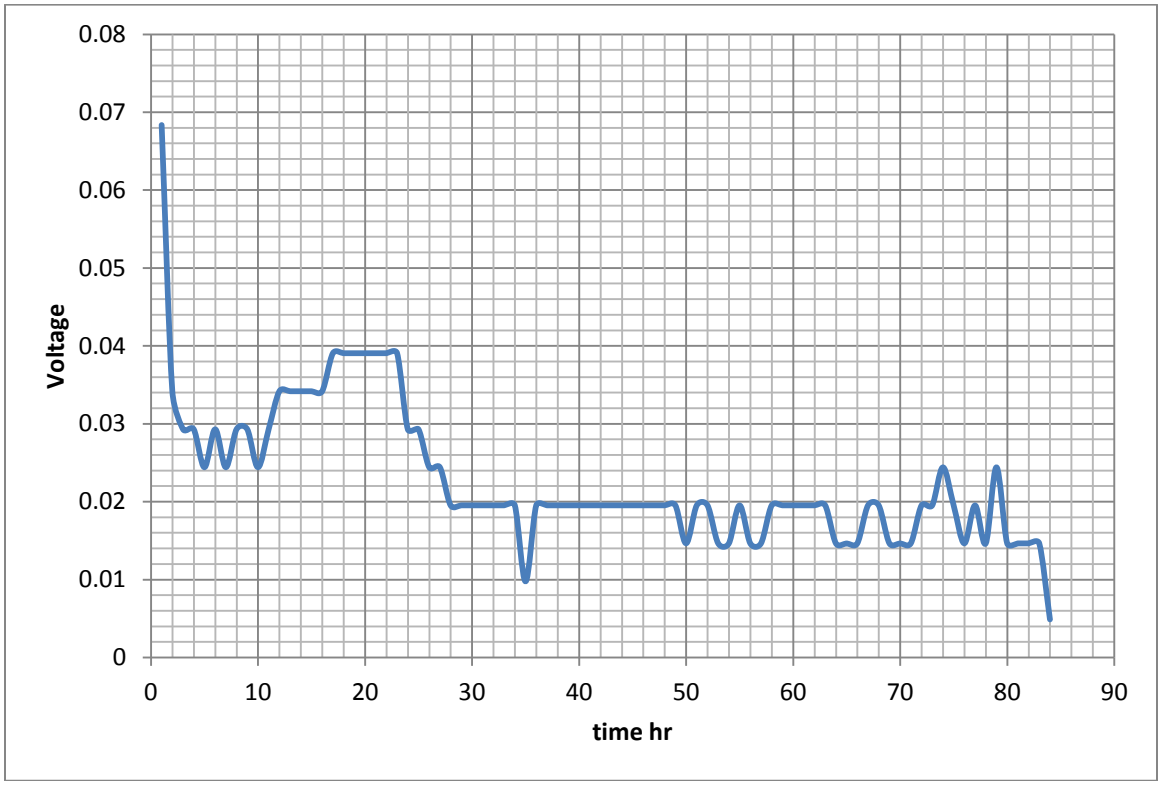
Table 4.9 Open Circuit Voltage(OCV) during inoculation period in trial 3

time	#13	#14	#15
Day1	0.177V	0.159V	0.111V
Day2	0.323V	0.201V	0.099V
Day3	0.178V	0.186V	0.095V
Day4	0.172V	0.183V	0.098V
Day5	0.165V	0.181V	0.097V
Day6	0.161V	0.184V	0.106V
Day7	0.162V	0.192V	0.108V

Table 4.10 COD removal results

Reactor #	Inlet COD	Outlet COD	Removal Efficiency
#13	2482mg/l	1402mg/l	43.51%
#14	2592mg/l	1338mg/l	48.38%
#15	2280mg/l	1636mg/l	28.25%

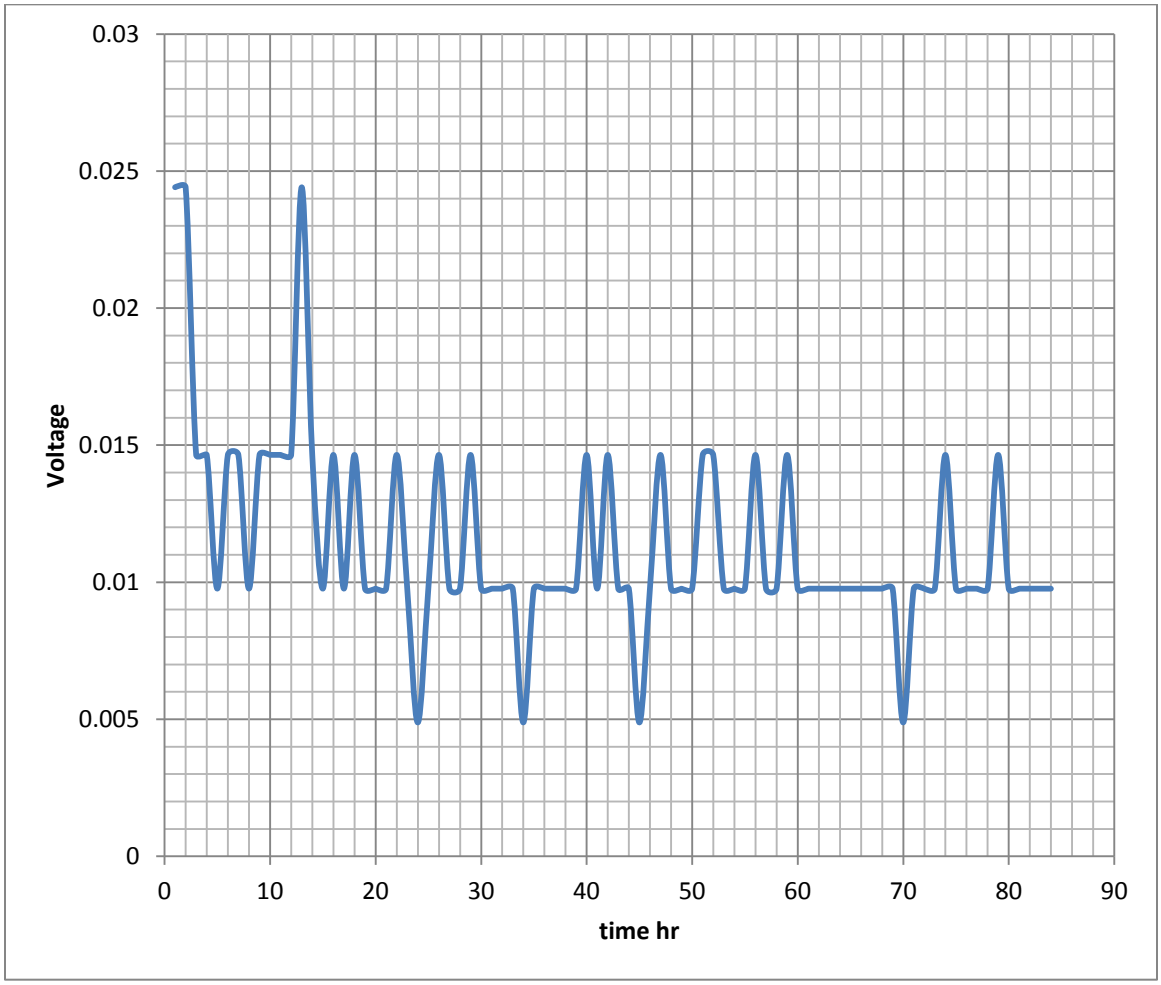
Figure 4.10 Power production for #13 reactor with sugar wastewater sample



From Figure 4.10, it gives the results for the 2cm cathode diameter reactor, the reactor

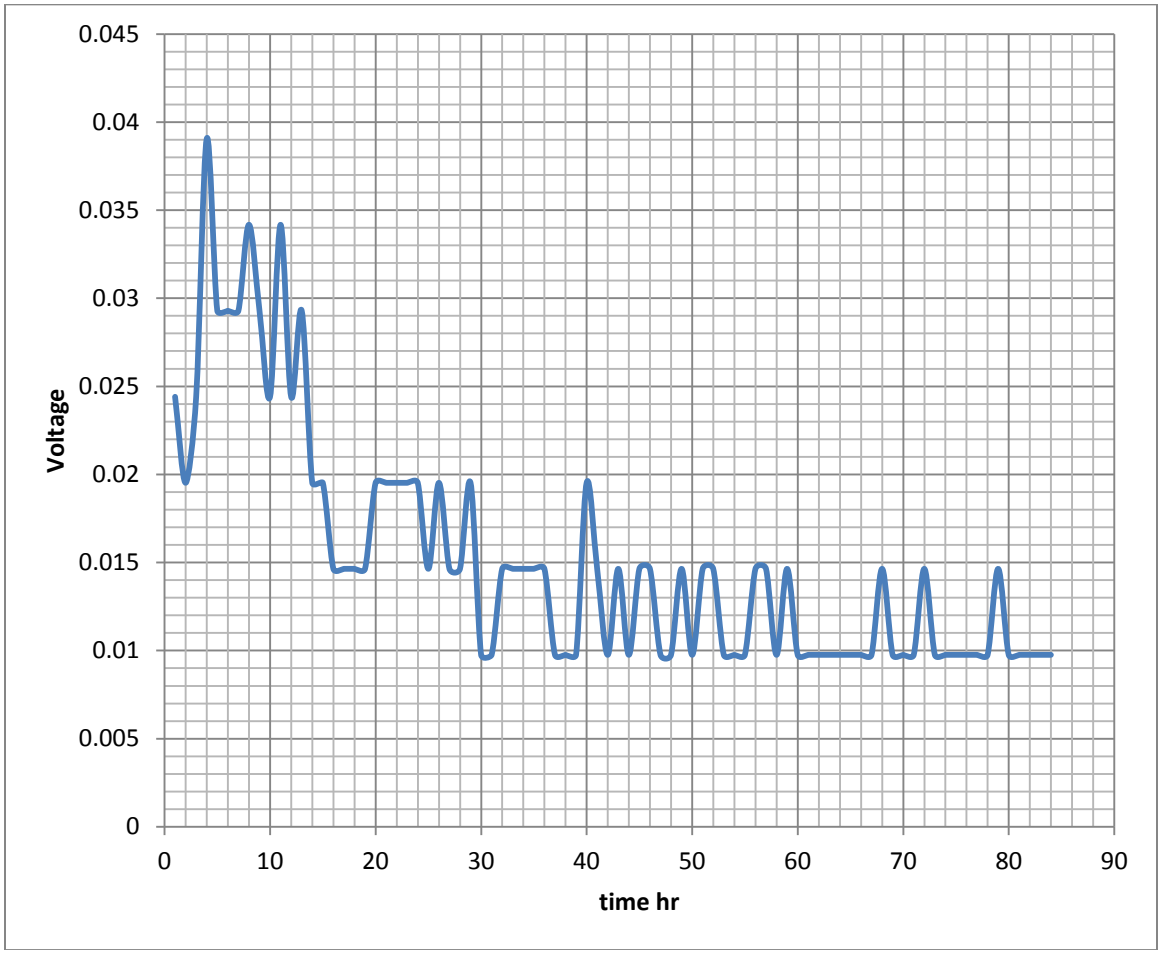
was run for about 84hr and inlet COD and outlet COD were 2482mg/l and 1402 mg/l respectively. The COD removal efficiency was 43.51%. The maximum voltage generation was 0.04Vand maximum power density was $4.87*10^{-3}$ W/m^2. The external resistance was 1000Ω and average voltage production was 0.023V and average current was $2.28*10^{-5}$A. Based on the above results, the coulombs efficiency was 1.68%.

Figure 4.11 Power production for #14 reactor with sugar wastewater sample



From Figure 4.11, it gives results for reactor for the 3cm cathode diameter reactor and the reactor was run for about 84hr and the inlet COD was 2592mg/l and outlet COD was 1338mg/l. The COD removal efficiency was 48.38%. The maximum voltage production is 0.024V and maximum power density was $8.44*10^{-4}$ W/m^2 . The external resistor used was 1000Ω. The average voltage was 0.011V and the average current was $1.1*10^{-5}$ A. Based on the above results, the coulombs efficiency was 0.71%.

Figure 4.12 Power production for #15 reactor with sugar samples



From the above Figure 4.12, it gives results for 4cm cathode diameter reactor and the

experiment was run for about 84hr and The inlet and outlet COD were 2280mg/l and 1636mg/l respectively. The maximum voltage production was 0.04V and maximum power density was $1.21*10^{-3}$ W/m^2. The COD removal efficiency was 28.25% and external resistor was 1000Ω. The average voltage production was 0.015V and average current was $1.53*10^{-5}$A. Based on the above results, the coulombs efficiency was 1.86%.

Table 4.11 Summary of power production in trial 3

Reactor	Resistor	Peak Voltage	Average Voltage	Average Current	Coulombs Efficiency	Power Density
#13	1000Ω	0.039062V	0.022844V	$2.2844*10^{-5}$A	1.68%	$4.87*10^{-3}$ W/m^2
#14	1000Ω	0.024414V	0.0113933V	$1.13933*10^{-5}$A	0.71%	$8.44*10^{-4}$ W/m^2
#15	1000Ω	0.039062V	0.0152878V	$1.5287*10^{-5}$A	1.86%	$1.21*10^{-3}$ W/m^2

Summary for trial 3:

From the table 4.9, the open circuit voltage was still relatively stable even though the open circuit voltage was not quite high, The reasons for this were discussed in the trial 2 summary. It maybe the nutrients were used up during the inoculation period or the available carbon source is not sufficient, so an external carbon source maybe needed in the inoculums. However, the contrast between power production figures, trial 3 power production was better than trial 2 even though the peak numbers are close. The better performance for trial 3 maybe the result of good biofilm growth on the anode surface and that one-time injecting of inoculums maybe helpful for biofilm growth. The COD removal efficiency in this trial is not as high as trial 2. The reason for this remains unclear. However in this trial, 50% COD removal efficiency gives the evidence that the

bacteria in the reactors are still workable. It is hard to compare Figure 4.10, 4.11 & 4.12 directly because of the irregular curve. But from the above 3 figures, the conversion from chemical energy in the organic matters into electrical energy did occur during the 84hr-runs.

Trial 4:

In this trial, both sugar and thin-stillage samples were tested and all of the reactor had same air-cathode area, $7.065*10^{-4}$ m^2. However in this trial, the inoculums was from the Stillwater Wastewater Treatment Plant-- Primary Clarifier Effluent rather than the digestors samples used in the previous trials. The inoculation period was also one-week but adopted one-time injection on the first day. The OCV was monitored daily during the inoculation period. Based on the low OCV value in the previous trials, the carbon source maybe not enough for bacteria, so in this trial's inoculation period sodium acetate was added into inoculums as the external carbon. The inoculums dissolved oxygen was controlled 0.9 mg/l by purging the solutions with nitrogen.

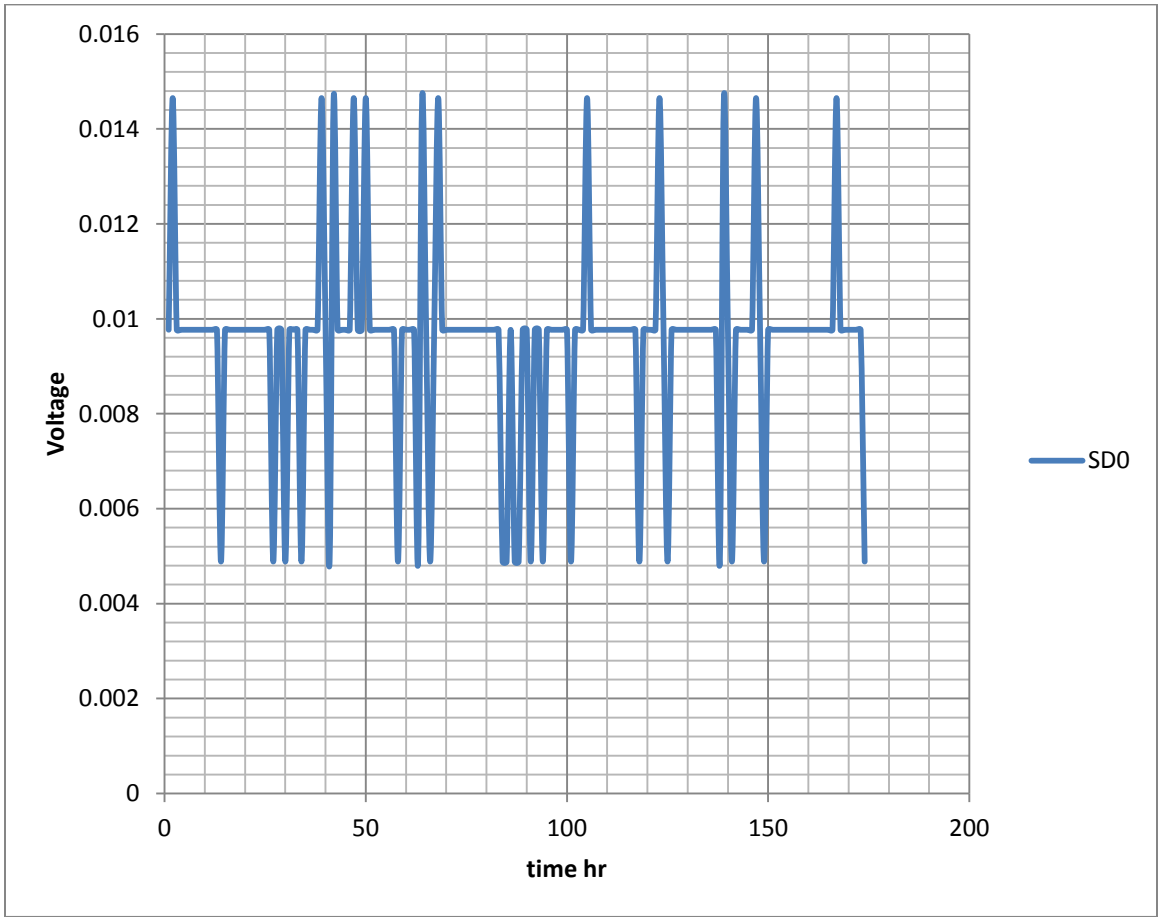
Table 4.12 Open Circuit Voltage (OCV) during inoculation period in trial 4

	#7	#8	#9	#10	#11	#12
Day1	0.164V	0.141V	0.247V	0.159V	0.168V	0.160V
Day2	0.187V	0.133V	0.223V	0.147V	0.185V	0.147V
Day3	0.166V	0.139V	0.253V	0.150V	0.195V	0.150V
Day4	0.168V	0.137V	0.250V	0.150V	0.197V	0.152V
Day5	0.182V	0.135V	0.244V	0.148V	0.197V	0.153V
Day6	0.184V	0.136V	0.149V	0.182V	0.197V	0.173V
Day7	0.166V	0.137V	0.173V	0.195V	0.225V	0.184V

Table 4.13 COD removal result

Reactor	Inlet COD	Outlet COD	Removal Efficiency
#7	1650mg/l	208mg/l	87.40%
#8	2290mg/l	316mg/l	86.20%
#9	3230mg/l	520mg/l	83.90%
#10	1000mg/l	718mg/l	28.2%
#11	1510mg/l	1262mg/l	16.42%
#12	1850mg/l	N/A	N/A

Figure 4.13 Power Production for #7 with sugar samples



From the Figure 4.13, the reactor was operated for a total 174 hours. The COD removal efficiency was 87.40% during this period. The average voltage and current were 0.01 V and $1.0*10^{-5}$ A respectively. The external resistor was 1000Ω. The maximum voltage was 0.015V and maximum power was $2.1456*10^{-7}$ Watts. Based on the above results, the maximum power density is $3.037*10^{-4}$ W/m^2 in this running cycle.

Figure 4.14 Power production for #8 reactor with sugar samples

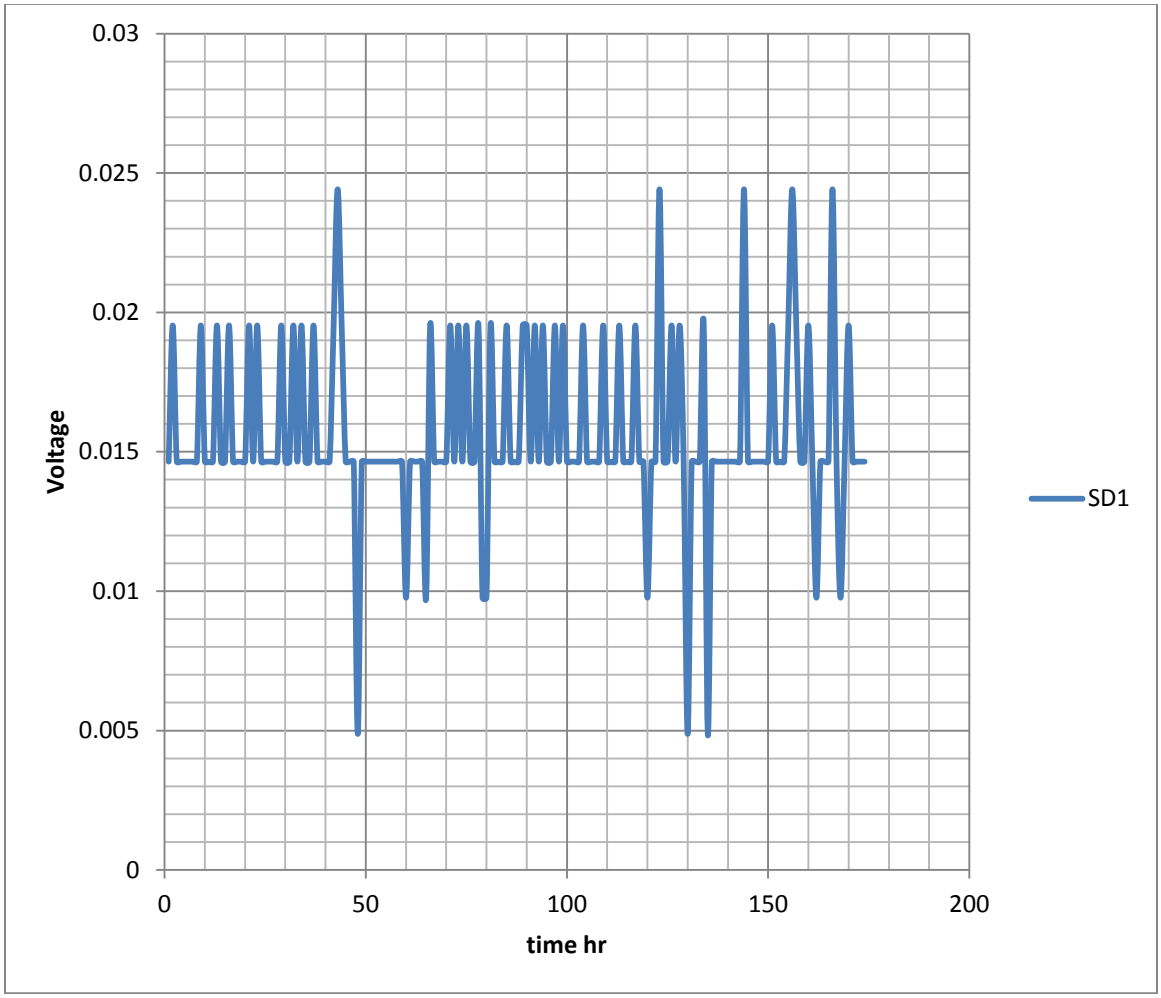
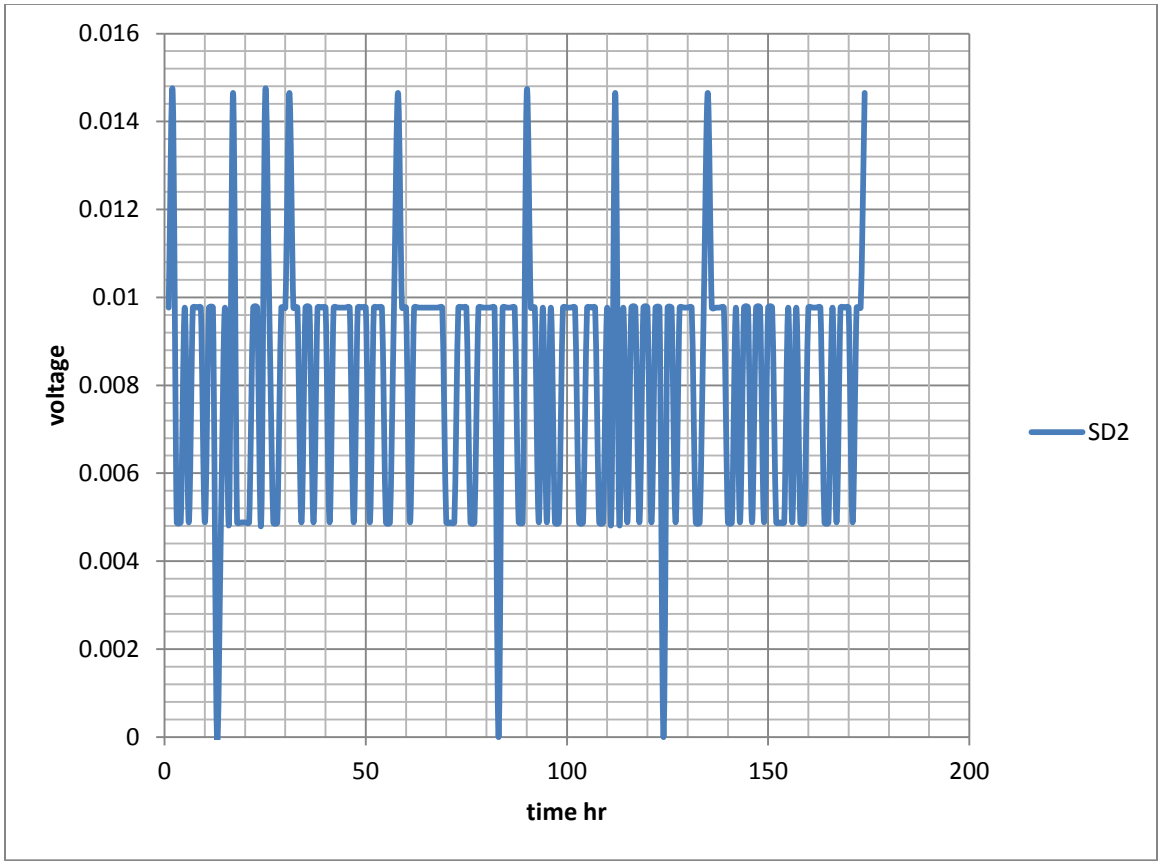


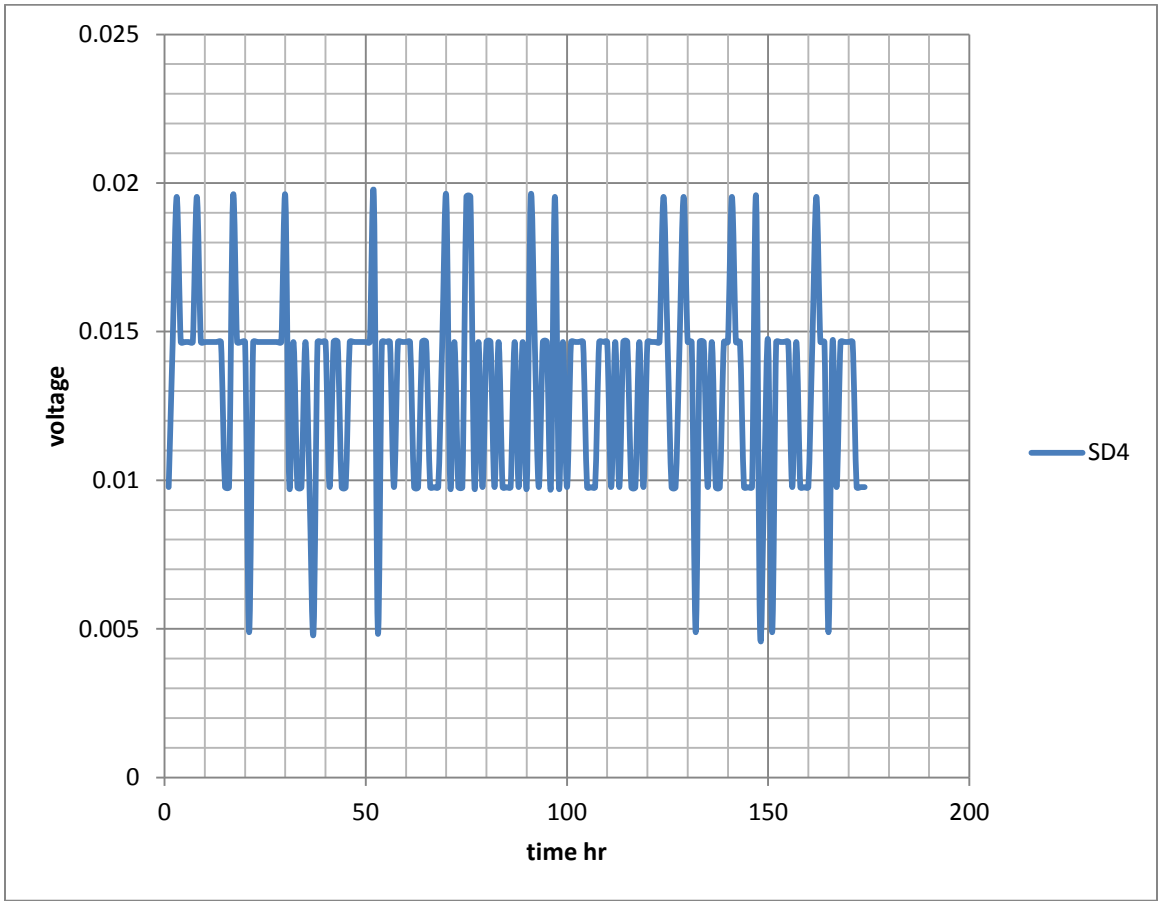
Figure 4.14 shows the reactor was run for 174 hr. The inlet and outlet COD were 2290mg/l and 316mg/l respectively and the COD removal efficiency was 86.20%. The maximum voltage and power were 0.024 V and 6.0 $*10^{-7}$ Watts. The external resistor was 1000Ω. The average voltage and current were 0.016V and 1.6 $*10^{-5}$ A. Based on the above results, the power density was $8.44*10^{-4}$ W/m^2.

Figure 4.15 Power production for #9 reactor with sugar samples



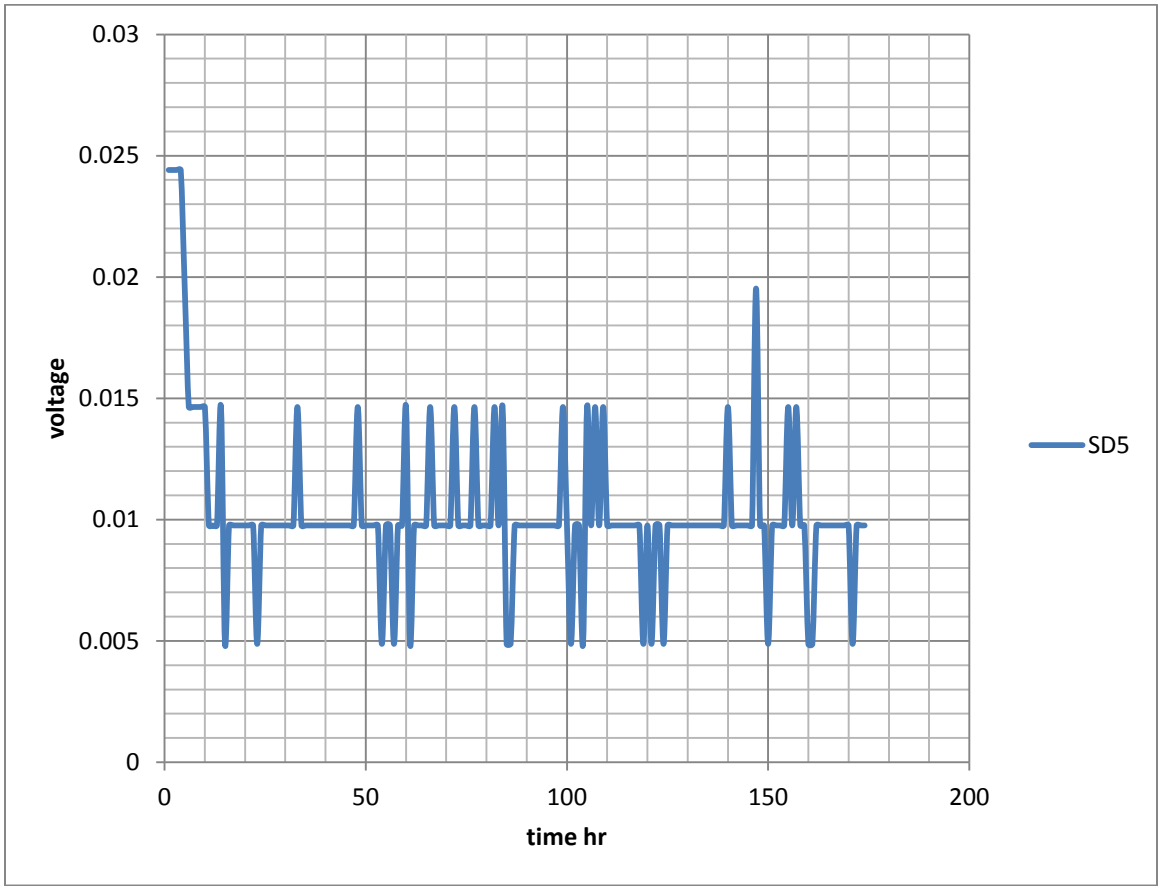
The reactor shown in Figure 4.15 was run for 174 hrs. The inlet and outlet COD were 3230mg/l and 520mg/l respectively. And COD removal efficiency was 83.90%. The maximum voltage and power were 0.015 V and $2.15*10^{-7}$ Watts respectively. The external resistor was 1000Ω. The average voltage and current were 0.0082V and $8.19*10^{-6}$ A respectively. Based on the above results, the power density is $3.037*10^{-4}$ W/m^2

Figure 4.16 Power production for #10 with thin-stillage samples



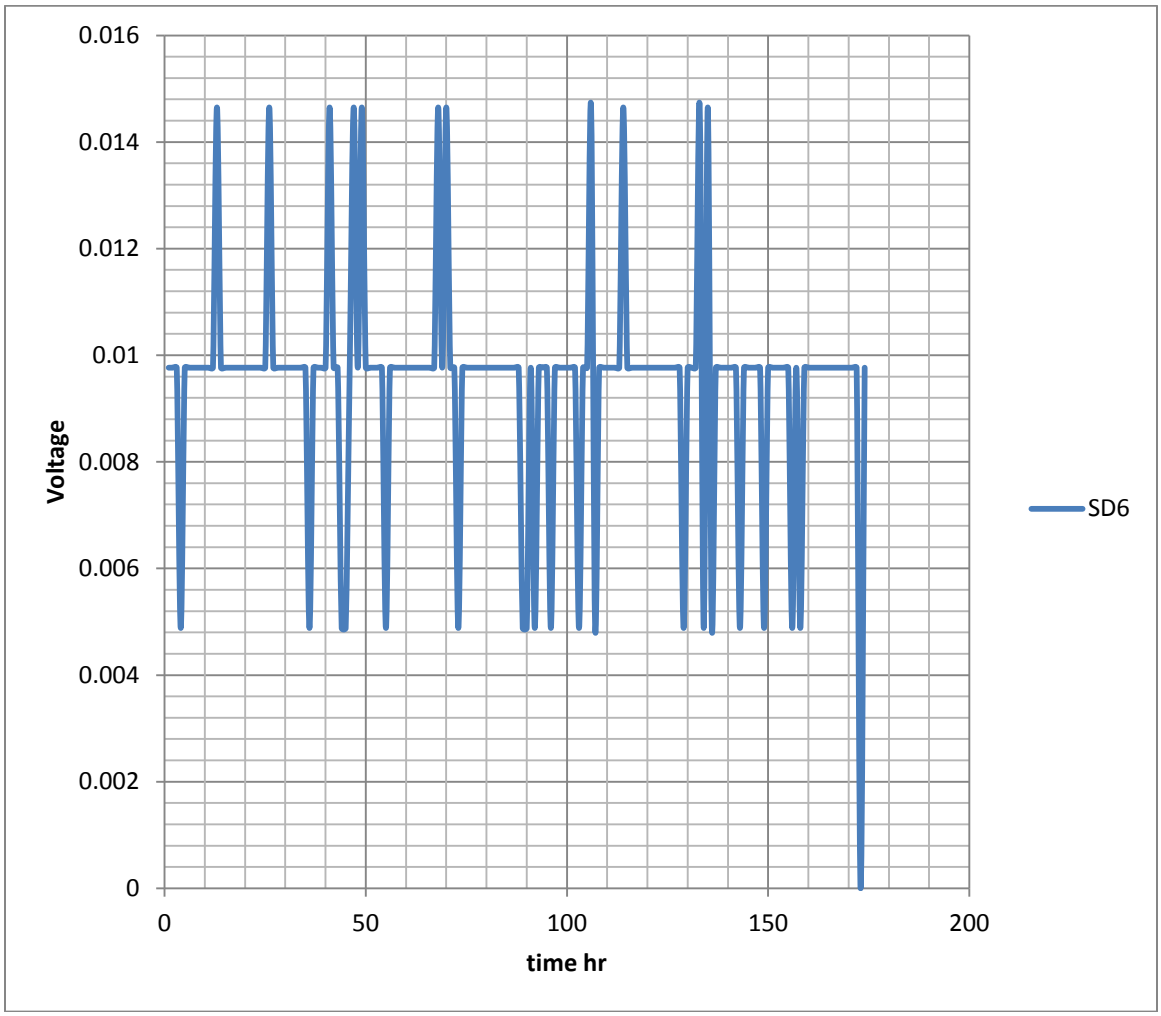
From Figure 4.16, it can be seen that the reactor was also run 174hr. The inlet and outlet COD were 1000mg/l and 718mg/l respectively, the COD removal efficiency was 28.2%. The maximum voltage and power were 0.02V and $3.8*10^{-7}$ Watts. The external resistance was 1000Ω. The average voltage and current were 0.013V and $1.3*10^{-5}$ A respectively. Based on the above results, the power density was $5.4*10^{-4}$ W/m^2.

Figure 4.17 Power production for #11 reactor with thin-stillage sample



As shown in Figure 4.17, the reactor was run for 174 hr. The inlet and outlet COD were 1510mg/l and 1262mg/l respectively and the COD removal efficiency was 16.42%. The maximum voltage and power were 0.02V and $3.8*10^{-7}$ W. The external resistor was 1000Ω . The average voltage and current were 0.01V and $1.0*10^{-5}$ A. Based on the above results, the power density was $5.40*10^{-4}$ W/m^2.

Figure 4.18 Power production for #12 reactor with thin-stillage samples



The reactor results shown in Figure 4.18 indicate it was operated for 174hrs. The inlet

COD was 1850mg/l and outlet COD was unknown. The maximum voltage and power was 0.015V and $2.15*10^{-7}$ Watts respectively. The external resistor was 1000Ω. The average voltage and current were 0.0095V and $9.5*10^{-6}$A respectively. Based on the above results, the power density was $3.04*10^{-4}$ W/m^2.

Table 4.14 Summary of power production in trial 4

Reactor	Resistor	Maximum Voltage	Average. Voltage	Average Current	Coulombic Efficiency	Power Density
#7	1000 Ω	0.015V	0.0095V	$9.51*10^{-6}$A	1.08%	$3.04*10^{-4}$W/m^2
#8	1000 Ω	0.024V	0.0156V	$1.56*10^{-5}$A	1.28%	$8.44*10^{-4}$W/m^2
#9	1000 Ω	0.015V	0.0082V	$8.19*10^{-6}$A	0.5%	$3.04*10^{-4}$W/m^2
#10	1000 Ω	0.020V	0.0131V	$1.31*10^{-5}$A	3.77%	$5.40*10^{-4}$ W/m^2
#11	1000 Ω	0.020V	0.0104V	$1.04*10^{-5}$A	3.39%	$5.40*10^{-4}$W/m^2
#12	1000 Ω	0.015V	0.0095V	$9.49*10^{-6}$A	N/A	$3.04*10^{-4}$W/m^2

Summary of trial 4:

In this trial, the bacteria source came from Stillwater Wastewater Plant primary clarifier effluent rather than the digestor as was used in the previous trials. Ten ml of 300mg/l sodium acetate was added in inoculums as external carbon source. In the previous trials, the bacteria used only carbon that already existed in the digestors samples. Compare table 4.6 with table 4.9, the bacteria from the different source and extra carbon source did not make a big difference in terms of OCV in the inoculation period. From the table 4.10, generally speaking, the sugar wastewater samples were more easily degraded than thin-stillage. For example, the sugar samples COD removal efficiency remained at 85% whereas the thin-stillage ones just reach 30%. The reason is because the sugar wastewater

samples contain more simple, easy-degraded substances. Reactor 12 outlet COD was over spectrophotometer measuring range (0-1500 mg/l) even though the inlet COD was just 1850mg/l. The reason for this is unknown. Based on this, that is also why in Table 4.14 the coulombic efficiency is not available. From Table 4.11, the power was produced even though it was not ideal , the electrical results are quite similar to the previous trials.

Table 4.15 Comparison of findings in this study with others

	COD removal efficiency	CE	Power Density
Liu (2004)	55%	28%	262 mW/m^2
Oh.	65%	71%	213 mW/m^2
Min (2005)	Not mentioned	55%	38 mW/m^2
Sugar in this study	87.40%	23.34%	147 mW/m^2
Thin-stillage in this study	46.67%	49.57%	0.84 mW/m^2

Summary of Table 4.15

From table 4.15, it can be seen that the sugar sample's COD removal efficiency remains higher than other samples. As discussed above, the reason for this is because the sugar sample contains more simple constituents than others. For instance, in Liu's experiment, the domestic wastewater was used as wastewater samples for bacteria. Thin-stillage sample's coulombic efficiency is higher than others except Oh's experiment. The CE reached 49.57% means that in this reactor, most of organic matters that was biodegraded based on the electrons-generating bacteria. For the power density parameter, the number in this study remains lower than others, especially thin-stillage samples. The reason for this maybe because of the poor reactor's starting up or reactor's tiny leakages for oxygen

diffusion.

CHAPTER V

Conclusion

The concept of the MFC and its working principles are introduced in this study. From this study's four trials, it not hard to conclude that some types of bacteria indeed can produce electrons through their usual metabolism. By analyzing the four trials results, the voltage production is determined by several factors. Anaerobic conditions can affected the electricity-generating bacteria performance, even though COD removal efficiency was good. Thus the voltage production was low. The condition of biofilm growth also can affect power production, for instance, the number of bacteria on the electrode and how robust the biofilm.

In these four trials, the reactor with the sugar COD of 3000 mg/l gave the best results compare to other samples. Obtaining a peak voltage production reached 0.32 V. The other reactors also produced the power even though it was quite low. The reason for this is not clear. It maybe because of excessive oxygen diffusion or a limited biofilm layer. Also from these four trials, it is clear that the candy manufacture wastewater samples are more easily biodegraded rather than thin-stillage because of its simple constituents.

To sum up, microbial fuel cells (MFC) showed remarkable removal efficiency for industrial wastewater samples and it could be a novel method for treating wastewater in the future because of its low cost even though current research scales remains on the laboratory level. A suggestion for the future research is test a two-chambers reactor because it can provide an ideal anaerobic environment for the biofilm formation on the electrode. Also, the future research can focus on various MFC-based technology such as Microbial Desalination Cell(MDC) or apply MFC technology to bio-electrochemical removal of nitrogen.

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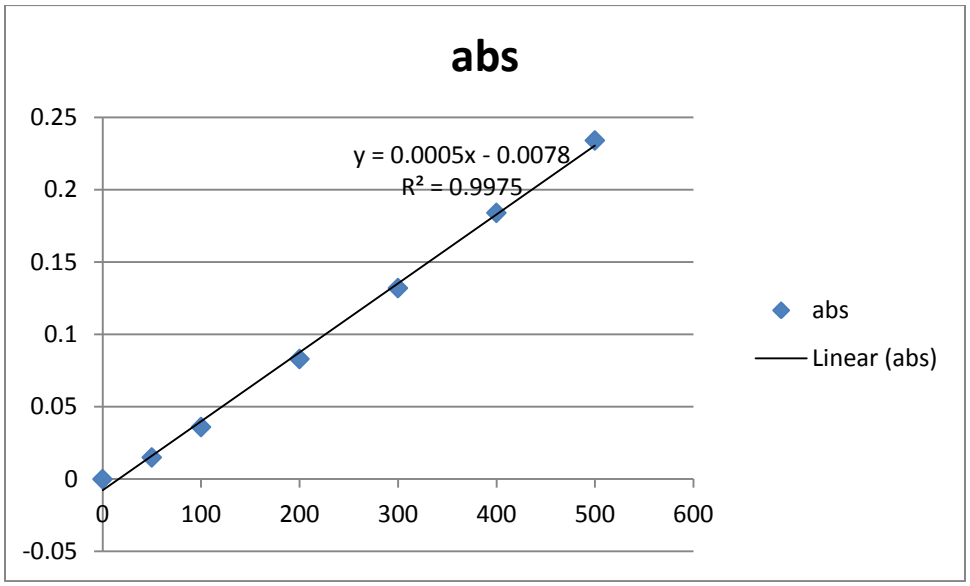
APPPENDIX A

Determination of industrial wastewater COD

Low-range

COD mg/l	500	400	300	200	100	50	0
Absorbance	0.234	0.184	0.132	0.083	0.036	0.015	0



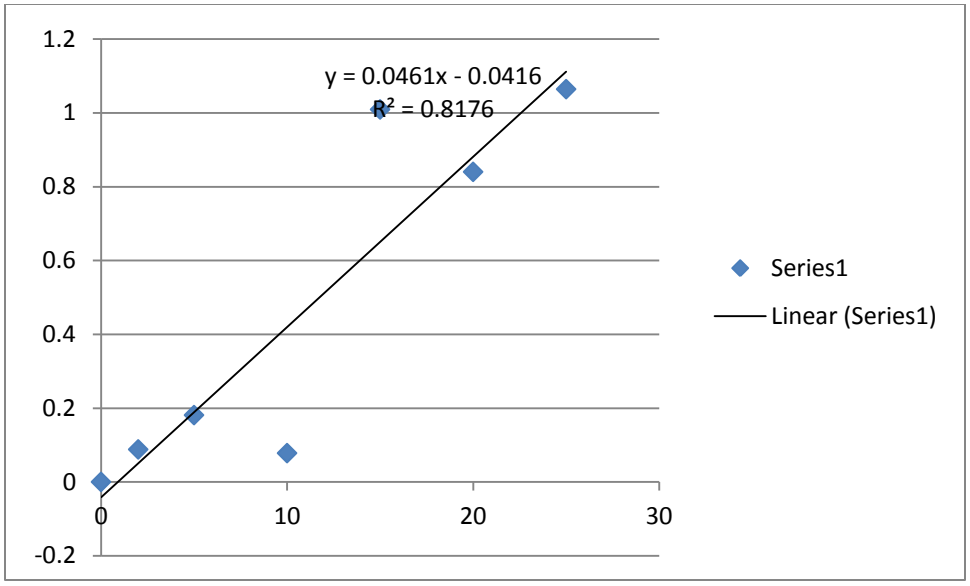
Thin-stillage:	1/100	1/120	1/150	1/180	1/200
Absorbance:	0.469	0.422	0.456	0.268	0.245
COD mg/l:	95360	103152	139140	99288	101120

Sugar:	1/100	1/120	1/150	1/180	1/200
Absorbance:	0.194	0.165	0.128	0.089	0.087
COD mg/l:	40360	41472	40740	34848	37920

Appendix B

Determination of Phosphate Concentration in Wastewater

Conc. PO_4 mg/l	25	20	15	10	5	2	0
Absorbance	1.064	0.84	1.009	0.078	0.181	0.088	0



Thin-stillage	1:120	1:150	1:180	1:200
Absorbance:	0.583	0.527	0.335	0.288
Phosphate:	1626mg/l	1850mg/l	1470mg/l	1430mg/l
Sugar	1:120	1:150	1:180	1:200
Absorbance:	0.022	0.007	0.01	0.015
Phosphate:	165mg/l	158mg/l	201mg/l	246mg/l

Appendix C

Raw BOD testing data

Thin-stillage	Day1	2	3	4	5	6	7	8	9
	10	11	12	13	14	15	16	17	18
	19	20	21						
1:10 000	6.77 mg/l	5.59mg/l	4.41mg/l	3.35mg/l	2.35mg/l	1.49mg/l	1.01mg/l (7.25)	6.28mg/l	4.93mg/l
	4.15mg/l	3.62mg/l	3.19mg/l	2.98mg/l	2.86mg/l	2.68mg/l	2.54mg/l	2.47mg/l	2.37mg/l
	2.19mg/l	2.04mg/l	2.03mg/l						
1:12 000	6.68mg/l	4.65mg/l	3.55mg/l	2.57mg/l	1.55mg/l	0.58mg/l	0.19mg/l (9.12mg/l)	7.79mg/l	6.46mg/l
	5.55mg/l	4.79mg/l	4.14mg/l	3.87mg/l	3.72mg/l	3.58mg/l	3.44mg/l	3.12mg/l	2.84mg/l
	2.64mg/l	2.45mg/l	2.38mg/l						
1:20 000	6.68mg/l	6.00mg/l	5.52mg/l	4.78mg/l	4.20mg/l	3.67mg/l	3.31mg/l	2.73mg/l	2.06mg/l
	1.54mg/l	1.10mg/l	0.75mg/l (6.81mg/l)	6.37mg/l	6.18mg/l	5.95mg/l	5.80mg/l	5.66mg/l	5.42mg/l
	5.3	5.19mg/l	5.16mg/l						

	2mg/l								
Thin-stillage (BOD Water)									
1:10000	8.73mg/l	6.14mg/l	4.02mg/l	2.74mg/l	2.21mg/l	1.89mg/l	1.61mg/l	1.34mg/l	1.24mg/l
	0.93mg/l	0.84mg/l							
1:12000	8.71mg/l	6.94 mg/l	5.12 mg/l	4.27mg/l	3.49mg/l	3.18mg/l	2.94mg/l	2.71mg/l	2.61mg/l
	2.41mg/l	2.32mg/l							
1:20000	8.74mg/l	7.69mg/l	6.59mg/l	5.90mg/l	5.55mg/l	5.42mg/l	5.23mg/l	5.06mg/l	4.97mg/l
	4.86mg/l	4.78mg/l							
Thin-stillage (BOD W+Sludge)									
1:10000	9.11mg/l	5.20mg/l	2.67mg/l	0.94mg/l (9.56mg/l)	7.76mg/l	6.23mg/l	5.28mg/l	4.16mg/l	3.12mg/l
	2.2	1.49mg/l	7.47mg/l	6.66mg/l	5.8	4.96m	N/A	4.32mg/l	3.5

	6mg/l	(8.21mg/l)			3mg/l	g/l			6mg/l
	2.95mg/l	N/A	2.20mg/l						
1:12000	9.08mg/l	5.44mg/l	3.04mg/l	1.56mg/l (8.32mg/l)	6.82mg/l	5.51mg/l	4.53mg/l	3.59mg/l	2.65mg/l
	1.86mg/l	1.17mg/l (7.13mg/l)	6.51mg/l	5.83mg/l	5.21mg/l	4.50mg/l	N/A	3.93mg/l	3.43mg/l
	2.91mg/l	N/A	2.27mg/l						
1:20000	9.08mg/l	6.32mg/l	4.48mg/l	3.12mg/l	2.08mg/l	1.23mg/l(9.54 mg/l)	8.59mg/l	7.49mg/l	6.65mg/l
	5.87mg/l	5.16mg/l	4.63mg/l	4.12mg/l	3.58mg/l	3.05mg/l	N/A	2.37mg/l	1.87mg/l
	1.38mg/l	N/A	0.75mg/l						
Sugar(BOD Water)									
1:10000	8.76mg/l	8.59mg/l	6.51mg/l	5.89mg/l	5.42mg/l	5.20mg/l	5.09mg/l	4.96mg/l	4.93mg/l
	4.60mg/l	4.40mg/l							
1:12000	8.77mg/l	8.61mg/l	6.79mg/l	6.21mg/l	5.82mg/l	5.65mg/l	5.60mg/l	5.51mg/l	5.46mg/l
	5.32mg/l	5.22mg/l							

1:20 000	8.80mg/l	8.56mg/l	7.41mg/l	6.94mg/l	6.65mg/l	6.58mg/l	6.56mg/l	6.52mg/l	6.47mg/l
	6.35mg/l	6.33mg/l							
Sugar 1:10 000 (BOD Water+S)									
1:10 000	9.17mg/l	7.31mg/l	5.39mg/l	4.18mg/l	3.18mg/l	2.37mg/l	1.75mg/l	1.19mg/l (9.67mg/l)	8.96mg/l
	8.25mg/l	7.62mg/l	7.21mg/l	6.69mg/l	6.19mg/l	5.55	N/A	5.31mg/l	4.71mg/l
	4.06mg/l	N/A	3.56mg/l						
1:12 000	9.17mg/l	7.42mg/l	5.62mg/l	4.37mg/l	3.51mg/l	2.61mg/l	2.01mg/l	1.43mg/l (8.40mg/l)	7.85mg/l
	7.10mg/l	6.39mg/l	5.92mg/l	5.40mg/l	4.91mg/l	4.31mg/l	N/A	3.73mg/l	3.24mg/l
	2.76mg/l	N/A	2.12mg/l						
1:20 000	9.16mg/l	7.41mg/l	5.88mg/l	4.83mg/l	4.08mg/l	3.34mg/l	2.82mg/l	2.30mg/l	1.89mg/l
	1.38mg/l	0.92mg/l (9.15mg/l)	8.57mg/l	7.97mg/l	7.34mg/l	6.46mg/l	N/A	6.18mg/l	5.60mg/l
	4.83mg/l	N/A	4.33mg/l						

Note: The number in red color in table means at that day aeration to water was given at 3:00PM.

The Equation for calculating k:

$BOD_t = BOD_u (1 - e^{-kt})$

Where BOD_t is Biological Oxygen Demand value at t day

BOD_u is ultimate Biological Oxygen Demand

t is time for measuring BOD

$BOD_t = (DO_i - DO_t)/P$

Where DO_i is dissolved oxygen concentration at initial time;

DO_t is dissolved oxygen concentration at t day

P is dilution ratio

Appendix D

Electrical Calculation:

External Resistance= 1000 Ω

Inlet COD= 3135 mg/l Outlet COD=1164mg/l

COD Removal Efficiency= (3135 mg/l-1164mg/l) / 3135 mg/l * 100% = 62.87%

Average Voltage= 0.099804701 V, Average Current = $9.9804701 * 10^{-5}$ ampere

Total Coulombs = $9.9804701 * 10^{-5} * 480 * 3600 = 172.4625233$ C

$C_t = (96485 * 1.971 * 0.032 * 4) / 32 = 760.68$ C

Coulomb Efficiency = 172.4625233/ 760.68 * 100 % = 22.67 %

Power (maximum) = 0.322266 * 0.322266 / 1000= $1.038553748 * 10^{-4}$ W

Power Density = $1.038553748 * 10^{-4} / 7.065 * 10^{-4} = 0.147$ W/ m^2

Note: the power density was normalized to anode surface area (0.0007065m^2).

VITA

JIAN LI

Candidate for the Degree of

Master of Science

Thesis: APPLICATION OF AIR-CATHODE MICROBIAL FUEL CELL TO INDUSTRIAL WASTEWATER

Major Field: Environmental Engineering

Biographical:

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Name: Jian Li Date of Degree: December 2011

Institution: Oklahoma State University Location: Stillwater, Oklahoma

Title of Study: APPLICATION OF AIR-CATHODE MICROBIAL FUEL CELL TO INDUSTRIAL WASTEWATER

Pages in Study: 78 Candidate for the Degree of Master of Science

Major Field: Environmental Engineering

Scope and Method of Study: Using the single chamber air-cathode to test how much COD could be biodegraded and how about power production in this process. Also discussing the relationship between air-cathode area and the time needed to obtain the maximum power output. COD removal efficiency, power density and coulomb efficiency are three parameters in more detailed.

Findings and Conclusions:

Electricity is generated by using Microbial Fuel Cell with PTFE coated with cathode surface. Although not all of reactors have successful start-up, in these four trials, the maximum COD removal efficiency reached 87.40%, Coulomb Efficiency reached 49.57% and power density obtained was 147mW/m^2. In this study, the results show that there is no relationship between air-cathode surface area and peak voltage. The above results and figures show that using microorganism to biodegrade industrial wastewater and produce the power back to utility is feasible at laboratory level, how to large-scale application for manufacture plant and wastewater treatment plant cast a problem for current MFC research.

ADVISER'S APPROVAL: John. N. Veenstra