Chapter 2

Design And Performance Evaluation Of Green Energy Conversion System

2.1 Introduction

Sustainable electricity production is becoming one of the substantial concerns of the 21st century. As nuclear power is alternatively available to sustainable fossil fuels, it is far from sustainable but natural sources such as hydroelectric systems, windmills, and solar energy have been identified as some of the more promising alternatives as renewable energy resources. However, many regions do not lend themselves well to some or all of these options. As a new technology, green energy conversion based microbial fuel cells (MFCs) have quickly gained attention from researchers in sustainable energy production.

A plenty of recent studies have investigated these systems operating with wastewater as a fuel or energy source (Moon, Chang and Kim, 2006; Min, Kim, Oh, Regan and Logan, 2005; He, Minteer, and Angenent, 2005; Aelterman, Rabaey, Clauwaert and Verstraete, 2006; You, Zhao, Jiang and Zhang, 2006). Typical wastewater treatment systems with an appropriate biological treatment under aerobic conditions are utilized to biodegrade the organic components in the wastewater. Similarly, MFCs use microorganisms to biodegrade natural ingredients under anaerobic conditions and through this process, electrons are liberated and provide the current produced by the MFCs. MFC research has evolved over the last few decades. Old MFC studies concentrated on simple systems with single microorganisms and simple substrates (Kim, Choi, Jung and Kim, 2000).

Several kinds of microbes are found to behave ideally under anaerobic conditions, readily freeing electrons during biodegradation of the substrate, including some

Shewanella and Geobacter species (Bond and Lovley, 2003; Ringeisen, Ray and Little, 2007). The use of electron mediators are described in early research, but the concept of membrane-less and mediator-less MFCs became prominent only in the late 1990s and continued to be more widely researched over MFCs operated with mediators (Gil et al., 2003; Moon et al., 2006). Across the past decade, many advances have continued performed continually with respect to system design and materials, including the development of the single-chamber microbial fuel cell (SCMFC), which eliminates much of the problem associated with the low solubility of oxygen in water by directly contacting air with the cathode (Park and Zeikus, 2002; Liu and Logan, 2004; Cheng, Liu, and Logan, 2006).

Further studies begin to focus on naturally diverse microbial systems and substrates, such as those provided in wastewater. Moreover, research exists demanded in many areas, including the use of multiple MFC reactor systems, the influence of various operational parameters, overall MFC performance and system responses to disturbance and upset. The study above aspired to develop and test two MFCs using different electron acceptors while being operated in parallel and appropriating waste activated sludge as the anolyte and the substrate for biological activity. System acclimation, operation, performance, and microbial community ecology are studied throughout commencement up and a series of carbon source pulse tests (CSPTs). In this chapter, the MFC systems and experimental methodology are used throughout this research work which is described in detail. The materials required to build the MFCs are listed, and the system design does the outline.

The design and operation of the experiments remain reported with supporting documentation are outlined in detail. The full data analysis methodology is referenced, including analytical methods that are presented in this section. Results are presented and

discussed in brief, as it is the focus of this chapter to describe the investigation methodology thoroughly. Conclusions based on system design and overall performance are given. Chapter 3 provides microbial community ecology evaluation, while chapter 4 presents a detailed comparison of Bio dry cell-based MFC performance and system response results.

2.2 Materials and System Design

This section is subdivided into four major sub-sections: (i) the construction and operation of the microbial fuel cells, (ii) the electrical system for parameter measurement and system control, (iii) the ancillary equipment for system operation and some system variable measurement and (iv) the electrolytes. The overall system design and development are explained in detail in Section 2.3.

2.2.1 Microbial Fuel Cells (MFCs)

The MFC converts the chemical energy of organic compounds from chemical bonds into electrical energy as a bioreactor under anaerobic conditions through catalytic reactions of microorganisms. Experimentally, it is confirmed to generate the electrical power directly by using bacteria to break down the organic substrates utilizing in this approach. The energy crisis of the 21st century has created the technological interests in MFCs among researchers, scientists, technocrats and academics. Without net carbon emission into the ecosystem is negligible with MFC and this biotechnological approach provides an idea for electric power generation from biomass. This approach is also used to break down organic matters in wastewater treatment facilities.

The columbic efficiency and power output are significantly affected by the MFC anodic chamber, types of microbe in the MFC configuration and experimental conditions (Logan and Regan, 2006). The current study dedicates to decreasing the operating and constructional costs and performance improvement of the MFCs. For many diverse

applications, different microbial electrochemical technologies are developed, including water desalination, wastewater treatment, remote energy resources, biofuel production, and biosensors. The energy and current densities would always be limited relative to chemical fuel cells and batteries in the areas of electrical energy conversion systems. The presented technologies have other advantages that electrons are donated or accepted from an electrode, versatility production in the chemicals and utilization range of fuels based on the self-sustaining nature of the microorganisms. The first MFC is proposed and assembled in August 2016 and the second MFC in Nov 2016. The only difference between the two MFCs is the use of acrylic glass in the first MFC and Nanofiltration membrane (NF) in the second MFC as a proton exchange medium. However, the PVC net centerpiece in the first MFC which is subsequently replaced with an identical NF layer in October 2016. For this research, the two MFCs are considered to be structurally indistinguishable. Table 2.1 lists the materials required to build the MFCs. The NF layers soak at room temperature in sulphuric acid before rinsing and MFC construction. The MFC center plates are constructed to ensure that the Na on® held remedied accurately. Once the MFC body held composed, silicone is used to seal the chambers except for the lids. The graphite anodes remained sealed along with one set of graphite cathodes using silicone. The covers are remained sealed with a rubber gasket, and the rest of the MFC things and wires are included the following silicone sealing.

Table 2.1: Microbial Fuel Cell Components

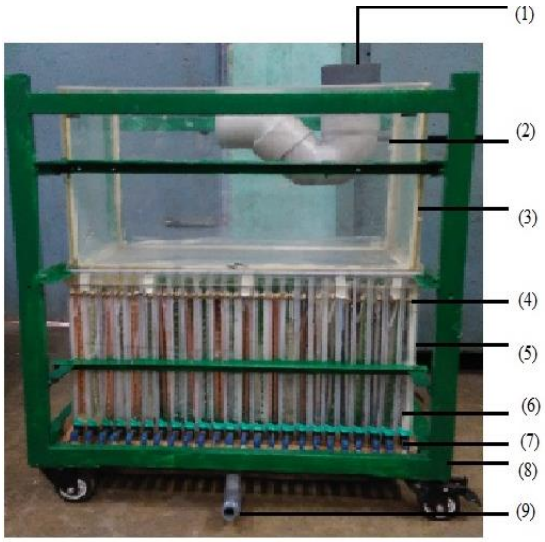
Component/material	**Specification**
Activated carbon electrodes (10 pieces) for each fuel cell	Dimensions (L * W* D): (100 x 90 x 5) mm e^+effective surface area, A =141cm^2 surface sanded with grit 120 paper for roughness

	boreholes at top (diam=1mm, depth=20mm) for wire connection (1 per electrode) boreholes through face 15mm from top (diam=5mm) to suspend electrodes from lid (3 per electrode)
Acrylic glass plates (2 identical)	Clear cast acrylic Glass, Central Stores, CSIR-NAL, Bangalore Dimensions (L*W*D): (168 x 127 x 8.8) mm 24 electrode ports in each cassette: 12 on anode and 12 on the cathode side. The multi-functional port on the anode side of each plate (1/2 inch NPT) allows for standard adapters, third electrode or sensors (pH, temperature, oxygen) ¼ inch NPT on the anode side of each plate for processing gas evacuation nozzle. Sampling port on the cathode side of each plate (boreholes for ½ inch NPT left untapped)
Front and back plates (2 front and 2 back, identical Lengthwise symmetrical)	Clear cast crystal glass (see above) Dimensions (l* w* d): (127 x 90 x 8.8) mm 4 threads (10/32 in) from the top of each for connections to plates 6 boreholes (diam=0.205in) on each, to connect plates with the bottom plate and side wall plates. ds (7/16-20) in each front and each backplate for the adapter fittings, located to allow possible central access to and from resulting chambers.

Sidewall plates (4 identical)	Clear cast acrylic glass (see above) Dimensions (l*w*d): (150 x 81 x 8.8) mm 3 threads (10/32 in) at top of each for plate connection, matching plate dimensions. 2 threads (10/32 in) one at either side of each to connect with front and backplates. Central transverse trench (depth = 3.8mm, width =8.9mm) on centreline of each, allows tighter centre plate construction.

The identical MFCs consist of an anodic and cathodic chamber, each with approximately 500 mL of working volume. The working volume represents the amount of anolyte or catholyte in the system. The remaining size in the chambers is allowed for a small top space volume of approximately 10 mm between the surface of the electrolyte and the MFC lid and the volume occupied by the electrodes. Figure 2.1 shows an entirely constructed MFC. The ports: 1-9 are described in Table 2.1 which may hold as observed in the picture.

The Tedlar bags are attached to the process of gas evacuation nozzles in the lid of each MFC. Prior to the connection, the bags are completely evacuated, so no air or residual gases would continue to introduce in the system.



(a)

(b)

(c)

Figure 2.1: Constructed MFC (MFC#1)

The Tedlar bags are attached to the process of gas evacuation nozzles in the lid of each MFC and before gets connected, the Tedlar bag containers are evacuated, so no air or residual gases are introduced in the system. The bags provide a collection system for

any gases produced during MFC operation since positive pressure in the top space would force system gas into the Tedlar bags. The two MFCs in this study are labeled MFC#1 and MFC#2. MFC#1 is the original prototype, later modified with a Naon ® centerpiece, and operated with dissolved oxygen (DO) saline catholyte. MFC#2 is modeled after MFC#1 and incorporated Naon® from its inception. MFC#2 worked with a ferricyanide catholyte. The electrolytes are described further in Section 2.2.4.

2.2.2 Electrical System

The electrical system is designed to meet two prominent objectives, firstly, the cell voltage of both MFCs is to be controlled at a set value during operation and secondly, automated collection of potential power and current measurements is required. The potential difference of each cell has been observed and recorded using a multimeter to set the value at millivolts range 200 mV for first 24 hours. For the next 48 hours the voltage has been set for range 500 mV and finally the range has been set for 1000 mV to observe the potential difference by open circuit.

Table 2.2 lists the components of the electrical system are designed to meet the above objectives. The MFCs are connected to the potentiostat in parallel to ensure the same cell voltage for both MFCs. The multimeter is attached to the circuit of the MFC#1, allowing the current in MFC#1 to be directly measured. Since the potentiostat measures the total flow generated by both MFCs, the current owing through the second MFC is observed from the difference between the two measurements and the output signals from the multimeter and potentiostat passed through a data collection unit and sent to a lab computer for automated voltage and current data recording.

Figure 2.2 and Figure 2.3 provides a basic wiring diagram to illustrate how the MFC system is controlled and monitored with simultaneous recording of data. The pumping circuit having capacitors 10 Nos. each 4000 MFD /16 Volts has been connected in

parallel for boosting the current and series for boosting the voltage. The load of 1 W 12 V, 500 milliamps (mA) brushless motor is used to test the on load parameter using digital multimeter is as shown in figure 2.2.

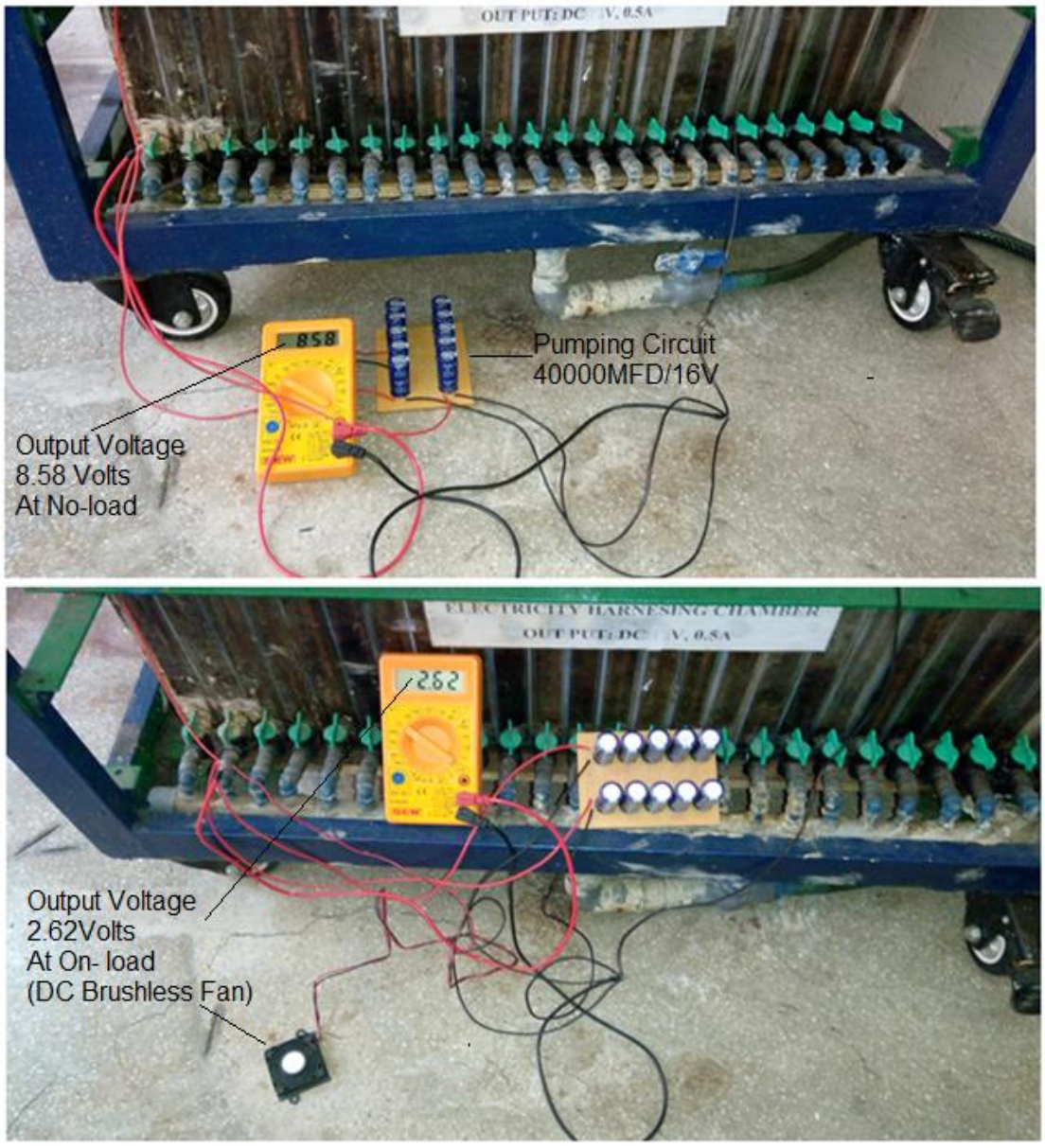


Figure 2.2: Electrical measurement of MFC (MFC#1 and MFC#2)

Table 2.2: Electrical System Components

Equipment's/Measuring devices	**Specification**

	EG and G PAR 173, dual channel, BNC voltage output current range from 200µampere to 200 miliampere. Control voltage ±2 Volts
Portable DC power analyser	EG and G PAR 179 Digital Coulometer installed for signal output, BNC cable Potentiostat/ Galvanostat connections. Signal input and system control: two cables set with alligator clips, attach to electrode wires Keithely 160B Standard banana plug input and output
Digital Multimeter	^ signal input: two banana plug to alligator clip cables. ^ signal output: one banana plug to BNC cable ^ Model 401
eDAQ e-corder	Signal input: up to four BNC connections, three used (system voltage, total current, MFC#1 current) ^ signal output: USB 2.0 A/B for connection to lab computer
Lab computer	Departmental standard: 1 GHz processor, 256 MB RAM, ^ network data storage under user allocated space ^ windows XP Professional OS ^ USB port for signal input associated software: eDAQ Chart 5.0 software for continuous voltage,

current recording, allows calculation of individual MFC currents, coulombs, and power.

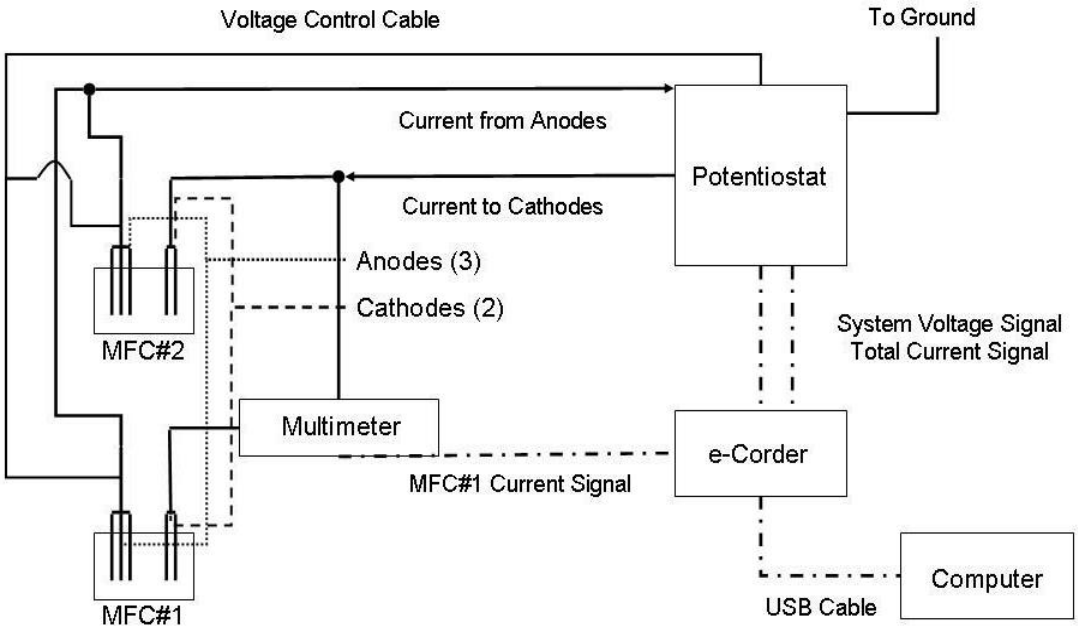


Figure 2.3: Electrical Layout Diagram of MFC

2.2.3 Ancillary Equipment

Several other pieces of equipment are required such as an incubator, two stirrer plates, an air pump, and a dissolved oxygen (DO) meter and probe. Table 2.3 lists these additional components with their associated specifications. The system is operated with MFCs, stirrer plates, air pumps, and DOES exploration inside the incubator. The incubator is used to control the housed system at 37°C. Both MFCs are placed on stirrer plates to agitate the waste activated sludge in the anode compartments via magnetic stir-bars.

The air pump is used to bubble air through the catholyte of MFC#1. The air is held to pump through ports on the front and rear parts of MFC#1 into the cathode chamber, which is left open to the atmosphere via the untapped sampling port in the MFC lid. Each DO probe and meter are employed to measure dissolved oxygen in the catholyte of

MFC#1 to ensure that DO concentrations remained relatively constant throughout MFC operation. Figure 2.4 illustrates the overall system layout.

Figure 2.4: Potentiostat and Multimeter with Data Collection System beside Incubator

Table 2.3: Ancillary System Components

Components	**Specifications**
Incubator	^ Thelco GCA Precision Scientific Model 6M Interior glass doors for system viewing with minimal

	Temperature disturbance ^ metal shelving for multiple levels Ceiling vent used as wiring access between external electrical Components and system power supply.
Magnetic StirrerPlates	One corning PC351, one Cole-Parmer Instrument company ^ Model 4658 ^ standard dial control for stirrer speed
Air pump	^ Tetratec Deep Water DW 12 (KSB) used for tank aeration ^ standard tank tubing connecting the pump to the plastic manifold Two output from the plastic manifold, standard tank tubing Connecting couplers and hose clamp Plastic manifold to MFC #1 cathode chamber
Dissolved Oxygen (DO) Meter and Probe	VWR Symphony SP70D Probe kept immersed in DI water when measurements not taken Probe placed in catholyte through untapped sampling port in the cathode side of the MFC plate

2.2.4 Electrolytes

In MFC#1, the air creates a bubble through a phosphate-buffered, saline catholyte to provide a source of dissolved oxygen. Dissolved oxygen concentrations as close to saturation as possible stayed prepared. In MFC#2, a phosphate-buffered, 0.05 M

ferricyanide solution is used. In this cell, ferricyanide serves as the electron acceptor through its redox reaction to form ferrocyanide. The anolyte is the same for both MFCs. Waste activated sludge from the Waterloo region of wastewater treatment plant remains in use as an initial anolyte and biological inoculants. Both the ferricyanide catholyte solution and the wastewater anolyte are subjected to the same sampling and feeding system.

The aforementioned technique is required weekly batches of waste activated sludge and a new bunch of ferricyanide solution about every twenty days. The liquid level of MFC#1 is maintained with deionized water to make up for evaporation losses, while the air is provided a constant supply of oxygen.

2.3. Experimental Design and Operation

The discussion of the experimental design and procedures are separated into four sub-sections:

(i) Overall system operation,

(ii) Overall system performance evaluation,

(iii) Organic waste and operational measurements,

(iv) Sampling and feeding regimen,

(v) Electrical measurements,

(vi) Wastewater and operational measurements and

(v) Analytical methods are described in Section 2.4.

2.3.1 System Operation

In Section 2.2, the components of the microbial fuel cells, electrical equipment, and ancillary equipment are discussed. Two consecutive experimental results are carried out during this project; the first experiment lasted 28 days, while the second is 182 days in

duration. The first experiment is tested the entire setup and various analytical techniques. Most of the results are related to MFC performance and presented in this thesis and obtained from the second experiment. Figure 2.2 illustrates the wiring setup for system operation.

The potentiostat, multimeter, e-recorder and lab computer are located outside the incubator, while the MFCs, stirrer plates, DO probe and air pump are managed inside the incubator. The incubator is operated at 37°C and the MFCs which perform under a controlled voltage of 0.35 V between the anodes and cathodes for the duration of the experiments. This regulated voltage is chosen for comparison with previous studies and as an operational midpoint between MFC short circuit (V=0) and an average of the open circuit potential of the two MFCs (average V ≈0.6).

2.3.2 Sampling and Feed System

The MFCs are designed with ports on the front and rear to allow for continuous and fed-batch operation. The MFCs are stayed operated under fed-batch conditions throughout both experiments. The use of a continuous flow system for the wastewater anolyte and catholyte solutions is recommended for future studies. However, these ports are used for sampling and feeding the wastewater anolyte in both MFCs via syringes and tubing. The aforementioned discussions ensure that the anode chamber remained anaerobic during operation. Ferricyanide catholyte sampling and feeding are accomplished via syringe and piping at the untapped sampling port on the cathode side of the MFC#2 lid. The catholyte in MFC#1 is not subject to the same sampling and feeding system as the other electrolytes.

The air is bubbled through this electrolyte, and the untapped sampling port on the cathode side of the MFC#1 lid is left open. In the proposed work, it necessary to top up

the electrolyte levels every 48 ±3 hours with deionized water to replace water that evaporated during operation.

Sampling and feeding of both MFCs are scheduled every 48 ±3 hours throughout both experiments and for both MFCs. During the first experiment, the sampling and nutrition for the two MFCs are vacillated due to constraints with chemical oxygen demand and total Kjeldahl nitrogen analytical equipment. Throughout the second experiment, this constraint is raised, and the sampling and feeding for the two MFCs are aligned to reduce analysis times. The sample and feed volumes are 100 mL, taken and delivered in two 50 mL portions.

The wastewater anolyte is stored in a refrigerator, while the fed ferricyanide catholyte is collected at room temperature. The sample wastewater anolyte is fractionated and preserved in Nalgene® bottles in a freezer until analysis. Wastewater fraction is involved in splitting the sample into a total sample, which is represented as a fraction of the original sample, and a soluble sample, which is obtained through centrifugal and filtering processes. Total samples are stored without modification and preserved through refrigeration. Soluble samples are prepared by centrifuging (Beckman Model TJ-6 Centrifuge) a portion of the original sample at a speed of 7000 RPM for 25-30 minutes and then passing the resulting liquid through a 1.5 µm glass microfibre filter (Whatman Grade 934-AH). The substrate is preserved by adding concentrated sulphuric acid until the sample pH is approximately achieved value 2 and finally it is refrigerated. Ferricyanide catholyte samples are taken 100 mL in volume to maintain a similar hydraulic residence time to the anolyte in each MFC.

Duplicate 1 mL portions of the ferricyanide catholyte samples are removed and placed in 1.5 mL sample vials before discarding the remainder. The 1 mL ferricyanide catholyte sample duplicates are stored at room temperature until analysis. Detailed

fractional and preservation methods are observed in Appendix B along with the overall sampling and feeding procedure.

2.3.3 Electrical Variables

Three electrical variables stayed are covered throughout the second experiment, the cell voltage, total current, and MFC#1 current. From these variables, the current for MFC#2 is calculated along with the total coulombs of electricity and power produced by each MFC. The calculation of the electrical quantities from measurements is reported in Section 2.4.

2.3.4 Operational and Wastewater Variables

Throughout the experiments, a variety of operational and wastewater variables are covered. The associated analytical methods are explained in Section 2.4. These variables include several parameters to monitor the system environment in addition to the parameters which is directly related to system evaluation.

The chemical oxygen demand (COD) is a sum of the amount of oxidized material in a given sample. It is a standard wastewater variable that is a measure of the potential chemical energy in the wastewater anolyte. Throughout this study, the COD levels of both the total samples and the soluble portions are determined. The ratio of soluble COD to complete COD is monitored since some biological activity can result in the soluble particulate matter that is comprised of a large percentage of the total COD.

Therefore, after some treatment, cumulative COD may be decreased while soluble COD may be increased. The Kjeldahl nitrogen (TKN) and Free and Saline Ammonia (FSA) are nitrogen-specific wastewater quality measurements. These concentrations are monitored in the wastewater anolyte to describe the behavior of the nitrogen-containing species.

TKN is a fraction of Total Kjeldahl nitrogen (TKN) and free, and saline ammonia (FSA) are nitrogen-species wastewater quality measurements. These concentrations are monitored in the wastewater anolyte to define the behavior of the nitrogen-containing species. TKN is a fraction related in the same manner as COD to determine the soluble portion of the TKN. The ratio of soluble TKN to total TKN is also observed.

FSA, by its very nature, is a soluble nitrogen-containing species and is a portion of the soluble TKN. In the proposed technique, another fraction of the total TKN that is of interest, since ammonia is often the dominant nitrogen-containing product in wastewater treatment processes.

In addition to these wastewater components, the pH of the wastewater anolyte samples is also measured. The pH is monitored to ensure no significant fluctuations in anolyte acid-base chemistry. The wastewater pH is measured directly from the soluble portions of wastewater anolyte and feed, and no further analysis is required. Ferricyanide ions in MFC#2 functioned as the electron acceptors. The change in ferricyanide concentration throughout MFC#2 operation is indicative of electricity production.

As electrons passed through the circuit to the cathode, the ferricyanide continued diminished to ferrocyanide. The average concentration is found in duplicate analytical ferricyanide samples and compared before the system current and coulombs of electricity produced during operation.

Measurements of dissolved oxygen concentration are made throughout the operation of MFC#1 to ensure that the oxygen levels do not fluctuate to any numerous degrees and no direct analysis is required. The dissolved oxygen concentration is measured directly as mg/L and % saturation, and no further investigation is added.

Samples of the cover space gas are obtained and taken throughout the operation of both MFCs. It is continued to expect that the gas mainly consists of nitrogen, carbon dioxide, and possibly methane. Gas chromatography is used to determine the percentages of each of these gases in 1 mL samples. Duplicate 1 mL samples are obtained from each MFC, but due to the low volume of the cover space, it is not possible to take some representations, which may have reduced the high variability in methane concentration measurements.

2.4 Analysis

The description of the analytical methods is divided into several sub-sections. The electrical parameter analysis is described first, followed by the examination of the following wastewater measurements: COD, TKN and FSA, and anolyte pH. The investigation of the catholyte determinations, ferricyanide concentration for MFC#2 and DO concentration for MFC#1, follow the wastewater measurement analysis. The analytical methods for the cover space gas are described in the sub-section. Specific analysis methods are explained in detail.

2.4.1 Electrical Parameters

The electrical data are collected using the eDAQ e-recorder 401 units, lab computer and Chart 5.0 Software and then interpreted using the Chart 5.0 software, provided with the e-recorder 401 unit.

The events occurred consigned to Microsoft Excel for general analysis and time plots. As described earlier, three electrical variables are directly measured, the cell voltage (V), total current (I), and MFC#1 current (I_1). The current resulting from MFC#2 (I_2) held calculated from Equation 2.1. The amount of electricity in coulombs (Q(t)) produced by the entire system or by an individual MFC is calculated using Equation 2.2.

Finally, the power generated by the entire system or by a specific MFC is calculated using Equation 2.3. With these equations, the current, voltage, power, and coulombs are monitored and recorded for each MFC.

$$I_2 = I\text{-}I_1 \tag{2.1}$$

$$Q(t) = \frac{Z.t}{O.t.dt} \tag{2.2}$$

$$P = VI \tag{2.3}$$

Regularly, current and power are summarised in the literature normalized to the anode or cathode surface area, where they are usually equal. However, the field of interest is only the effective, or employed surface area. Since there are only two cathodes, an active electrode surface area (EESA) of 282 cm^2 is used to normalize the current and power values. With increased internal resistance due to the MFC design, it is likely that only a small fraction of this area, which is approximately equal to the proton exchange membrane surface area, is primarily appropriated.

In this thesis work, a path is provided of the least resistance for proton shuttling to complete the electrical circuit. As such, an effective membrane surface area (EMSA) of 7 cm^2 was used to normalize the current and power values as well. These two effective active surface areas likely bound the actual useful surface area employed during the experiments.

2.4.2 Chemical Oxygen Demand (COD)

Following sample fraction and preservation, the samples collected for COD analysis are stored at 4°C. The steps for the analysis of the COD wastewater anolyte and feed samples are listed below:

i. Sample dilutions: total 1:20 or 1:10, soluble 1:2 or none

ii. Digestion preparation: triplicate total and soluble samples, calibration standards, digestive reagents

iii. Digestion: 3.0 hours at 150°C

iv. Optical Density (OD) measurements: λ = 600 nm, the calibration curve is generated, sample values are recorded

During the first step, preserved samples are diluted with deionized water. Following dilution, triplicate 2.5 mL volumes of each wastewater sample are added continuously to 10 mL COD digestion vials. A set of COD calibration standards held prepared at 0, 25, 50, 100, 200, 300, 400, 600, 800, and 1000 mg COD/L, and 2.5 mL of each standard existed combined to 10 mL COD digestion vials. If the previous COD digestion is used the same batch of reagents, only a 0 and a 1000 COD calibration standards are prepared to confirm the above calibration curve. If affirmed, the previous calibration curve may be reused.

After sample and standard addition, 3.5 mL of the sulphuric reagent and 1.5 mL of the chromatic reagent held combined to each digestion vial. Recipes for these reagents last presented along with the overall procedure in Appendix C. Once the reagents are added, the trials are capped, shaken and placed in a block heater to digest for 3 hours at 150 °C. During the following digestion, the vials are allowed to cool before being cleaned with ethanol and tissues. Optical density determinations at a wavelength of 600 nm are obtained and recorded for each sample and standard using a spectrophotometer (Hach DR/2010 Portable Datalogging Spectrophotometer).

The COD values are obtained by reading the calibration curve. Refer to the standard method for water and wastewater analysis, 5220D Calorimetric Method, as published by the American Public Health Association - American Water Works Association - Water Environment Foundation. A cumulative COD balance applied to

each MFC for the duration of the second experiment yields performance characteristics concerning the amount employed in electricity production and the total amount of COD is reduced. The total accumulation of COD (COD_{Acc}) for each MFC was calculated using Equation 2.4:

$$COD_{Acc}=COD_{Feed}+COD_{CSP}-COD_{Smpl}-COD_{Elec}-COD_{Gas} \quad (2.4)$$

where,

COD_{Acc} = cumulative COD accumulation in MFC (mg)

COD_{Feed} = cumulative COD of feed wastewater anolyte to MFC (mg)

COD_{CSP} = cumulative COD of carbon source pulses injected into MFC (mg)

COD_{Smpl} = cumulative COD of sample wastewater anolyte from MFC (mg)

COD_{Elec} = equivalent cumulative COD of electricity produced during MFC operation (mg)

COD_{Gas} = equivalent cumulative COD of methane gas produced during MFC operation (mg)

The COD_{Feed} and COD_{Smpl} values are obtained from measured sample results and known volumes. COD_{CSP} and COD_{Gas} are calculated from theoretical values for the substances, while COD_{Elec} is determined from the coulombs of electricity (Q) produced during MFC operation. The theoretical COD values are estimated from the mass of oxygen required to oxidize the mass of the substance added. The calculation of COD_{Gas} is described further in Subsection 2.4.7. From the coulombs of electricity produced, the moles of electrons are measured. These are related to the moles of oxygen required to oxidize enough organic matter to generate the same amount of electrons. The moles of oxygen are converted to the corresponding mass in each case (COD_{CSP}, COD_{Gas}, COD_{Elec}).

2.4.3 Total Kjeldahl Nitrogen (TKN) and Free and Saline Ammonia (FSA)

Nitrogen sources and ammonia are wastewater contaminants of concern in most treatment systems and also nutrients for biological growth. Similarly to COD analysis, several steps followed sample partitioning and preservation, as listed below:

i. Sample dilutions: total 1:2 or none, no soluble sample dilution, FSA 1:26
ii. Digestion preparation: total and soluble samples, calibration standards, digestion standards, digestive reagent
iii. Digestion: 1.5 hours at 200°C then 3.5 hours at 380°C
iv. Dilutions: digested samples and standards diluted to 100 mL
v. Ammonia Analysis: dialysis unit for detection of ammonia in digested and FSA samples

During the first step, preserved samples are held diluted with deionized water. In the following dilution, 1.0 mL of each sample obtained is added to a semi-macro TKN digestion vial with a total capacity of approximately 80 mL. A set of TKN calibration standards is developed at 0, 125, 250, 500, and 1000 mg NH4-N/L. Also, glutamic acid standards are prepared at 125 and 500 mg NH4-N/L, based on the ideal ammonia composition after digestion. These standards are used to ensure that sample digestion is completed. Glutamic acid standards at 250 and 375 mg NH4-N/L are also used in beginning digestions and analyses to increase the number of digestion standards and condense in full metabolism. Following preparation, 1.0 mL of each standard is held computed to a semi-macro TKN digestion vial. After sample and standard addition, 3.0 mL of the digestive reagent is added to each of the semi-macro TKN digestion vials.

Once the reagent is combined, two glass boiling beads obtained are added to each vial, and the vessels are located in a block heater for digestion. The digestion took place for 1.5 hours at 200 °C and then for 3.5 hours at 380°C. Following digestion, the digested samples and standards are diluted with deionized water to 100 mL by rinsing

each digestion vial into a graduated cylinder three times. Because the original sample and standard volume are added to the bottles is 1.0 mL, this constitutes a 1:100 dilution. A Brann and Luebbe AA3 ammonia analysis system is used to determine the ammonia content in the digested samples and standards as well as the FSA samples.System's calibration standards are required at 0.5, 1.0, 5.0, 10.0, and 30.0 mg NH4-N/L.

Analytical cups for each digested standard are prepared in at least duplicate, with triplicate and quadruplicate analysis in earlier analyses to ensure good performance. Each sample is analyzed in duplicate. The digested standards are used to construct a calibration curve for digested samples, while the analyzed glutamic acid standards provided a correction factor for digestion completion. FSA samples are compared to the system calibration standards to obtain FSA concentrations. FSA samples are non-digested, so the comparison to non-digested system calibration standards prevents any digestion biases from being applied to the FSA sample measurements. Refer to the standard methods for water and wastewater analysis, 4500-NorgC Semi-Micro Kjeldahl Method and 4500-NH 3G Automated Phenate Method, as published by the American Public Health Association - American Water Works Association - Water Environment Foundation.

2.4.4 Anolyte pH

The organically extracted wastewater pH is continued to measure throughout the second experiment. The measurement is made using a standard pH probe and meter on the soluble wastewater anolyte samples before preservation. As mentioned earlier, the conservation of the water-soluble example has required the addition of sulphuric acid, so pH measurements stay accompanied before this step.

2.4.5 Ferricyanide

The catholyte ferricyanide concentration is the primary variable for the cathode side of MFC#2.

The procedure to determine the concentration is proffered below:

i. Serial dilution: duplicate samples diluted to 1:100
ii. Optical Density (OD) measurements: λ = 420 nm, sample absorbance values recorded

A calibration curve of ferricyanide concentration versus optical density at a wavelength of 420 nm is established in advance of both experiments and used afterward. The calibration curve is valid for levels up to 0.05 M, which was the feed concentration for both analyses.

Following serial dilution of the samples, OD measurements are taken at a wavelength of 420 nm using a spectrophotometer (Spectronic Genesys 2). Sample OD values are compared to the calibration curve to obtain ferricyanide concentrations. The feed system for the fresh ferricyanide catholyte solution allows a relatively constant ferricyanide concentration is prepared throughout system operation.

A simple molar balance yields the amount of ferricyanide reduced to ferrocyanide at the cathode. Equation 2.5 shows this balance. The moles of ferricyanide reduced to ferrocyanide are equal to the moles of electrons gained from the cathode. These are related to the moles of oxygen that are theoretically required to liberate these electrons through oxidation. The equivalent mass of oxygen is equal to the COD mass. This value is held matched to the COD_{Elec} found for MFC#2 through coulombic analysis.

$$Ferri_{Reacted} = Ferri_{In} - Ferri_{Out} \quad (2.5)$$

where,

$Ferri_{Reacted}$ = moles of ferricyanide reacted during MFC operation (moles), $Ferri_{In}$ = moles of ferricyanide added to MFC#2 during operation, includes start-up (moles)

$Ferri_{Out}$ = moles of ferricyanide removed from MFC#2 during operation, includes shut down (moles).

2.4.6 Dissolved Oxygen

The data of Dissolved oxygen (DO) are obtained to use as indicators of electron acceptor concentrations in the cathode of MFC#1. It is difficult to calculate the total amount of oxygen that reacted at the cathode of MFC#1 for comparison to the COD Elec found for MFC#1. However, it is essential to ensure that the DO concentration in the phosphate-buffered saline catholyte of MFC#1 remained relatively constant. Low DO concentrations would be theoretically hinder the electricity production, inducing the anodic side of the MFC and limiting MFC performance on the cathode side. It remains solicited that the catholyte strength in both MFCs relatively constant to minimize any cathodic limitations impacting the system performance.

2.4.7 Cover Space Gas

The cover space gas theoretically contains nitrogen, originating from any air that may enter the system, along with carbon dioxide and methane from system operation. Analysis of the cover space gas samples is accomplished using gas chromatography. The cover space gas volume (V Total) is obtained approximately from system design dimensions and known anolyte measures to be 10 mL. The steps which are required for the analysis described as follows:

i. Gas chromatography system setup: power up the d carrier gas, Peak software
ii. Triplicate air sample injection: the prime system with air, 2-minute runtime each
iii. Cover space gas sample injection: samples injected, 2-minute runtime each
iv. Gas composition: calculated against the known system calibration curve
v. Gas volumes: cover space gas volume estimated, with composition gives individual gas quantities

The gas chromatography (GC) system consists of the GC unit (SRI 310C Gas Chromato-graph, silica gel carrier medium), helium carrier gas cylinder and lines, a thermal conductivity detector and a lab computer with Peak Simple 3.29 software for data collection. A calibration curve is established using gas standards before any experimental result. Methane is the component of interest since nitrogen is an inert in the system and carbon dioxide has a zero COD equivalence. Cover space gas samples exert with every sample/feed cycle, resulting in gas samples every 48 hours. Cover space gas samples are only 2 mL in size, while the headspace is approximated as 10 mL, leaving 8 mL of cover space gas and probably methane to confound later measurements. However, the sample/feed procedure for the wastewater anolyte is assumed to effectively reset the cover space gas composition and eliminate methane presence. Thus, the amount of methane is calculated for each sample which is supposed to independent of previous methane calculations.

Since the gas composition of each example is provided the volumetric fraction of each component including methane (X_{CH4}), the methane volume in each sample (V_{CH4}) is held for readily calculation from Equation 2.6:

$$V_{CH4} = X_{CH4} \times V_{Total} \tag{2.6}$$

A cumulative methane volume was calculated from the sum of each cover space gas sample result and converted to a molar equivalent using Equation 2.7, derived from the ideal gas law.

The mass of oxygen required to fully oxidize this amount of methane provides the theoretical COD equivalent (COD_{Gas}) for use in the COD balance in Equation 2.4.

$$N_{CH_4} = \frac{P_{sys} \times V_{CH_4}}{R \times T_{sys}} \tag{2.7}$$

where,

N_{CH4} = number of moles of methane produced

Psys = system operative pressure: 1 atm (abs)

V_{CH4} = volume of methane produced in liters

R = gas constant: 0.08206 L*atm/mol*K

T_{sys} = system operative temperature: 310.15 K

The presence of oxygen in the cover space gas is assumed to be negligible, considering the anaerobic conditions maintained in the anodic chamber. However, during GC analysis, any trace amounts of oxygen would be measured as part of the total nitrogen component of the cover space gas. The GC analytical method is unable to distinguish between these two gases.

2.5 Results and Discussion

Following the analysis of the data, several signs cant conclusions remained drawn from the results. A few of these results are presented and discussed below, in the same order as in the previous section. Since the primary focus of this chapter is to introduce and describe the MFC experiments, a more thorough examination of the results moves demonstrated in Chapter 4.

2.5.1 Electrical Parameters

A summary of the electrical parameter results from the second experiment is given in Table 2.4 for MFC#1 and Table 2.5 for MFC#2. The controlled voltage is maintained at 0.3V throughout the investigation, though it stood abandoned to 0.25V following sample/feed procedures during the first few months of operation. This is due to a reversal of the current flow direction immediately following the sample/feed procedure. After approximately 2 hours of service at 0.25V, the controlled voltage is set back to 0.3V. Results are presented in approximately 15-day intervals to highlight the changes during

the acclimation period and the carbon dosing period. The acclimation period is defined as the operational time before the carbon source pulse tests (CSPTs) and lasted from August 5th, 2016 to October 20th, 2016. The carbon dosing period encompasses the CSPTs from February 20th, 2017 to April 23rd, 2017. There is also a post-experimental monitoring period from April 23rd, 2017 to June 5th, 2017, which completed the 182-day duration of the second experiment. On April 19th, 2017 the anolyte in both MFCs continued manually stirred for 5 minutes before the sample/feed procedure. Current and power production levels are observed to rise and remain high for over two weeks.

A constant voltage, current, and power are proportional to each other, so the trends shown in Table 2.4 and Table 2.5 for these two parameters followed a similar pattern. There are several exciting trends to note:

MFC#1: current/power is relatively stable throughout the acclimation period addition of sodium acetate significantly increased current/power production from sludge.

MFC#1

- The addition of glucose and glycerol is maintained to observe an increase in current/power production from sludge and the addition of bovine serum albumin drastically increased current/power production from sludge.
- Following CSPTs, the system is returned to previous current/power production levels
- current/power densities are calculated with EMSA approached literature values derived from electrode surface areas, on the order of 150 mW/m^2 (Oh and Logan, 2006). Current/power densities are calculated with EESA are significantly less than the same.

Table 2.4: Electrical Parameter Results for MFC#1

Date	Current and Current Density	Power and Power Density	Total Coulombs

							produced	
	(mA)	**(mA/m^2)**		**(mW)**	**(mW/m^2)**		**(C)**	
Densities calculated with acclimation Period		EESA	EMSA		EESA	EMSA		
December 21st, 2016	0.0244	0.87	34.9	0.0086	0.30	12.3	85.726	
January 5th, 2017	0.0172	0.61	24.6	0.0052	0.18	7.43	188.456	
January 20th, 2017	0.0340	1.21	48.6	0.0102	0.36	14.6	280.197	
February 5th, 2017	0.0386	1.37	55.1	0.0116	0.41	16.6	379.802	
February 20th, 2017	0.0235	0.83	33.6	0.0071	0.25	10.1	420.637	
CS Dosing Period								
March 5th, 2017	0.0593	2.10	84.7	0.0178	0.63	25.4	520.243	Post Sodium Acetate
March 20th, 2017	0.0456	1.62	65.1	0.0137	0.49	19.6	617.674	Post Glucose
April 5th, 2017	0.0654	2.32	93.4	0.0196	0.70	28.0	760.586	Post Glycerol
April 19th, 2017	0.2296	8.14	328	0.0690	2.45	98.6	965.529	Post BSA
May 5th, 2017	0.2550	9.04	364	0.0765	2.71	109	x	Anolyte mixed Apr 19th
May 20th, 2017	0.1700	6.03	243	0.0510	1.81	72.9	x	
June 5th, 2017	0.0350	1.24	50.0	0.0105	0.37	15.0	x	

MFC#2

- Current/power is relatively stable throughout the acclimation period.
- Current/power is relatively stable throughout the carbon dosing period.
- Following CSPTs, the system is returned to previous current/power production levels
- Current/power densities calculated with the EMSA are on the same order as literature values derived from electrode surface areas, on the order of 150 mW/m^2 (Oh and Logan, 2006) current/power densities calculated with the EESA are significantly less than the same literature values, on the order of 150 mW/m^2 (Oh and Logan, 2006).

Table 2.5: Electrical Parameter Results for MFC#2

Date	**Current and Current Density**			**Power and Power Density**			**Total Coulombs produced**
	(mA)	**(mA/m^2)**		**(mW)**	**(mW/m^2)**		**(C)**
Densities calculated with acclimation Period		EESA	EMSA		EESA	EMSA	

December 21st, 2016	0.2796	9.91	399	0.0980	3.48	140	501.662	
January 5th, 2017	0.2659	9.43	380	0.0799	2.83	114	900.679	
January 20th, 2017	0.2706	9.60	387	0.0815	2.89	116	1240.002	
February 5th, 2017	0.2439	8.65	348	0.0734	2.60	105	1623.378	
February 20th, 2017	0.3186	11.3	455	0.0958	3.40	137	2015.667	
CS Dosing Period								
March 5th, 2017	0.2788	9.89	398	0.0839	2.98	120	2389.976	Post SodiumAcetate
March 20th, 2017	0.3087	11.0	441	0.0929	3.29	133	2776.565	Post Glucose
April 5th, 2017	0.3251	11.5	464	0.0977	3.46	140	3219.783	Post Glycerol
April 19th, 2017	0.2999	10.6	428	0.0902	3.20	129	3639.926	Post BSA
May 5th, 2017	0.3900	13.8	557	0.1170	4.15	167	x	Anolyte mixed Apr 19th
May 20th, 2017	0.3400	12.1	486	0.1020	3.62	146	x	
June 5th, 2017	0.2900	10.3	414	0.0870	3.09	124	x	

The power densities are calculated from EESA and EMSA which represent the theoretical minimum and maximum power densities for each MFC.

It is understandable to conclude that the real estimable housing area is surrounded by EESA and EMSA. If the actual active surface area is close to the EESA, power densities are very low during system operation, while the opposite is reliable if the EMSA is closer to the actual useful surface area. The proposed future MFC designs incorporate a larger PEM and equivalent, evenly-spaced, single electrodes. The addition of the carbon sources increases the current and power levels slightly, but only for short periods. Those above are due to their relatively low COD equivalence and the unsustained addition of the carbon sources. Spot sample values for the current, no matter how well placed, are a poor indicator of overall performance. MFC#1 operated at a much lower current than MFC#2 due to the air-activated catholytes.

Therefore, the long term effects of the carbon source pulse tests are more easily identified by looking at the coulomb production averaged over time. Table 2.6 presents

the average coulomb production for each period in Tables 2.4 and 2.5. From Table 2.6, the MFCs show similar electrical behavior concerning each carbon source pulse test.

Sodium acetate increased daily coulomb production by approximately 15% over acclimation period levels for both MFCs glucose decreased daily coulomb production to acclimation period levels for both MFCs glycerol increased daily coulomb production by about 30% and 10% over acclimation period levels for MFC#1 and MFC#2, respectively.

- Bovine serum albumin increased daily coulomb production by approximately 180% and 20% over acclimation period levels for MFC#1 and MFC#2, respectively
- Organics instants in the wastewater anolyte are oxidized by micro-organisms in the wastewater anolyte. This biocatalytic reaction is occurred either at the anode surface or within the bulk anolyte solution.

Because the anode side of the MFC is under anaerobic conditions, the liberated electrons could either:

- Travel through the anode to the cathode to reduce the associated electron acceptor if the reaction took place at the anode surface, or chemically reduce carbon in solution, resulting in the production of methane if the reaction took place in the bulk anolyte solution.

Table 2.6: Daily Coulomb Production for MFCs

Start-End Dates	**MFC#1 (Q/day)**	**MFC#2 (Q/day)**
December 5−21, 2016	5.20	30.41
December 21, 2016−January 5, 2017	6.90	26.79
January 5−20, 2017	6.12	22.62

January 20−February 5, 2017	6.23	23.96	
February 5−20, 2017	2.73	26.18	
February 20−March 5, 2017	7.66	28.80	Sodium Acetate dosing
March 5−20, 2017	6.51	25.83	Glucose dosing
March 20−April 5, 2017	8.95	27.77	Glycerol dosing
April 5−19, 2017	14.58	29.88	BSA dosing

When the reaction takes place at the anode and electrons travel through the circuit, coulomb production occurs. When the reaction takes place in the bulk anolyte resulting in methane production, coulomb production does not happen. Therefore, a decrease in coulomb production likely favors methanogenesis in the bulk solution over response at the anode and coulomb production. At a microbial level, if glucose results in a competitive growth then the advantage for methanogens and electron-producing micro-organisms may have at a relative disadvantage, resulting in a lower coulomb output. It is interesting that this phenomenon is remarked in both MFCs. Also of interest, return to pre-CSPT current/power production levels during the post-experimental monitoring period. Nevertheless, this may have been due to a `washout' effect from the sample/feed procedure.

2.5.2 Chemical Oxygen Demand (COD)

The COD results from the second experiment are presented in Table 2.7. The COD totals continue to give as sums throughout the acclimation and carbon dosing periods. Some approximate proceeds from the post-experimental monitoring period are manifested in Table 2.8. The analytical error ranges are available for the COD balance variables in both tables, based on a 95% confidence interval and triplicate analysis.

Table 2.7: Cumulative Chemical Oxygen Demand Results without Post-Experimental Period Extrapolations

COD Variable	**MFC#1 (mg)**	**MFC#2 (mg)**
COD_{Feed}	19120 2500	19120 2500
COD_{CSP}	92.9 4.6	92.9 4.6
COD_{Smpl}	5070 1810	5470 1930
COD_{Elec}	88.4 3.0	318.6 59.7
COD_{Gas}	141.7 278.3	175.2 148.3
COD_{Acc} (from Equation2.4)	13914.8 4594.7	13255.3 4642.6

As can be seen in Table 2.7, the system mass transfer terms, COD_{Feed}, Sample, Acclimation, constitute a majority of the overall balance. The COD_{CSP} associated with the carbon source pulse tests, is very small in comparison, as it is the COD_{Elec} associated with electricity production and the COD_{Gas} associated with methane production. During system design, it remained understood that the sub-optimal geometry would lead to lower current/power production than previously published values (Oh and Logan, 2006), but the impact on the overall COD mass balance is not thoroughly investigated. The balance on both MFCs indicates an unusual large COD accumulation term. The COD accumulation terms are 73% and 69% of the total sludge feed for MFC#1 and MFC#2, respectively. During the post-experimental period, sampling and feeding are continued, as electricity and methane are produced. Based on the acclimation and carbon dosing periods, approximate values for the COD balance terms are extrapolated for the post-experimental period. Analysis of feed and sequent samples are abandoned during this period, and a representative sample for the accumulation term is not taken immediately following the carbon dosing period.

A representative sample is required for the scraping of the anode surface, which is avoided to preserve any bioculum activity during the post-experimental period. The COD results with the extrapolated values are included as shown in Table 2.8.

Table 2.8: Cumulative Chemical Oxygen Demand Results with Post-Experimental Period Extrapolations

COD Variable	**MFC#1 (mg)**	**MFC#2 (mg)**
COD_{Feed}	24800 3240	24800 3240
COD_{CSP}	92.9 4.6	92.9 4.6
COD_{Smpl}	6690 2390	7200 2550
COD_{Elec},Gas	307 375	658 277.4
COD_{Acc} (Equation 2.4)	17900 6010	17040 6070

As the post-experimental period results are extrapolated continuously from the previous operational results, the same general trends may be observed. Following the system shut down, samples to determine the COD accumulation is remained taken from both MFCs. The MFCs are opened up, and the accumulated wastewater sludge on the lid, anodes, and within the anodic chamber held actively stirred into the anolyte. These sample volumes are 100 mL, constituting 20% of the entire anolyte for each MFC to minimize the possibility of unrepresentative samples. The steady accumulation is found to be 6244.0 mg and 6135.7 mg for MFC#1 and MFC#2, respectively. From the results of the accumulation term analysis, a discrepancy of 11660 mg and 10900 mg is observed for MFC#1 and MFC#2, respectively. This constitutes approximately 47% of the total feed to MFC#1 and 44% of the inclusive feed to MFC#2. Although it is likely that the measured accumulation samples would provide low estimates of the COD accumulation, it continued not expected that the discrepancy would be of such a large magnitude. There are several possible causes for this:

i. cover space gas leakage leading to the loss of methane from the system and unmeasured COD_{Gas}

ii. oxygen presence in the anodic chamber providing a chemical short circuit of the MFC and unmeasured COD loss through oxidation

iii. liquid phase anolyte leakage to MFC surroundings, leading to the loss of wastewater anolyte and the associated COD

iv. other sources of error in addition to the calculated analytical error, such as operator and measurement error

Cover space gas leakage is considered unlikely during MFC design and early operation. The Tedlar bags are attached to the headspace volume consistently showed little to no swelling and negligible amounts of methane when gas is available. However, if the discrepancy in the COD accumulation is due to methane leakage, it would only require a rate of approximately 25 mL/day or 1 mL/hr of methane production from each MFC. Carbon dioxide would not account for any of the COD balance discrepancies but may have stayed produced beyond the measured amounts. This would increase the leakage rate of any gas from the system, but only by an equivalent or lesser percentage. Therefore, the total leakage rate may have approached 50 mL/day, with methane, carbon dioxide and trace amounts of nitrogen leaving the system. Since these volumetric production rates are remarkably modest, a slight leak in the Tedlar bag system could account for the discrepancy.

Also, carbon dioxide and methane production in the cover space during MFC operation would cause a slight positive pressure, forcing the gas into the Tedlar bag. Oxygen present in the anodic chamber is considered a minimal and unavoidable side act of the sample/feed procedure. It is unlikely that oxygen is able to enter the anode side during the feeding process in particular. However, if the Tedlar bags are leaking, oxygen

could be introduced during sampling. If 100 mL of air is able to enter the anodic chamber during sampling, it would be quickly forced out during the feeding procedure. Any residual air would be a source of oxygen. If it remains estimated that approximately 2 mL of oxygen, 20% of the 10 mL cover space volume, is available in the anode chamber after the sample/feed procedure, this only represents about 2.5 mg of the undetected COD oxidation. If this leakage occurs throughout the entire second experiment, this would only describe 228.8 mg of undetected COD oxidation and would not be adequately explained the discrepancy in the determined COD accumulation. It is also unlikely that oxygen is able to leak into the anodic chamber continuously, considering the gas production and slightly positive pressure in the cover space.

Liquid phase anolyte leakage would provide a direct loss of COD from the anode chamber. However, this type of leak would be very noticeable and is not observed at any point during experimentation.

Although additional sources of error beyond the analytical mistake from the 95% condense level provided in Tables 2.7 and 2.8 are possible, it is unlikely to explain the full magnitude of the discrepancy in the COD accumulation measurement. The error associated with sample preparation would act both MFC samples and the feed that existed analyzed. It is possible that any under- or over-estimates would occur in both terms, and this could at least partially negate the acts on the COD accumulation term.

2.5.3 Total Kjeldahl Nitrogen (TKN) and Free and Saline Ammonia (FSA)

The TKN results from the second experiment continue manifested in Figure 2.4 for the feed, Figure 2.5 for MFC#1 and Figure 2.6 for MFC#2. Error bars are also included in the figures and are indicative of the analytical error calculated from duplicate samples at a 95% condense level. In Figure 2.4, the feed TKN between December 5th, 2016 and January 23rd, 2017 is interpolated based on the surrounding values. Unfortunately, direct

analysis is not carried out due to TKN digestion equipment constraints. The error bars are associated with these interpolated values essentially paints a black box with a width of the stated period and a height equal to the difference between surrounding values. Subsequent TKN measurements throughout the experiment suggest that this is a reasonable range for estimated TKN values.

2.5.4 Anolyte pH

The pH of the wastewater anolyte and feed waste activated sludge is measured for the last 38 days of the acclimation period and throughout the carbon dosing period. The results are presented in Figure 2.7. Most pH measurements indicate that the wastewater anolyte in each MFC remains close to neutrality. The feed pH is consistently slightly basic, maintaining values below a pH of 8.2. During biodegradation of the organic matter in the wastewater anolyte, protons are liberated in addition to the electrons for electricity production.

These protons theoretically migrated through the PEM to the catholyte to maintain electro-neutrality in the system. However, any accumulation of protons in the wastewater anolyte during operation would result in lower pH values for the wastewater anolyte. Although incredible, small amounts of proton accumulation could be a result of mass transfer limitation through the PEM due to biofouling or particulate development on the membrane surface. MFC#1 consistently shows lower pH values than MFC#2. Another explanation for pH changes in the production of volatile fatty acids (VFAs). VFAs are a product of fermentation of the organics; a process that is likely partially active in the anaerobic anode chamber with few oxidizing agents present. The presence of VFAs would lower the pH. The higher current in MFC#2 allows for more oxidation of the anolyte and less accumulation of any VFAs, resulting in a higher pH than MFC#1

throughout the experiment. Also, the pH values observed during system operation are close enough to a neutral pH that biological activity would not be adversely accepted.

2.5.5 Ferricyanide

The ferricyanide concentration in the catholyte of MFC#2 is obtained and measured throughout the acclimation and carbon dosing periods of the second experiment. Ferricyanide effluent concentrations ranged from 0.34 mL to 0.46 mL throughout the research. The steady feed and effluent concentrations are used to determine the total amount of ferric iron reduced to ferrous metal. This value remained converted to a COD mass equivalent for comparison to the COD_{Elec} is obtained for MFC#2. The amount is calculated as 266.4 911.2 mg with a 95% condense level. The median value is in good agreement to the value obtained for MFC#2 (Table 2.7) on the source of the measured current, but the 95% condense range was significantly higher due to the ferricyanide analysis technique

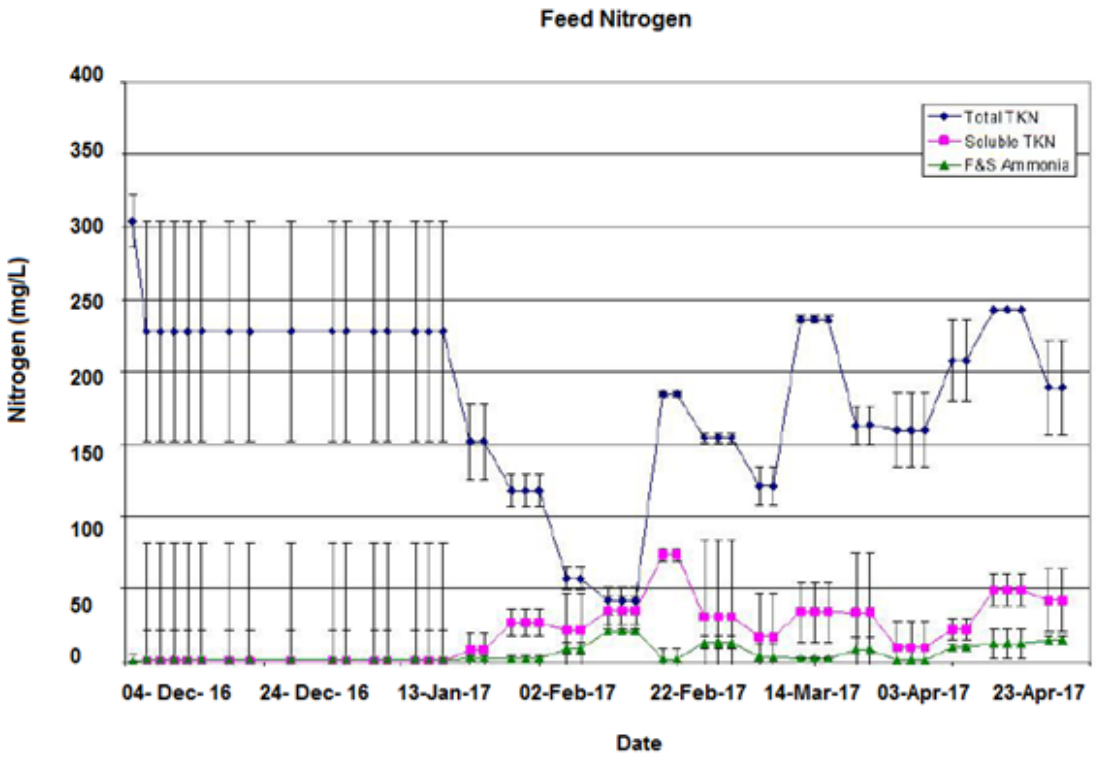


Figure 2.5: Feed TKN (Total and Soluble) and FSA

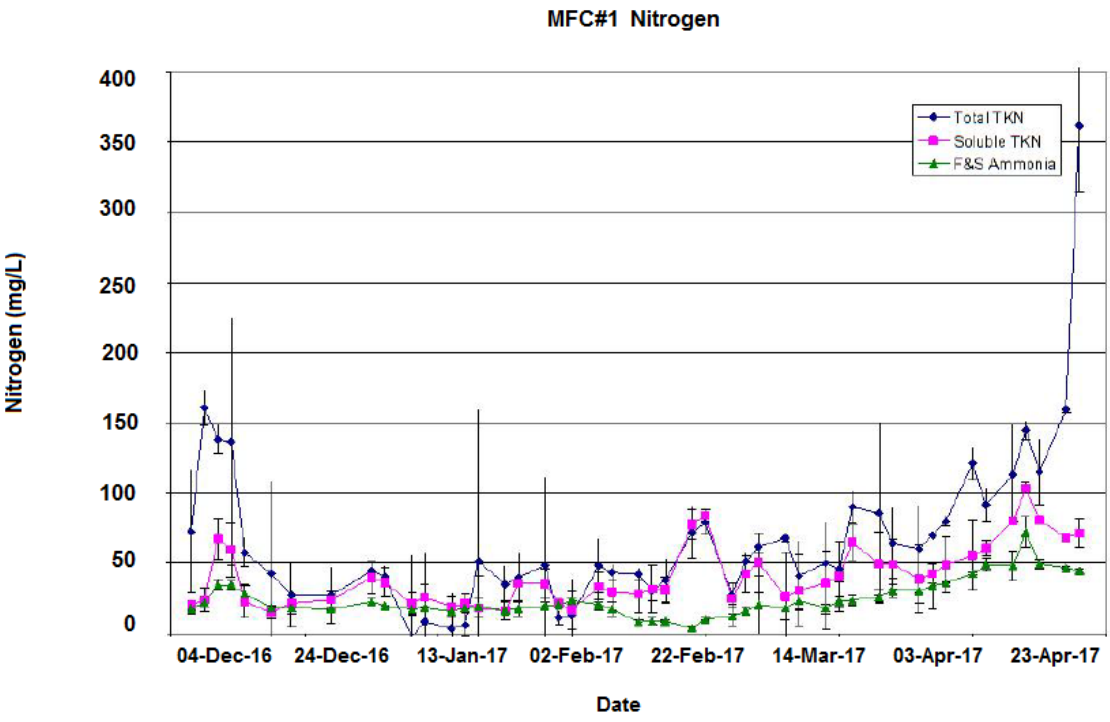


Figure 2.6: MFC#1 TKN (Total and Soluble) and FSA

2.5.6 Dissolved Oxygen

The DO of the phosphate-buffered catholyte for MFC#1 was measured for the last 40 days of the acclimation period and throughout the carbon dosing period. The results are presented in Figure 2.8.

The DO measurements are taken during the first few weeks of the carbon dosing period which are not deemed reliable since a recalibration of the DO meter is required. From Figure 2.8, it can be moved and seen that the DO ranged from approximately 45% −85% saturation or 3−6 mg/L during the acclimation period, while the DO ranged from 35%−75% saturation or 2−5 mg/L.

While the carbon dosing interval coincides with the higher current production observed in MFC#1 during the carbon dosing period. With higher current production, more oxygen would remain consumed from solution as electron acceptors. Due to the

range and relatively unstable DO measurements, it is difficult to identify a direct relationship that is outside of this expected theoretical relationship.

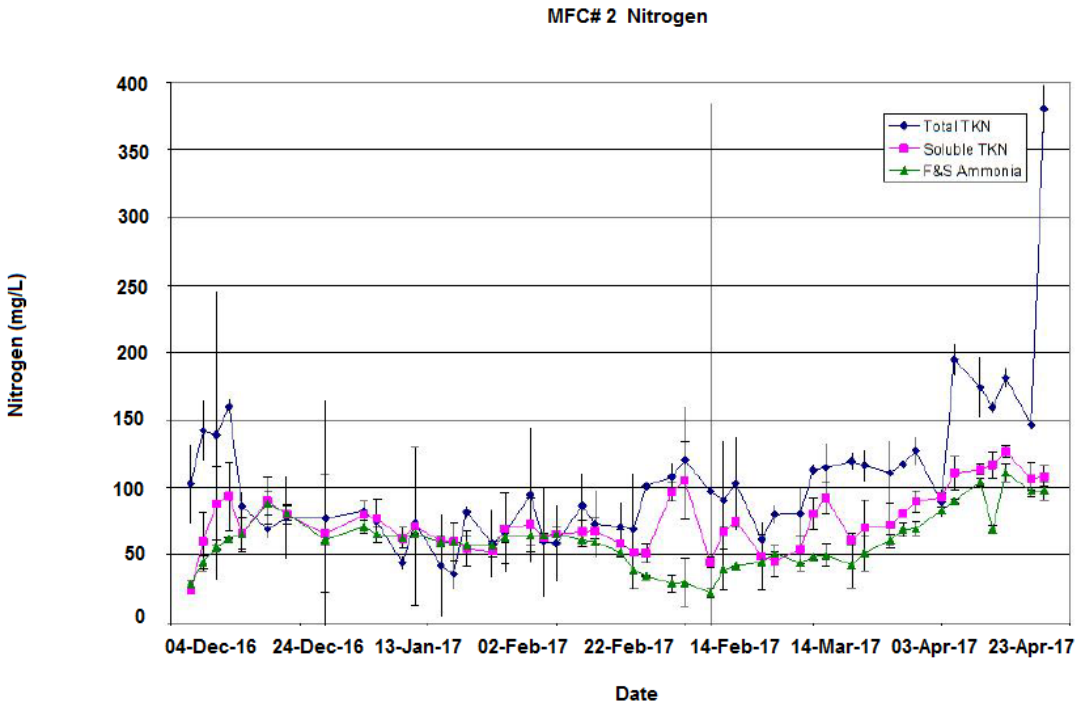


Figure 2.7: MFC#2 TKN (Total and Soluble) and FSA

Also, the ample range of oxygen concentration in MFC#1 introduces an uncertainty in the cathodic effects on coulomb production for MFC#1. A higher oxygen concentration is desirable throughout the second experiment to eliminate cathodic influences on MFC#1 performance, but unfortunately, the system is unable to maintain reliable high oxygen levels.

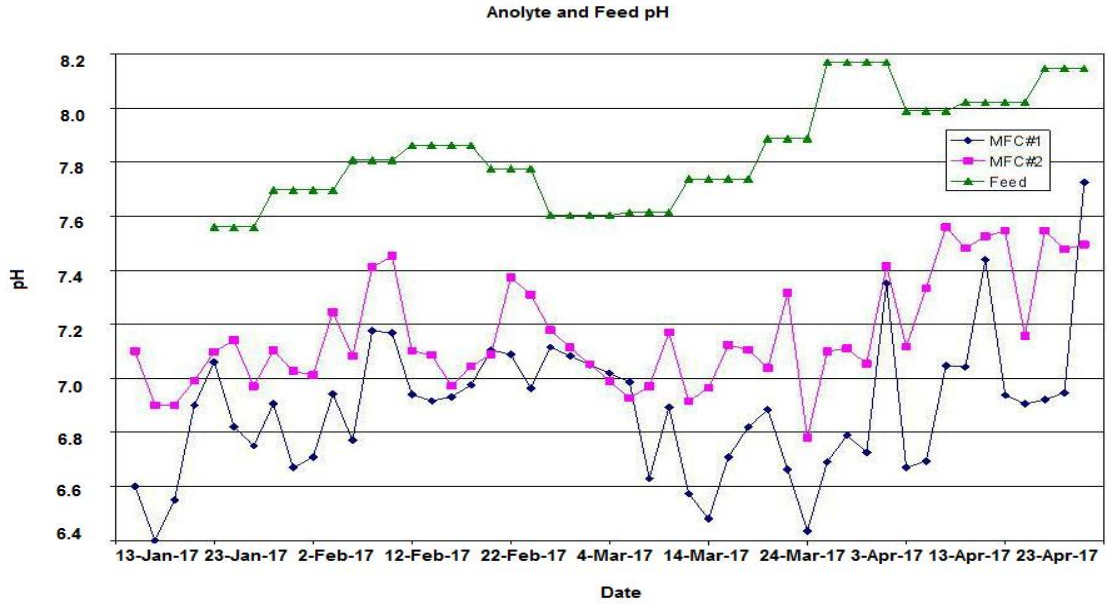


Figure 2.8: Anolyte and Feed pH

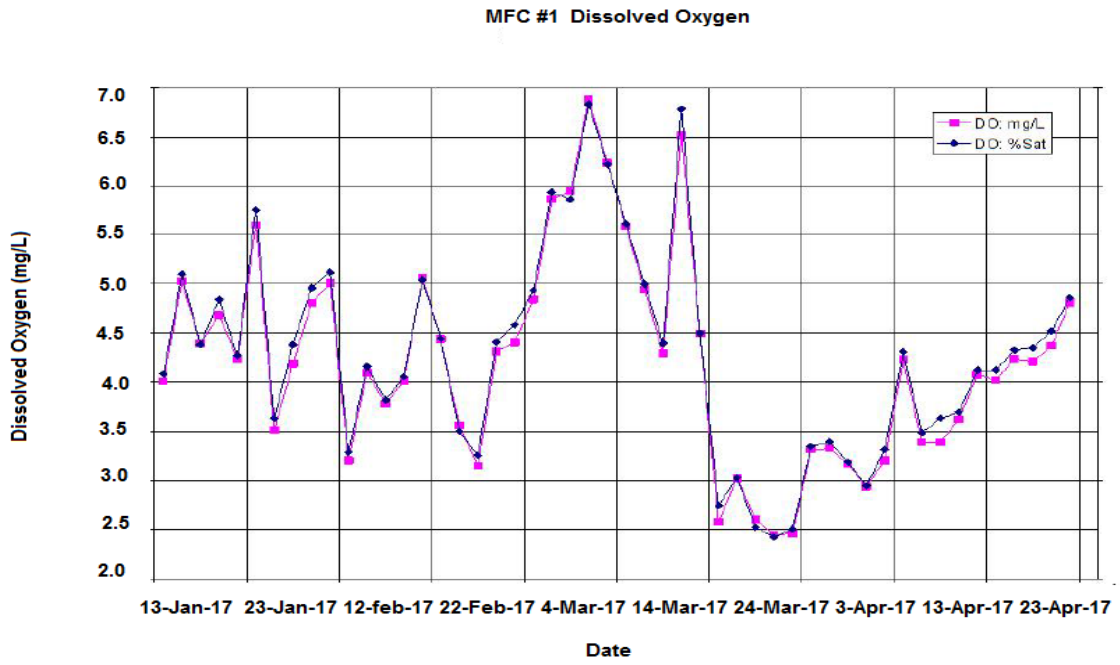


Figure 2.9: Dissolved Oxygen with time

2.5.7 Cover Space Gas

The main result from the cover space gas analysis is the COD_{Gas} term, which stands itemized in Table 2.7 with the COD results. This result is obtained which is based on an approximated cover space volume of 10 mL. Throughout the second experiment, the

quantities of methane produced to equal the COD_{Gas} values in Table 2.7 are 56.3 and 110.7 mL for MFC#1 and 69.7 and 59.0 mL for MFC#2, with a 95% condense level.

These production rates are much smaller, and it is believed that volumetric methane production is very close to negligible. However, as discussed with the COD results, methane production of only 25 mL/day could estimate the variance observed between the measured and calculated COD_{Acc} values. If the Tedlar bags are leaking, it is possible that this methane production took place and is unmeasured.

2.6 Conclusion

Two MFCs are operated in parallel successfully for 182 days, or approximately six months. The system is worked at a controlled voltage of 0.3V and under a fed-batch sample/feed protocol. Several system variables which remained measured throughout the experiment are the cell voltage, MFC current, waste activated sludge feed, and wastewater anolyte variables (COD, TKN, FSA, and pH), ferricyanide concentration in MFC#2 catholyte, DO in MFC#1 catholyte, and the cover space gas composition. The calculation of current and power densities is performed using two useful surface areas, EESA based on the entire cathode surface area and EMSA based on the Naon ® PEM surface area.

Power densities of up to 167 $mW/m^2$are observed from MFC#2 using the EMSA, while the same power production results in a power density of 4.15 mW/m^2 using the EESA. These areas represent upper and lower bounds on the effective surface area.

The power density thus calculated with the EMSA is comparable to previously reported literature values in similar systems operated with a glucose feed. A COD balance determines for each MFC, which is resulted in a COD accumulation term. Measurement of the final accumulation term results in an accumulation discrepancy of 11660.8 mg and 10901.1 mg for MFC#1 and MFC#2, respectively. Here is the remainder

of 40% of the overall COD_{feed} for each MFC. It is continuously recommended that the most likely cause for the COD discrepancy is greater methane production than that which is measured. TKN measurements further suggested that particulate matter is accumulating within the system. It is also held and noted that the addition of BSA appeared to increase the TKN leaving each MFC, as it is suspected and based on the BSA nitrogen content. The feed and anolyte pH is remained relatively close to neutrality, reducing the possibility of pH effects on biological activity in the anode chamber.

The change in ferricyanide concentration is consistent with that expected from the measured current in MFC#2. DO measurements generally showed oxygen concentration in the catholyte of MFC#1 to range between 30% and 80% of saturation. Lower oxygen concentrations remained observed during higher current production. Finally, the cover space gas analysis indicated the presence of nitrogen, carbon dioxide, and methane, but the overall production of these gases was found to be very low unless gas-phase leakage is prevalent. Methane production represents the suspected discrepancy in the COD balances for each MFC.