

**EFFECT OF HRT ON THE PERFORMANCE OF DUAL CHAMBER
CONTINUOUS FLOW MICROBIAL FUEL CELL (MFC) TREATING
DOMESTIC WASTEWATER**



Irfan Ahmad

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A thesis submitted in partial fulfillment of requirements for the degree of
Master of Science

In

Environmental Engineering

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2019

ii

CERTIFICATE

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LIST OF ACRONYMS

MFC	Microbial fuel cell
CFB	Carbon fiber brush
GR	Graphite rod
COD	Chemical oxygen demand
BOD	Biological oxygen demand
TOC	Total organic carbon
CEM	Cation exchange membrane
PEM	Proton exchange membrane
CE	Columbic efficiency
HRT	Hydraulic retention time
mM	Milli molar
Mg/l	Milli grams per liter
mV	Millivolt
OCV	Open circuit voltage
OLR	Organic loading rate
WWTP	Wastewater treatment plant
ARB	Anode respiring bacteria
mW/m ²	Milliwatt per square meter

ABSTRACT

Water scarcity has become the worldwide issue. In many applications such as crop irrigation, groundwater recharge and industrial processes, there is an increase in demand for domestic wastewater reclamation and recycling due to water shortages and expanding population. In order to accomplish high level of wastewater treatment, a large input of energy is required. The heavy demands of energy for traditional wastewater processes make it important to explore other treatment processes to minimize operational costs using more energy efficient processes such as anaerobic treatment processes. One of the process is microbial fuel cell (MFC). In a standard MFC process, anaerobic microbes are used in an anodic chamber to degrade organic compounds and thus treat wastewater. Bacteria-generated electrons are transmitted to the negatively charged electrode (anode) and from where they flow towards the positively charged electrode (cathode) connected by some conductive wire consisting of a resistor or operated under a load. In the current research two dual chamber MFCs were used with two different categories of electrodes installed in each of reactor chamber. One of the electrodes was carbon fiber brush (CFB) and the other was graphite rod (GR). Domestic wastewater was utilized as a substrate and the reactors were run in a semi continuous flow at HRTs of 48, 36, 24, 12, 8, 4 and 2 h. Both reactors were run at 1000 Ω internal resistance. Maximum COD removals of 80.3% and 73.9% were achieved for CFBMFC and GRMFC at an HRT of 48 h respectively, which indicates higher COD removals are obtained at longer HRTs. Voltage generation and power production in both reactors were continuous. At an HRT of 8 h maximum voltage of 319 mV and 308 mV was generated for CFBMFC and GRMFC respectively. Similarly, at the same 8 h HRT, maximum power production was 58 mW/m² and 77 mW/m² for GRMFC and CFBMFC respectively. Power generation showed decreasing trend with increasing HRT. The CE was in the range of 4.2 to 5.44% for both MFC reactors with CFBMFC showed relatively higher CE than GRMFC. Thus, the current research shows that domestic wastewater can be treated in an MFC along with the subsequent power generation. The power generation and treatment performance of an MFC can be enhanced by using suitable electrodes such as carbon fiber brushes and by optimizing HRT.

CHAPTER 1 INTRODUCTION

1.1 Background

Due to expanding population and huge water consumption, water scarcity is becoming the worldwide issue. In many applications such as crops irrigation, groundwater revival and industrial processes, there is an increment in demand for domestic wastewater recovery and reuse due to water deficiencies and expanding population. As water and energy are related to accomplish high level of purification, a large input of energy is required. In the last few years, the overall world energy need has increased drastically (Sharvini et al., 2018). Fossil fuel depletion, environmental pollution and energy crisis has diverted worldwide attention towards more renewable energy resources. Conventional wastewater treatment methods, most commonly activated sludge and further biological processes are also very energy intensive processes. This high demand of energy for wastewater treatment puts more pressure on the overall energy grid. Aerobic treatment processes also generate big quantities of sludge waste that is very expensive to dispose and treat (Ge et al., 2013). The very high demands of aerobic processes make it essential to explore and study other methods of treatment, to decrease operational costs by optimizing processes or using more energy efficient processes such as anaerobic treatment processes (McCarty et al., 2011).

Domestic wastewater treatment is a problem because to manage its huge quantity, it needs large infrastructural investment. Domestic wastewater contains average COD, enough nutrients, a neutral temperature, large volume, enhanced microbial consortium, and easy availability. Within sewage there are essentially three forms of energy stored: (i) organic material ($\sim 1.79 \text{ kWh} / \text{m}^3$); (ii) Elements such as nitrogen and phosphorus ($0.7 \text{ kWh} / \text{m}^3$); and (iii) heat energy ($7 \text{ kWh} / \text{m}^3$) (McCarty et al., 2011). Energy available in the source of domestic wastewater can be categorized as chemical and heat energy. Chemical power ($\sim 26\%$) is accessible in carbon forms (measured as demand for chemical oxygen, COD) and nutrient compounds (nitrogen, N and phosphorus, P). Thermal energy retains a significant part of this power potential (74 percent) that heat pumps can capture. Chemical

energy can be obtained effectively while it is not possible to obtain thermal energy except by using a thermal pump and under the sewage origin temperature (Gude et al., 2013).

Efficient treatment of domestic sewage can be achieved by the MFC. Over the past decade, MFCs are very useful in converting wastewater's chemical energy into electrical energy. In a standard MFC process, anaerobic microorganisms are used in an anodic chamber to oxidize organic compounds and thus treat wastewater. Bacteria-generated electrons are transmitted to the negatively charged electrode (anode) and move towards the positively charged electrode (cathode) connected by an electrically conductive material consisting of an external resistor (Electricity generation running the device) (Logan et al., 2006).

Majority of the microbial fuel cell research was conducted in a batch mode (However, the batch system has several disadvantages, such as the depletion of substrates about restricted nutrients and the toxicity of by-products (Bailey and Olis, 1976). Ceaseless stream innovations have a few preferences; (1) medium piece can be upgraded for ideal profitability; (2) optional metabolite generation can likewise be controlled; (3) development energy and active constants were determined accurately, (4) the technique prompts reproducible outcomes and solid information; (5) it accomplishes greatest efficiency per unit volume and (6) less work escalated nonstop development (Rahimnejad et al., 2011). In continuous mode studies, removal levels are typically determined based on concentrations of reactor and permeate COD as a function of HRT (Fan et al., 2012; Moon et al., 2005). With shorter HRTs, COD removal rates usually reduce (Zhang et al., 2013). Thus, while at these shorter HRTs high energy densities are attained, higher HRTs are required to decrease COD concentrations appropriate for release of wastewater (Ahn and Logan, 2012).

The current study investigates the treatment of domestic wastewater in MFC operated in a semi continuous flow mode.

1.2 Objectives of the Study

The primary objectives of the current study include;

- To study the effect of different types of electrodes (graphite rod and carbon fiber brush) on the performance of MFC.

- To study the impact of HRT on treatment performance (COD removal) and power production.

1.3 Scope of the Study

The scope of this current study includes;

- Modification of available lab scale double chamber MFC for semi continuous process
- Use of anaerobic sludge as an inoculum
- Usage of domestic wastewater as a sole carbon source (Substrate).
- Use of two different electrodes (graphite rod and carbon brush) for best performance.
- Analysis of the MFC performance for power production, COD removal, columbic efficiency and internal resistance.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview of Microbial Fuel Cell (MFC)

Microbial fuel cells (MFCs) and wastewater biological systems are an important and evolving scientific and technological field that mixes biological activity with conventional abiotic electrochemical reactions. (Logan et al., 2006; Logan and Rabaey, 2012; Logan and Elimelech, 2012; Rinaldi et al., 2008).

In 1911 Potter ascribed the idea of using microorganisms to produce electrical energy. Since then, along with Cohen's 35-unit set-up, further ideas and practical advances have been studied. Recently in the late 90's the research on artificial mediators led to the growth of the so-termed "analytical MFC" that is use until now. In the 1980s, scientists wanted to provide low-cost and consistent energy to third world countries, heading to a revolution in the design of microbial fuel cells. Allen and Peter began to understand the electron carrying string and made substantial technological advances that made it possible to create the basic design of MFCs (Mercer, 2012). However, the use of MFCs is yet in the pilot phases in third world countries due to the difficulties of make simpler the design enough to allow disadvantaged countryside farmers to construct them.

Significant progress has already been made from these early examples in understanding electron transfer processes, developing effective bio-electrocatalytic edges and developing effective, small-cost and sturdy electrode ingredients, but there is still plenty space for enhancement and work to be accomplished before MFCs are industrialized. Just extremely rare MFC arrangements with device volumes greater than 1 Liters have been tried, not like several conventional fuel cells (inorganic) which have now achieved an advanced state in their process of development.

2.2 MFC Mechanism

Figure 2.1. Shows that there are two halves or parts of a basic MFC: aerobic and anaerobic. The aerobic chamber has a positively charged electrode (Cathode) and, along with the assistance of an aerator, it is aerated or bubbled with oxygen.

The anaerobic compartment has a negatively charged electrode (Anode) and is kept tight to prevent the oxygen from flowing into the anode compartment. A semi-permeable membrane splits up two chambers to stay the oxygen out of the anode compartment whilst allowing the passage of hydrogen ion (H^+).

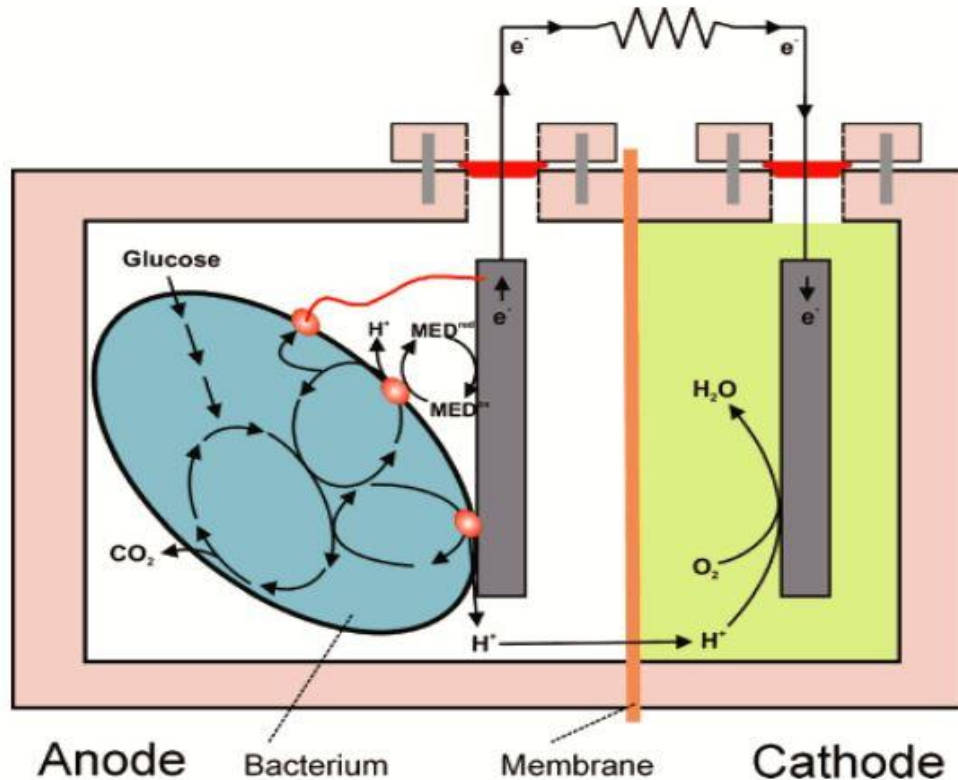


Figure 2.1 Working Principle of an MFC

A mixture which contains food and bacteria is added / circulated in the anaerobic compartment. The food usually consists of organic substance such as fructose and acetate and domestic sewage in our case. By splitting food particles into H^+ ions CO_2 and electrons, the bacteria present in the chamber metabolize food. Bacteria use electrons to generate energy through the process of electron passage. The MFC inhibits the electron transport system by utilizing a facilitator to deliver electrons to the anode.

2.3 MFC Designs

MFCs have many different possible formations.

2.3.1 Dual Chamber MFC

DCMFC, constructed in "H" form, is the most commonly used and cheapest design (Figure 2.2). It consists of two chambers or compartments which are interconnected by a pipe that contains a strainer and is mostly a proton membrane (PEM) for example Nafion (Ali et al., 2015; Prakash et al., 2015; Khan et al., 2013) or Ultrex CMI-7000 (Sotres et al., 2015) or a plain salt bridge (Sevda & Sreekrishnan, 2012).



Figure 2.2 Dual Chamber MFC



Figure 2.3 Salt bridge

Also called proton exchange membrane (PEM), CEM enables only protons to go through. It does not normally allow oxygen or any other electron acceptor to pass through. The membrane is usually sandwiched between two chambers/bottles as shown in (Figure 2.2). The salt bridge (salt and agar is filled in tubes connecting the two bottles) can also be used instead of CEM but the power production is lower because of the very elevated internal resistance (Figure 2.3). This is the type of MFC which is used in our study.

2.3.2 Air Cathode MFC

The cathode does not need to be put in liquid and different compartment while consuming O_2 in the cathode. The cathode cylinder is positioned in straight interaction with atmosphere (Figure 2.4a & 2.4b) (Liu and Logan, 2004). Relatively higher energy densities have been obtained when aqueous cathode is substituted by air cathode. The cathode and anode are mounted in the simplest arrangement on one of the two sides of conduit, through

the anode installed beside a plane sheet and the other electrode facing the oxygen and water into another side (Figure 2.4b).

The membrane in air-cathode system is used to primarily keep water from leaking into cathode. The membrane also minimizes O_2 diffusion into anode compartment. The leakage of O_2 into anode chamber decreases the coulombic efficiency (It described the percentage of electrons retrieved as present versus the highest regeneration possible) (Liu and Logan, 2004). Air cathode single chamber MFC when treated anaerobic sludge produced a maximum power of 5.79 W/m^3 (Gao et al., 2014).

2.3.3 Other designs

Several variants of the basic models have arisen to enhance power density and ensure continuous feeding through the compartment (as opposed to the normal designs that were all run in batch mode).

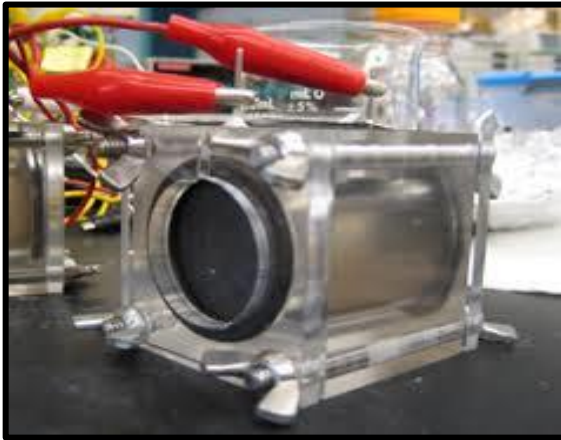


Figure 2.4a Air-cathode single-chamber, a simple “tube” arrangement



Figure 2.4b Flat plate layout in which a reactor is cut into the blocks to allow fluid to flow through the electrode in a serpentine pattern

Systems were designed for an external cylinder like reactor which has a condensed inner pipe of the cathode (Liu et al., 2004a) (Figure 2.5d) besides an external cathode internal cylindrical reactor (anode consisting of granular media) (Janicek et al., 2014) (Figure 2.5a). Another modification is the layout of the device as a reactor whose liquid moving uninterruptedly through permeable anodes to a barrier from where it moves towards the

cathode compartment (Minteer et al., 2012) (Figure 2.5b). Arrangements were planned to look like HFC where a PEM between cathode and anode is sandwiched (Figure 2.5c).

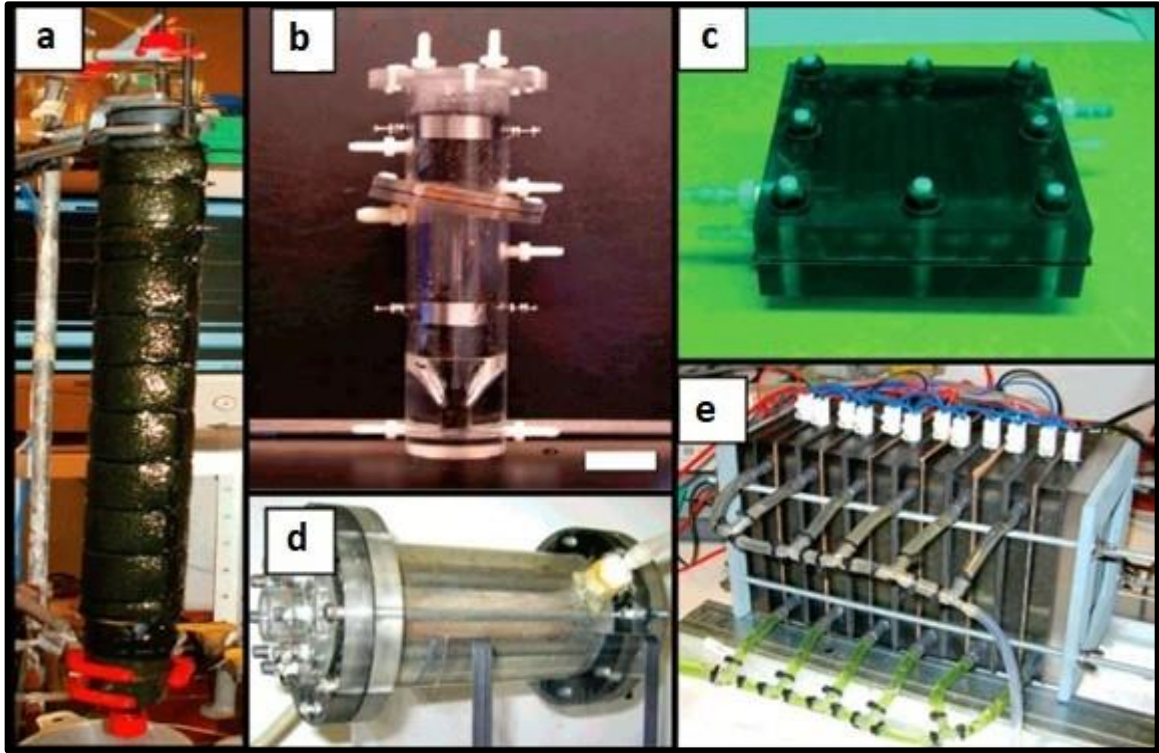


Figure 2.5 (a) Internal graphite bed anode and exterior cathode up flow, tube-shaped MFC (Rabaey et al., 2005); (b) The membrane is inclined upstream, tube-like MFC with anode under and cathode overhead. (Minteer et al., 2014); (c) plane plate design (Min et al., 2004); (d) Solo chamber design with an internal concentrated air cathode enclosed by an anode chamber with graphite rods (Liu et al., 2004); (e) Slanted MFC, which includes six separate MFCs in one wedge of reactor (Aelterman et al., 2006)

MFCs can be installed with structures molded like a sequence of plane flat like plates or connected in series to improve the overall voltage of the device (Aelterman et al., 2006) (Figure 2.5e).

2.4 Materials of Construction

2.4.1 Anode

The anode has a major impact on the formation of biofilm and the transmission of electrons between the microbe and the acceptor of electron. The anode must

be (a) conductive, (b) biocompatible (c) chemically stable (d) non-corrosive and (e) mechanically stable.

2.4.1.1 Conventional Carbon-based materials

Products built on carbon are the main materials used in MFC science. This contains graphite rod, carbon felt, graphite fiber comb, carbon paper and carbon granules (Figure 2.6). Most commonly used electrode in MFCs is graphite, because it is very inexpensive, chemically stable and electrically conductive (Figure 2.6e). Graphite rod in a membrane less MFC for the treatment of sewage produced a power density of 6.73 mW/m^2 (Ghangrekar et al., 2008). A CFB is made of carbon fibers which is curled across conductive corrosion-resistant metal cords (titanium wire) (Figure 2.6a). Carbon fiber brush anode when paced between dual cathodes produced additional power (1.72 mW) than with single cathode (1.12 mW) using domestic wastewater as a substrate (Kim et al., 2015). It is very attractive and highly recommended because of its more outward surface area and minimal electrical electrode resistance. Carbon paper and carbon fiber, which are often used in hydrogen fuel cells, are now used as flat-plate electrodes in MFCs. (Figure 2.6c & 2.6b). When used as an anode in single chamber air cathode MFC for domestic sewage treatment, carbon paper generated a power of $1070 \text{ mW} / \text{m}^2$ with COD removal of 70% (Cheng et al., 2011). Similarly, slaughterhouse wastewater (COD 4850 mg/l) was feeded in dual chamber MFC with carbon paper electrodes, the MFC generated a power of 578 maw/m^2 (Kasturi et al., 2011). Table 2.1 shows some benefits and drawbacks of various carbon anodes. In one another study, carbon cloth was coated with carbon black and polytetrafluoroethylene (PTFE) and it yielded a power output of 50.6 mW/m^2 which was almost double of uncoated electrodes (Li et al., 2017). Graphene also has a high potential to be used as an electrode in MFC. When modified graphene was used as an anode in dual chamber MFC for the treatment of acetate it produced a maximum power of 2142 mW/m^2 which is far greater than when other carbon materials were used in the same MFC for the treatment of acetate (Hou et al., 2014).

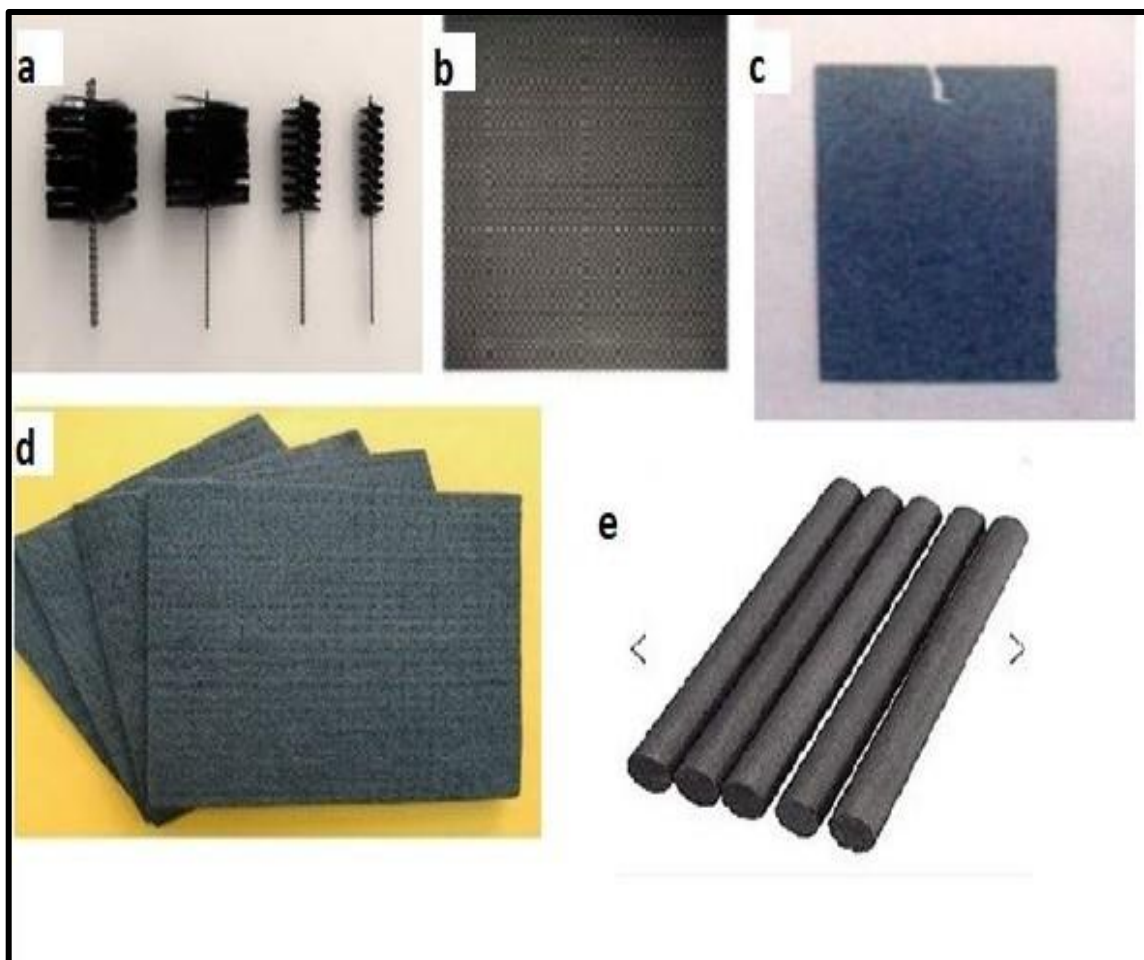


Figure 2.6 Carbon based anodes used in MFC (a) Graphite Brush (Logan et al., 2007) (b) Carbon cloth (Wang et al., 2009) (c) Carbon Paper (Logan, 2008) (d) Carbon Felt (Nam et al., 2010) (e) Graphite rod (Liu et al., 2004a)

Table 2.1 Comparison of anode material characteristics used in MFC

Anode Stuff	Benefits	Drawbacks	Reference
Graphite rod	Easy availability, Enhanced electrical conductivity and inexpensive	Surface area is hard to raise	Liu et al., 2005a
Graphite Fiber Brush	Simple to produce, very high surface area	Clogging	Ahn et al., 2010
Carbon Felt	Large aperture	High resistance	Kim et al., 2002
Carbon Paper	Simple to connect wiring	Lack of toughness, Fragile	Kim et al., 2007
Carbon Cloth	Big porosity	Costly	Ishii et al., 2008

2.4.1.2 Non-carbon-based anodes

In MFC experiments, many metal anodes can be used such as corrosion resistant stainless-steel (Tanisho et al., 1989), But even slight copper ions are toxic to bacteria species does not make copper beneficial. Also used as an anode with *Geobacter sulfurreducens* was MFC with highly conductive metal such as gold and a sturdy current of $1175\mu\text{A}/\text{cm}^2$ was produced (Baudler et al., 2015). Some other metals specially platinum was also used as an anode in one study, but it was found unsuitable (Heijne et al., 2008).

2.4.2 Cathode

Materials of cathode have a major effect on MFC's power generation. The perfect cathode materials should have elevated redox potential and be able to readily capture electrons. Graphite, carbon paper and carbon cloth are the most widely utilized items.

2.4.2.1 Platinum (Pt) based Catalyst

The performance of the cathode can be increased by using some active catalyst and platinum Pt. is the most commonly used (Watanabe et al., 2008). Platinum can favor the kinetics for electro-oxidation. The MFC using carbon paper containing Pt as a cathode showed a power density of $124 \text{ mW} / \text{m}^2$ (0.2 mg-Pt cm^2) that was three times greater when using only carbon paper (Deng et al., 2011). Platinum, however, is very costly material, reducing its practical applications. The price of Pt catalyst coating is \$0.0447 for 1 cm^2 area (Morris et al. 2007). Also, during the lifetime of Pt., it undergoes corrosion from oxidation which results in the loss of active surface area.

2.4.2.2 Non-Pt based Catalyst

Due to very high cost of Pt many non-Pt based electrodes are also used as cathodes. Table 2.2 shows some of the catalyst that are used in MFCs.

Table 2.2 Non-Pt. Catalyst based cathodes in MFC

Kind of Catalyst	Cathode materials	P_{max} (mW/m ²)	Reference
MnO _x	Carbon cloth	161	Roche et al., 2010
PbO ₂	Ti Sheeting	78	Zhou et al., 2011

CoTMPP	Carbon Cloth	369	Cheng et al., 2006
B-MnO ₂	Carbon cloth	3.773*	Zhang et al., 2009
Co/Fe/N/CNT	Carbon cloth	751	Deng et al., 2010

*W/m³.

2.4.3 Membrane

Most of the MFC models requires a membrane to split anode compartment from cathode compartment. The membrane only allows protons to pass through and does not usually allow oxygen to pass through substrates or electron acceptors. With its practical applications in mind, the membrane plays a crucial role for designing MFCs. It is because the performance and unit cost are significantly affected by the architecture, product choice and membrane geometry.

The most widely used PEM is Nafion (Choi et al., 2011; Shahgaldi et al., 2014) which can be bought from many international suppliers (e.g. Aldrich and Membrane international Inc.). Nafion's use as a cation exchange membrane (CEM) was, however, correlated with operational challenges. For example, a reducing pH in the anodic chamber and an improved pH of cathodic chamber in a dual chamber MFC were observed since the anode rate of creation of protons and the cathode utilization rate of protons were considerably quicker than the Nafion PEM transportation of protons. (Choi et al., 2011). For the treatment of wastewater using microfiltration membranes (MFM) and active sludge inoculation, the quality of a single MFC air-cathode compartment. Once CEM was paired with MFM, a great decrease in internal resistance from 672Ω to 248Ω was noticed, resulting in an approximately two times increase in the extreme power density of fuel cell with MFM compared to MFC with CEM. CE increased from 4.17% to 5.16% when using MFM instead of a membrane less device (Sun et al., 2009). Ultrex CMI - 7000 (Membranes intl. Inc.) was utilized in MFC systems (Babanova et al., 2017) and is considered more economical than nafion. Ultrex CMI 7000 is a solid, polymer cross-connected structure with many sulphonate groups comprising divinyl benzene (Ismail and Jaeel, 2013). Though its positive charges connection and shear strength are equivalent to

Nafion, its quality in MFCs is lesser than Nafion (Stores et al., 2014) due to high load (Rahimnejad et al., 2014).

2.4.4 Salt bridge

Salt bridge is employed as an alternative for membrane because of its simple and inexpensive use. In this type of MFC, ions are rendered sandwiched among the two compartments by means of a salt connection comprising of a glass conduit loaded with certain electrical materials (Min et al., 2005). To prevent the mixing of two fluids agar is usually mixed in the glass tube. In the MFC, a salt bridge composed of a 2 per cent potassium chloride - containing agar (10 per cent) layer crammed among two perforated plexiglass sheets, used as a divider (Dalvi et al., 2011).

Salt bridge MFC has usually high columbic efficiency when compared to the CEM MFC because of its low oxygen permeability (Liu and Li, 2007). Nevertheless, due to very high internal resistance, Salt Bridge MFC displayed low power density. Under similar conditions, a phosphate buffer solution salt bridge was stated to have considerably greater internal resistance than the Nafion membrane (Min et al., 2005). Similar results for the wastewater treatment from the food processing industry were obtained in the salt-bridge MFC, where the topmost power density obtained was considerably lesser as compared to PEM MFC (Mansoorian et al., 2013). Findings above indicate that when salt bridge is used as a separator in MFC reactors, elevated internal resistance is a big task. The internal resistance can be reduced by choosing concentrations and composition of electrolytes appropriately (Li et al., 2011). It is also possible to reduce the output of the salt bridge MFC by increasing the salt bridge area in connection with the anode and cathode chambers (Jatoi et al., 2016).

2.5 Factors affecting the performance of MFCs

MFC performance is affected by several external and internal factors such as reactor design, separator materials, electrodes, catalysts, substratum type, substratum concentration, operating mode, hydraulic retention time (HRT), electron acceptors, ionic strength, pH and temperature. Some of these factors are

discussed in the previous sections so this section only summarizes the remaining important factors.

2.5.1 Substrate type

One of the most important parameters that effects the overall performance of the MFC is the substrate (Liu et al., 2009). Most substrates that can be utilized in MFCs to generate electricity from simple compounds to complex organic matter mixtures found in wastewater. Table 2.3. Summarizes some of the substrate types used in MFCs.

Table 2.3 Substrates types used in MFCs

Type of Substrate	Concentration (g/l)	Inoculum	Type of MFC (with electrode surface area and/or cell volume)	Current density (mA/m ²) at max. power	Reference
Acetate	1.28	Domestic wastewater	H-shaped reactor with carbon paper sheets	729	Sun et al., 2014
Glucose	2	Luria-Bertani medium, having 10 g peptone, 5 g yeast extract and 10 g sodium chloride per liter, was used to cultivate E. coli	Dual chamber MFC with DPC dispersed in 1 wt% poly (tetrafluoroethylene) solution on carbon felt (3cm ²)	3600	Chen et al., 2014
Sucrose	1.14	Mixed microbial culture	Single chamber air cathode MFC with carbon clothes used as electrode materials	1000	Catal et al., 2019
Brewery wastewater	3.197 ± 0.979	Lagoon sediment and diluted brewery wastewater	Tubular dual chamber MFCs with carbon fiber cloth electrodes (anode 1.59 m ² and cathode 2.59 m ²)	40 A/m ³	Lu et al., 2017

Domestic wastewater	545 mg/L	Mixed culture of MFC operated effluent	Single chamber MFC with carbon fiber brush (50 cm ²)	800	Stager et al., 2017
Synthetic wastewater	510 mg/L	Anaerobic culture from a pre-existing MFC	Double chamber MFC with stainless steel as anode (170 cm ²) and carbon graphite rods as cathode (150 cm ²)	0.008	Jadhav and Ghangrekar, 2009

2.5.2 Substrate Concentration

Substrate concentration effect on MFC is directly associated with a microbial community in the anode compartment. Different types of communities of microorganisms can be established depending on the kind of inoculum used and optimum values of substrate concentration can differ due to which it is difficult to find out an optimum range for this factor. One study investigated the influence of date syrup and concentration of glucose in MFCs inoculated with *Saccharomyces cerevisiae*. It was observed that optimal concentration for both substrates was 3g / l and that low substrates can play a important role in MFC output (Ghoreyshi et al., 2011). In one study it was found that when same substrate (acetate) with different concentrations (500, 2000 and 3000 mg/l) were used in a dual chamber MFC, highest current density (795 mA/m²) was achieved at 3000 mg/l of COD (Ziaullah, 2017). However, these results cannot be inferred to different case studies without looking into further details.

2.5.3 Operation mode

MFCs can be worked in various modes; batch, fed-batch, repeated (semi-continuous) fed-batch and continuous mode. There is a regular method of substitution of anolyte and catholyte in batch mode. In fed-batch process growth limiting substrate is added to the MFC while constantly adding and withdrawing the same anolyte and catholyte volume from the system to maintain the total volume constant. Ultimately, semi-continuous mode, the mixture of batch and continuous service can be considered. The anolyte or catholyte is fed at regular intervals during this process while the effluent is discontinuously drained

(Pannell et al., 2016) reported that continuously fed MFC achieved stable power density and C.E after 48 days of operation while fed batch MFC performance dropped after 36 days of operation. It was noticed that the current rise from 0.5 to 49 mA following the continuous feeding of anolyte and catholyte solutions to the compartments at 1.5 mL / min was around 5 hours after semi-continuous feeding of anolyte / catholyte (Wang et al., 2011).

2.5.4 Hydraulic Retention Time

Hydraulic retention time (HRT) is a vital aspect that effects the performance of MFC particularly with wastewater treatment. Its effects both the power generation and the COD/BOD removal. Despite lower HRTs, COD removal levels are typically increasing (Zhang et al., 2013). While these shorter HRTs achieve high power densities, extended HRTs are required to lower COD levels appropriate for discharge of wastewater. For extended HRTs, current densities can also be relatively low, so that no useful electrical power can be generated at these high COD levels (Ahn and Logan, 2012). The influence of HRT (4, 2 and 1.1 hrs.) on MFC with flat plate electrode, constantly supplied with prominent concentrations of chemical oxygen (COD) concentrations of 246 ± 3 to 379 ± 9 mg / l. Results revealed increased power production and decreased efficiency of COD removal with decreased HRT (Min and Logan, 2004). One experiment observed the impact of HRT on a glucose-fed baffled air cathode MFC. The HRT varied with an influent COD of 1,000 mg / l between 6 and 1.5 h and the results indicated that the removal efficiency of COD decreased with HRT. With a reduction in HRT up to 2.5 h, electricity generation decreased, but an additional decline in HRT to 1.5 h caused in a decrease in electricity production. Similarly, the HRT effect on a DC air cathode MFC supplied with a preliminary influent concentration of 30000 mg / l glucose (COD 1/4 32,100 mg / l) was also investigated. The reactor was run at 26, 16, 12.3, 6.7 and 3.4 h HRTs for this reason and it was found that the peak power was reached at 6.7 hr HRT (Rahimnejad et al., 2011).

2.5.5 Ionic Strength

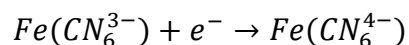
Increasing the electrolyte's ionic strength in an MFC will significantly increase power output as internal resistance is decreased. Improving the ionic power of the electrolyte solution can significantly boost power output by growing NaCl (equal to 400 mM) or potassium chloride (equal to 300 mM). (Liu et al., 2005a; Logan and Oh, 2006).

Nonetheless, internal resistance allocation of single-chamber MFCs reveals that resistance due to electrolyte holds for 36–78% of entire resistance, which can be reduced from 208 to 85.9% by expanding the concentration of phosphate buffers from 50 to 200 mM (Fan et al., 2008). In most of the old studies, the utmost ionic activity was held at lower stages because of the use of varied crops that are obtained from fresh water and cannot withstand very elevated salt concentrations (Rabaey et al., 2004, 2005).

2.5.6 Electron acceptors

Similar electron acceptors have similar chemical and physical properties (e.g. potential for oxidation) and thus affect electricity generation efficiency in MFCs. The most ordinary electron gainer used in the cathode compartment of MFC is oxygen (O₂) because of its elevated oxidation potential also that it only yields a very cleanse H₂O after reduction. Nonetheless, previous work shows that oxygen is generally an energy-consuming process in the cathode compartment (Strik et al., 2010). While airborne oxygen can also be used directly with an air cathode, it also has some drawbacks, such as contact problems in the cathode and the necessity for pricey substances (Heijne et al., 2007).

In addition to increasing power generation and reducing operating costs, the use of alternative electron acceptors can also enhance the scope of MFC applications. In addition to oxygen, the mostly used electron acceptor is ferricyanide. In one experiment, carbon electrode using ferricyanide provided higher power of 50 to 80% output than O₂ with cathode made up of carbon coated with Pt. because of higher mass transmission efficiencies and higher cathode potential (Penteado et al., 2017).



Some of the recalcitrant compounds can also be employed in the cathode chamber as an electron gainer (Jayashree et al., 2015). Nitrate can also be used in the positive cathode compartment as an electron gainer (Oon et al., 2017). In this situation, the denitrification process in the cathode compartment converts the nitrate to nitrogen gas. In addition to nitrate, other heavy metals e.g. copper (Tao et al., 2011), mercury and Fe (Wang et al., 2011) may also be utilized as electron gainers and may convert to less contaminated forms. Therefore, wastewater treatment & power generation both can be achieved simultaneously.

2.5.7 pH

pH is another crucial factor that effects the performance of MFC by controlling bacterial growth and biofilm formation. Bacteria are affected by the changes in pH thus bacteria adopt themselves by changing the production and formation of proteins related with various processes, comprising amino acid degradation, proton translocation, adjustment to acidic or fundamental conditions (Olson, 1993). Several studies have reported effects of anode compartment pH microenvironment on MFC efficiency. Several researchers found that acidic pH decreases the production of electricity (Gil et al., 2003) And low pH (5 and 6) has been reported to result in lower power output (He et al., 2008). The pH value between 7 - 9 was stated to be optimal for biofilm formation and quality of MFC (Sun et al., 2014)

2.5.8 Temperature

Temperature is another important factor that is kept constant in most of the MFC studies because variation in temperature affects the bacteria growth and biofilm formation and ultimately the overall MFC performance. (Ali et al., 2015) investigated the MFC performance using domestic wastewater at summer (37°) and winter (25°) temperatures Their calculated power density was 202 mW/m² for summer samples and 117 mW/m² for winter samples which showed that MFC performed better at higher temperature. In one study a temperature range of 10-50°C was described as “livable” for the biofilm while the values between 30 – 35°C have been termed as optimum (Sun et al., 2014).

2.6 Performance evaluation of MFC

Generally, two of the factors are main while contemplating the performance of an MFC, how well it is capable to utilize a given substrate and the amount of electricity it can produce. Although computing power output from current is a straightforward process in MFC but presenting data to the journals is not that easy. Although operational conditions such as reactor design, substrate type and compartment materials used by different researchers vary, but still unanimously acceptable standard parameters are needed. Some of the parameters are discuss in detail in this section.

2.6.1 Open circuit voltage

The OCV is the voltage of a reactor which is obtained in the absence of external resistance (infinity resistance). It can be determined after some time. The OCV must enter the emf cell theoretically. In practice however, due to various potential losses, the OCV is significantly lesser than the reactor cell emf. Such losses include concentration losses, activation losses, bacterial metabolic losses and ohmic losses. In one study OCV was reported to be 1.29 V utilizing landfill leachate as a substrate (Sonawane et al., 2017b). Similarly, when domestic wastewater was used as substrate the highest OCV was found to be 0.200 V (Jiang et al., 2013).

2.6.2 Power density

Power generated from the MFC system is often standardized to some of the characteristics of the reactor to permit assessment of the power output of various structures. The power yield is generally standardized to the projected anode surface area since the biofilm develops here and most of the bacterial and chemical reaction takes place (Rabaey et al., 2004; Liu et al., 2004b). The calculation of the power density is performed in the previous section.

Nonetheless, in many situations, the reaction on cathode is considered to restrict overall power generation (Cheng et al., 2006; Liu and Logan, 2006) or where the anode is a substance that cannot be expressed as its surface area (i.e., graphite brush; (Rabaey et al., 2005). Power density greatly varies on the type of

substrates, MFC configuration, types of electrodes and substrate concentration. It was stated that maximum power density of 481 mW/m^3 was attained for domestic wastewater using carbon fiber brush in membrane less MFC (Jiang et al., 2013). Similarly, when brewery wastewater was used as a substrate, 669 mW/m^2 of power density was achieved (Wen et al., 2010).

2.6.3 Polarization Curves

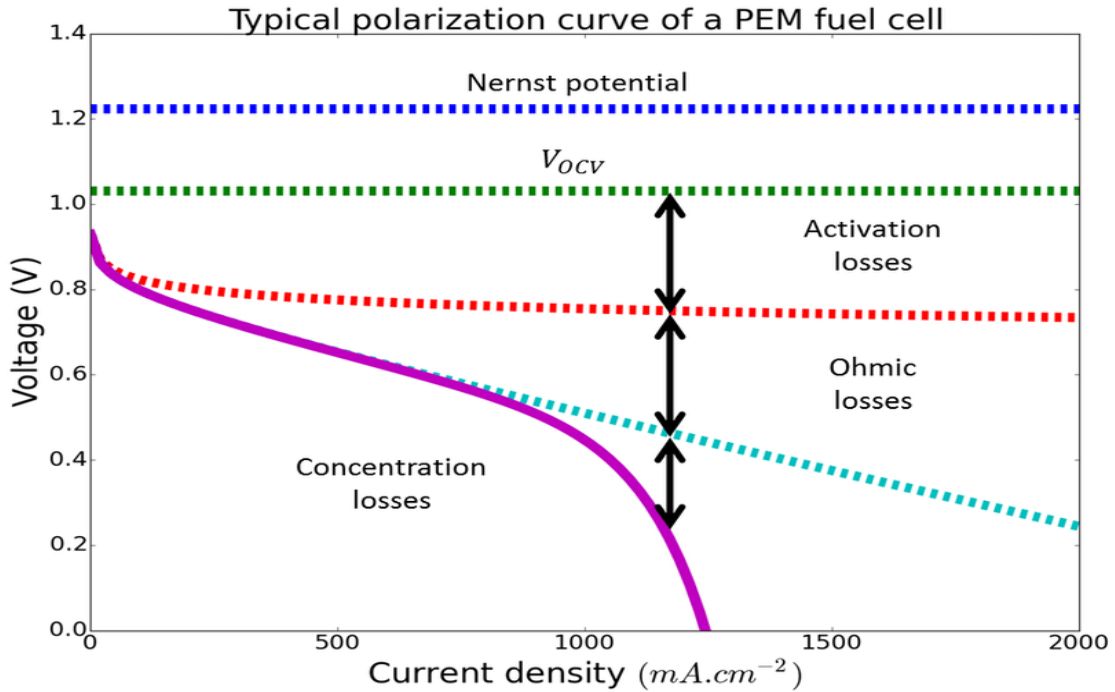


Figure 2.7 Polarization curve of a typical fuel cell (Agaesse, 2016)

Polarization curves are a useful method for evaluating and characterizing all fuel cell forms (Hoovers., 2002). Similarly, in the case of MFCs, polarization curve is also used for cell analysis. A curve of polarization describes the voltage as the current (density) value. Potentiostat is used for this purpose. If the availability of potentiostat is not possible then use a box of variable resistance to set external loads variable. The voltage is measured using a periodic load reduction and the electric current is determined using Ohms law. When using a resistance box to obtain a polarization curve, it is only necessary to take current and potential values by pseudo-state conditions are defined. Depending on the device and internal opposition, the creation of this

pseudo-stable state can take quite a few minutes or more. Figure 2.7 illustrates the typical polarization curve.

There are typically three zones in a polarization curve:

- i. At first there is a decrease in voltage, starting from the OCV at zero current: activation losses dominant in this area.
- ii. Voltage slowly falls and the drop-in voltage is impartially linear with current: ohmic losses are the main losses
- iii. At elevated currents the depression of the voltage is very sudden: concentration losses (mass transport effect) dominant is this zone

2.6.4 Columbic Efficiency

Coulombic efficiency (C.E) is defined as the proportion of total Coulombs transmitted from the substrate to the anode, to full Coulombs if current is provided by all substrate removal. The calculation of C.E for batch and continuous mode is discussed in the previous section.

The use of other types of electrons gainers by microorganisms, which are already found in the wastewater, decreases coulombic efficiency and those that travel like oxygen through the CEM. Competitive processes and bacterial growth are some of the other factors that causes reduction in coulombic efficiency. For fermentation or methanogenesis, microbes that are not able to use the electrodes as electron gainers are probably to use available substrates. When domestic wastewater was used as a substrate lower CEs were obtained (He et al., 2016; Zhang et al., 2015; Ahn and Logan, 2013). CE was found to be 14% when domestic sewage was used as a substrate in membrane less MFC (Jiang et al., 2013). It was also reported that CEs are higher for continuous flow tests (35.3 to 46.7%) at an HRT of 2 to 8 h as compared to batch fed tests (Wu et al., 2017).

2.6.5 Treatment Efficiency

Most important factor for the evaluation of MFCs is its treatment efficiency. It is determined based on BOD, COD or by the removal of Total organic carbon (TOC). The most important factor is the removal of COD as it is a normal

determination of efficiency in wastewater treatment, and for Columbic efficiency calculations it is necessary to remove COD. The COD removal process calculation is already discussed in the previous section. COD removal efficiency depends on many factors such as HRT, bacterial growth, biofilm thickness, substrate concentration and so on. But the COD removal efficiency does not depend on the influent COD concentration (Rodrigo et al., 2007). It was reported that when domestic wastewater was treated at continuous flow conditions, higher HRT achieved more COD removal (80 – 95 %) (Wu et al., 2017). This is because at higher HRTs the fermentative bacteria become dominant and will consume more food/organic matter due to the less availability of organic matter. When sewage wastewater (COD 400 mg/l) was used as a substrate in MFC with graphite rod electrode (anode and cathode), 82.7% COD removal was achieved (Ghangrekar et al., 2008). Similarly, when domestic wastewater was used in dual chamber MFC, COD removal efficiencies of 64.8 ± 1.7 , 48.3 ± 1 and $32.8 \pm 1.9\%$ were achieved at an HRTs of 8.8, 4.4 and 2.2 h respectively (Kim et al., 2015).

2.6.6 Internal Resistance

There are two aspects of an MFC's internal resistance: ohmic and non-ohmic resistance (Fan et al., 2008). Ohmic loss resistance in MFCs can be lessened by increasing the geometric region among anode and cathode (generally the length of the exposed CEM), closely placing the electrodes and utilizing high conductivity solutions (Benetton et al., 2010). Non-ohmic resistance includes transfer of the loads and resistance due to diffusion (Larminie and Dicks, 2000), which can be reduced by enhancing the estimated surface area of anodic and cathodic electrodes and by choosing decent catalytic electrodes. The internal resistance is determined by the polarization curve slope. In one MFC study, when synthetic wastewater was used as a substrate the reactor module showed an internal resistance of 1.2Ω with OCV of 732 mV (Wu et al., 2016). In one other study, acetate was utilized as a substrate in two dual chamber MFCs with carbon felt anodes and carbon fiber brush cathodes. The open circuit voltages (OCV) of the MFCs had no remarkable difference (~ 0.72 V) while the reactors showed the internal resistances of 82.5 and 65.1 Ω respectively (Zhang et al., 2015).

CHAPTER 3

MATERIALS AND METHODS

The experimental setup for this research, consists of construction of two lab-scale MFCs in order to be used in semi-continuous operation. Inoculum was prepared to be used as a source of bacteria and domestic wastewater was used as a substrate. The following sections explain different materials and methods used in the current research.

3.1 MFC Construction

Two identical lab-scale double chamber MFCs were built using translucent acrylic sheets. Working volume of each chamber was 1.8L. These MFCs were constructed in a H-shaped design and both compartments were split by CEM (CMI-7000, Membranes Internationals, Inc., USA) (Figure 3.1)

The CEM surface area was approximately 64 cm² and it was first soaked for 24 hrs. in deionized water and then in 5% sodium chloride solution for 12 hours before using it to permit hydration and expansion. The CMI-7000 membrane was selected for the study as it has an excellent proton conductivity, thermal and chemical stability with much less water permeability (Khanal, 2011).

In order to investigate their effect on MFC performance two types of electrodes were used. In one of the MFC setups, graphite rods were utilized as electrodes for each compartment (Figure 3.2a). The effective length and diameter of graphite rods were 7.3 and 4.5 cm resulting in an effective surface area of 22 cm². The rods were roughened by sandpaper before installation to improve the bacterial connection. In another MFC setup, carbon fiber brushes (The Mill-Rose Company, USA) were used as an electrode (Figure 3.2b). The brush was constructed of a core of a titanium wires with graphite fibers. It had 5.9 cm diameter, 6.93 cm brush section and 14.85 cm overall length of titanium stem with carbon fiber fill 400,000 tips. The specific surface area of brush to be calculated was 183 cm². The brush was soaked in deionized water and heated at 100°C for 30 minutes before use for disinfection purpose. A copper wire was linked to each electrode and extended outside the MFC setup to simply develop an electrical circuit for electron transport.

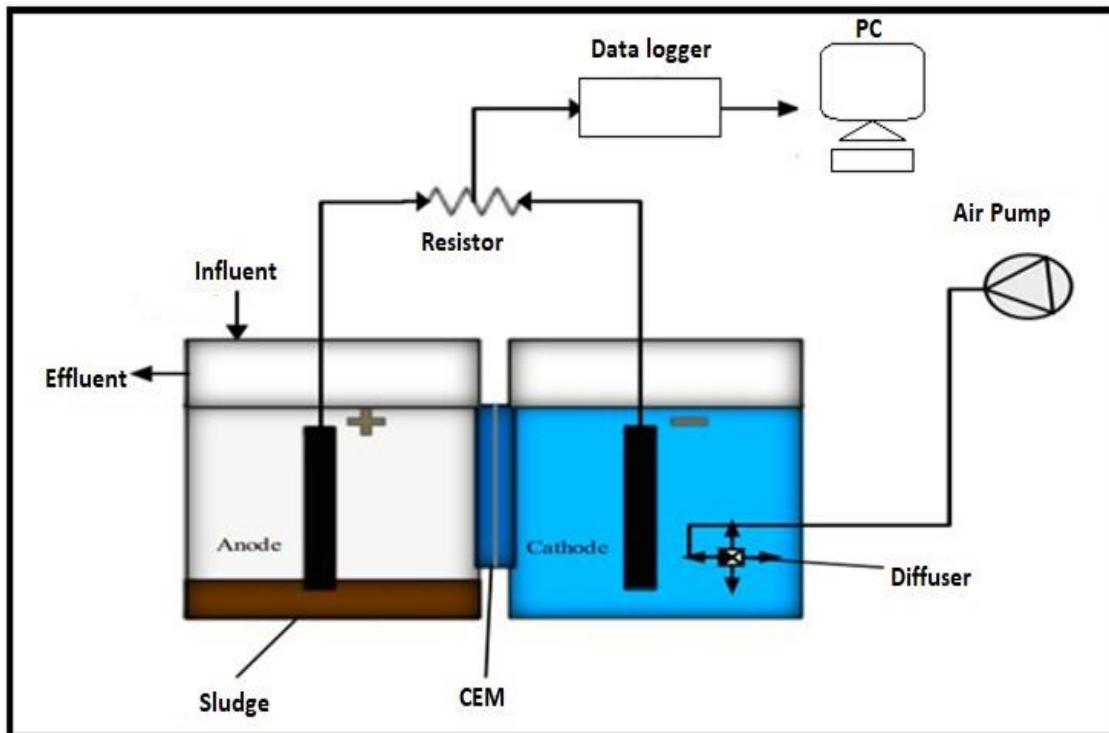


Figure 3.1 Schematic diagram of MFC used in the study

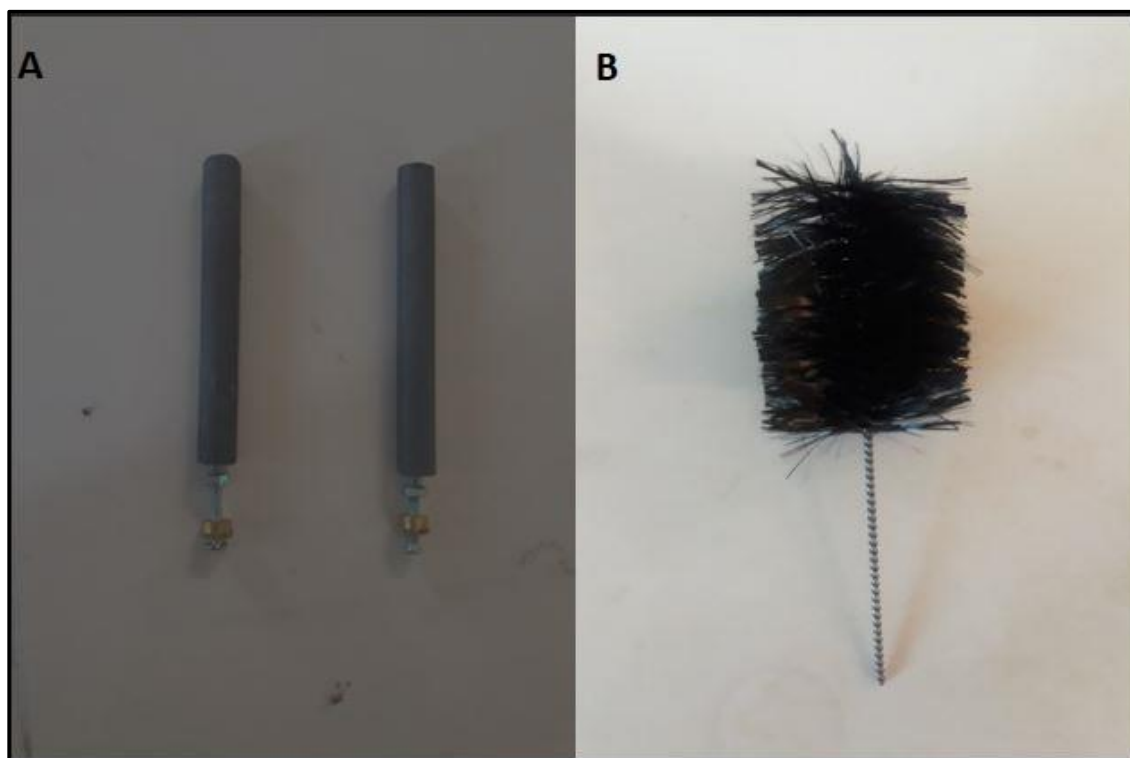


Figure 3.2 (a) Graphite rods (b) Carbon fiber brush, used in the study

Table 3.1 CMI – 7000 membrane technical specifications

Functionality	Strong acid CEM
Polymer structure	Gel polystyrene cross linked with divinylbenzene
Functional group	Sulphonic acid
Ionic form	Sodium
Color	Brown
Standard thickness (mm)	0.45 ±0.025
Electrical resistance ($\Omega \cdot \text{cm}^2$) 0.5 mol/L NaCl	<30
Maximum current density (A/m^2)	<500
Permselectivity (%) 0.1 mol KCl/kg 0.5 mol KCl/kg	94
Water permeability ($\text{ml}/\text{hr}/\text{ft}^2$) @5psi	<3
Mullen Burst test strength (psi)	>80
Thermal stability ($^{\circ}\text{C}$)	90
Chemical stability range (pH)	1-10

3.2 MFC Inoculation and Wastewater

Activated sludge was collected from the NUST MBR treatment plant (Islamabad). It was utilized as an inoculum for the anodic chamber of MFC reactor. Before using the activated sludge in MFC reactor, it was placed in a container which was air sealed and purged with N_2 gas to favor anaerobic conditions (Figure 3.3). This anaerobic environment favored the growth of mix culture of anaerobic microorganisms. No wastewater was added to the culture during this period of acclimation (Asensio et al., 2016). After the acclimation process completed the sludge was fed into the MFC reactors and wastewater feeding was started into the reactor.

Domestic wastewater was collected from the NUST campus, Islamabad. Wastewater was collected twice a week and was stored in refrigerator at 4°C . Table 3.2 shows the characteristics of the domestic wastewater used in the current study.

Table 3.2 Domestic wastewater characteristics, used in a study

Parameters	Average	Standard deviation
COD (mg/l)	287	±29.3
sCOD (mg/)	109	±31.6
Electrical conductivity (µS/cm)	819	±139.2
pH	7.33	±0.18

3.3 MFC Operation

The overall operation of the MFCs has been divided into two phases; (i) Startup phase which was conducted in four batches, (ii) Semi - continuous phase. Table 3.3 shows the overall sequence of MFC operation. Domestic wastewater was fed into the anodic chamber with an HRT of 96 h. The batch mode continued for 16 days with total number of four batches. The first batch was operated in OCV conditions and after its completion the circuit was completed by linking a 1000 Ω resistance for the rest of the three batches. Anode compartment was sparged with N₂ gas before the start of each batch which reduces the electrons loss to O₂. After the batch phase was completed, the operation was shifted into semi-continuous mode. In this mode, wastewater was fed and removed continuously. The MFCs were operated at different HRTs. All the experiments were carried out in 30±2 °C temperature - controlled water bath. The external resistance was 1000 Ω (and varied only in case of polarization study), Because this resistance helps to shorten the exoelectrogenic biofilm growth time compared to lower resistance (Hong et al., 2011). The other compartment of the MFC was filled with 100mM phosphate buffer solution of pH 7 and was continuously aerated with fishery pump (3.5L/min) to supply oxygen (Figure 3.3).

Table 3.3 Overall Sequence of operation for MFCs

Sr. No	HRT (h)	OLR (kg COD/m ³ -day)	Operation time (days)
Batch Mode for Startup			
1	96	0.08	4
2	96	0.08	4
3	96	0.08	4

4	96	0.08	4
Semi Continuous Mode			
1	48	0.16	9
2	36	0.20	7
3	24	0.30	7
4	12	0.58	6
5	8	0.85	6
6	4	1.76	5
7	2	3.34	3

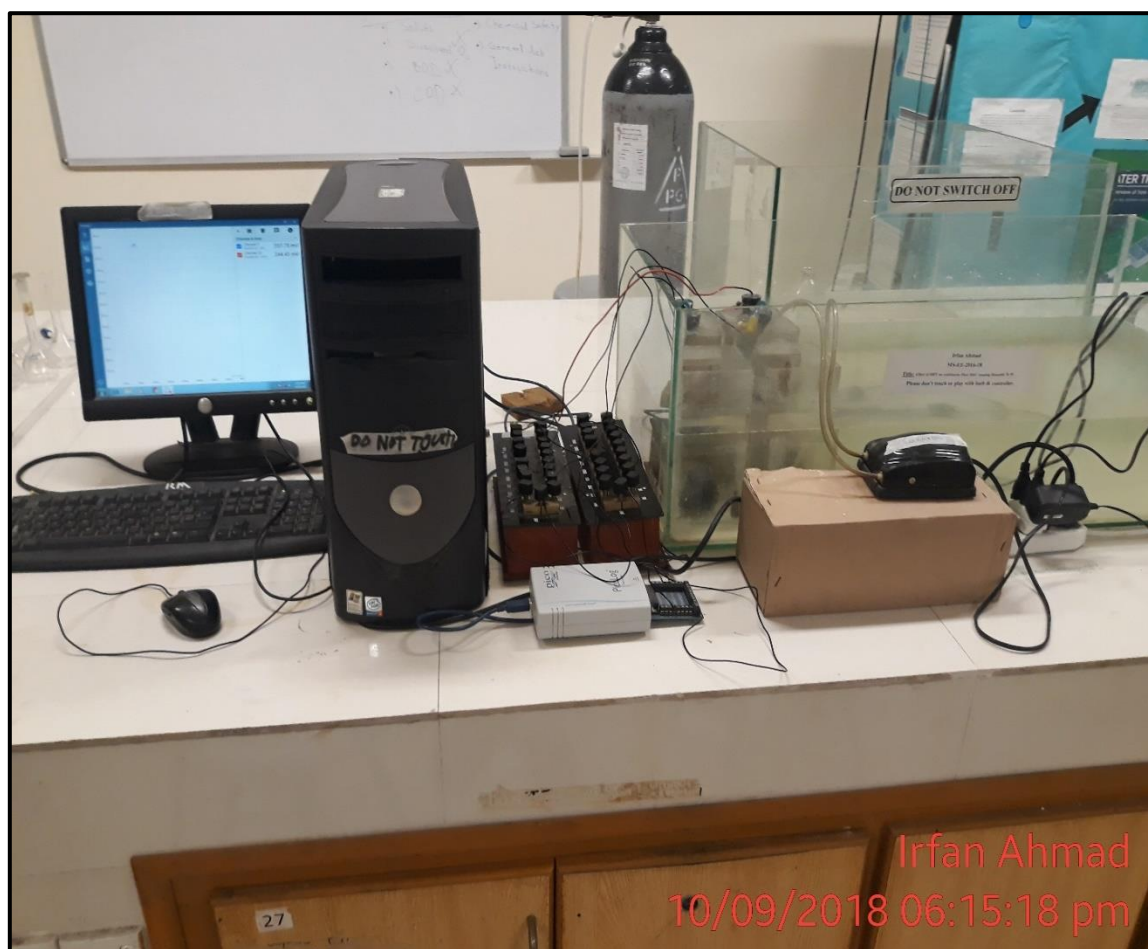


Figure 3.3 Complete setup of MFC Operation

3.4 Electrochemical and chemical measurements

Cell potential (V) was continuously monitored with data logger (PicoLog 1000 series, USA) which was connected to a PC (Figure 3.3). The data was recorded every 30 minutes

Where V is the cell potential across a resistor (V), R_{ext} is the external resistance (Ω), I is the current (A) and P is the power output (W).

Power density and current density are calculated as (Eqs. 3 and 4)

$$P.D = \frac{P}{A} \quad (3)$$

$$C.D = \frac{I}{A} \quad (4)$$

Where P.D is the power density (W/m^2), C.D is the current density (A/m^2) and A is the area of electrode (m^2).

Volumetric power density is calculated by (Eq. 5)

$$P.D_{\text{vol}} = \frac{P}{V} \quad (5)$$

$P.D_{\text{vol}}$ = power density in terms of anode volume (W/m^3) and V = volume of the anode chamber (m^3).

Columbic efficiency (C.E) for batch and continuous mode is calculated using: (Eqs. 6 and 7)

$$C.E = \frac{M \int_0^t I dt}{F.b.V_{\text{An}} \Delta\text{COD}} \quad (6)$$

$$C.E = \frac{MI}{F.b.Q \Delta\text{COD}} \quad (7)$$

Where M = Molar mass of oxygen, F = Faraday's constant (96485 C/mol-e-), b = 4 (quantity of electrons substituted for every 1 mole of O_2), V_{an} = Volume of substrate in the anode chamber, Q = volumetric inflow rate and ΔCOD = change in COD over time t.

The specific surface area of carbon brush electrode was calculated as: (Eq. 8)

$$A = 2\pi r^2 + 2\pi r h \quad (8)$$

where r is the radius of the brush and h is the brush length (Lanas et al., 2014).

CHAPTER 4 RESULTS & DISCUSSION

The study was performed to examine the effect of types of electrodes (Carbon fiber brush and Graphite rod) and the HRT on the treatment and power generation of DCMFC. In order to evade problems in data comparison, both MFCs were first operated in the batch flow and then in a semi continuous flow operation.

4.1. MFC performance during startup

Following inoculation, the operation of both the MFCs were started in a batch mode. Initially the MFCs were operated under open circuit conditions (OCV) in order to assess their performance when no load is applied. After that MFCs were run under closed circuit circumstances at a fixed load of 1000Ω . MFC performance is assessed and analyzed by carefully compiling data, plotting graphs and studying results.

4.1.1 Open circuit voltage (OCV) at startup

During the first batch of startup phase, the MFCs were operated under open circuit conditions. During the OCV, no external resistance was connected across each of the reactor. The OCV was recorded at an interval of 30 minutes and the recorded data was averaged every 24 h. The variations in the OCV with time represents three different stages as shown in Figure 4.1. The upsurge or increase in the initial stage of the operation indicates the formation of the microbial community. This stage is then followed by a steady stage where the microbial growth in a system saturates the anode and maximum OCVs were achieved in the both reactors. As already acclimatized sludge was used, so the first stage lasted for a short period of time and maximum voltage comes very quickly (Sonawane et al., 2017a). The maximum OCVs of 529 mV and 451 mV across anode and cathode were obtained for the CFBMFC and GRMFC respectively, during the second stage of operation. CFBMFC achieved 14.7% more OCV than the GRMFC because of the better biofilm growth due to its large surface area (Monayeri et al., 2006). Finally, the third and the last stage shows the decline in the performance which is the indication of substantial decrease in nutrients concentration (Sonawane et al., 2017a).

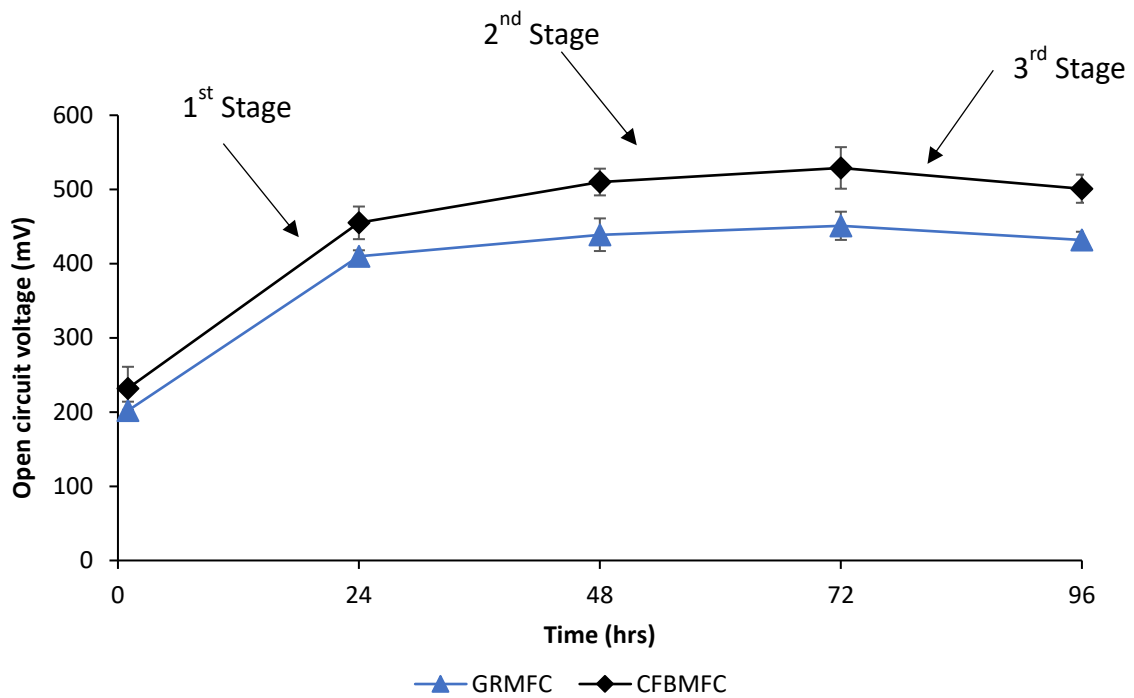


Figure 4.1 Changes in electrode potential with time under OCV

4.1.2 Voltage and power generation at startup

Following the OCVs measurement, the circuit was closed by connecting a resistor of 1000 Ω across the anode and cathode and the voltage was recorded at a time interval of 30 minutes. The reactors started generating electricity by utilizing organic waste existing in the sewage and were able to accomplish the wastewater treatment. A similar trend to that of OCV was also observed here. The maximum voltage was achieved initially after the formation of microbial community followed by a relatively steady phase.

Maximum voltage of 232 mV and 289 mV (Figure 4.2) corresponding to highest power densities of 24.5 mW/m² and 37.96 mW/m² (Figure 4.3) were achieved for GRMFC and CFBMFC respectively. There was 19.7% and 35.4% more increase in voltage and power generation in CFBMFC than in GRMFC respectively. Figure 4.2 and 4.3 shows that in CFBMFC, voltage and power reached a maximum value between 24 and 48 hrs. and then starts to decline. In GRMFC, the power and voltage reached to maximum value rather slowly and lower maximum values were achieved because of less mature biofilm growth due to small surface area of electrode.

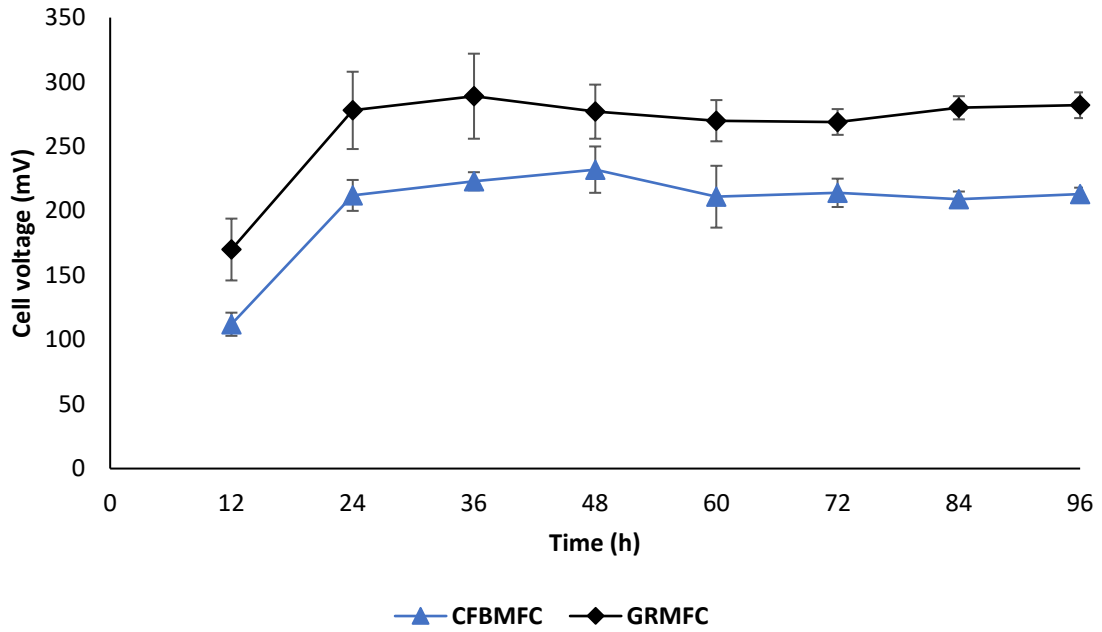


Figure 4.2 Variation in voltage with time under closed circuit conditions

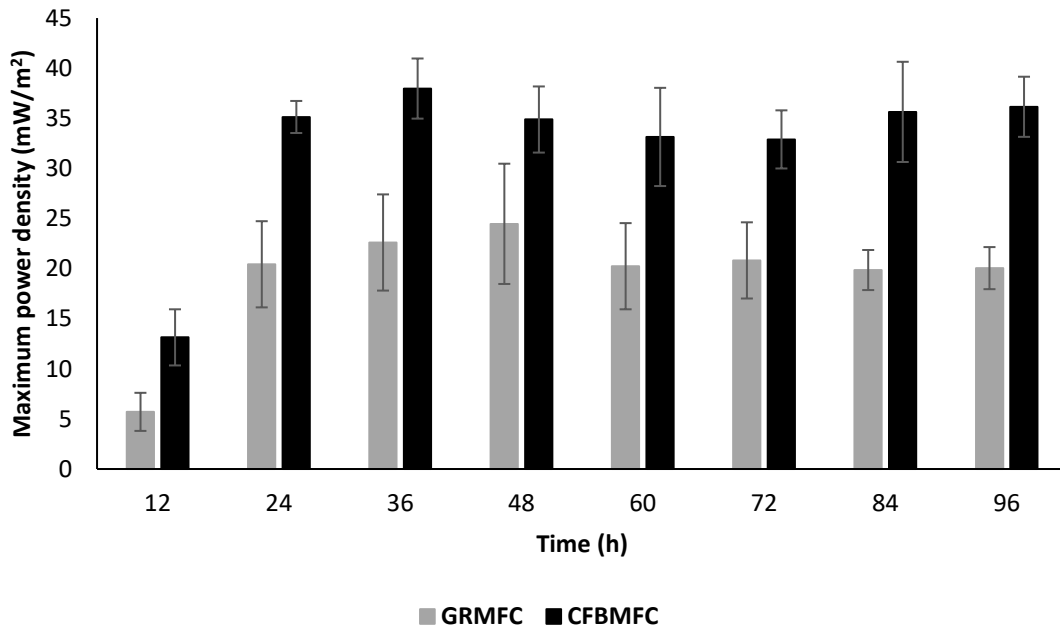


Figure 4.3 Maximum power density vs time under closed circuit conditions

4.1.3 COD removal by MFCs at startup

One of the important parameters is the COD removal which is helpful in the overall evaluation of the performance of MFC. COD test is used to find the availability of substrate in the MFC, either into electricity production, or by reaction that are competitive with some other electron gainers (e.g. O₂, sulfate and nitrate) or the growth of a biomass. During the startup batch run, COD removals of 60-70 % for GRMFC and 70-80% CFBMFCs were achieved. CFBMFC achieved overall 10% more COD removal than GRMFC because carbon fiber brush has thick attached growth biofilm along with suspended growth microorganisms which contribute to the overall COD removal (Monayeri et al., 2006)

4.2. MFC performance at semi continuous mode

After 12 days of batch run, the operation of both the MFCs were shifted into semi-continuous mode. In this mode of operation, wastewater was continuously fed and removed from the reactors. The known amount of substrate was fed manually using syringe four times a day. Similarly, the same amount of effluent was removed four times a day through effluent valves. The external resistance was 1000 Ω in both of MFC reactors like that in a batch mode.

4.2.1 Continuous voltage generation at various HRTs

Figure 4.4 shows the continuous generation of voltage during the whole semi continuous operation. Voltage was recorded at a time interval of every 30 minutes and later it was averaged for 24 hours. Figure 4.4 shows the voltage generated at every operated HRT. The reactors were generating voltage when they were shifted into semi continuous mode as they were already operating in batch mode. At a starting HRT of 48 hours the reactors undergo a sudden increase in voltage following a steady phase. When the voltage was stabilized at 48 hours HRT during the 8th day of operation, HRT was changed into 36 hours. There was a sudden decrease in voltage generation due to change in conditions, as bacteria stabilizes to the new HRT the voltage gradually starts to increase and reaches a maximum of 267 mV and 280 mV for a GRMFC and CFBMFC respectively. At this stage CFBMFC achieved 4.64% more voltage than GRMFC. Similarly, when voltage starts to stabilize and there was very little variation in voltage generation, HRT was shifted from 36 hours into 24 hours. The reactors were operated at each HRT until or unless voltage generation was stable.

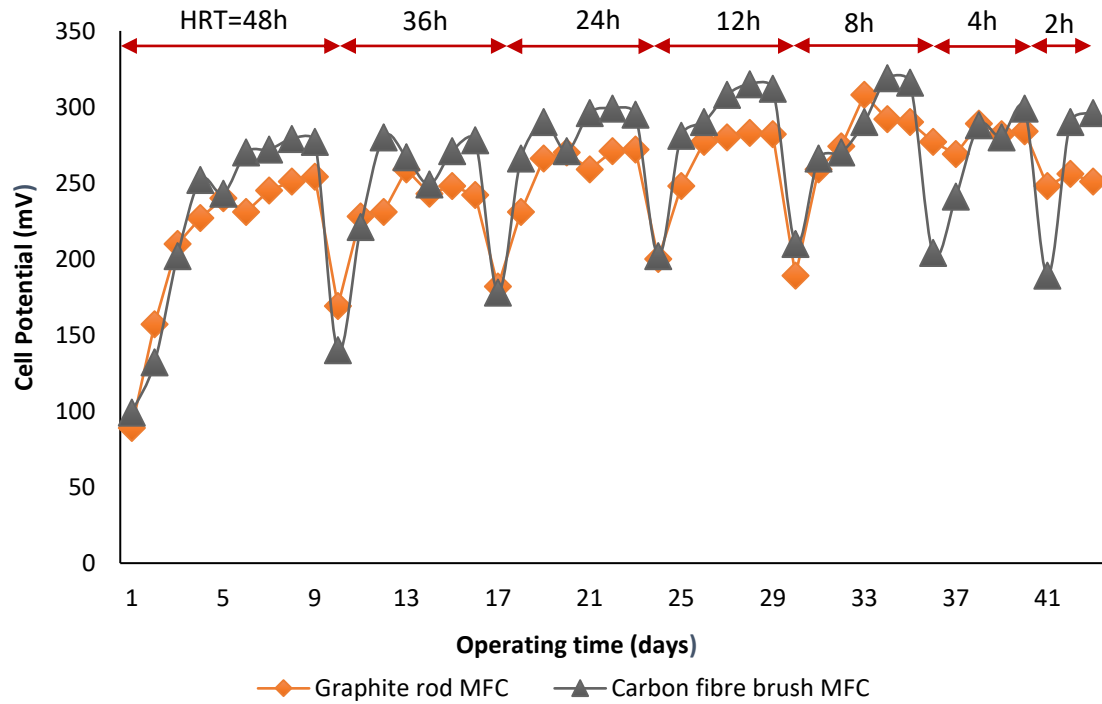


Figure 4.4 Continuous cell voltage generation for different electrodes and HRTs

Figure 4.4 is showing the results of voltage generation for both reactors. It can be seen from the graph lines of both the reactors that with the decrease in HRT there is an increase in voltage production. The reason for that is at longer HRTs there is lower average substrate (COD) concentrations and less substrate availability for bacteria to release subsequent electrons (Ahn and Logan, 2012). It can also be seen that carbon fiber brush MFC has achieved overall higher voltage generation than graphite rod MFC. This is because carbon fiber brush, due to its large surface area had a thicker biofilm development and more active microorganisms which released a greater number of electrons thus achieving high overall voltage generation than plain graphite rods. (Feng et al., 2010).

4.2.2 Effect of HRT on the power generation of both MFCs

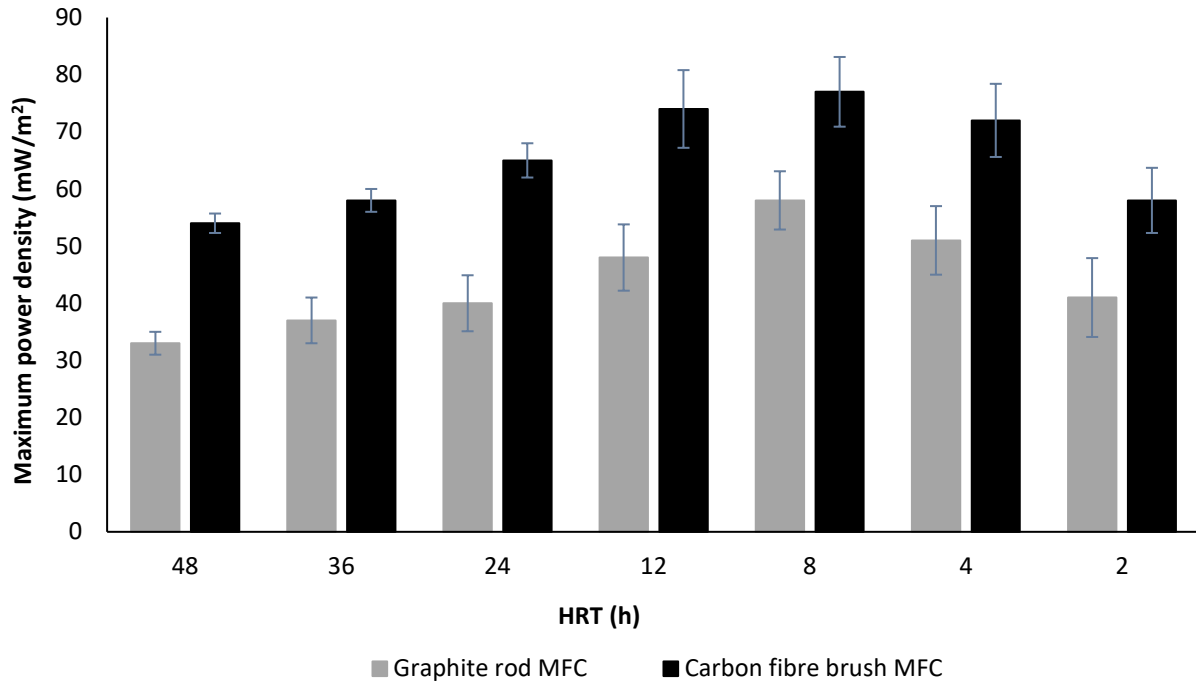


Figure 4.5 Maximum power density vs time for different electrodes used

Both MFC reactors generated power density at each operated HRT corresponding to the voltage generation. Figure 4.5 shows the maximum power density generated at each operated HRT. Maximum power density of 77 mW/m² and 58 mW/m² was achieved at 8 h HRT for carbon fiber brush and graphite rod MFC which shows that CFBMFC has achieved 24.6% more power density than GRMFC for the same HRT respectively. This is because CFB has a great durability, which gives it a greater specific surface area for bacteria thus generating more power densities (Feng et al., 2010). Figure 4.5 also shows that with the decrease in HRT from 48 h to 8 h power density for both reactors followed an increasing trend and then started to decline with further decrease of HRT to 4 hrs. and 2 hrs. respectively. GRMFC and CFBMFC showed 43.1% and 30% increase in power density when HRT was decreased from 48 h to 8 h respectively. The reason for the following trend is again that at longer HRTs there is lower average substrate concentrations thus resulting in lower power densities at higher HRTs (Ahn and Logan, 2012).

4.2.3 COD Removal and CE during Semi-Continuous Phase

The COD removal and CE are two important parameters used in the evaluation of an MFC.

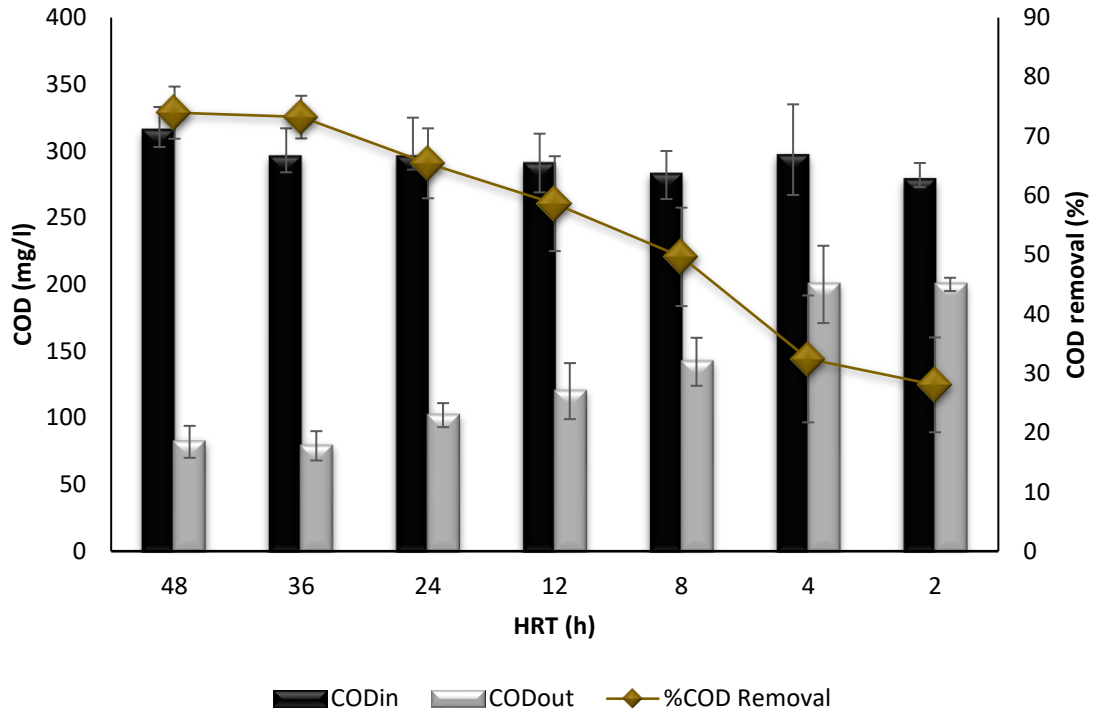


Figure 4.6 COD removal in GRMFC

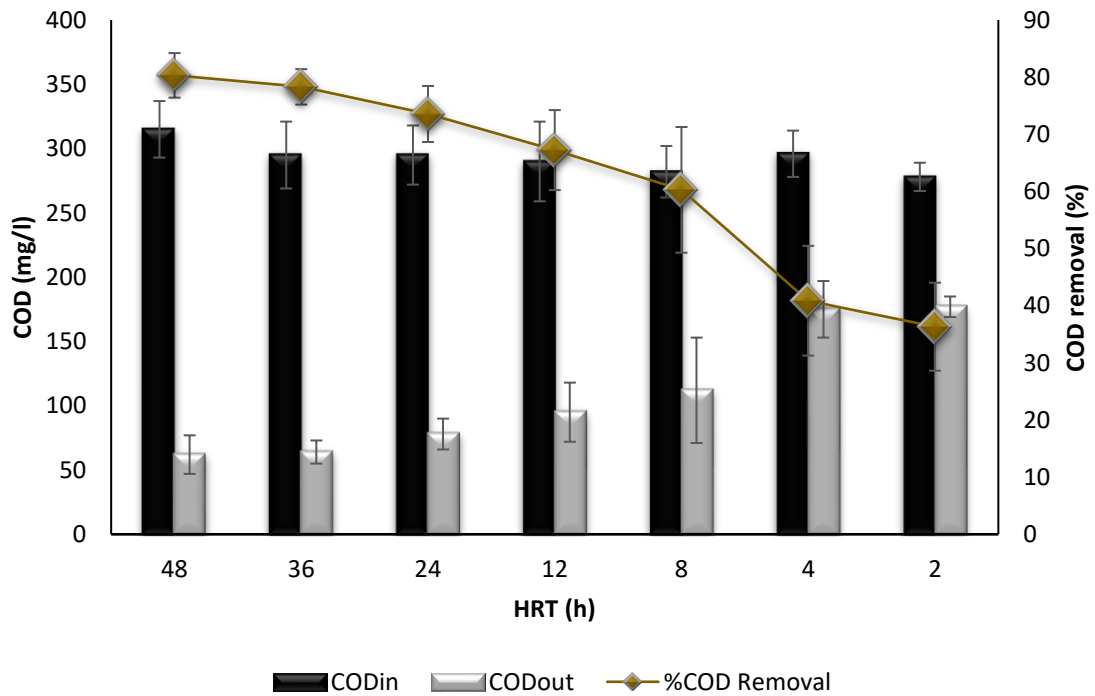


Figure 4.7 COD removal in CFBMFC

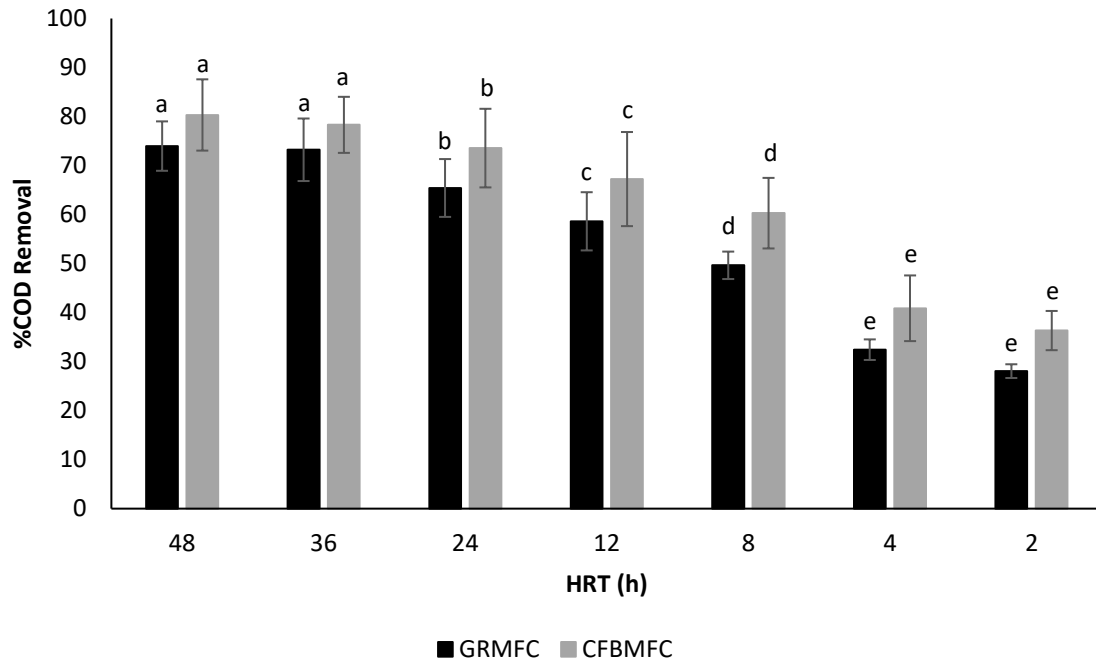


Figure 4.8 %COD comparison of GRMFC and CFBMFC

Figure 4.8 is showing the comparison of COD removal in both reactors. CFBMFC has achieved 7.97% more COD removal than GRMFC at a maximum HRT of 48 h. The reason for higher COD removal in CFBMFC is that in CFB reactors due to large surface area of brushes there was a thicker biofilm development which resulted in efficient removal of COD (Zhang et al., 2013). Similarly, when HRT was increased from 2 h to 48 h there was 54.8% and 52% increase in COD removal efficiency in CFBMFC and GRMFC respectively. Figure 4.8 also indicates the statistical analysis of the data. The p-value of the data was determined for both reactors and data were analyzed separately for each reactor at each operated HRT. The graph displayed that the data is not much significantly different at longer HRTs of 48 and 36 h but showed a significant difference at HRTs of 24, 12 and 8 h because the conditions were less stable due to high organic loading rates at these HRTs. The CE was determined based on the total substrate utilization into electric current. In the current study COD removal of 70-80% was achieved for both reactors (Figure 4.6 & Figure 4.7). Figure 4.6 and 4.7 shows the overall COD removal in graphite rod and carbon fiber brush MFC at each operated HRT respectively. Maximum COD removals of 73.9% and 80.3% were achieved for graphite rod and carbon fiber brush MFC at an HRT of 48 hrs. In

both reactors the COD removal declined with the decrease in HRT. COD removal rates generally decrease with shorter HRTs because at shorter HRTs there is high organic loading rates and due to short time availability there is not enough contact time between the substrate and microorganisms so a part of the organic compound present in the substrate remains untreated resulting in overall high CODs in the effluent (Zhang et al., 2013).

The CE was in the range of 4.2 to 5.44% indicating that significant number of electrons were lost (Figure 4.9). The CE is not directly related to power density since it is not a kinetic factor. Thus, due to space competition in the anode biofilm, low density of ARB could be the reason associated with the low CE which may lead to low power density (Ismail & Habeeb, 2017). Also, COD removal is inversely proportional to CE. Several studies have shown that lower CE with higher COD removal was potentially caused by non – exoelectrogenic bacteria in the solution which basically utilizes the electrons in other metabolic processes (Kim et al., 2008; Liu et al., 2005b; Strycharz-Glaven et al., 2011). Many factors may contribute to the loss of electrons, including substrate utilization for the growth of bacteria, methanogenesis, fermentation and the transfer of electrons by substrate to other type of electron gainers such as oxygen, SO_4^{2-} and nitrate in the solution (Prestigiacomo et al., 2016).

Figure 4.9 illustrates the CE at various operated HRTs. Maximum columbic efficiencies for both reactors were achieved at 48 h HRT with 4.2% for graphite rod MFC and 5.44% for carbon fiber brush MFC, which shows that CFBMFC has achieved 22.8% more CE than GRMFC respectively.

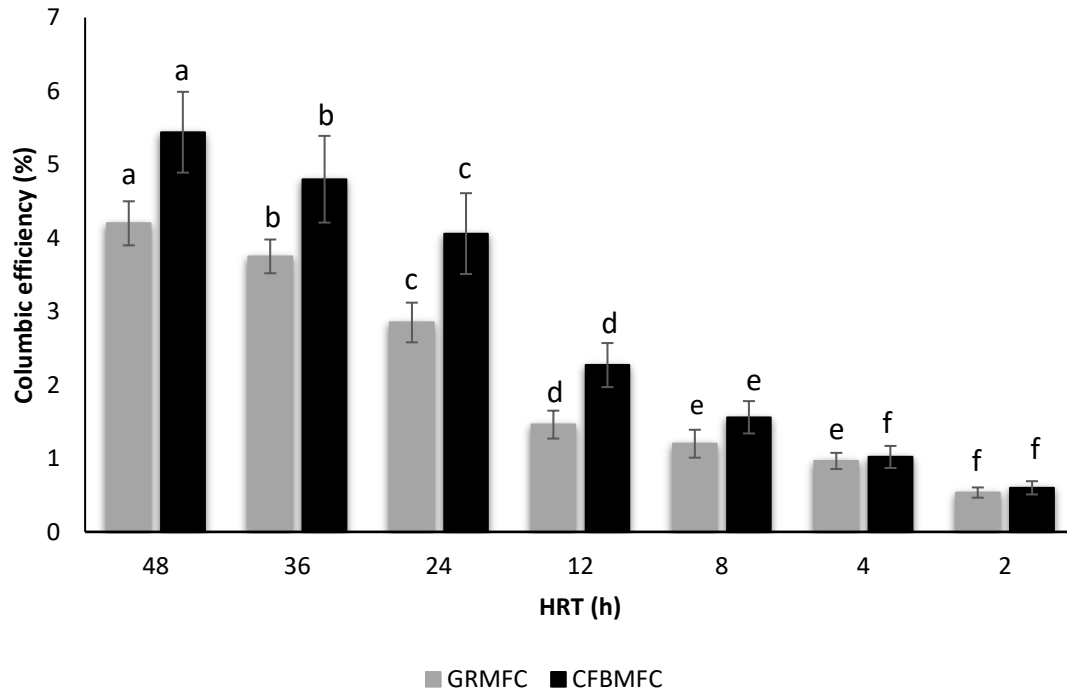


Figure 4.9 CE at various HRTs

Figure 4.9 also indicates that with the increase in HRT the C.E is also increased. It is because at greater HRTs, microorganisms have more time to degrade the organic matter completely and thus electrons are efficiently transfer to the electrode. While at lower HRTs, organic matter is not completely oxidized, and energy is lost in the form of unoxidized substrate. Figure 4.9 also shows that carbon fiber brush electrode MFC achieved a relatively higher C.E than that of graphite rod electrode MFC. The reason for that is the dense biofilm development on carbon brush anode having a large surface area than that on the graphite rod anode having low surface area (Wu et al., 2017). Similarly, Figure 4.9 shows the statistical analysis of the data. The p-value of the data was determined for both reactors at each operated HRT and the results showed that the data was significantly different at longer HRTs for both reactors while there was not much difference at shorter HRTs of 8, 4 and 2 h respectively.

4.3. Polarization Curves at different HRTs

Polarization curve data was achieved by changing the external resistance from 10 to 10000 Ω in decreasing order after a steady state of operation as shown in figure 4.6 & 4.7.

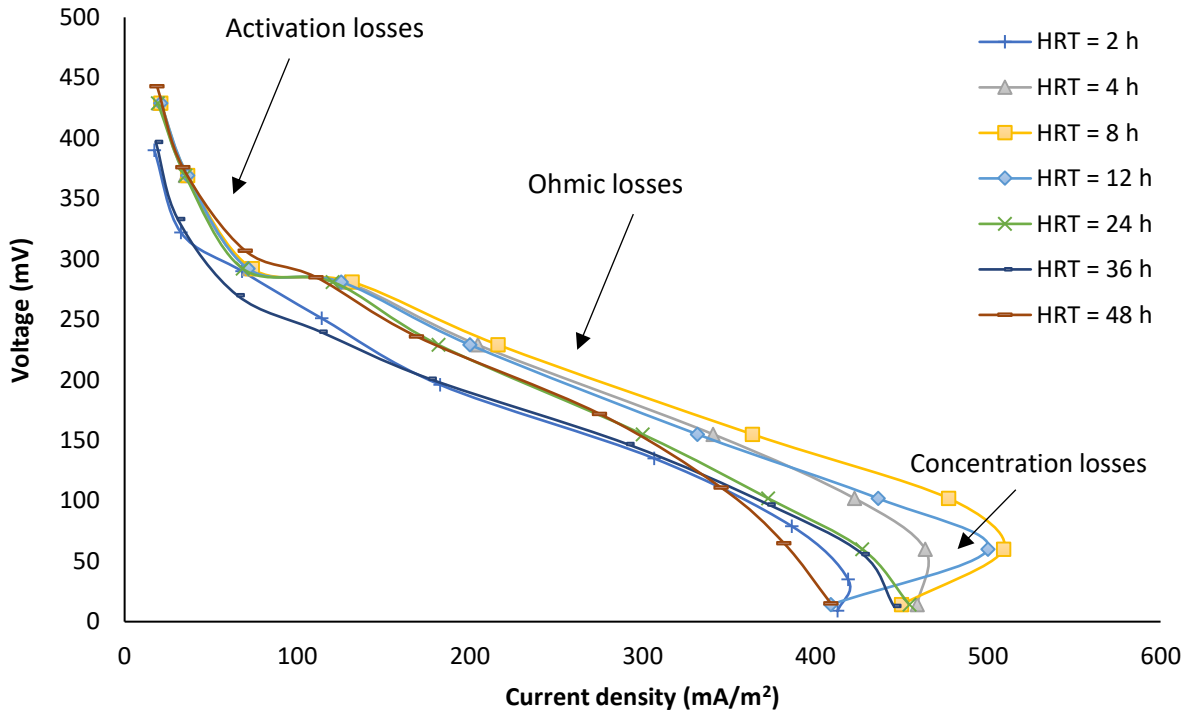


Figure 4.10 Polarization curves for GRMFC

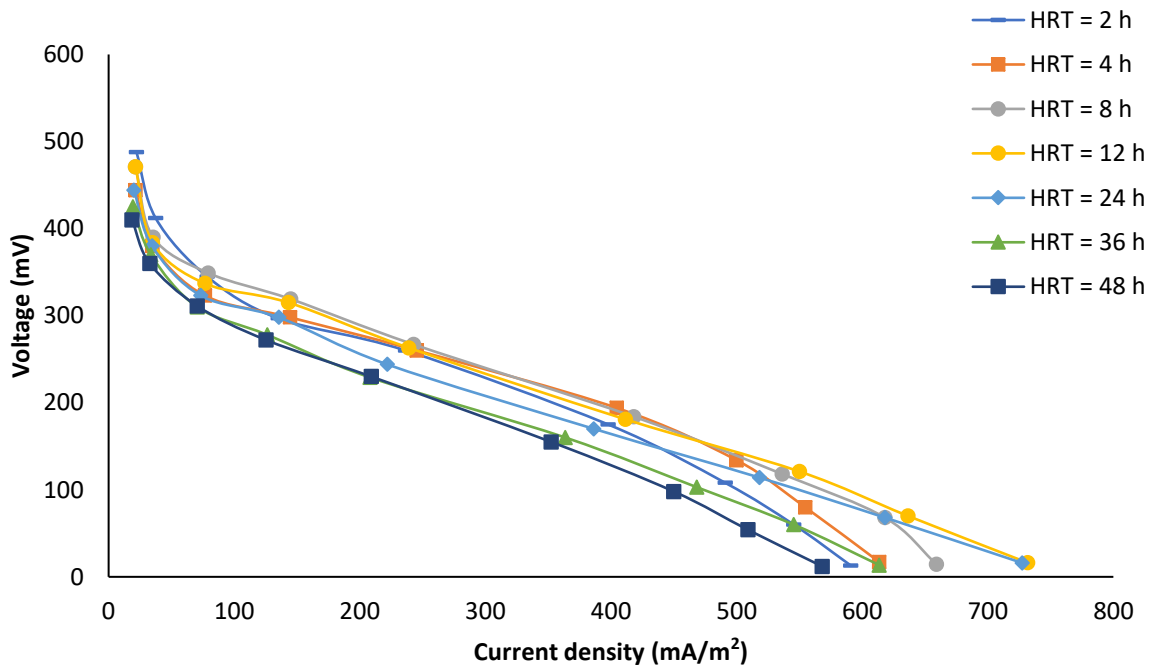


Figure 4.11 Polarization curves for CFBMFC

Polarization curves of both the reactor shows that as cell potential decreases current density increases with increase in external resistance. Maximum current density of 509 mA/m² and 731 mA/m² were achieved for graphite rod and carbon fiber brush MFCs which shows that CFBMFC achieved 30.3% more current density than GRMFC respectively. The cell potential drops suddenly at lower external resistance, but the current was relatively higher in all polarization tests.

Figure 4.10 shows the polarization curves of a graphite rod MFC at each operated HRT. Generally current density improved with the decrease in HRT and the maximum current density of 509 mA/m² was accomplished at an HRT of 8 h. Similarly figure 4.11 shows the polarization curves of carbon fiber brush MFC operated at each HRT. In this MFC reactor maximum current density of 731 mA/m² was accomplished at an HRT of 12 h. Higher current density in carbon fiber brush MFC reactor is an indication of better growth of microorganisms due to large surface area of carbon fiber brushes (Feng et al., 2010).

Internal resistance was estimated from the slope of the polarization curve (Logan et al., 2006). Table 4.1 shows the internal resistance at each operated HRT for both MFC reactors.

Table 4.1 Internal resistance at different HRTs

HRT (h)	Internal resistance of GRMFC (Ω)	Internal resistance of CFBMFC (Ω)
48	418	292
36	381	275
24	368	244
12	332	248
8	311	242
4	340	270
2	357	317

Polarization curve is usually divided into three regions which gave an idea about the type of losses in the MFC reactor. In the 1st portion, there is a sharp initial reduction of voltage due to the activation losses. After that voltage drops more slowly and linear with current which is basically the indication of ohmic losses. In the third and final region quick drop

of voltage at greater currents due to the concentration losses (Rismani-Yazdi et al., 2008). In this current study the internal resistance is mostly because of ohmic losses as the linear part of the current & voltage is dominant. The main reason for the ohmic losses is probably due to the uncoated electrode (cathode) (Zhou et al., 2011).

4.4. Power curves at different HRTs

Power curve is a helpful tool in MFC systems which is used to obtain the highest attainable power in some MFC reactor. These curves are obtained from the polarization data and plotted as a function of power density against current density. Figure 4.12 & 4.13 shows the power curves for graphite rod and CFB MFCs attained during steady state phase. It shows the maximum power density of 58 mW/m² and 77 mW/m² for graphite rod MFC and carbon fiber brush MFC respectively. Both MFC reactors achieved maximum power density at an HRT of 8 h with CFBMFC achieved 24.6% more power than GRMFC. The reason for maximum power density at an HRT of 8 h is due to low internal resistance of the reactors then at other operated HRTs (Table 4.1). The greater the internal resistance the lower will be power density because substantial number of electrons will be lost to overcome the internal resistance (Khater et al., 2015).

Power curves of both the reactors shows that with the increase in HRT, power density tends to decrease. There was 42% decrease in power density when HRT was increased from 8 h to 48 h in GRMFC respectively. The large reduction in power for both types of MFCs at larger HRTs was likely due to the lower average COD concentration in the reactor, as low CODs are known to reduce current production by the anode (Liu et al., 2004b).

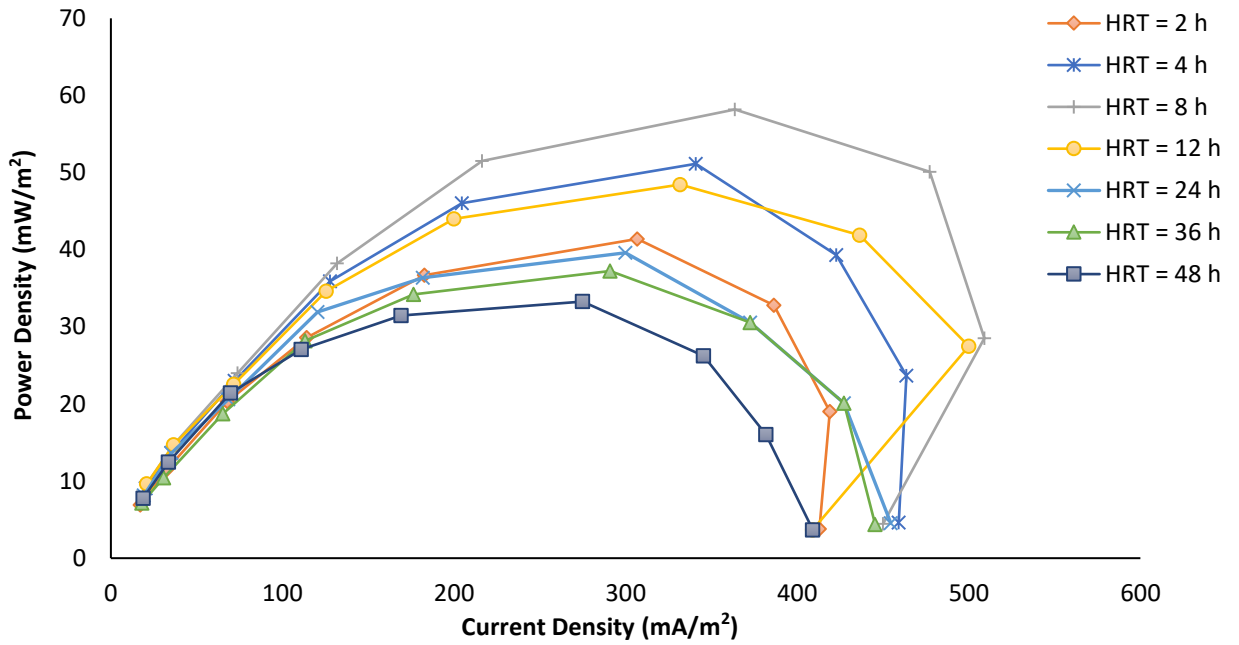


Figure 4.12 Power curves of GRMFC

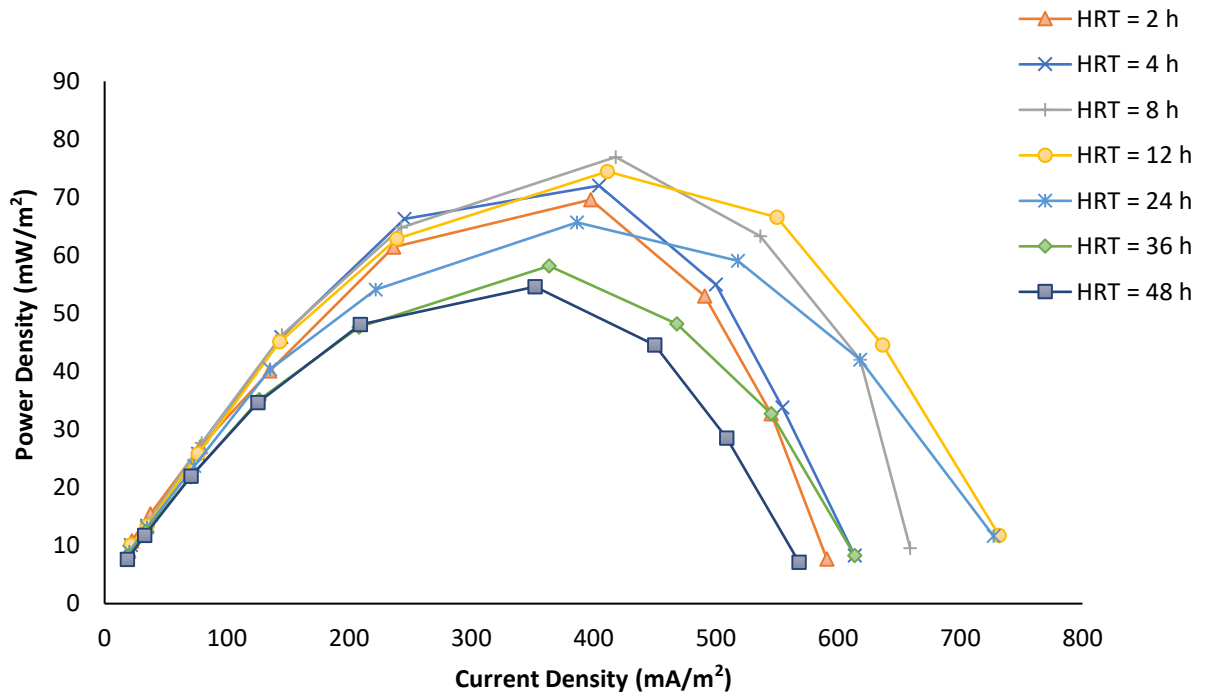


Figure 4.13 Power curves of CFBMFC

4.5. Effect of HRT on the pH of both reactors

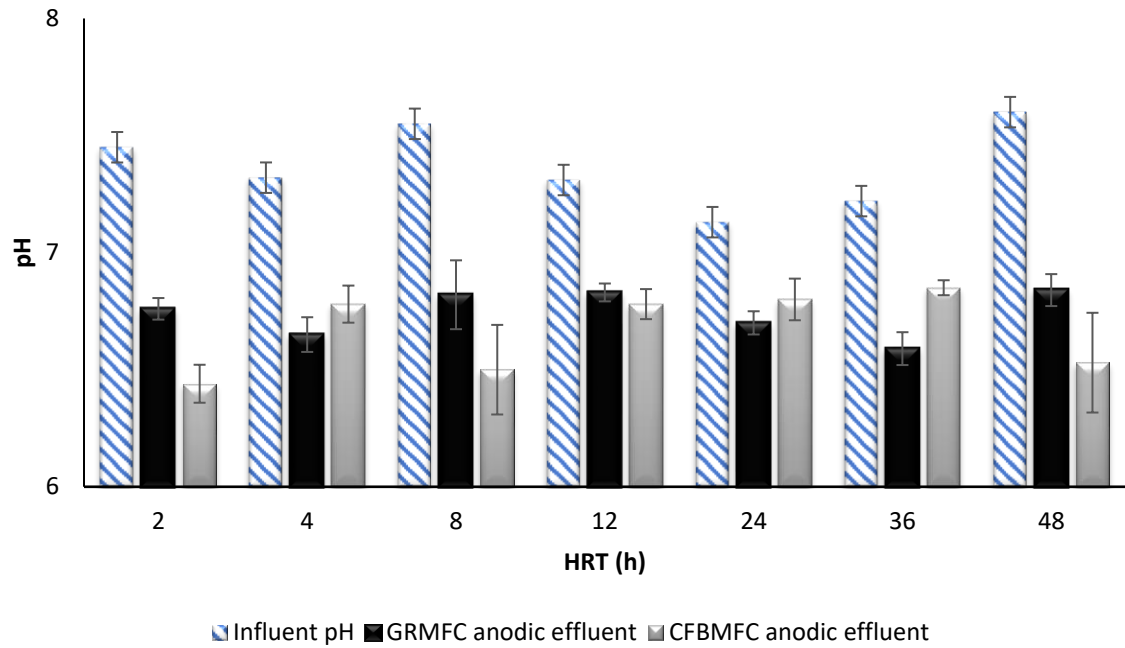


Figure 4.14 Influent & effluent pH in GRMFC & CFBMFC

Anodic pH is the most useful chemical parameter for determining the electrochemical accomplishment of the microbial anode, which in turn affects the overall MFC performance. Figure 4.14 shows pH of both the influent and anodic effluent of the graphite rod and carbon fiber brush MFC reactors. The pH of the influent domestic wastewater was found to be in a range of 7 – 7.6. Figure 4.14 shows that at each operated HRT, pH of the anodic effluent tends to decrease in both reactors, this is mainly because of the release of protons during the bacterial degradation of organic matter. Previous studies suggest that controlling the anodic pH close to neutral pH condition would allow the electroactive biofilm to function better and thus will enhance the overall performance of MFC (Zhang et al., 2013).

4.6. Energy Balance

The overall energy expenditure of the CFBMFC is calculated as:

4.6.1 Energy Produced

Maximum volumetric power density of CFBMFC = 94 mW/m³ at an HRT of 8 h

	$= 94/1000 \text{ W/m}^3$
	$= 0.094 \text{ W/m}^3$
	$= 0.00001175 \text{ kWh/m}^3$
COD utilized at an 8 h HRT	$= 145 \text{ mg/l}$
	$= 0.0145 \text{ kg/m}^3$
Total energy produced	$= 0.00001175/0.0145$
	$= 0.0000810 \text{ kWh/kg COD}$
4.6.2 Energy Consumed	
Pumping Power requirements	$= Q.d.E / 1000 \quad (\text{Kim et al., 2010})$
$Q = 1.5\text{L}/8\text{h}$, $d = 9800 \text{ N/m}^3$, $E = 0.15\text{m}$	
$Q = 0.0000000521 \text{ m}^3/\text{s}$	
Power requirement	$= 0.0000000521 \times 9800 \times 0.15 / 1000$
	$= 0.0000000766 \text{ kW}$
	$= 0.0000006125 \text{ kWh}$
Average influent COD	$= 287 \text{ mg/l}$
	$= 0.0000006125/0.287$
Pumping energy requirement	$= 0.000002134 \text{ kWh/kg COD}$
Aeration Power requirements	$= Q.d.E / 1000 \quad (\text{Kim et al., 2010})$
$Q = 3.5\text{L}/\text{min}$, $d = 11.418 \text{ N/m}^3$, $E = 0.15\text{m}$	
$Q = 0.00005833 \text{ m}^3/\text{s}$	
Power requirement	$= 0.00005833 \times 11.418 \times 0.15 / 1000$
	$= 0.0000000999 \text{ kW}$
	$= 0.0000007992 \text{ kWh}$

Average influent COD	= 287 mg/l
	= 0.0000007992/0.287
Aeration energy requirement	= 0.000002784 kWh/kg COD
Total energy consumed	= 0.0000021341 + 0.000002784
	= 0.000004918 kWh/kg COD
Net Energy	= 0.0000810 - 0.000004918
Net Energy	= 0.00007612 kWh/kg COD

CHAPTER 5

CONCLUSIONS & RECOMMENDATIONS

5.1. Conclusions

To evaluate the effect of different HRTs on the performance of microbial fuel cell, two types of electrodes were used: carbon fiber brush and graphite rod respectively. The system developed here was able to continuously generate electricity from the organic matter present in the domestic wastewater while accomplishing wastewater treatment. These are the following conclusions that can be drawn from the current work.

- The HRT greatly affect the performance of an MFC reactor. It was found that longer HRTs are needed in order to achieve higher COD removals. COD removals of 80.3% and 73.9% were achieved for CFBMFC and GRMFC at an HRT of 48 h. Similarly, columbic efficiency also increased with the increase in HRT and maximum CEs of 5.44% and 4.2% were achieved at an HRT of 48 h for CFBMFC and GRMFC respectively. The relatively low CEs shows that the electric current was the least significant in both MFCs.
- Voltage and Power generation were found to decrease with the increase in HRT, but the maximum power was generated at an HRT of 8 h. Extreme power densities of 77 mW/m² and 58 mW/m² were achieved for CFBMFC and GRMFC respectively. Similarly, the maximum current densities of 509 mA/m² and 731 mA/m² were achieved for graphite rod and carbon fiber brush MFCs respectively.
- Carbon fiber brush electrodes in MFC showed overall better performance than graphite rod electrodes both in terms of COD removal and power production.

5.2. Recommendations

Following recommendations are noteworthy for further study:

- Ohmic losses were the main reason for high internal resistance, which is mainly due to CEM, electrodes and interconnections used. Using some better quality CEMs or coating a catalyst on electrode will be able to reduce this internal resistance.
- Single chamber MFC can be used instead of dual chamber MFC to eliminate the need of aeration thus reducing the overall cost of MFC.

- CE can be enhanced by reducing the oxygen access from cathode compartment. Thus, that type of membrane can be used which has better proton permeability but less oxygen diffusion properties.
- Keeping the electrodes distance minimum, ohmic resistance can be reduced thus improving the power density of MFC.

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APPENDIX

Here are the some of the calculations of the various parameters that are used in the current study.

1) Voltage

$$\begin{aligned}\text{Voltage} &= 280 \text{ mV (measured using data logger)} \\ &= 0.28 \text{ V}\end{aligned}$$

2) Current

$$\text{Resistance} = R = 1000 \Omega$$

$$\text{Working volume of anode compartment} = V_{\text{an}} = 1.8 \text{ L}$$

$$\text{Surface Area of Anode} = 22 \text{ cm}^2 = 0.0022 \text{ m}^2$$

According to ohm's law

$$V = IR$$

$$I = \frac{V}{R}$$

$$= \frac{0.28}{1000} = 0.00028 \text{ A}$$

$$\text{Current Calculated} = 0.28 \text{ mA}$$

3) Power

$$\text{Power} = P = V \times I$$

$$= 0.28 \text{ V} \times 0.00028 \text{ A}$$

$$= 0.0000784 \text{ W}$$

$$\text{Power} = 0.0784 \text{ mW}$$

4) Power density

$$\text{Power density} = \frac{P}{A_{\text{an}}}$$

$$= \frac{0.0784}{0.0022}$$

$$= 35.6 \text{ mW/m}^2$$

So, the Power density calculated is 35.6 mW/m²

5) Current density

$$\text{Current density} = \frac{I}{A_{\text{an}}}$$

$$= \frac{0.00028}{0.0022}$$

$$= 0.127 \text{ A/m}^2$$

So, the final calculated current density is 0.127 A/m²

6) Volumetric power density

$$\text{Volumetric Power density} = \frac{P}{V_{an}}$$

$$= \frac{0.0784}{1.8}$$

$$= 0.043 \text{ mW/L}$$

So, the volumetric power density is 0.043 mW/L

7) Coulombic Efficiency

$$\text{Coulombic Efficiency} = \text{CE} = \frac{M \int_0^t I dt}{FbV_{an}\Delta\text{COD}}$$

Where,

M = Molecular weight of oxygen = 32 g/mol

I = Current = 0.00028 A

T = HRT = 96 h = 345600 s

F = Faraday's Constant = 96485 Coulombs/mol

b = Number of electrons exchanged per mole of oxygen = 4

$$\Delta\text{COD} = \text{COD}_{\text{in}} - \text{COD}_{\text{out}}$$

$$= 320\text{mg/l} - 80 \text{ mg/l}$$

$$= 240 \text{ mg/l}$$

$$\Delta\text{COD} = 0.24 \text{ g/l}$$

$$V_{an} = 1.8 \text{ L}$$

$$\text{CE} = \frac{32 \int_0^t I dt}{(96485)(4)(1.8)(0.24)}$$

$$= \frac{(32) [(0.00028)(345600) - (0.00028)(0)]}{166726} \quad (t = 96 \text{ h} = 345600\text{s})$$

$$= 0.01857$$

So, the coulombic efficiency is found to be 1.86%

8) Internal Resistance

The internal resistance can be determined from the slope of the polarization curve. From the polarization curve shown below

Equation of the slope $y = -0.7285x + 351.93$

As $y = mx$

Here, Slope $m = 0.7285 \Omega\text{m}^2$

$m = 0.7285/0.0022$ (Surface area of anode = 0.0022 m^2)

$m = 331 \Omega$

So, the internal resistance is 331Ω

Polarization curve

