Chapter 1

Prologue

1.1 Introduction

The present invention: GECS is related to Renewable Energy Conversion System. The personal power utilization scheme: GECS is used to capture energy produced by naturally occurring microbial metabolism from organic-rich materials such as food scraps, manure, plant waste, etc to run electrical household appliances and other electrical lighting loads. The reliable energy is obtained cleanly by using the developed GECS. Consequently, the GECS for personal power generation and utilization performs this function at a low cost and contributes to reducing environmental pollution. Environmentally beneficial and sustainable power production is coming to the forefront of both research and world issues. Organic waste and wastewater treatment are also a priority in the developing global community. Microbial fuel cells (MFCs) are an alternative energy technology that can simultaneously treat organic waste and wastewater. MFC is one of the recent popular researches which provides the potential to address the wastewater and organic waste treatment. To achieve the eventual goal of scaling up MFC technology for commercial and industrial applications, moreover, research on MFC technology is needed in many areas to design, configure, and integrate into existing technologies, operation and system stability (Du, Li, and GU, 2007).

In this chapter, the theory on MFCs is presented along with principles of wastewater and organic waste treatment as they pertain to MFCs. The research objectives and thesis structure follow a short literature review that focuses on several pivotal studies in the evolution of MFCs as well as some of the more recent, promising discoveries.

1.2 Literature Review

While MFCs are a relatively new technology, the concept of utilizing microorganisms to generate electricity is incipiently known in the 18th century. In 1911, Prof. Potter in botany at the University of Durham, UK, described the electricity production gained from cultures of yeast and Escherichia coli. It was the first time that the biological process was observed producing bioelectricity.Potter was the first person successful to demonstrate a half cell using microbes to produce electricity in 1912. The results of these experiments are not published for almost 20 years. Some studies on microbial and biofuel cells are reported between the 1950s and the 1980s, though little attention is paid to this technology (Bullen, Arnot, Lakeman, and C., 2006). The vast majority of the advances made in MFC research have occurred over the last 5 to 10 years and also with renewed interest in alternative fuels and water treatment, The history started with the relationship between biology and electricity when Galvani in 1791 observed electric current generation with twitching of frog's leg. Fifty years from then, in 1839, Grove created first fuel cell. In his experiment, Grove reversed the process of electrolysis of water, where hydrogen and oxygen were also combined back to water and electricity produced during the process as described by Ieropoulos et al. (2005). Further progress made by Cohen in 1931 that could produce more than 35 V through half fuel cells connected in series as reported by Singh and Songera (2012). Palmore and Whitesides (1994) reported the increased demand for biological fuel cells during 1960s due to the space race as the USA space program was interested in this technology. Rao and Drake (1969) showed that using platinum as the working electrode, glucose can be used as fuel to produce power and in 1976 they identified the clear principle of the biological fuel cell (Rao et al. 1976). The name and concept of MFCs were first explored from 1980s (Roller et al. 1984). The concept of combining wastewater treatment and MFCs was introduced in

1991(Habermann and Pommer 1991). MFC research has been the trend from a surge in popularity and relevant research. Bennetto et al. are one of the first groups to consistently pursue MFC research in the 1980s and 1990s (Allen and Bennett, 1993). The use of wastewater or other waste streams as an anolyte/substrate became more widely studied (Moon, Chang, and Kim, 2006; Min, Kim, Oh, Regan, and Logan, 2005; He, Minteer, and Angenent, 2005; Aelterman, Rabaey, Clauwaert, and Verstraete, 2006; S. J. You, Zhao, Jiang, and Zhang, 2006). Some studies have also investigated the production of hydrogen gas from wastewater under fermentation conditions in MFCs (Logan, Oh, Kim, and Van Ginkel, 2002; Liu, Grot, and Logan, 2005). First, MFC designs employed two separate chambers, one for the anode side and one for the cathode side (Bullen et al., 2006). Recently, an alternative design is proposed by Liu et al.(Liu and Logan, 2004; Liu, Ramnarayanan, and Logan, 2004). The single-chamber annular design, consisting of a central, hollow cathode, separated from the anolyte by the PEM. Multiple anode rods existed in the anode chamber, while the whole structure obtained encapsulated in an acrylic glass cylinder.

The performance depends on the efficiency of bacteria to transfer their electrons by metabolizing the organic matter to the anode. It also depends on the electrochemical reaction at the cathode (Rabaey and Verstraete 2005). Considering the above two, factors responsible for the affecting the performance of MFCs are type of microorganism, type of organic biodegradable matter or feed, pH and temperature of the system, electrode material, proton exchanger, internal and external resistance, catholyte, aeration in cathodic chamber (Du et al. 2007).

The electron acceptor is oxygen that passed through the center of the hollow cathode. The most significant advantage of this design is the exploitation of the relatively large concentration of oxygen in the air as opposed to water. Subsequent studies of MFCs

by this particular research group involved the single-chamber MFC. A subject of earlier studies in MFCs is the requirement for electron mediators that are involved in the transport of electrons to the anode surface (Bullen et al., 2006). Gil et al. (2003) amongst other groups found that electron transfer to the anodes may be self-medicated or unnecessary if biofilms form on the anode surface (Zhang, Xu, Diao, and Shuang, 2006; Prasad et al., 2007). A very recent study utilizes some of the accepted electron mediators from earlier studies to examine the mediators have on electricity production and fermentation within the anolyte (Sund, McMasters, Crittenden, Harrell, and Sumner, 2007). One particular electron mediator, resazurin, is found to increase electricity production while having little effect on fermentation rates.

A large number of studies on MFCs have focused on electrode materials and surface area impacts. The consequences of electrode materials have been tested by a few research groups, focusing on the use or addition of metals such as manganese, copper, and gold (Park Zeikus, 2002; Crittenden, Sund, and Sumner, 2006; Kargi and Eker, 2007).

The impact of electrode surface area, spacing relative size to the PEM on electricity generation have also continued to investigate (Oh & Logan, 2006; Ghangrekar and Shinde, 2007). It is seen that the PEM surface area is considerably smaller than the electrode surface areas, current production is found to be substantially limited. The aforementioned works held correlated to higher internal resistance in the MFC design.

The efficiency of conversion into electricity also depends on the components present in the waste matter. When we are talking about substrate or feed-in MFC, the composition and the concentration becomes very important because it has been observed that the microbial community present at the anode and the power output in MFCs is influenced by the nature of the feed. Pure chemical compounds such as glucose and other

monosaccharides like xylose, arabinose, fructose, mannose, galactose (Catal et al. 2008a), lactate (Lanthier et al. 2008), acetate (Logan et al. 2007), propionate (Oh and Logan 2005), sucrose (Behera and Ghangrekar 2009), mannitol and sorbitol (Catalet al. 2008b) have been used as feed. The abundance of organic waste in the form of wastewater makes this application attractive for large scale energy generation.

Wastewaters from different industries can be used as feed such as beer brewery (Köroğlu et al. 2014), chocolate industry (Patil et al. 2009), domestic (Ren et al. 2014), food processing (Oh and Logan 2005), dairy (Elakkiya and Matheswaran 2013) and synthetic wastewater amended with pure compounds mentioned above (Pant et al. 2010). MFCs capture energy in the form of electricity without any input of electricity and this makes it a promising technology. The approach of MFC is completely different than the traditional methods of aerobic and anaerobic degradation of wastewater. Kim and co-workers demonstrated the use of industrial wastewater sustained by starch for electricity generation in the late 1990s. However, the output of energy was low leading to curiosity regarding the applicability of this technology.

In 2004, MFC was used to treat domestic wastewater to practical levels with simultaneous electricity generation (Liu et al. 2004). This study was the turning point for the improvement amongst the operational parameters, though the power produced was considerably low (26 mW/m2) but very high compared to previous experiments.

The use of marine sediments in MFCs was already shown by Reimers et al. (2001) emphasizing the utility of a wide variety of substrates and microbial sources. Following these demonstrations, the primary goal was set to increase the efficiency of MFCs in order to make it scalable technology for the treatment of domestic, industrial and other types of wastewaters.

Water pollution, wet waste management in the urban and rural is a major problem in India and as mentioned, distilleries are prime polluting industries. Treatment of high COD distillery wastewater is a challenge. It is generally treated with Physico-chemical methods such as coagulation, adsorption and reverse osmosis. High 35 cost and tremendous sludge production are major inhibitions in the use of these methods. The alternate method of treating distillery wastewater is biological. These include aerobic degradation, anaerobic digestion, anaerobic filters, up-flow anaerobic sludge blanket reactors (Jain et al. 2002). Anaerobic treatment is preferred because of low sludge production. Amongst the anaerobic treatments, anaerobic digestion results in the formation of biogas – a utilizable form of fuel and hence preferred. Along with the fuel, it stabilizes the waste and destroys viral and bacterial pathogens (Chen et al. 2008). However, the wastewater even after anaerobic digestion, that is ADDW, has the potential to be a pollutant due to the accumulation of recalcitrant compounds and the presence of melanoidins (Ghosh et al. 2002) and presence of high COD (Singh 2010). The literature revealed the focus on decolorization and COD reduction of ADDW due to dark-colored melanoidins. Kumar et al. (1998) achieved maximum decolorization up to 71.5% whereas COD reduction was 90% using fungal cultures Coriolusversicolor and Phanerochaetechrysospotium. However, the decolorization and COD reduction was achieved in 12.5% (v/v) ADDW broth media. Ghosh et al. (2002) used two-stage bioreactor for the treatment of ADDW. They used bacterial species Pseudomonas putida U and Aeromonas strain Ema for decolorization and COD reduction studies. P. putida showed 60% color and 44.4% COD reduction, however, Aeromonas sp. could not decolorize ADDW though the COD reduction was more than P. putida (66%). Similar studies achieved the decolourization over a range of 67% to 81% (Adikane et al. 2006;

Mohana et al. 2007; Shayegan et al. 2005), whereas the COD reduction was 51% and 84% by Mohana et al. (2007) and Shayegan et al. (2005) respectively.

Biological treatments, using fungi such as Coriolus sp., Aspergillus sp., Aspergillusniger, Trametesversicolor, Phanerochaete sp., Phanerochaetechrysosporium, Coriolusversicolor, Coriolushirsutus and Penicilliumdecumbes, yeasts such as Citeromyces sp., and certain bacteria such as Bacillus sp., Pseudomonas fluorescence, and acetogenic bacteria have been reported (Jiranuntipon et al. 2009).

The use of platinum catalysts for the cathode has also been investigated (Zhao et al., 2005; Cheng, Liu, and Logan, 2006b). Relatively small loadings of platinum on the cathode surface have been observed to increase current densities over that of a non-catalysed carbon cathode. A few review papers that describe the state of the art of the MFC research have been published recently by researchers Bullen et al., 2006; Du et al., 2007; Davis and Higson, 2007. For a thorough review of MFC research for the design of Green Energy Conversion System (GECS) and state of the art which provides a collection of MFC-related literature.

Electrode materials can be improved for better performing by MFCs. For example, platinum and platinum black electrodes are superior to graphite, graphite felt and carbon-cloth electrodes for both anodes and cathodes (Du et al. 2007). Schröder et al. (2003) reported the use of platinized carbon cloth as anode and produced a current of 2 – 4 mA by using E. coli in a standard glucose medium, however, an unmodified carbon-cloth showed no current flow under the same operating conditions. The basic advantage of platinum is its higher catalytic activity for oxygen reduction than graphite materials and hence MFCs with platinum or platinum-coated cathodes show higher power densities (Moon et al. 2006; Oh et al. 2004). But platinum material is very costly and hence graphite material is preferred for electrodes. Electrode modification is actively

investigated by several research groups to improve MFC performances. Along with the anode material and its configuration, surface areas of electrodes represent an important parameter in MFCs, as the current output was found to increase with the increase in the thickness of the anode bed and with the approximate anode area (Di Lorenzo et al. 2010). In particular, a three-dimensional anode would allow a greater surface area for microbial attachment. Graphite granules have been widely used as both anode and cathode material (Aelterman et al. 2006; Heilmann and Logan 2006; Rabaey et al. 2005).

1.3 Research Objective

The research objectives established for this work are:

- To compare the impact of dissolved oxygen and ferricyanide as electron acceptors on the generation of electrical power from two MFCs for GECS operated identically with organic waste activated sludge feed.
- To compare the impact on the type of electron acceptor on the biological wastewater quality variables and any O^-gases produced during the generation of electricity.
- To evaluate the destination of COD fed to the system by calculating a COD mass balance on each MFC for performance evaluation of developed green energy conversion system.
- To evaluate the use of data transforms of ecological data before performing principal component analysis (PCA) for CLPP of the MFC anolyte microbial communities for design optimization of the green energy conversion system.
- To assess the effects of an acclimation period and the dosing of pure carbon sources to the anolytes on electricity production, anolyte wastewater quality, and microbial community profiles to gain a better understanding of MFC start-up periods and which types of carbon sources are responsible for electricity production.

- To propose enzymatic bio dry cells of the straightforward structure without the proton exchange membrane.
- To make the bio dry cell free from maintenance, reliable, efficient and performs as an energy server.
- The possible approach of this thesis is to bring this technology into real-world applications is the multiplication of units connected mutually as modules (stacks) for useful power levels.

1.4 Background of the Innovation

The MFC theory has two sub-sections and the principles and basic designs are presented, followed by organic waste principles applicable to MFC operation. Further, this chapter presents a detailed review of MFC technology with its design, history and working principle. The review discusses various parameters affecting the efficiency of MFC. It also discusses the utilization of wastewater and organic waste for the generation of electricity. It discusses various microorganisms responsible for the activity and a detailed review of the mechanism of transfer of extracellular electrons from bacteria to anode.

1.4.1 Microbial Fuel Cell (MFC) Design Principles

Broadly two MFC designs are available: (a) single-chambered MFC and (b) two-chambered MFC. The basic difference between the two depends on the number of reservoirs. In single-chambered MFC (Figure 1.1), both electrodes are in the single chamber.

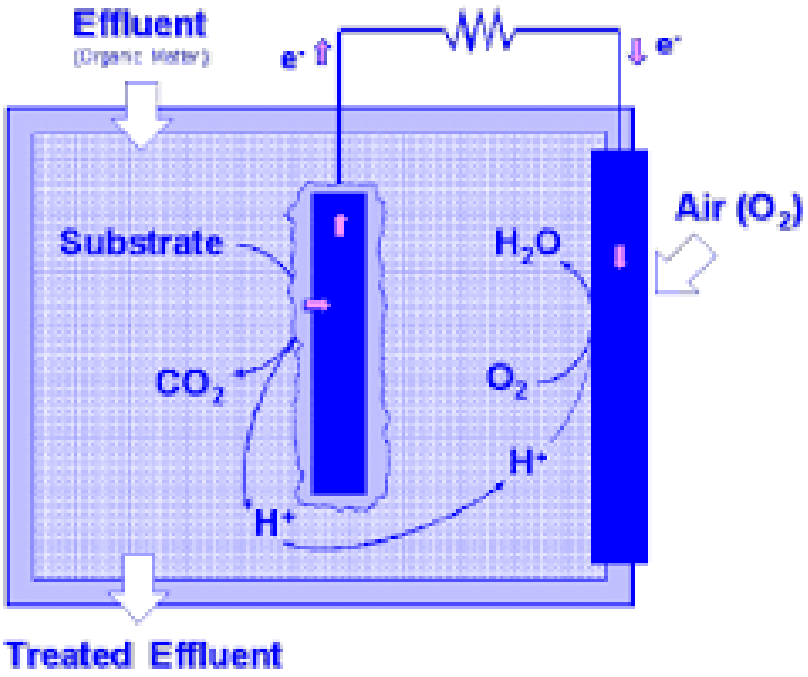

Figure 1.1: Basic Single-Chamber Microbial Fuel Cell (source)

The electrons generated at the anode by bacteria are accepted by oxygen at the cathode. The disadvantage is diffusion of oxygen at anode inhibiting bacteria from transferring electrons to anode, thereby, reducing the efficiency of electricity generation (Aziz et al. 2013). Liu and Logan (2004) reported a maximum of 0.49 W/m2 of power production using single-chambered MFC. Figure 1.2 gives the basic design of a dual-chamber MFC which is similar to that used in this thesis and to generate electricity, bacteria in the anode chamber utilize substrates in the anolyte to liberate electrons. Particles at the cathode surface reduce electron acceptors. The electrical circuit is connected using proton migration from the anolyte, through the proton exchange membrane (PEM) and to the catholyte where the electron acceptor is available. The anolyte consists of a substrate and the microbial community active in the substrate. In this thesis work, the anolyte which includes waste activated sludge as a substrate, and the bacterial consortium which is naturally present in the waste activated sludge. In MFCs, bacteria at the anode metabolize biodegradable matter for example glucose. During the metabolism they generate electrons

and protons. Electrons are transferred to cathode through external resistance; simultaneously protons are transferred to proton exchangers, thus completing the circuit and generating electricity (Figure 2.3) (Oh and Logan 2006; Oliveira et al. 2013; Rabaey and Verstraete 2005). Thus if biodegradable matter is available in abundance then microbes will continuously generate and transfer electrons and protons to anode resulting in continuous generation of electricity. For successful operation of MFC, particulate matter in the anolyte is needed to be remain solubilized before microbes come appropriately.

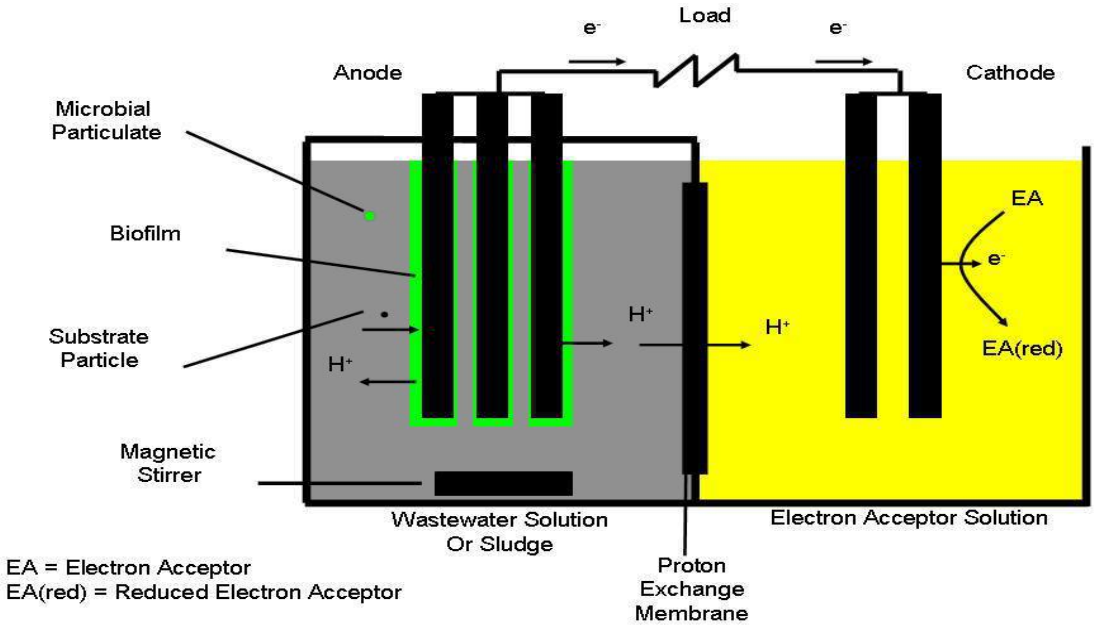

Figure 1.2: Basic Two-Chamber Microbial Fuel Cell (source)

The anolyte requires mixing throughout MFC operation to keep particulate components in suspension and to assist in the mass transfer of substrates to the anode surface. The aforementioned technology is implemented in the MFC as illustrated in Figure 1.1 by the magnetic stirrer in the anode chamber. The anode consists of an electrically conductive, non-toxic material, ideally conducive to bacterial attachment. In this study, the anodes are graphite plates. Most substrate utilization reactions resulting in electricity generation take place at the anode surface which allows liberated electrons to travel through the anode

and the rest of the electrical circuit. The attachment of the bacteria themselves to the anodes and form a biofilm, the electrons liberated during substrate utilization have a higher probability of traveling 5through the anode and electrical circuit as compared to being involved in competing for electron acceptor reactions within the anolyte. Alternatively, electrons may reach the anode surface from the anolyte solution if they continually conveyed via electron mediators.

Electron mediators are chemicals in the anolyte which shuttle electrons liberated during substrate utilization reactions in the anolyte to the anode surface. Theoretically, with each liberated electron, there is a corresponding proton released to the anolyte. The electrical circuit placed between the anodes and the cathodes consists of a load to introduce resistance to the system. In this work, a potentiometer controlled the voltage between the anodes and cathodes by varying the active opposition of the circuit load. The MFC is powering a device, the device represents the burden and associated resistance in the circuit.

The electrons are passed through the course to the cathode that consists of an electrically conductive material. For this thesis work, the cathodes and anodes are obtained which is made up of graphite plates. Reduction reactions for the electron acceptors take place at the cathode surface where the electron moves from the cathode towards the electron acceptor. The catholyte consists of an electron acceptor solution and the two different electron acceptors are associated such as dissolved oxygen and ferricyanide. Fundamental electron acceptor concentrations in the catholyte result in higher densities at the cathode surface to support the transfer of electrons.

The PEM provides a physical/chemical barrier between the anolyte and catholyte and acts as the physical barrier between the active anode and cathode chambers. Protons in the anolyte selectively migrate through the PEM to the catholyte to maintain

electroneutrality within the system process. A cover space gas exists in the anode chamber, and measurement of the gas composition and quantity allows for the determination of any O^-gas properties during MFC operation.

1.4.2 MFC and Organic waste Theoretical Principles and Variables

The main constraints in the construction of MFC are the use of material which can increase power production. The next issue is to minimize the cost as MFCs are scalable systems. The three main components of MFCs are anode, cathode, and membrane. One of the primary and essential factors is electrode material because it is related to the interaction with bacteria through anode and reaction between electron and proton with high reduction potential entity such as oxygen at the cathode. Since the anode deals with bacterial growth, they should have good biocompatibility, high surface area for the growth deposition and the development of biofilm along with high conductivity, chemical stability especially in wastewater, good adaptability, stability at different temperatures and pH, resistance to biofouling and should have low cost. Carbon materials satisfy almost all criteria and hence they are preferred as anode. Different forms of carbon materials are available such as cloth, fibers, and graphite plates, rods and granules (Hu 2009). The required properties of cathode are very similar to anode except for the fact that cathodes may not be biocompatible. However, when bio-cathodes are used in MFCs then biocompatibility should be taken into consideration.

In the case of oxygen used at the cathode, the cathode material should have certain amount of platinum which acts as a catalyst for the reduction of oxygen. But platinum is a costly metal and can be easily poisoned by microbial by-products such as hydrogen sulphide (Logan 2008). Thus to reduce the cost, materials similar to anode are used for cathode which lacks platinum and instead of oxygen potassium ferricyanide or potassium permanganate is preferred as they readily accept electrons (You et al. 2006). In case of

two-chambered MFCs, anodic and cathodic chambers are separated by proton exchanger with a basic function of selective transfer of proton from anode to cathode. The commonly used proton exchangers are salt bridge, cation exchange membrane (CEM) and proton exchange membrane (PEM). Considering the cost and the performance, ascending order will be PEM > CEM > salt bridge. Both PEM and CEM are permeable to gas but impermeable to water. This is another disadvantage apart from being costly is diffusion of 33 oxygen from cathodic chamber to anodic chamber reducing the efficiency of the system (Logan 2008). Yet, the diffusion is less than in case of single-chambered MFCs.The two electrical variables of concern in an electrochemical system are the voltage and the current. By definition, the product of these two variables is power. The flow of electrons from the anode to the cathode acts induced by the voltage difference between the two electrodes and the concentrations of readily available electron donors and acceptors at the anode and cathode surfaces, respectively.

The voltage obtained between the electrodes is measured in this study through automatic resistance adjustments made by the potentiostat. The current is measured and then power is calculated during MFC operation. The electron donor reaction at the anode is represented by Equation 1.1:

$$\text{Organics in waste} + H_2O \rightarrow CO_2 + NH_4 + HCO_3 + H^+ + e^- \quad (1.1)$$

This reaction is carried out by the bacteria in the anolyte or at the anode surface. The liberated electrons travel through the anode to the cathode via the electrical circuit where they react with the electron acceptors at the cathode, as described by Equation 1.2:

$$EA + e^- \rightarrow EA^- \quad (1.2)$$

where,

EA = oxidized electron acceptor

EA^- = reduced electron acceptor

Alternatively, sources of electrons in the anolyte is oxidized by competing electron acceptors in the anolyte and negating their electron capacity for electricity production. Since oxygen is such an electron acceptor which requires to eliminate from the anode anolyte chamber under anaerobic conditions. However, oxygen is not discharged from the anolyte, as it is present in some of the substrates.

A poor seal on the anode chamber may allow oxygen into the anolyte as well. Also, under anaerobic conditions, some nitrogen species such as nitrate and nitrite as well as carbon may act as electron acceptors. Thus, competing electron acceptor reactions may exist in the anolyte, as represented in Equations 1.3 through 1.5:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (1.3)$$

$$2NO_3^- + 12H^+ + 10e^- \rightarrow N_2(g) + 6H_2O \quad (1.4)$$

$$2N\,O_2^- + 8H^+ + 6e^- \rightarrow N_2(g) + 4H_2O$$

$$HCO_3^- + 9H^+ + 8e^- \rightarrow CH_4(g) + 3H_2O \quad (1.5)$$

The organic wet waste characteristics measured in this study are chemical oxygen demand (COD), soluble and total Kjeldahl nitrogen (TKN) and pH. COD is a measure of the quantity of oxidizable material in the MFC anolytes, while the TKN is a measure of the amount of nitrogen in the MFC anolytes. The COD is indicative of the amount of energy that the anolyte may supply as electrons to the anode. TKN and Free and Saline Ammonia (FSA) measurements allowed the tracking of the nitrogen components in the anolytes in the form of particulate and FSA. It is observed that at increased levels of FSA witnessed particulate components in the anolyte containing nitrogen are solubilized.

Under anaerobic conditions, carbon acts as an electron acceptor, as illustrated in Equation 1.5 where it leads to methane production, which covers as an O^-gas in the headspace of the anode chamber. Also, under anaerobic conditions, fermentation processes can lead to the generation of volatile fatty acids, which tend to lower the pH in

the anolyte. A more thorough description of the design, principles, associated equations, procedures and methods used in this thesis as produced in Chapters 2 through 4.

1.5 Thesis Organization

This thesis comprises of five chapters. Chapter 1 presents theoretical principles applicable to MFCs, the research objectives and a brief literature review. Chapter 2 presents the design parameters of MFCs for the GECS and the associated apparatus. Chapter 2 also illustrates and evaluates the MFC system operation and overall performance in addition to the full COD mass balance. Chapter 3 introduces the use of Bio dry cell-based GECs to collect power output data from the organic wastes. The work included the materials, anaerobic sampling, and BDC technology methods, data treatment, data transform and principal component analysis for interpretation of results. Transforms of data from all BDC are estimated, while the microbial ecology remains performed for the experiment. Chapter 4 presents the full comparison of the three Soil-based MFCs concerning electricity production, organic waste quality, and microbial ecology. The analysis continues conducted in sections that describe the acclimation period and each of the three SMFCs in the carbon source dosing period. Chapter 5 presents the main conclusions from Chapters 2 through 4 and establishes a set of recommendations for future work and analytical test data and collected literature to date, respectively, and do present as soft copy.