Effect of Various Operating Parameters on Power Generation from Mediator Less Microbial Fuel Cell

by

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A project report submitted in partial fulfillment of the requirements for the degree of Master of Science in Energy Science and Engineering

Khulna University of Engineering & Technology
Khulna 9203, Bangladesh
May 2019

Declaration

This is to certify that the research work entitled "Effect of Various Operating Parameters on Continuous Power Generation from Mediator Less Microbial Fuel Cell" has been carried out by Md. Abdul Halim in the Department of Energy Science and Technology, Khulna University of Engineering & Technology, Khulna, Bangladesh. The above research work or any part of this work has not been submitted anywhere for the award of any degree or diploma.

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Approval

This is to certify that the research work submitted by Md. Abdul Halim entitled "Effect of Various Operating Parameters on Continuous Power Generation from Mediator Less Microbial Fuel Cell" has been approved by the board of examiners for the partial fulfillment of the degree of Master of Science in the Department of Energy Science and Engineering, Khulna University of Engineering and Technology, Khulna, Bangladesh in May 2019.

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Acknowledgement

At first, I would like to express my praise and gratitude to the Merciful and Almighty Allah, who makes me capable to successfully complete this study.

I would like to express his deepest and sincerest gratitude to his supervisor Dr. Mohammad Ariful Islam, Professor Department of Mechanical Engineering & Head, Department of Energy Science and Engineering, Khulna University of Engineering & Technology (KUET), for his unyielding guideline, forceful encouragement and after all constructive criticism at every stage of the research.

My sincere gratitude and thanks are extended to Prof. Dr. Quazi Sazzad Hossain, the honorable Vice- Chancellor of KUET, for the financial support given to this project without which this work could not be completed.

I express my heartful gratitude to the laboratory staffs department of Leather Engineering, Khulna University of Engineering & Technology (KUET), for their entireness help to perform laboratory test.

I would be very much grateful to Md. Ibrahim and Md Rasel Mollah, undergraduate student, department of Chemical Engineering, Jashore University of Science and Technology (JUST), for their amiable cooperation and support.

Finally I would like to acknowledge the encouragement of my family without their support it is not possible to run my research work.

Md. Abdul Halim

May, 2019

Dedication

To my family members, supervisor and all the teachers.

Abstract:

Microbial fuel cell (MFC) is the most adaptable renewable energy technology for its multidimensional applications. This bioreactor converts the chemical energy stored in decomposable organic and inorganic compound into electricity with the help of bacteria. The whole process occurred in an air free environment. Significant amount of research works has been carried out to improve the yield of MFC. In this research work, three MFCs were constructed using locally available materials. Local window glass was used to construct the body of MFC, Agar-agar solution and bandage cloth were used for salt bridge. Several experiments were performed in batch mode to investigate the effects of various operating parameters such as electrode material, electrolyte source, pH and concentration. To investigate the effect of electrode materials, three anode materials (carbon felt, Zinc and carbon rod) were used and copper was used as cathode with every cathode. Zinc-copper combinations gave 28.2% higher power than carbon felt-copper and 57.1% than carbon rod-copper. For operating pH, pH 6, pH 8 and pH 10 were investigated, where maximum power generated from pH 8, its value was 680.625 mW. To investigate better electrolytic source municipal waste water, river water (Bhairab) and hospital waste water was studied and maximum power (5.907mW) generated from Bhairab river water. Additives affect the power generation of microbial fuel cell; urine mixed waste water generates 52.13% and 9.6% higher power than raw waste water and fish waste mixed waste water respectively. 10% urine mixed electrolyte gives maximum voltage (1146 mV) but top power obtained from 15% urine mixed waste water. To get better yield source of electrolyte (Bhairab river water), electrode combinations (Zinc-copper), operating pH (pH 8) and 15% urine as additive can be used.

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Abbreviation

CO	: Carbon Monoxide
CO_2	: Carbon Dioxide
SO_2	: Sulfur Dioxide
NO_2	: Nitrogen Dioxide
CH_4	: Methane
REN	: Renewable Energy Policy Network
Mtoe	: Million tonnes of oil equivalent
NASA	: National Aeronautics and Space Administration
USA	: United States of America
BOD	: Biochemical Oxygen Demand
COD	: Chemical Oxygen Demand
Cu	: Copper
H_2	: Hydrogen
OCV	: Open-circuit Voltage
NH_4^+	: Ammonium ion
Na^+	: Sodium ion
K^+	: Potassium ion
Mg^{2+}	: Magnesium ion
Ca^{2+}	: Calcium ion
Fe	: Iron
Cr	: Chromium
Mn	: Manganese
P	: Power
Zn	: Zinc
CC	: Carbon cloth
Na	: Sodium
N	: Nitrogen
Mg	: Magnesium

Si	: Silicon
Cl	: Chlorine
P	: Phosphorus
K	: Potassium
S	: Sulphur

Units of measurements

%	: Percent
GW	: Giga Watt
°F	: Degree Fahrenheit
mA	: Milliampere
μW	: Micro Watt
cm^3	: Centimeter cube
μJ	: Micro Joule
°C	: Degree Celsius
m/s	: Meter per second
μm	: Micro meter
cm	: Centimeter
W/m^3	: Watt per meter cube
kWh	: Kilowatt hour
V	: Volt
mg/L	: Milligram per litter
mL/min	: Millilitre per minute
L	: Liter
M	: Molar
v/v	: Volume per Volume

CHAPTER I

INTRODUCTION

1.1 General

Crisis of energy is becoming more and more significant day by day. To alleviate this problem an alternative solution is needed, which can meet this demand of energy also can control the environmental pollution. Fossil fuels (coal, oil and gas) have significant impact on environment. In industrial revolution period fossil fuels was the main energy source. Due to the economic growth the most important challenge for the growing world is to manage the global energy demands. Petroleum, natural gas and coal known as fossil fuels are the main resources of energy. When this fossil fuel burns, discharges a massive volume of carbon dioxide (CO_2) and various greenhouse gases as CO, SO_2, NO_2 and CH_4, which affects human health and environment [1]. Around 80% of the total greenhouse gas emission comes by this process. The reserves of fossil fuels are getting less and also concerns about continued contributions of additional carbon dioxide to atmosphere that affect climate changes, therefore, the need for new energy sources with less environmental impact also increases [2]. All the human activities need energy consumption, and many sources are implied. A lot of economic and social factors as economic development, scientific and technological progress and world population growing determine a permanent increasing energy demand. The actual energy consumption relies mostly on fossil fuels, which are non-renewable and un-uniformly distributed in the earth crust. The energy supplying for all countries can be provided only by the international trade using different method for transport. The requirement of energy is increasing; previously fossil fuels maintained the major demand of energy requirement. The consequence of using much fossil fuel is the tremendous depletion of fossil fuel resources and ecological imbalance [3]. So, an environmental and economic sustainability an unconventional, renewable and carbon free energy sources are great demand for the scientist. Energy directly affects every function of modern life. In future

biofuels and hydrogen fuels will be the most important energy sources. The main energy carriers are electricity, which can be produced from all primary energy sources.

1.2 Sources of energy

A non-renewable resource cannot reuse within a meaningful human time-frame. Organic rich materials are the main component of this energy. These organic materials converted into oil and gas in sufficient amount of heat and pressure. The important part of non-renewable resources is minerals, metal-ores, fossil fuels (coal, petroleum, and natural gas) and groundwater with certain aquifers. The main source of energy is shown in Figure 1.1.

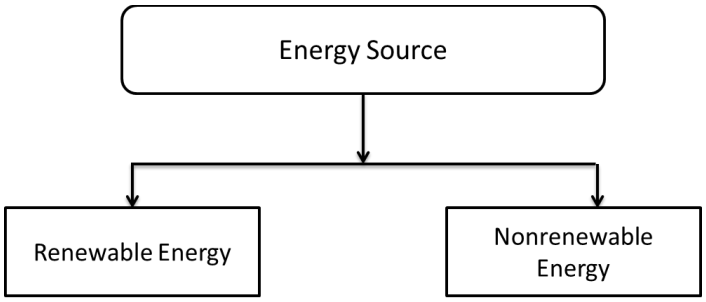


Figure 1.1: Sources of energy

Numerous renewable energy sources such as solar, wind, hydro, tidal, waves, and geothermal heat can be certainly replaced on a human timescale. Solar energy is one type of renewable energy. The natural light or heat that comes from sunlight is known as solar energy. Though solar energy is open and endless, only two constituents named collector and a storage unit are required to use this energy [4]. In 1839 Edmund Becquerel discovered how electricity comes from solar energy; the use of solar power for heating purpose was discovered firstly [5]. In 1954 Bell Laboratories firstly demonstrate the technology [6]. The markets for solar technologies are growing day by day though solar energy contributes only a small fraction of global energy production. Several hundreds of years ago human used wind power for pumping water and milling grains, finally it used for producing electricity with the help of turbines. Kinetic energy from falling or flowing water from dam or waterfall is used to produce electricity is known as hydropower plants. Hydropower is the most efficient, cost-effective and globally friendly

resources of producing electric energy. Biomass can produce organic matter that stored energy, which naturally reproduced. Again it is used directly as a solid fuel and can produce heat and electricity through thermal process using turbine. In destructive distillation process biogas can be produced from biomass which is rich in methane. Landfill is a natural but longer process converts the solid waste into methane-rich-gas, which is used for generating fuel [7]. Bio-alcohols (e.g. bioethanol) can also be obtained from biomass, is satisfies energy demand also protect environment [8]. By using fermentation process of corn, potato, beet and wheat bioethanol could be produced [9]. When humans modify energy balance can affects ecosystem.

The research and technical development are occurred significantly in the field of renewable energy. The fossil fuel based energy sources will rapidly collapse, so the cost of energy will be increased. This gives a clear idea for the urgency to switch to a sustainable attitude in generating power and reduce greenhouse gas emissions by at least 18% below the 1990 levels by the year 2020 [10]. So this susceptibility of unoriginal source of energy conducts the researchers to think about reliable sources of fuel. This can regenerate sharply and able to supply a region with its long-term energy needs for the future demand. This represents a strong argument in favor for the importance of developing renewable energy sources.

1.3 Demand of energy with population

With the increasing number of population the demand of food, water and energy have been reached a critical point, which is shown in Figure 1.2. Normally, more than 7 billion people live on the earth, which is estimated to reach 9.6 billion by the 2050 [11]. From the year 1973 to 2014 the global demand of energy goes double from 6,101 Mtoe (million tonnes of oil equivalent) to 13,699 Mtoe. [12]. Nowadays around 80% of the supplied energy comes from fossil fuels [12] which have a negative impact on the environment.

So that to minimize the uses of fossil fuel environmental friendly fuel sources are very emergency for future world. The demand of power in the form of electricity is ever increasing. Fuel cell is the most promising technology which can be a good alternative of fossil fuel.

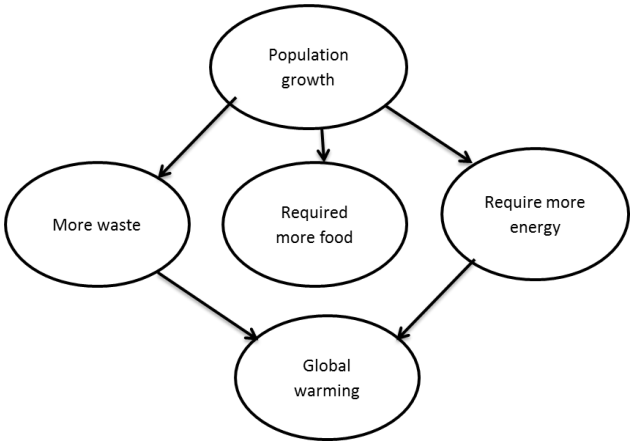


Figure 1.2: The impacts of population growth on environment

1.4 Fuel cell as energy harvesting technique

A fuel cell is a system that converts the chemical energy of the fuel into electrical energy. The chemical bonding energy contains in fuel change into electricity through the electrochemical reaction occurred in fuel cell, here proton associates with oxygen or another oxidizing agent. Primarily fuels cell are categorized based on the electrolytes which are used. The classification is done considering the electro-chemical reactions, used catalyst, temperature and other factors. The construction and types affect the applications of these cells. Currently numerous varieties of fuel cells are available in the market, but each have their own compensations, restrictions, and possible applications. The market of fuel cell is rapidly growing as it will reach 50 GW by 2020. Various types of fuel cell are shown in Figure 1.3.

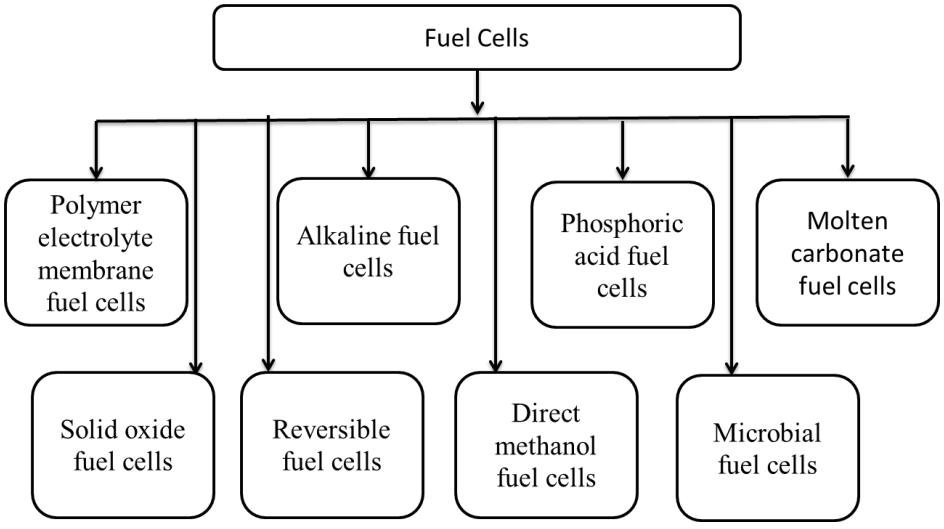


Figure 1.3: Classification of fuel cells

Polymer electrolyte membrane (PEM) fuel cells: This type of fuel cells also called as proton exchange membrane fuel cells. The prime benefit of PEM is; it can deliver high power density, having low weight and volume. Here electrolyte is used as solid polymer and platinum or platinum alloy containing carbon. To operate this cell only hydrogen, oxygen and water are required. The reaction occurred in this fuel cell are:

$$Anode: H_2 \rightarrow 2H^+ + 2e^- \quad (1.1)$$

$$Cathode: {}^1/_2\, O_2 + 2H^+ + 2e^- \rightarrow H_2O \quad (1.2)$$

Relatively low temperatures around 60-1400C are required to operate this cells. Main applications of these cells are in transportation systems. Some traveller automobiles, such as buses and cars PEM are particularly suitable for their startup time and weight-to-power ratio. Figure 1.4 shows the most common polymer electrolytic membrane fuel cell.

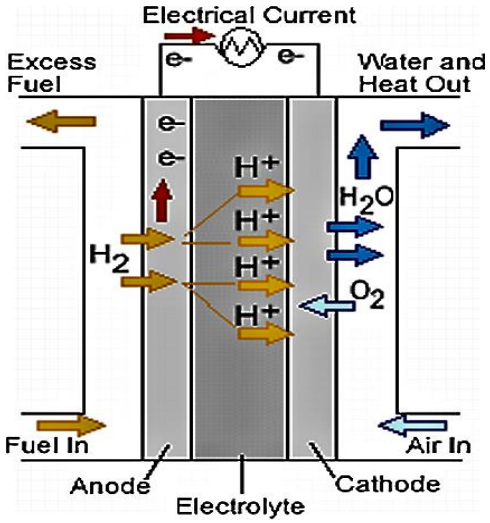


Figure 1.4: Schematic of polymer electrolytic membrane fuel cell

Alkaline fuel cells: Alkaline fuel cells (AFCs) are mainly used in U.S. space program. Here mixture of potassium hydroxide (KOH) with water is used as electrolyte. The reaction occurred in this fuel cell are:

$$Anode: H_2 + 2OH^- \rightarrow H_2O + 2e^- \quad (1.3)$$

$$Cathode: {}^1/_2\, O_2 + H_2O + 2e^- \rightarrow 2OH^- \quad (1.4)$$

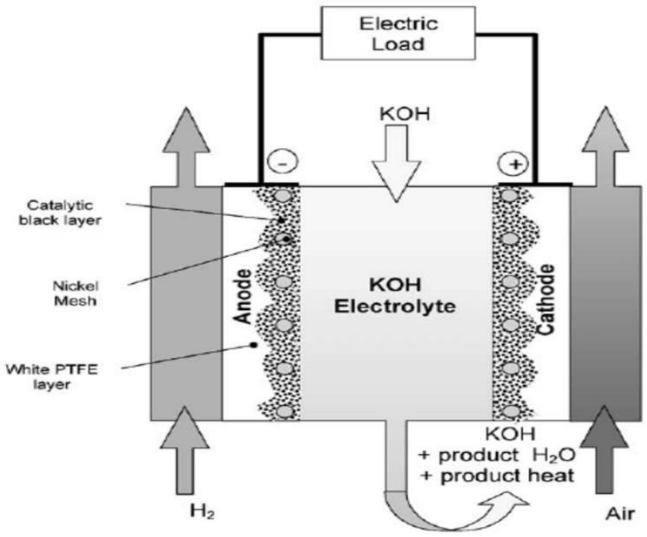


Figure 1.5: Schematic of alkaline fuel cell

In AFCs the optimum operating temperature ranges is 150-200^{0}C. In recent years, polymer membrane used AFCs have been developed. The only difference of AFCs from usual PEM fuel cells, in AFCs alkaline membrane is used, whereas, PME used acid membrane. The performance depend on the electro-chemical reaction occurred in the fuel cell, the performance of AFCs is high for its higher rate of electro-chemical reactions. About 60% of AFCs is widely used in space craft. Control of the poisons, occurred by carbon dioxide (CO_2) is the prime challenge for this type of cells. In fact, in AFCs carbonate from CO_2 in the air intensely affect the cell yield and stability. Figure 1.5 represents alkaline fuel cell.

Phosphoric acid fuel cells: in this fuel cell liquid phosphoric acid is used as electrolyte and a porous carbon with silicon carbide matrix is used as electrodes. The reaction occurred in this cell are given below:

$$Anode: H_2 \rightarrow 2H^+ + 2e^- \tag{1.5}$$

$$Cathode: {}^1/_2\, O_2 + 2H^+ + 2e^- \rightarrow H_2O \tag{1.6}$$

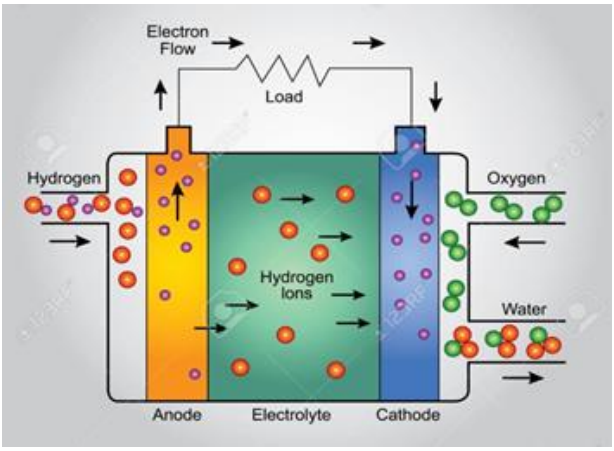


Figure 1.6: Schematic of phosphoric acid fuel cell

The optimum operating temperature is 180-200^{0}C. This fuel cell is the first generation update fuel cell used commercially. To produce motionless power generation phosphoric acid fuel cell is mainly used. A common phosphoric acid fuel cell is shown in Figure 1.6.

Molten carbonate fuel cells: Now days molten carbonate fuel cells (MCFCs) are used in electrical utility, industrial and military applications. The operating temperature of MCFCs is higher than 650°C. Molten carbonate salt with a mixture of chemically inert ceramic lithium aluminum oxide matrix is used as electrolyte. For reducing operating cost in anode chamber non porous metal catalyst is used. A model molten carbonate fuel cell is shown in Figure 1.7. The cell reactions are:

$$Anode: H_2 + {CO_3}^{2-} \rightarrow H_2O + CO_2 + 2e^- \quad (1.7)$$

$$Cathode: {}^1/_2\, O_2 + CO_2 + 2e^- \rightarrow {CO_3}^{2-} \quad (1.8)$$

The prime demerits of MCFC technology for its operating condition high temperature and corrosive environment which decries its life time.

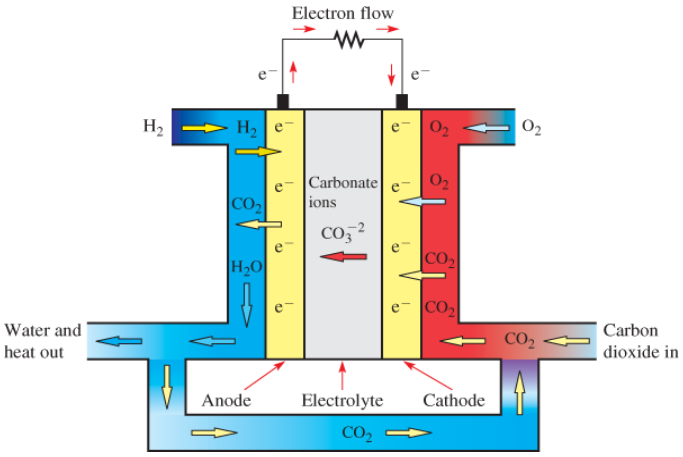


Figure 1.7: Schematic of molten carbonate fuel cell

Solid oxide fuel cells: Non porous ceramic compound is used as electrolyte in solid oxide fuel cells (SOFCs). It can convert 60% energy present in fuel into direct electricity. The anodic as well as cathodic reactions are:

$$Anode: H_2 + O^{2-} \rightarrow H_2O + 2e^- \quad (1.9)$$

$$Cathode: {}^{1}/_{2}\, O_2 + 2e^- \rightarrow O^{2-} \quad (1.10)$$

Solid oxide fuel cells can work at relatively high temperature at 1,000°C (1,830°F). Precious metal catalyst is not used here, so this fuel cell is very cost effective. Figure 1.8 represents a solid oxide fuel cell.

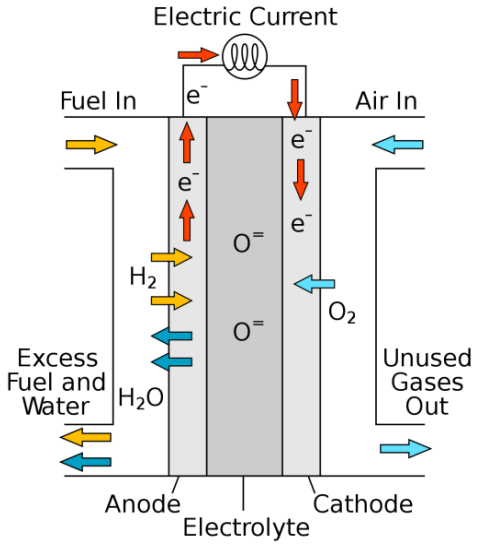


Figure 1.8: Schematic of solid oxide fuel cell

Reversible fuel cells: Electricity is produced in reversible fuel cells (RFCs) by the combination of oxygen with hydrogen which generates heat and water as byproducts. However, reversible fuel cell can decompose water and produce hydrogen and oxygen fuel by consuming current from solar and wind power, or any sources through a process known as electrolysis. In spare cases RFCs can deliver power, can stock extra energy as hydrogen, which act as intermittent energy source. The figure of reversible fuel cell is shown in Figure 1.9.

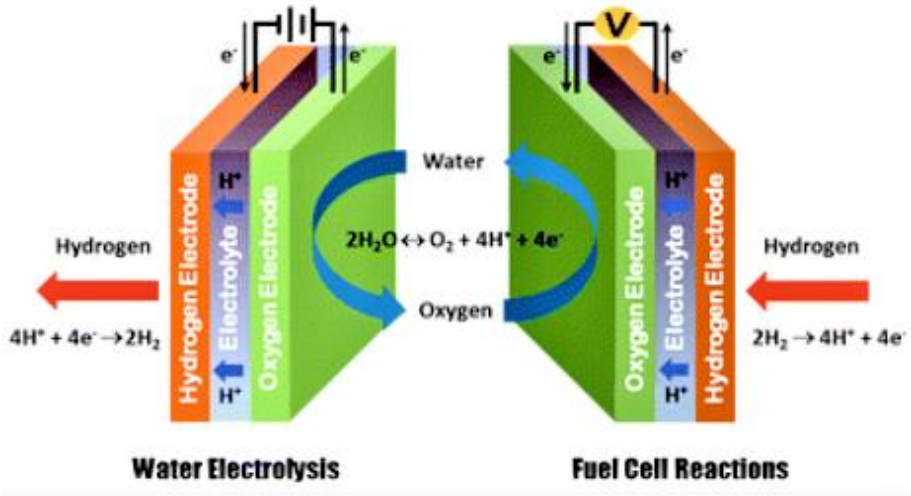


Figure 1.9: Schematic of reversible fuel cell

Direct methanol fuel cell: Normally methanol, ethanol, and hydrocarbon fuels are used directly as feed. Here pure methanol combined with water and used as fed in anode chamber.

The cell reactions are:

$$Anode: CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \quad (1.11)$$

$$Cathode: {}^{2}/_{3}\, O_2 + 6H^+ + 6e^- \rightarrow 3H_2O \quad (1.12)$$

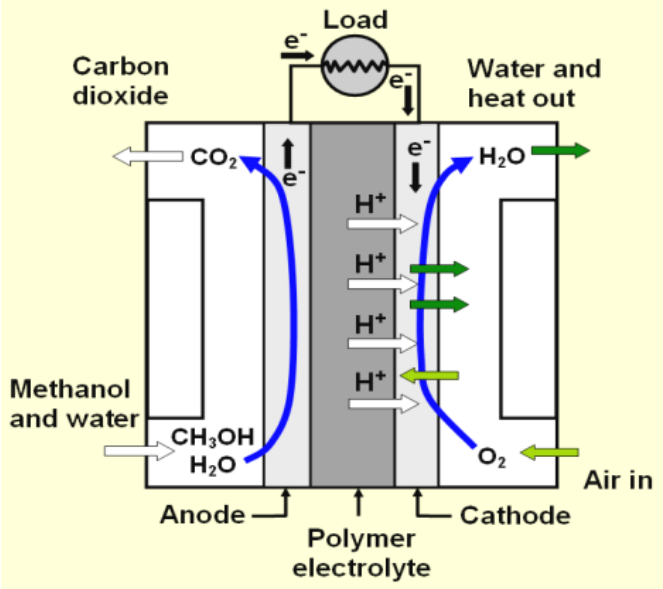


Figure 1.10: Schematic of direct methanol fuel cell

Like others direct methanol fuel cell has no fuel storage problems. Again energy contain of methanol is higher than hydrogen but less than diesel oil and gasoline fuel. This is mostly used in portable fuel cell applications such as cell phones or laptop computers. Figure 1.10 represents direct methanol fuel cell.

Microbial fuel cell: Microbial fuel cell (MFC) known as biological fuel cell, act as bio-electrochemical system by using bacteria this cell produce electric current. In the early 20th century the first demonstration on MFCs was done, using a mediator helps to transfer electron from bacteria to the anode chamber. Whereas, in the year of 1970 mediator less MFCs was emerged, here the bacteria transfer electrons to cathode [13]. Commercially, in 21st century MFCs were used to treat wastewater. Microbial fuel cells will be a promising alternative for future human beings and the planet we live on. Various researches are done so far the applications of MFCs will help to aid the reduction of our need of fossil fuels and allow us to gain energy from wastes products. The model microbial fuel cell is shown in Figure 1.11.

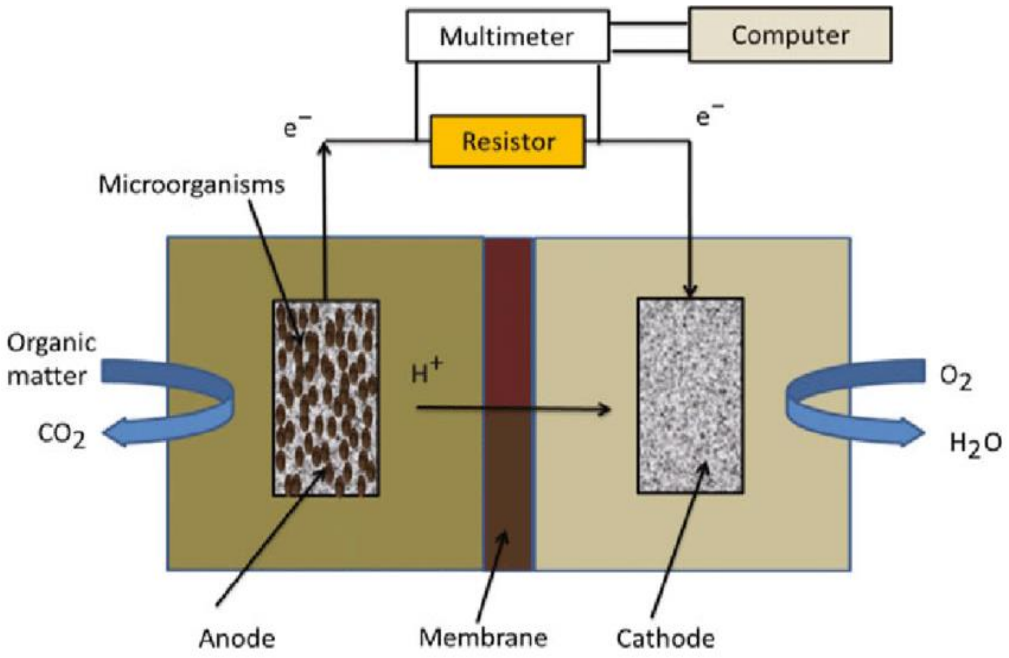


Figure 1.11: Model of microbial fuel cell

1.5 Fuel cell technology

A fuel cell is an electrochemical cell that converts the chemical energy of a fuel (often hydrogen) and an oxidizing agent (often oxygen) into electricity through a pair of redox reactions. Figure 1.12 shows the classification of fuel cell technology.

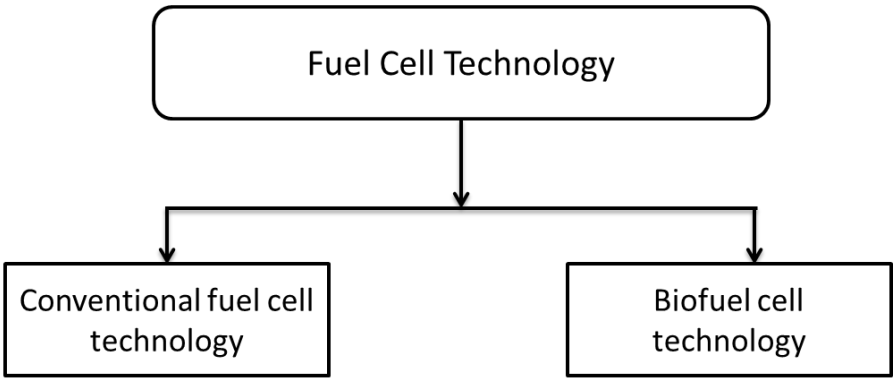
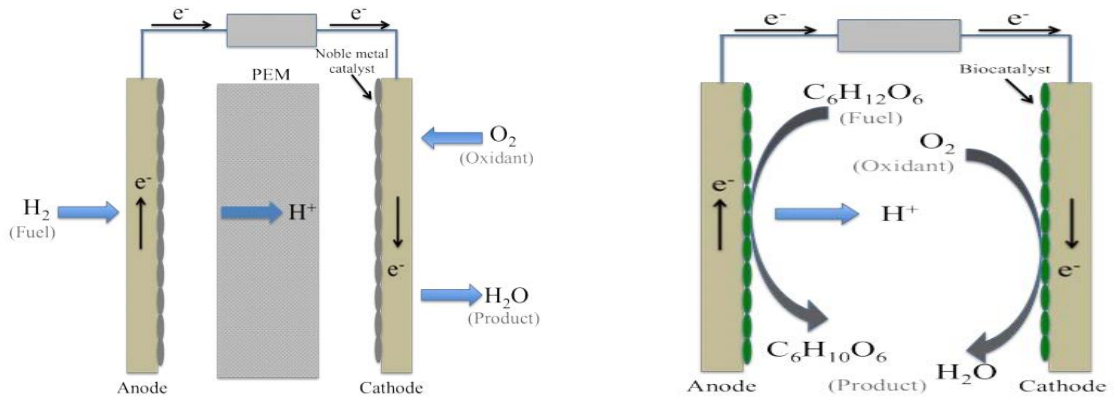


Figure 1.12: Classification of fuel cell technology

1.5.1 Conventional fuel cell technology

Fuel cells offer an exciting technology to harvest electrical energy from biomass by bridging biological components together with electrochemical devices. Fuel cells have been developed for use with a variety of different fuels, the most common being hydrogen. Fuel cells have become a

widely studied energy conversion technology due to their high efficiency: simplicity in terms of moving parts; and wide-range of configurations, fuels, and applications. A fuel cell is like a battery that converts chemical energy into electrical energy. However, a battery holds a closed amount of energy and once it is depleted, the battery must be recharged. While a fuel cell uses an external source of chemical energy and can operate as long as it is supplied with a source of oxygen and a source of hydrogen. In a hydrogen fuel cell, electricity is generated efficiently from the oxidation of hydrogen, coupled to the reduction of oxygen, with water as presented in Figure 1.13-a. Hydrogen is supplied to the anode and split into an electron and a proton via electrochemical reactions. Electrons are released in the process and flow from the anode to the cathode through an external circuit as an electric current [14]. Platinum is the most commonly used electro-catalyst in fuel cells. Platinum is very efficient in oxidizing hydrogen and enabling high currents to be produced. The major disadvantage is that platinum is expensive and its availability limited, resulting in an expensive method of energy production. At the cathode, oxygen reacts with electron and proton that have travelled through the electrolyte to form water.



(a) (b)

Figure 1.13: Schematic presentation of (a) conventional PEM fuel cell and (b) enzymatic biofuel cell.

1.5.2 Biofuel cell technology

A biological fuel cell (biofuel cell) is the offspring of two technologies: biotechnology and fuel cells. Like conventional fuel cells, a biofuel cells are composed of two electrodes (anode and cathode) separated by a membrane that is selective for the passage protons. Microbial biofuel cells (abbreviated as microbial fuel cell or MFCs) employ living cells (microorganisms) to catalyze the oxidation of the fuel, whereas enzymatic biofuel cells (EFCs) use enzymes for this

purpose [15]. MFCs or EFCs transform chemical energy into electrical energy via electrochemical reactions involving microorganisms or enzymes, which are shown in Figure 1.13 b. Enzymatic fuel cells employ enzymes as biocatalysts instead of conventional noble metal catalysts. The operation of these cells is the same as in conventional fuel cells; fuel is oxidized at the anode side. Enzyme helps to oxidize the sugar (glucose) into electrons and hydrogen ions, which is shown in equation 1.13:

$$Glucose\ (C_6H_{12}O_6) \rightarrow Gluconolactone\ (C_6H_{10}O_6) + 2H^+ + 2e^- \qquad (1.13)$$

The electrons that released are driven through an external electrical circuit to the cathode, where they combine with the final electron acceptor (typically oxygen) and protons to form water, which is shown in equation 1.14:

$$^1/_2\, O_2 + 2H^+ + 2e^- \rightarrow H_2O \qquad (1.14)$$

The principle of operation of the conventional polymer electrolyte membrane (PEM) fuel cell and an enzymatic fuel cell (EFC) are presented in Figure 1.13 b. Even though the BFCs have been known for almost a century since the first microbial BFC was demonstrated in 1911 [16], the first enzyme-based biofuel cell was reported only in 1964 using glucose as biofuel [17]. Enzyme-based biofuel cells remain limited by short active lifetimes, low power densities and efficiency. In microbial fuel cells (MFCs) the microorganisms assist redox reactions for producing electric power. MFCs have longer lifetimes (up to several years) than EFCs. In both microbial and enzymatic fuel cells, mediators are required to transfer electrons from the oxidized fuel to the electrode surface. The drawback of utilizing a mediator is toxicity and sustainability of the system. Most mediators are not easily re-oxidized in the anodic chamber. Therefore continuous replacement of mediators is required [18]. It was found that some microorganisms have the ability to produce their own mediators to promote extracellular electron transfer (endogenous mediators). The electrons transferred to extracellular space can be utilized to generate anodic current [15].

1.6 Microbial fuel cells

Luigi Galvani observed the bioelectric phenomenon first in 1790 but microbial fuel cells (MFCs) were not discovered until the beginning of the 20th century. A variety of carbon sources act as

electron donors have been demonstrated to generate electricity. In 1911, M.C. Potter was the first to observe and describe how microbial conversions could create power and electrical current [17]. He monitored the electrical effects associated with fermentation in a galvanic cell based on platinum wires and a pure culture of yeast and discovered the first bio-based battery. The concept was presented again in the literature in 1931 by Cohen, who connected several cells to generate 35 volts with a low current (2mA) [19]. From 1911-1960, there was very little interest or advances in this field. MFCs became popular in the 1960s, when the "NASA" in USA proposed the idea to use MFCs to supply their applications in space missions from human waste. It was discovered that current and power output could be enhanced by using electron mediators to improve the electron transfer rate from microorganisms to the anode. The truly research and application of MFCs were not advanced until the 1990's. Although the addition of chemical mediators as methylene blue in these first MFCs, output currents and power densities were still low. In 1999, first report was published that species She wanella could transfer electrons directly in mediator-less microbial fuel cells [19], which eliminate the uses of mediator in MFCs. Such improvements were attributed to the minimized distance that the mediator had to travel between the electrode and bacteria and consequently minimizing the distance between electrodes of the MFC. This design exhibits a higher output current and power density resulting from using direct electron transfer bacteria. In that period, MFC's field publication released research fundamentals, methods, and only few designs [20]. Contributions from material science, environmental engineering, electrical engineering, biology, microbial physiology and electrochemistry have made recently the study of MFCs a truly interdisciplinary endeavor [2, 21].

The basic concept of a MFC incorporates anodes and cathodes connected by an electrical load, separated by a membrane. In the anode chamber, the fuel such as acetate or lactate is oxidized by a monoculture biofilms or bacterial microorganisms, releasing electrons and protons. In the anode chamber, it is essential that oxygen would not be present near the anode surface, as the electrode will function as the terminal electron acceptor for organisms associated with MFCs. The anode compartment is therefore an anaerobic region (i.e. no oxygen) where the anaerobic bacteria are located while the cathode compartment is an aerobic region (i.e. oxygen is present). An electrochemical reaction of reduction of oxygen and/or other molecules associated with wastewater, such as nitrates, occurs at the cathode of MFC [22]. The electrons produced through

the oxidation of organic matter are transferred to the anode electrode, in the anode compartment, and travel through a wire and the electrical load to the cathode electrode. Protons are diffused through the membrane from the anode compartment to the cathode to combine with the electrons and oxygen to form water. A catalyst at the cathode or a catholyte solution must be used to facilitate this reaction. Small amount of CO_2 is produced by the reaction, when CO_2 is accumulate its concentration is raised but after the formation of water this concentration is decreased.

The reactor is often divided by a proton exchange membrane into the anodic and cathodic compartments to form a two-chambered MFC. The proton exchange membrane allows the transport of positively charged ions (protons) from the anode to the cathode, thereby maintaining pH and electro-neutrality. The main drawback of using these separators is that they affect the fuel cell performance due to high Ohmic resistance contribution [23]. The basic MFC which is used in MFCs research, such as examining the performance of new electrode materials, is a conventional 'H' shaped MFC, dual chamber, containing two bottles separated by a tube containing the proton exchange membrane like Nafion [24]. This two-chamber design would be difficult to apply to larger systems for continuous wastewater treatment.

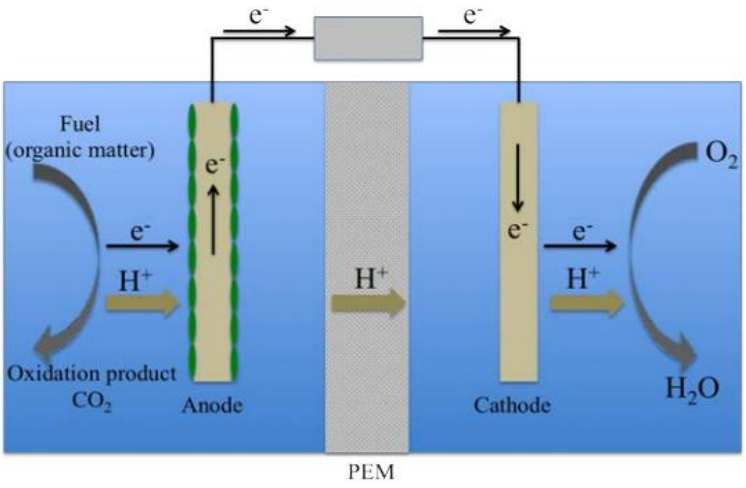


Figure 1.14: Schematic representation of dual chamber MFC system.

A simpler design where the proton exchange membrane could be eliminated will offer more perspective for energy harvesting. In a single chamber MFC design, the proton exchange membrane is either removed or pressed against the anode or cathode to form Membrane

Electrode Assemblies (MEAs) shown in Figure 1.14. New design consisted of an anode placed at the bottom and a floating cathode placed at the top in a glass cylindrical chamber. The basic advantage of exposing the cathode directly to air is to eliminate any limitation in oxygen supply to the electrode due to mass transport issues. These modifications minimize the internal resistance and increase the power generation. Moreover this design is more suitable for large geometry scale and thus wastewater treatment [25]. This design is therefore chosen in this study.

1.6.1 Energy content of substrate used for microbial fuel cell

Due to the continuous population growth numerous industries are established, which increases the volume of waste water. To run conventional wastewater treatment process is very expensive, also consume much more energy. Most of the countries in Europe spend around 1% of their total energy to treat wastewater. Normally wastewater contains 3 to 10 times more energy [26] than needed to treat it. So if 14.7 kJ contains in every g of COD, the total energy available around the world for 6.8 billion people is $(2.2 - 4.4) \times 10^{18}\,\mathrm{J/year}$, which is equivalent to 52-104 million tons of oil fuel [26].

Huge amount of energy is required to treat the large amount of waste water comes from domestic, industrial and agriculture operations. Again from the decomposition of organic substances, large amount of activated sludge is produced. Recently European Union produce annually 10 million tons of activated sludge, whereas, in USA this value is around 8.2 million tons. In China this value increased from 4.4 million tons to 6 million from year 2010 to 2016 [27]. For treating this huge sludge they cost around 25% to 65% of their total operation cost, so it becomes a major obstacle for treatment plants [28]. In other consideration sludge mainly consist higher content of organic particles. To recover energy from activated sludge various methods are used, such as, anaerobic digestion is used to produce methane, anaerobic fermentation for hydrogen fuel, for fertilizer utilization sludge composting [29]. Microbial fuel cell and anaerobic hydrogen production are the two main technologies used to harvest energy [29]. Various energy sources along their power density and conditions are shown in Table 1.1.

Table 1.1: Power densities come from various energy sources [30-34].

Energy Source	Power density	Conditions
Solar (direct sunlight)	100 mW/cm^3	
Thermoelectric	60$\mu W/cm^3$	From 5 °C
Blood Pressure	3$\mu J/cm^3$/cycle	
Ambient airflow harvester	2.3$\mu W/cm^3$	At 20 m/s
Microbial fuel cell	1010$\mu W/cm^3$	Continuous flow mode wastewater

Several years ago it was understood that bacteria found in waste water which can convert the organic material into electricity. Both economic and environmental benefits are occurred for energy production from waste water. Besides taking energy in the form of electricity, electricity can be used to power the wastewater treatment plant (WWTP) besides cleaning the water. The aim of using this technology is to decrease the energy and cost of cleaning wastewater by using the microorganisms found in the wastewater to harvest green electrical energy to operate the plant [35]. To harvest that energy MFCs can be used. Again MFCs is suitable as bio-electrochemical device. Capturing energy as a molecular bio-hydrogen by the fermentation of organic matter in wastewater treatment process could also be investigated to improve energy recovery in WWTP [36]. Researcher are investigating how to hydrogen can produce from waste water by using micro-organism. In this context, wastewater treatment plants could be self-sufficient and may even contribute energy to the grid. It was reported that a potential energy of 330 kWh could be produced from a WWTP that produces 7500 kg/day of waste organics [37]. At this point, it is quite clear that MFCs in WWTP will not be considered with green energy generators from sun, wind or hydraulic storage, in terms of power density and peak power. What is true for the sludge in WWTP is also true for a large number of organic waste matters in agriculture [38]. On a small scale, a MFC should be considered as energy harvester for sensor nodes.

1.7 Research on microbial fuel cell

Microbial fuel cell technology becomes very attractive for energy production and waste water management. MFCs can produce energy from poor waste such as sludge or waste water which

provides inexpensive waste treatment. In the past ten years, MFCs as a new source of bio-energy have been extensively reviewed various terminology and measurements, state of the art information on MFCs and recent improvements in MFC technologies [38], electrodes performance and limitations in MFCs and practical implementation of Bio Electrochemical Systems BESs. MFCs can degrade a wide range of organic matter for producing electrical energy amplifies the number of publications (see Figure 1.15).

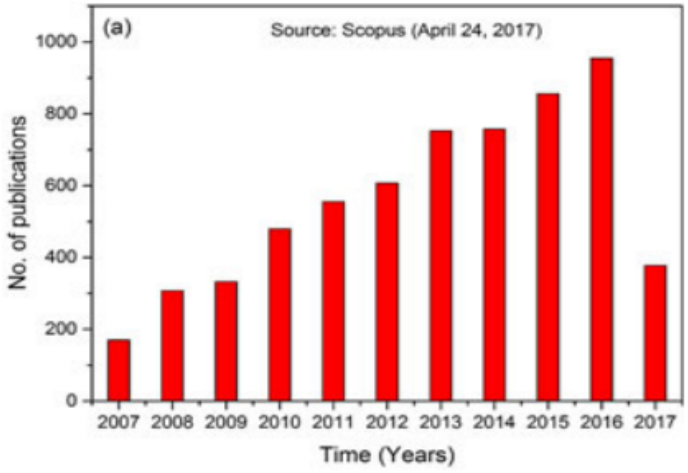


Figure 1.15: Volume of publications published for microbial fuel cell

For a variety of materials and diversity of configurations MFCs are widely used as research topics. To generate electricity both single and double chamber MFC reactors can be constructed. Already many materials have been tested for electrode materials and membrane [39]. A more multifaceted, fixed MFC is studied for the inquiry of presentations of several MFCs coupled in series and in parallel. These schemes are verified under a range of operating conditions including changes in temperature, pH, electron acceptor, reactor size, electrode surface areas and operation time [40]. Energy harvesting from MFCs requires a specific design of power management system to deal with their characteristics (low power, low voltage). Electrical management of microbial fuel cells are reported only few papers [41].

1.8 Application of microbial fuel cell

Microbial fuel cell is a potential source of energy. The application of microbial fuel cell is various. The applications of MFCs are the following:

Power generation

Devices such as wireless networks which required low power are very applicable for microbial fuel cell. Any types of organic materials can be used as feed for microbial fuel cell, including joint cells to waste water treatment plants. Dual and single-chamber mediator less MFCs is used to treat various chemicals and synthetic waste water [42]. Higher power can be obtained from the biofilm covered graphite based MFCs [43]. For smaller scale applications microbial fuel cell is very useful. In some cases where electrodes need only 7 μm thick and 2 cm long [44] microbial fuel cell can replace a battery for its renewability. Microbial fuel cell can operate at the temperature ranges from 20 °C to 40 °C and also at pH of around 7 [45]. Aquatic plants such as algae worked as a base for power stations.

Education

Soil based microbial fuel cell can be used in various scientific disciplines such as microbiology, geochemistry, electrical engineering etc. Commonly available such as soils can be used to made refrigerator items. For home science projects and classrooms kits can use MFCs. Thomas Jefferson High School for Science and Technology used microbial fuel cells being in their IBET (Integrated Biology, English, and Technology) curriculum. International Society for Microbial Electrochemistry and Technology (ISMET Society) provides several educational videos and articles.

Biosensor

The current which is generated from microbial fuel cell is proportional to the energy contents present in feed electrolyte. The concentration of solute present in waste water can be measured (as a biosensor) by using MFCs. BOD is commonly assessed in wastewater, which can be determined by hatching samples for five days with microorganism. MFC can be used as BOD sensor for getting real time BOD values. Here nitrate and oxygen act as an electron acceptor; BOD values are estimated using BOD sensors in presence of these electron acceptor. This can be avoided by inhibiting aerobic and nitrate respiration in the MFC using terminal oxidase inhibitors such as cyanide and azide [46]. Such BOD sensors are commercially available.

Microbial fuel cells are used as environmental sensors by the NAVY of United states. For NAVY in undersea condition such as high salt concentrations, changing temperatures and

inadequate nutrient supply, MFCs can function with a combination of salt-tolerant microorganisms [47]. To detect organic contaminants in freshwater, MFC act as a self-power and autonomous BOD/COD biosensor.

Bio recovery

To reduce Cu^{2+} ion to copper metal and producing electricity a microbial fuel cell is developed in 2010. To produce hydrogen microbial fuel cell is also used [48].

Waste water treatment

Microbial fuel cells are widely used in waste water treatment process. In anaerobic digestion process it reduces pathogens in waste water. However, it operates at temperatures upwards to 30^0C a helical flow is created through spiral spacers so that, increase electricity generation.

1.9 Limitations of microbial fuel cell

Electrochemical energy can be produced by using microbial fuel cell. For various applications recently huge number of research have been done for expanding microbial fuel cell. Although there are many advantages of Microbial Fuel Cell, there are some limitations. These are:

Low power density: Power density which obtained from MFCs is very low considered to batteries, fuel cells, motors, etc. Its power density is expressed as W/m^3, which is alternatively known as volume power density. It refers how quickly the cell can deliver energy.

Higher primary cost: the design and constructional cost of microbial fuel cell is higher relative to its power generation.

Activation losses: Voltage drop occurred mainly due to activation losses in cathode chamber for low and medium temperate fuel cells. Tafel equation can be used to calculate the voltage drop occurred due to activation polarization.

Ohmic losses: Normally microbial fuel cell has high internal resistance; Ohmic losses have significant effect on its performance. Ohmic losses mainly occurred for the flow of electrons

from electrode through the electrolyte. The cell connections and electrode materials also increase Ohmic losses.

Microbial losses: In microbial fuel cell microorganism transfer electrons from a lower potential substrate to a higher potential electron acceptor using a close circuit. The last electron acceptor is anode, but if its potential turn's too low then electron transport will be blocked. So saturation of the electrolyte may give more energy to the microorganisms [49].

Concentration losses: Gas transport losses are known as concentration losses. In electrochemical process reactant is consumed at the anode, which occurred concentration gradient. So, loss of potential occurred for the primary substrate mass concentration.

1.10 Objectives of the research work:

The main objectives of this research work are given below:

(i) To design and construct of a mediator less microbial fuel cell.

(ii) To measure the power generation from various wastes.

(iii) To investigate the effect of various electrodes on power generation.

(iv) To optimize the pH and concentration of electrolyte.

1.11 Organization of the thesis

This project work has been presented in five separate chapters containing diverse aspects of the study. Outline of the various chapters is given below.

Chapter-II	Comprises a comparative study of past work, Principle of MFC and MEC, the constructing and operational parameters.
Chapter-III	Contains the elaborate description of cell construction, operation, data collection and analysis.
Chapter-IV	Presents the experimental data in tabular, graphical form including detailed discussion and comparison with previous work.
Chapter-V	Sketches final conclusions based on measured data, discussion along with several recommendations for the future work.

CHAPTER II

LITERATURE REVIEW

2.1 General

In this section, the historical background of fuel cell and hydrogen energy are described. The bio-electrochemical system of microbial fuel cell is shown here. With suitable figures the basic principle of microbial fuel cell and microbial electrochemical are also shown in this part. The design and operating parameters which affects the performances of microbial fuel cell are also discussed here.

2.2 Previous studies

M. C. Potter in 1911 developed the first idea for obtaining energy from bacterium and able to construct an aboriginal microbial fuel cell [50]. In 1931 complete microbial fuel cell was developed by Barnet Cohen, he also able to produce over 35 volts [51] from series connection. Delduca used clostridium butyricum bacteria in 1963 to produce hydrogen by the fermentation of glucose [52], but the process was unreliable due to unstable nature of microorganism [52]. This unstable nature of hydrogen production from microorganism was resolved by Suzuki in the year 1976 [53]. One year later in 1977 he developed the current model design of the microbial fuel cell [53]. Allen and Peter in 1980 able to understand the reaction and electron transport chain occurred in microbial fuel cell. Finally they developed a design which led a revolution in the field of microbial fuel cell for third world countries [54]. B-H. Kim a researcher from the Korean Institute of Science and Technology, developed mediator less microbial fuel cell in 1999 [55] later it became commercial. In 2007 University of Queensland, Australia developed a complete prototype microbial fuel cell [56]. *Geobacter* and *Shewanella* species were used by S. Kim in 2008 to improve the performance of MFCs [57], and microbial community beyond electricity generation. Normally voltage generated from microbial fuel cell decreases linearly with time. In year 2011 Barua et al. [58] observed that cow dung, drain waste water, rice washing water and

biogas plant slurry can extend the generated voltage. Ashoka et al. [59] studied various combinations of electrode materials for developing the performance of microbial fuel cell. Muralidharan et al [60] examined the effect of salt bridge over the production of electricity from microbial fuel cell.

2.3 Hydrogen

Energy density of hydrogen is very high, so the recent attention paid to the use of hydrogen. For backup power and transportation systems hydrogen fuel is extensively used. Additionally, many food and petrochemical industries used H_2 as fuel. Hydrogen mainly produced from fossil fuels (48% comes from natural gas, 30% from refinery off-gases, 18% from coal and the rest from electrolysis process). Every year around 65 million tons of hydrogen produced in whole world. The main source of hydrogen is non-renewable; therefore, finding new technologies for production of hydrogen from renewable sources is the prime concern in recent scientists. The currently available technologies for production of hydrogen are electrolysis, biological production methods, algae and photosynthetic bacteria [61]. The most common and efficient technology for hydrogen production is electrolysis; however, the required energy input for electrolysis is high (4.5-5 kWh/m^3) [62]. Indeed, all the aforementioned technologies either require a high input of energy or are not efficient technologies. So, an efficient environmental friendly and cost effective technology is very argent for production of hydrogen.

2.4 Bio-electrochemical systems (BESs)

During 1911, the concept of current generation from live microorganisms was found by Potter [63] but in the 1970s and 1980s, real interest in this concept started to grow, and since then, the number of studies regarding bio-electrochemical systems has increased. Bio-electrochemical systems (BESs), such as microbial fuel cells (MFCs) and microbial electrolysis cells (MECs), can be defined as a promising technology that can produce electricity or H_2 from the organic material present in wastewater using microbial biocatalysts. In other words, BESs can convert the chemical energy in the chemical compounds into electricity (MFC) or H_2 gas (MEC). This mechanism is shown in Figure 2.1. Thus, these systems have the ability to produce clean and sustainable energy from different waste sources. In a MFC, electrochemically active microorganisms are attached to one or both electrodes to catalyze the redox reactions in cells. In

MFC, electrical energy is produced, whereas in MEC, H_2 gas is produced. In both MFCs and MECs, bacteria are used in the anaerobic anode chamber to oxidize and transfer the chemical energy in the organic matter into electricity or H_2. In the MFC cathode chamber, various elements (oxygen, nitrate, and ferricyanide) can be used as an electron acceptor. In an MEC, an anaerobic cathode is used to reduce the electrons and protons to produce H_2. Recently, many studies have focused on developing MFC to be used in real life situations [64].

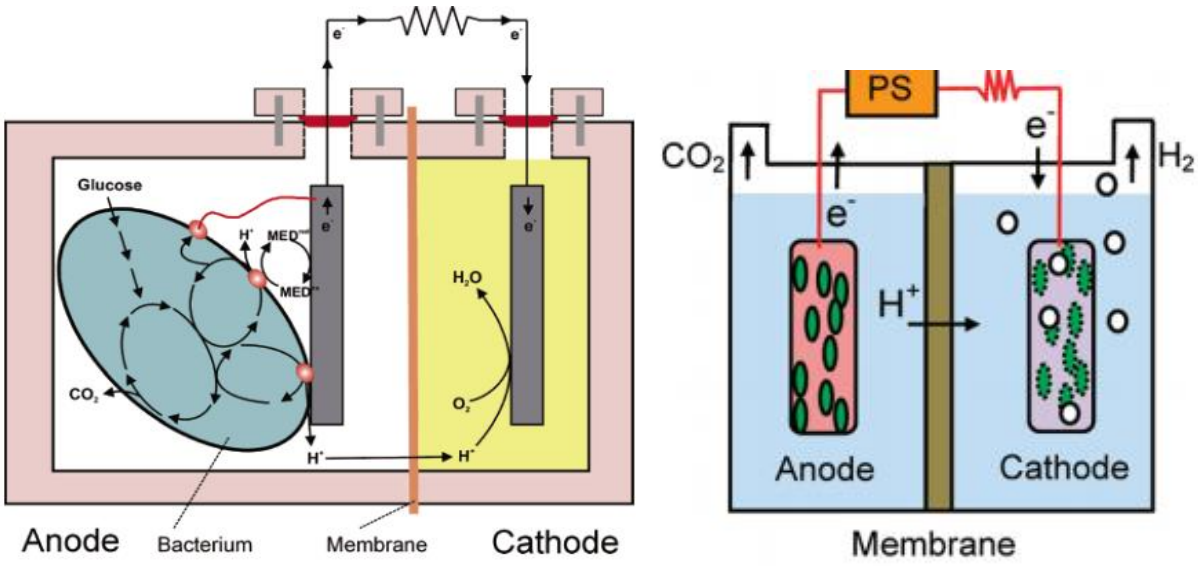


Figure 2.1 Schematics of dual chamber (a) MFC and (b) MEC (adapted from [31, 65])

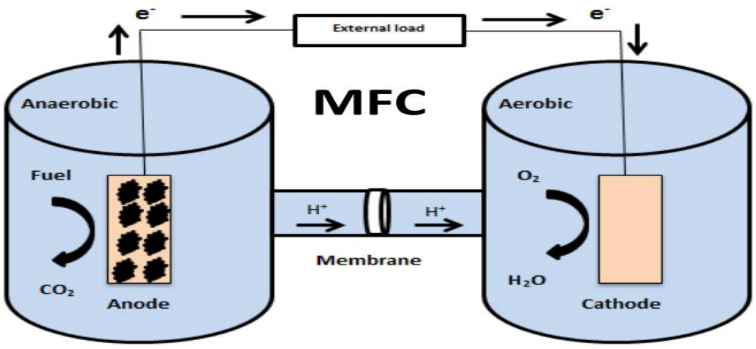
Treating wastewater in the conventional wastewater processes require 0.3–0.6 KWh/m^3, but wastewater can be considered a valuable resource of energy, as it contains an energy content equivalent to 10 times the amount required for conventional treatment [66]. Therefore, utilizing wastewater in such a way that the energy in the wastewater can be extracted is essential. Furthermore, MFCs have demonstrated the ability to treat efficiently different types of wastewater, such as low strength domestic wastewater, industrial wastewater, swine wastewater, digestion sludge [67]. Beside energy generation and H_2 production, MFC s have been used for different applications, such as methane production, nitrogen removal, sulphate removal, hydrogen peroxide, nickel removal, metal recovery and nutrient recovery [68].

2.5 Principle of MFC and MEC

Microbial fuel cells (MFCs) are defined as devices that use bacteria as the catalysts to oxidize organic and inorganic matter and generate current [31]. A standard MFC contains two main

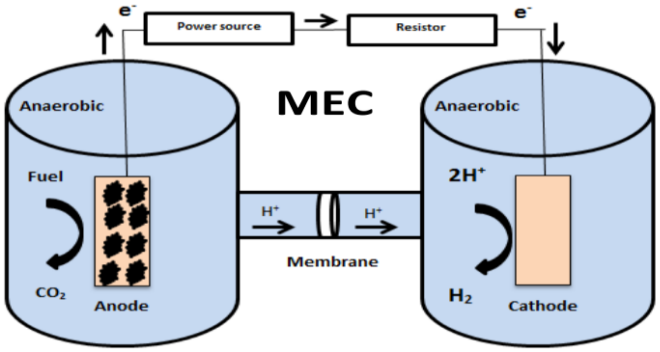
chambers: an anode and a cathode. The two chambers are separated by an anion or cation exchange membrane. Electrons, protons and carbon dioxide are released into the solution by oxidizing the organic matter using the bacteria in the anaerobic anode chamber. Electrons are transferred to the anode (negative terminal) and flow to the cathode (positive terminal) through an external resistor. Electrons are transferred to the anode electrode either directly, indirectly, or by a mediator, such as methylene blue. During the movement of the electrons through the resistor, current is generated. Protons are transferred to the cathode side through the membrane and combined with an electron acceptor (oxygen) in the cathode to complete the circuit (shown in Figure 2.2). Electromotive force (emf) is defined as the potential difference between the anode and the cathode [31]. Theoretically, the maximum electromotive force attainable in MFC is 1.1 V with acetate oxidation and oxygen reduction using half-cell reaction, but due to the different losses in the system, the emf is lower than 1.0 V [31]. The open circuit voltage (OCV) is the voltage when no current is flowing between the anode and the cathode. Cell emf should be close to the OCV; however, in practice, emf is greater than OCV due to the losses in the system. Microbial electrolysis cell (MEC) is a system that is able to produce hydrogen from biomass. MECs are similar to MFCs but with some changes, as a power source is connected to the anode and cathode to apply a small amount of voltage to the circuit. An MEC was designed recently by two research groups [69], and it is similar to the MFC concept, where in the anode chamber, the electrochemically active bacteria oxidize the organic matter and transfer the electrons to the electrode. In an MEC, a power source is used to apply the relatively small amount of energy to overcome the thermodynamic limit for hydrogen evolution [65]. In addition, the cathode chamber in an MEC is operated under anaerobic conditions to produce H_2. The anode reactions in both MFCs and MECs are the same if acetate is the carbon source (shown in table 2.1). Hydrogen production rate and current density have been used to evaluate MEC performance [65]. Electrons can be transferred to the anode by different methods: electron mediators or shuttles, bacteria nanowires and indirect transfer. Chemical mediators can enhance the movement of the electrons, but they are expensive and harmful to the environment. If no mediators are used, then the system can be classified as a "mediator-less system"

a)



$CH_3COO^- + 4H_2O \rightarrow 2HCO_3^- + 9H^+ + 8e^-$ $\qquad$ $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

b)



$CH_3COO^- + 4H_2O \rightarrow 2HCO_3^- + 9H^+ + 8e^-$	$8H^+ + 8e^- \rightarrow 4H_2$

Figure 2.2 a) Microbial fuel cell and b) Microbial electrolysis cell (equations adopted from [31]).

Table 2.1 Electrode reactions and potentials of MEC, MFC, and water electrolysis systems.

System	Anode reaction	Cathode reaction	Δ Potential
MFC	$CH_3COO^-+4H_2O \rightarrow 2HCO_3^-+9H^++8e^-$	$O_2+4H++4e^- \rightarrow 2H_2O$	1.085 V
MEC	$CH_3COO^-+4H_2O \rightarrow 2HCO_3^-+9H^++8e^-$	$2H++2e^- \rightarrow H_2$	-0.135 V
Water electrolysis	$2H_2O \rightarrow O_2+4H^++4e^-$	$2H++2e^- \rightarrow H_2$	-1.22 V

To generate high cell potential from the reaction, the anode chamber in the MFC should be operated at very low potential (anaerobic) and at the same time, the cathode chamber should be operated at very high potential (aerobic) [31]. For instance, in an MEC, the theoretical anode potentials can be calculated in terms of half-cell reactions (acetate is the carbon source) [65]:

$$E_a = E_a^{\circ} - \frac{RT}{8F}\left(\frac{[CH_3COO^-]}{[HCO_3^-]^2[H^+]^9}\right) \quad (2.1)$$

where Ea°(0.187) V is the standard potential for acetate oxidation, R (8.314 J/K/mol) is the universal gas constant, T (K) is the absolute temperature, and F (96485 C/mol e^-) is the Faraday's constant. The anode potential is = - 0.279 V. The theoretical cathode reaction can be calculated as follows [65]:

$$E_{cat} = E_{cat}^{\circ} - \frac{RT}{2F}\ln\frac{P_{H_2}}{[H^+]^2} \quad (2.2)$$

Where E_{cat} (0) V is the standard electrode potential for hydrogen and PH_2 is the hydrogen partial pressure under standard biological conditions. The cathode potential is = - 0.414 V; therefore, the equilibrium voltage is Eeq= Ecat – Ea= (- 0.414 V) – (- 0.279 V) = - 0.135 V The negative equilibrium voltage means that additional voltage (at least 0.14 V) is required to produce hydrogen from acetate. In practical terms, the applied voltage should be more than 0.2 V due to the losses in the system. According to Logan et al. (2008), at least 0.2 V is needed to produce H_2 in an MEC, and that amount of energy is much lower than that required for water electrolysis. The energy input in MEC and water electrolysis is 1 kWh/m^3 H_2 and 4-5.5 kWh/m^3 H_2 respectively [70].

2.6 MFC design

MFC can be designed in different shapes and structures based on their applications. During the last decade, many studies have focused on improving the design and the cell materials to optimize energy generation, H_2 production and reduce the losses in MFC s. MFC performance is dependent on physical, chemical, and biological parameters including external resistance, substrate oxidation by bacteria, cathode reduction, protons and electrons movement [71]. Therefore, all of these parameters should be considered during the designing process to optimize the performance.

2.6.1 Dual chamber MFC

The dual chamber cell is the most common type of MFC, which is mainly used in laboratory studies. A dual chamber MFC contains two main chambers (anode and cathode), and these are separated by an ion exchange membrane. Each chamber contains an electrode, which is connected to a wire and linked to an external load. Electron acceptors, such as oxygen, ferricyanide, are used in the MFC cathode for cathodic reduction reaction. Phosphate buffer solution (PBS) is commonly used in the MFC and MEC cathode to maintain a constant pH, as the reduction of oxygen (MFC) and the consumption of protons (MEC) results in a pH increase. High catholyte pH has a negative influence on MFC performance and causes a significant potential loss of the cathode [31, 65]. Therefore, in most MFC studies, PBS is commonly used as a catholyte due to the excellent performance in maintaining the pH balance during system operation. However, PBS is not suitable for practical applications of the MEC due to its high cost and the need to avoid phosphate release into the environment. In MFC, using a chemical such as a ferricyanide as a catholyte can be expensive and it presents a hazard to the environment. The advantage of dual chamber MFC is that anode and cathode reactions (oxidation and reduction) are separated, which makes it possible to extract useful products. The main disadvantage of dual-chamber MFCs is the high internal resistance due to the distance between the electrodes. In addition, using a cation exchange membrane in some applications can be challenging due to the transportation of cations (i.e. NH_4^+, Na^+, K^+, Mg^{2+} and Ca^{2+}) from the anode to the cathode, which leads to a pH gradient and reduces the performance of the MFC [72].

2.6.2 Single chamber MFC

Due to the high internal resistance and high designing cost for scaling-up a dual chamber MFC, the single chamber was developed to enhance MFC performance. In a single chamber MFC, both anode and cathode share the same chamber (anode chamber), where the anode is immersed in the anolyte, and the cathode is exposed to the air [31], where in a single-chamber MEC, both anode and cathode are immersed in the electrolyte. The distance between the electrodes in single chamber MFC is small compared to in a dual-chamber MFC and this enhances the MFC's performance. Furthermore, using a single chamber is an energy and cost effective system where no aeration or any other chemicals should be used at the cathode. In MEC studies, using a single chamber MEC for hydrogen production has shown a negative effect on MEC performance

because the hydrogen was consumed by hydrogen trophic methanogens. Therefore, a dual-chamber MEC was suggested to prevent methane production [73].

2.7 MFC components

The main components of MFCs are anode, cathode and ion exchange membrane. All these components are discussed below:

2.7.1 Anodes and cathodes

Energy generation and H_2 production in BES can be affected by many factors, such as BES design and electrode materials; therefore, selecting the material for the electrodes is crucial for enhancing BES performance. Thus, different electrode materials have been studied in BES research. The ideal electrode material should have (1) good electrical conductivity and low resistance, (2) chemical stability and anti-corrosion, (3) a large surface area, and (4) appropriate mechanical strength [31, 71]. Many electrode materials have been used in MFC and MEC studies, and the most common material is carbon material, which includes carbon cloth, carbon paper, reticulated vitreous carbon (RVC) and carbon felt. These materials were selected for their stability in microbial cultures, high electric conductivity, and large surface area [71]. Furthermore, many techniques, such as electrode heat pre-treatment, ammonia electrode treatment, and electrode catalysts [71], have been employed to enhance anode performance. However, using these methods could increase the cost of the reactor. Cathode electrode and catalyst performance have a great impact on the reduction reactions in the cathode chamber. Most of the cathode electrodes are coated with precious metals, such as platinum, which are used as catalysts. Selecting an appropriate catalyst on the electrode surface can lower the activation energy and enhance the reaction rate [71]. In bio-cathode systems, microorganisms are used as a catalyst on the cathode surface to enhance the MFC performance instead of artificial mediators or catalysts using nitrate, sulphate, tetrachloro-ethene, fumarate, perchlorate, and trichloroethene, CO_2, H^+, Fe(III), Cr(VI), U(VI) and Mn(IV) as electron acceptors and without the help of exogenous. Recently, inexpensive and durable electrode materials have been used to reduce the cost of MFC materials. For example, corrugated cardboard has been used as an inexpensive and high-performance electrode material in MFCs [74]. The MFC achieved 86% of the value obtained by the MFC that used a carbon paper anode.

2.7.2 Ion exchange membrane

The ion exchange membrane is another important part that has a significant impact on BES performance. The membrane separates the anodic and cathodic reactions. Many types of membrane have been used in MFC studies (cation exchange membrane, anion exchange membrane, membrane-less MFC, polymer membrane, and porous membranes); the usage of these membranes is dependent on the system applications. The presence of an ion exchange membrane between the anode and the cathode prevents substrate crossover and leads to the production of a pure product, which is pure hydrogen gas (MEC), and nutrient or metal recovery. Unfortunately, the membrane also increases the resistance of the system, resulting in increased specific energy consumption per m^3 of produced hydrogen. Some disadvantages were observed when separators were used in MFC studies: (1) oxygen diffusion from the cathode to the anaerobic anode in the MFC, which lowered the coulombic efficiency and microorganism activity [37], (2) pH splitting between the anode and the cathode especially when a cation membrane was used (high pH at the cathode and low pH at the anode), which resulted in low system performance, (3) membrane resistance, which is influenced by the electrolyte, pH and electrolyte concentration [75]. Thus, selecting the appropriate membrane is crucial in a MFC.

2.8 Electrochemically active microorganisms

The role of microorganisms in MFCs and MECs is very important, as it is responsible for oxidizing the organic matter and transferring the electrons from the substrate to the electrode. Microorganisms such as Aero-monas, Geobacter and Shewanella have shown their ability to generate current, and these genera are able to transfer electrons to the outer membrane without the assistance of electron carriers [65]. Anaerobic respiration is the main process for the electrochemical active bacteria to transfer electrons from organic compounds to an electrode. Thus, understanding bacteria structure and community can enhance BES performance by selecting the inoculation source and appropriate operational conditions. In MFC, Shewanella and E. Coli were found to generate electricity [76], whereas in an MEC, Geobacter is used to create a proton gradient across the cell membrane to generate hydrogen [77]. Diverse microbial communities can be found in wastewater, and the presence of these communities is essential for energy generation in BESs. Electrochemical active bacteria can be obtained from wastewater,

anaerobic digested sludge and sediments. Wastewater is commonly used for MFC and MEC inoculation, so it is expected that multiple microbial communities can be established in these systems. However, the microbial communities and community structure in MFCs and MECs can be different due to operational conditions. In an MFC, oxygen is used as an electron acceptor in the cathode, whereas in an MEC, the system is operated completely under anaerobic conditions. The operation of an MEC under anaerobic conditions can help the anaerobic bacteria (exoelectrogen Geobacter and methanogenic bacteria) to grow, whereas in an MFC, the microbial structure and the performance can be affected by oxygen diffusion [78]. The microorganism structure and communities vary depending on different operational conditions and system architectures and on the electron donors and acceptors in each system [25]. To a certain extent, the microbial communities in the MFC show an indication of the situation of microbial activity in the system, and any change in environmental conditions can lead to changes in microbial communities. In addition to the role of the major microorganism communities in MFC, minor communities can contribute significantly in MFC performance [79]. Three main transfer mechanisms have been discussed in previous studies, namely, direct electron transfer via outer membrane c-type cytochromes, direct electron transfer via conductive pili (microbial nanowires), and indirect electron transfer via endogenous metabolites [79].

2.9 The impact of operational conditions and components on MFC performance

The operational conditions and components of MFCs have a great impact on electricity generation (MFC). Thus, MFCs are influenced by operational conditions and reactor components, such as substrate concentration, electrolyte volume, cathode aeration flow rate, pH, and external resistance.

2.9.1 Substrate

The substrate is an important parameter for MFC performance, as it provides the organic matter (carbon source) for the microorganisms in the anode chamber. The efficiency of the MFC to convert the organic waste into bioenergy depends on the characterization of the waste material [80]. The microorganisms oxidize and degrade the organic matter to produce electrons and protons. Then, the electrons are transferred through the resistor to the cathode chamber. In the cathode, protons, electrons and electron acceptor are combined together to produce water. MFCs

have been used for different types of substrate, including synthetic wastewater [81], domestic wastewater and industrial wastewater [82]. The synthetic substrate (acetate and glucose) is the common type of substrate that is being used in laboratory-scale MFCs due to their simplicity. However, a complex substrate that is rich in complex organic matter helps in the growth of many active microbes. The concentration of the substrate is a key factor in MFC performance. For example, COD has a great impact on MFC performance, where increasing COD increases the current density and the generated power [83]. However, overdosing the MFC with a substrate leads to saturation and decreases the amount of power studied the impact of COD on power generation. In their study, an air cathode MFC was fed with COD ranging from 200 to 8000 mg/L. Power generation increased with the increase in COD up to 4000 mg/L and then started to decrease. With regard to COD removal efficiency, the efficiency decreased with the increase in COD. The study showed that increasing COD increased the power and decreased COD removal efficiency. Therefore, the substrate concentration should be controlled in such a way that a balance is found between the removal efficiency of the substrate and the production of current.

2.9.2 External resistance

External resistance is the link between the anode and the cathode electrodes, where the electrons transfer through it. External resistance in a MFC controls the ratio between the generated current and the voltage. Based on Ohm's law, the generated current in a MFC is totally dependent on the external resistance [31], and to obtain the highest power in the MFC, the external resistance value should be equal or close to the internal resistance [84]. Large losses in MFC performance may occur if the incorrect external load is selected. Using low external resistance leads to a decrease in the voltage and an increase in the current and vice versa. COD removal is influenced by the value of external resistance, where at low external resistance; COD removal is higher than high external resistance. Furthermore, studies have shown that external resistance has a significant effect on biofilm diversity and formation in the anode chamber [85, 86]. Therefore, selecting the optimum external resistance helps to enhance MFC performance.

2.9.3 Cathode aeration

In a dual chamber MFC, oxygen is commonly used as an electron acceptor due to the high potential. Therefore, providing the optimum amount of oxygen in the cathode chamber is

essential to optimize MFC performance. Researchers have obtained a variety of results cathode aeration flow rate in a dual chamber MFC varied from 10-200 mL/min [83, 86]. A linear correlation was found between the generated current and cathode aeration flow rate (lower or equal to 100 mL/min). In contrast achieved a maximum volumetric power density at a high cathode aeration rate (300 mL/min) [87]. All of these studies confirmed that cathode aeration is the major limiting factor for the operation of an MFC, thus identifying that the optimum cathode aeration flow rate is crucial to optimize MFC performance.

2.9.4 Anolyte and catholyte volumes

MFCs have been designed with different structures and scales, some in lab scales (micro-meters to liters) and some in pilot scales (120 L) [88]. However, the impact of anolyte and catholyte volumes on MFC performance has not been studied in depth. Logan et al. (2015) [89] studied the impact of the volume of the anode and cathode chamber on the current and showed that increased chambers volume and maintained electrode surface area in the anodes and cathodes decreased the generated energy because of an insufficient electrode surface area for capturing all the substrate as electrical current.

2.9.5 pH

The pH is another important factor that has an influence on MFC performance, especially on the life and growth of microorganisms. The pH difference between the anode and the cathode occurred when proton transport through the Nafion is slower than the proton production rate in the anode chamber (pH decreased) and the proton consumption rate in the cathode chamber (pH increased) [72]. The pH buffer is commonly used in dual-chamber BESs to maintain the solution pH and increase the solution conductivity, as the pH buffer plays an important role in facilitating proton transfer and reducing internal resistance in MFCs. Studies have found that the microbial activity is very active at a neutral pH, while it is slower at a pH less than 6 and higher than 7.5 [90]. A pH >7.5 is favorable for methanogens, which contributes to COD removal and results in a low value of current. Thus, the performance of the MFC decreases when the pH gradients occur [91]. Studied the impact of pH on dual chamber MFC performance and anodic biofilm. The study demonstrated that operating the MFC under acidic pH conditions led to a reduction in the output voltage and power. In addition, acidic conditions accelerated COD removal. The same

observation was found for MECs, where increasing the pH difference led to a decrease in H_2 production in the system. Furthermore, some studies found that MFC internal resistance decreased when the pH difference between the anode and the cathode was increased, as the higher pH difference increases the proton flux rate through the PEM. In contrast, increasing the cathode pH negatively affects MFC performance; based on the Nernst equation, a unit of pH difference between the anode and the cathode means an extra potential loss of about 0.06 V will occur in the system [92].

2.9.6 Temperature

Temperature is a critical factor that influences MFC performance, as it has a significant impact on the growth and reproduction of microorganisms, which can affect both intracellular biochemical processes and extracellular chemical or biochemical processes. Many researchers have studied the impact of temperature on MFC performance, and it has been demonstrated that the generated current increased by 80% when the temperature was increased from 30 to 40 C° [92]. Similarly, Min et al. (2008) [93] showed that increasing the temperature from 22 to 33 C° increased the power density by 62%, while Wei et al. (2013) [94] demonstrated that increasing the environmental temperature from 25 to 45 C° enhanced the microbial activity in the system and that the activity decreased significantly when the temperature was increased to 50 C°. In contrast, other studies showed that the performance of MFC was better at low temperatures (8-22 C°) than at high temperatures (20-35C°) [95]. Therefore, further studies are needed to fully understand the impact of temperature on MFC performance.

CHAPTER III

METHODOLOGY

3.1 General

In this section, design and construction procedures of MFC are discussed with detailed description of construction materials. The reactor configuration and operation of the whole processes (salt bridge preparation, cell construction, micro-organism collection, electrode preparation, and data collection and performance analysis) are also discussed.

3.2 Design of microbial fuel cell

A double chamber MFC is designed in this work. It consists of two reactor cells, two electrodes and a salt bridge. Each cell has the volume of $7500 cm^3$ (length 25 cm, width 15 cm and height 20 cm) and surface area of electrode is $27 cm^2$. The length of salt bridge is 4 cm. The final design of the microbial fuel cell is shown in Figure 3.1.

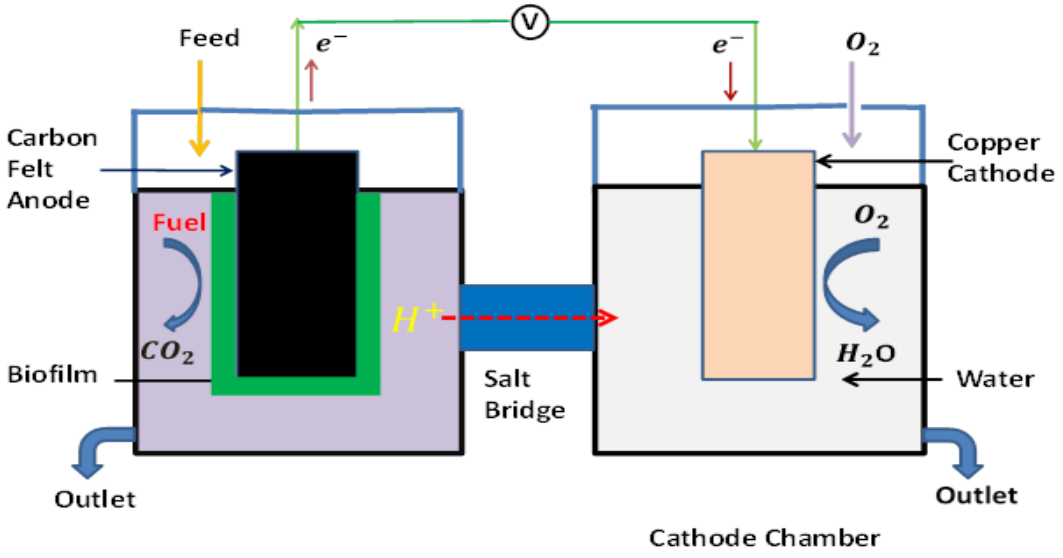


Figure 3.1 Double chambered mediators-less MFC

3.3. Construction of microbial fuel cell

Three microbial fuel cells of same dimensions and features are constructed in this work using locally available materials. Glass having a thickness of 5 mm was used to construct the body of the cell. Materials which were used for constructing the microbial fuel cell are shown in Table 3.1

Table 3.1 List of materials and photos used for constructing microbial fuel cell

Name	**Photograph**
Glass	
Carbon felt	
Zinc plate	
Copper plate	
Carbon rod	
Glass Bonding Epoxy (M-seal)	
Connecting wire (copper wire)	

3.4. Dual-chamber reactor configuration and operation

Various steps to construct and operation of the MFC is discussed below:

3.4.1. Construction procedure of the reactor

For the construction of the reactor, six (06) pieces of glass (5 mm thickness) were used. Before using the glass, it should be cleaned properly and cut in desired size. Then the glass pieces were connected via M-seal and construct a rectangular shape. After construction, the middle portion of inner side of each chamber was drilled according to the size of salt bridge. Two holes at the center of upper part of cathode chamber was drilled to create passage for wire and air ventilation. Again one hole at the center of upper part of anode chamber was drilled to create passage for wire. Finally the salt bridge pipe was inserted into the drilled holes of the chambers and fixed it with M-seal. The constructed MFC is shown in Figure 3.2.

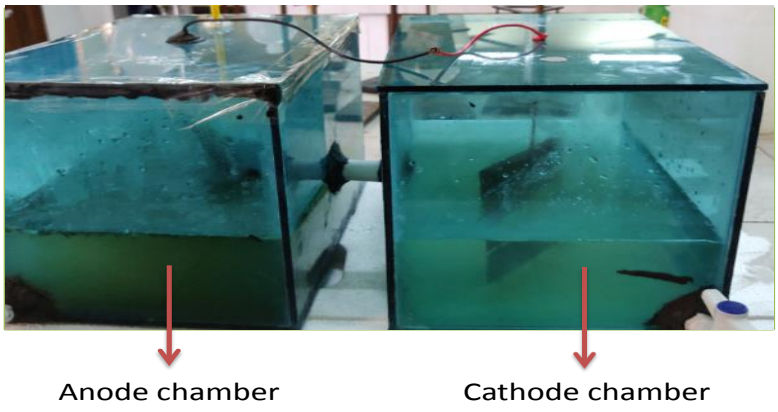


Figure 3.2 Photograph of the constructed microbial fuel cell

3.4.2. Preparation of salt bridge

For the preparation of salt bridge, firstly 0.1M salt solution was made by using finely ground salt such as table salt, which dissolves much faster than coarsely ground salt (rock salt). Then agar salt is added in the solution and warmed the solution, so the agar will begin to melt, warm it until agar becomes liquid. After completion of mixing, some pieces of bandage cloths were kept for two to three hours into the solution. A short PVC pipe with 4 cm long and 1 cm diameter was filled with the surgical gauze which absorbed the agar-salt solutions. The prepared salt bridge is shown in Figure. 3.3.

Figure 3.3 Photograph of the salt bridge for MFC

3.4.3. Collection of microbes

Locally available microorganisms (Escherichia coli, Anabaena, Rhodospirillum and some cyanobacteria) were used in all experiment, to culture these organisms firstly, organic rich bottom feeders were collected from the local pond. For proper growth of microorganisms, 1 (w%) of cow dung and 0.2 (w%) of sugar were mixed with bottom feeders and kept in an anaerobic condition for 24 hours.

3.4.4. Collection of the electrolytes

In order to expand the application of MFCs, a great variety of organic electrolytes were tested or pretreated to test for electricity generation. Here municipal waste water, river water and hospital waste water were used as electrolyte. These electrolytes were collected from municipal drain, Bhairab River and Jashore sador hospital respectively and additives such as urine from local dairy farm and fish waste from local market. Figure 3.4 shows the source of electrolyte and additive

Figure 3.4 Source of electrolyte and additive

3.5. Reaction

The reactions occurred in anode and cathode chamber are the follows:

Anodic reaction:

$$Organic\ compound\ + 2H_2 \rightarrow CO_2 + H^+ + e^- \quad (3.1)$$

Cathodic reaction:

$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \quad (3.2)$$

3.6. Data acquisition

Data acquisition is one of the most important parts in any research. In this research, generated voltage and current of MFCs were measured using a digital multi-meter (HiDANCE DT-9205A) in twenty four hour interval up to maximum 18 days.

3.7 MFCs performance analysis

Power, power density and current density were calculated using measured data. Finally, all these data were represented graphically and compared with previous work.

3.7.1. Power measurement

Power (P) in watts (W) was calculated by multiplying voltage with current;

$$P = I \times E \quad (3.1)$$

$$\text{Or, } P = {}^{E^2}/_{R} \quad (3.2)$$

3.7.2. Current density and power density calculation

Current density (j) and power density (PD) were calculated in terms of electrode total surface area or anodic volume;

$$j = \frac{I}{A} \quad (3.3)$$

$$PD = {}^{P}/_{A} \quad (3.4)$$

Where A is the total anode electrode surface area in square meters (m^2).

3.7.3 Chemical Oxygen Demand (COD) calculation

The organic matter present in the water sample is oxidized by potassium dichromate in the presence of sulfuric acid, silver sulfate and mercury sulfate to produce carbon dioxide and water. COD can be calculated by using equation 3.5.

$$\mathrm{COD} = \frac{8 \times 1000 \times \mathrm{DF} \times \mathrm{M} \times (\mathrm{V_B} - \mathrm{V_S})}{\text{Volume of sample (in ml)}} \quad (3.5)$$

Where,

DF-Dilution Factor

M-Molarity of standardized Ferrous Ammonium Sulfate solution

V_B-Volume consumed in titration with blank preparation

V_S- Volume consumed in titration with sample preparation

CHAPTER IV

RESULTS AND DISCUSSION

4.1 General

Various operating parameters such as electrode materials, sources of electrolyte, pH and additives have significant effects on the performance of MFC. This chapter mainly discussed the effect of various operating parameters on power generation from the experimental outcomes of this research work. Various operating parameters such as electrode materials [96], distance between the electrodes [97], pH [95], external resistance [97], temperature [97], conductivity [98], and organic matter of the sediment [99] affects the power generation of microbial fuel cell. The performance of MFCs increased for long term operation, when electro-genic biofilm formed on electrode surface.

4.2 Effects of electrode materials on power generation

The main target of this research was to investigate the effect of electrode materials on the output of MFC. The experiment was performed at room temperature using municipal waste water as electrolyte and pH of the electrolyte was maintained at 8, Three electrode combinations were used such as, carbon felt-copper, Zinc-copper, carbon rod-copper and distance between the electrodes was 7 cm. Here municipal waste water (pH 8) from Jashore sador was used as electrolyte. Performances of the three MFCs were monitored continuously maintaining same operating condition except electrode materials. Electrode materials have direct effects on the voltage and current obtained from MFC [100].

Amount of voltage generation with time for various electrodes are shown in Figure 4.1. This figure indicates voltage versus day curve for electrodes carbon felt-Cu, zinc-Cu, carbon rod-Cu used in MFC. When Zn-Cu was used as electrodes, at first day voltage was found 571mV. Then it increased gradually and obtained maximum voltage at 855mV at day 7. After this voltage gradually decreased from day 8 and reached the lowest value of 338mV at day 18.

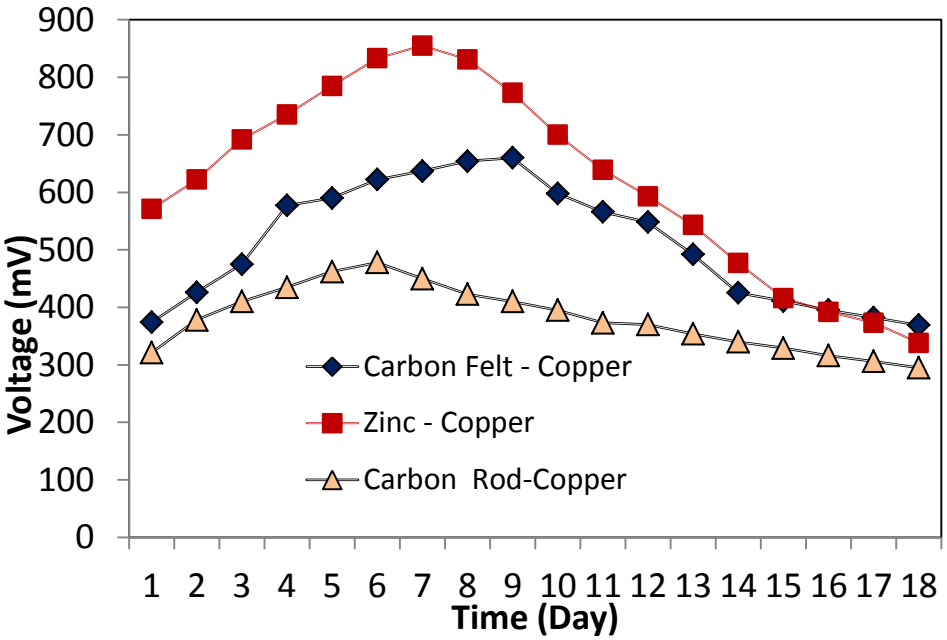


Figure 4.1 Effect of electrode materials on generated voltage

When carbon felt-Cu combination was used in MFC as electrodes, observed at first day voltage was 374mV. Then successive increase of voltage was observed and reached its maximum value of 660mV at day 9. From day 10 to 18, voltage was decried step by step and reached its lowest value of 369mV. In the case of MFC in which carbon rod-Cu electrode combination was used as electrodes, the output voltage was lower than the other two electrode combinations. From day 1 to 6 the obtained voltage increased from 321mV to 478mV. After that it was decreased and became lowest at day 18. Here found minimum value was 295mV. Total amount of potentials were obtained 9201mV, 11168mV and 6845mV for carbon felt-Cu, Zn-Cu and carbon rod-Cu electrodes combination respectively. This finding is much higher than Wang et. al [101], they used single chamber MFC with oxytetracycline mixed waste water and various Carbon cloth (CC) electrodes (unmodified CC, graphene-modified CC, and polyaniline-graphene-modified CC) and after the stable operation they got the maximum output voltages of 61mV, 87mV, and 118 mV, respectively.

Variation of current density with time for various electrodes used in the MFC is shown in Figure 4.2. When carbon felt–Cu was used as electrodes, current density was calculated 38.496mA/m^2 in first day, which increased gradually with the advancement of days. At day 9, current density

was 71.674mA/m^2 which was the maximum, then reduced gradually from day 9 to 18 and lowest value was 71.674mA/m^2 to 27.251mA/m^2. When Zn-Cu was installed as electrodes then the lowest value found was 50.244mA/m^2.

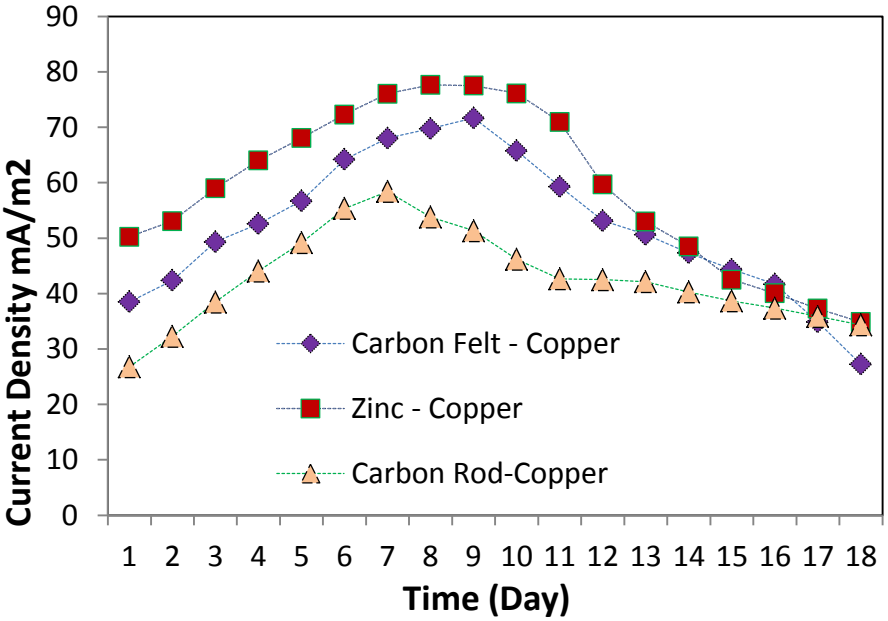


Figure 4.2 Variation of current density with time for various anode materials

At day 8, current density reached its maximum value of 77.633mA/m^2. After obtaining the maximum value current density decreased from day 9 to day 18. Here, obtained lowest value was 34.356mA/m^2. For carbon rod-Cu electrode, current density ascends from 26.787 to 58.425mA/m^2 and after that value reduced randomly from 53.804 to 34.356mA/m^2. Total current density obtained for Zn-Cu was 1060.841mA/m^2 which was higher than carbon felt-Cu (937.471mA/m^2), and carbon rod-Cu (769.726mA/m^2). Kamau et. al [102] used copper wires, graphite rod electrodes with cow dung as substrate and got maximum 23.29 mA/m^2. However, in this work carbon rod-Cu electrodes provided maximum 58.425 mA/m^2 for municipal waste water, and which is four time higher than Kamau et al [102].

Figure 4.3 shows the impact of electrode on power density with time similar to voltage and current density the higher value was obtained for zinc-copper electrode combination and the maximum value was 65.02 mW/m^2 , where as it was 47.31 for carbon felt-copper and 26.46 for carbon rod-copper electrode combination. In all the cases, power densities around one to eight days the value increased then decreased gradualy.

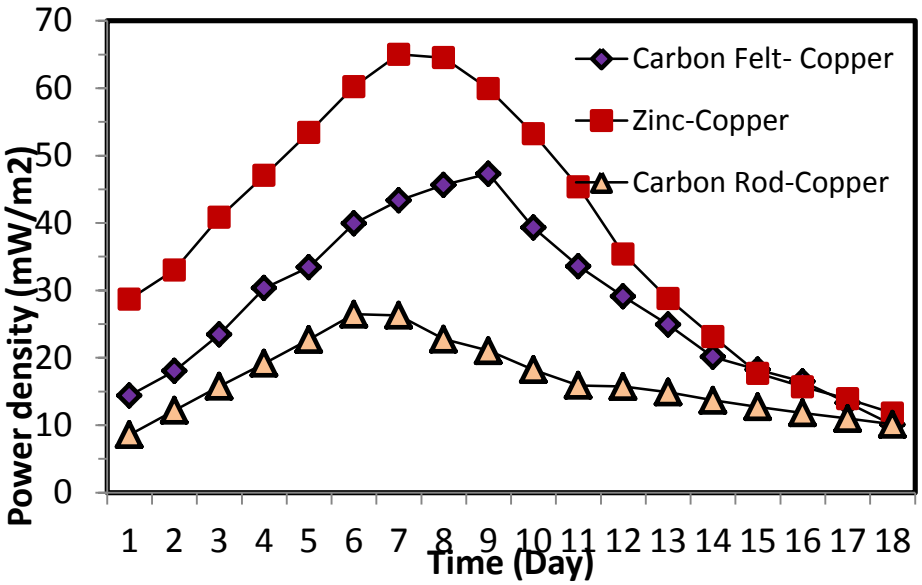


Figure 4.3 Variation of power density with time for various anode materials

Table 4.1 shows the total yield obtained for combinations of various electrodes. In total 18 days of operation zinc copper electrode combination generated voltage, current density and power density were 11168 mV, 1060.841mA/m^2 and 697.669mW/m^2 respectively. These values were higher than carbon felt-Cu and carbon rod-Cu electrode combination. COD removal is very important for waste water treatment. In this experiment the COD removal percentage were 86%, 76% and 74% for these three electrode combinations respectively.

Table 4.1 Total yield obtained for various combinations of electrode

Operation	MFC running process	Measurement	Total value
Electrode materials	Zinc-Cu	Voltage	11168 mV
		Current density	$1060.841 mA/m^2$
		Power density	$697.669 mW/m^2$
	Carbon felt-Cu	Voltage	9201mV
		Current density	$937.471 mA/m^2$
		Power density	$501.008 mW/m^2$
	Carbon rod-Cu	Voltage	6845mV
		Current density	$769.726 mA/m^2$
		Power density	$299.158 mW/m^2$

Table 4.2 COD removal percentage for various combinations of electrode

Electrode combination	COD Removal (%)
Zinc-Copper	86%
Carbon felt-Copper	76%
Carbon rod-Copper	74%

4.3 Effects of electrolyte pH on power generation

pH of electrolytes plays a vital role in bioreactor performance [83]. Similarly, the electrolyte pH plays a vital key role in MFC's power output. In MFC operation, power output drastically reduces at the acidic pH range below 6 [83]. It means, low pH conditions showed an adverse effect on electrochemically active bacterial population, which in turn leads to a drastic drop in power production. It is clear that pH will strongly influence the performance of MFC both in batch feed and continuous mode of operation. An ideal pH range for preferred fuel cell configuration was stated to be in the middle of 7–8 [34].

To identify the effect of pH on the output of MFC for municipal waste water several experiments were performed. These experiments were done at room temperature and Zn-Cu was used as electrode materials, where the electrolyte pH was maintained at pH 6, pH 8 and pH 10. All these experiments were done at same operating condition and pH of electrolyte was only variable.

Figure 4.4 and 4.5 represents the variation of pH on voltage, and current obtained from microbial fuel cell. From here it's seen that voltage went from 886 mV to 1019 mV, 953 mv to 1125 mV and 823 mV to 975 mV for pH 6, pH 8 and pH 10 respectively in first four days, then declined in a regular manner for pH-6 and pH-8, whereas pH-10, after 7 days voltage dropped sharply. As well as voltage, current spike in first few days goes a maximum value of 535 µA, 618 µA and 580 µA respectively, then current decreased in a similar way to voltage. In all the cases, in the operation of 15 days the final voltage (568 mV, 595 mV and 525 mV) and current (205 µA, 275 µA and 298 µA) were reached for pH (6, 8, 10) respectively, with time both voltage and current decreased for the formation of biofilm fall on the anode surface. It is noticeable that for pH 8 both voltage and current goes the peak value 1125 mV, where Zhang et al. [91] got 445 mV at pH 7 and graphite felt as electrodes, and 618 µA which is better than Biffinger et al. [103] where

found 400 µA between pH 6–7 by using graphite felt electrodes and He et al. [90] got current density 223.8 mA/m^2 using graphite felt as electrodes whereas, we got maximum current density 241.2 mA/m^2 both result obtained at pH 8, where we used iron and copper electrodes and waste water as electrolyte. So, pH 8 was used for further experiment. Our findings is very much resemble with He et al. [90], who express that highest current is obtained between pH of 7 and 8, but this values were lower at pH of 9 and pH below 7.

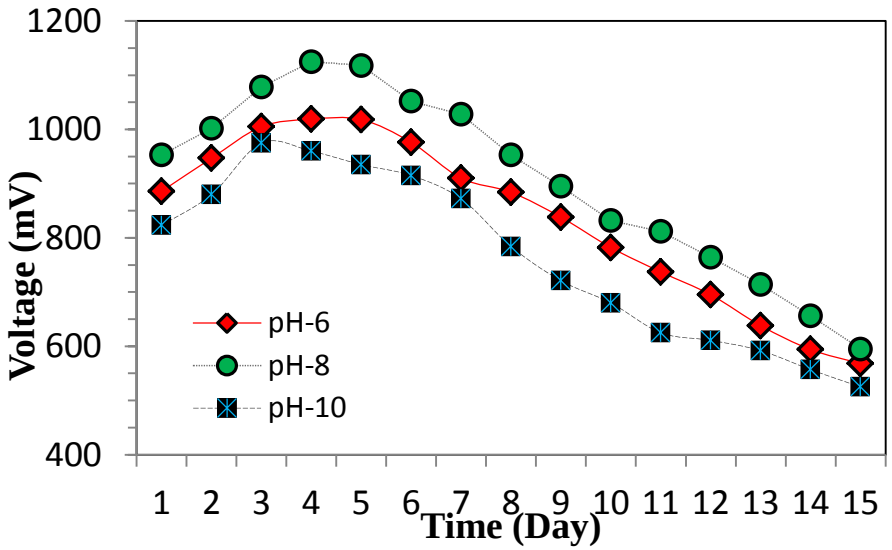


Figure 4.4 Effect of pH on the generated voltage

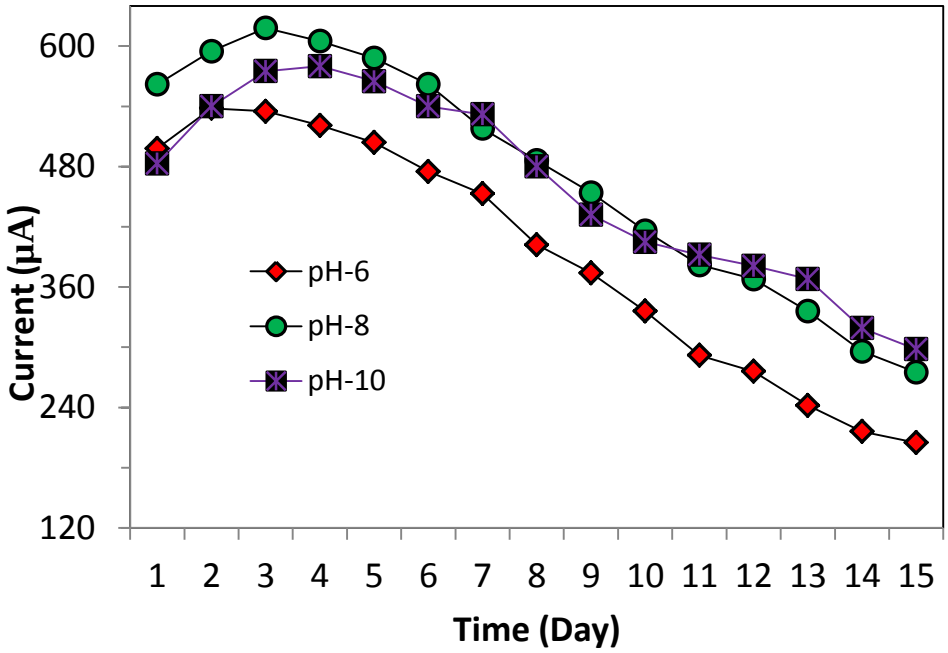


Figure 4.5 Effect of pH on generated current

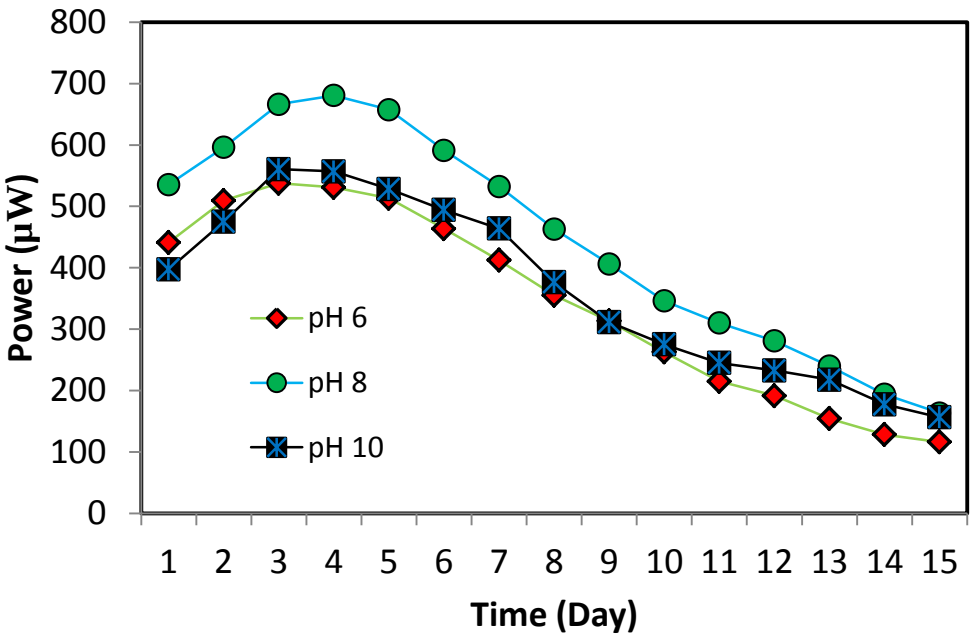


Figure 4.6 Effect of pH on generated power

In total running period pH 8 MFC generated voltage 7.95 % and 15.63 %, whereas current 16.91 % and 2.42 % higher from pH 6 and pH 10 respectively. Figure 4.6 shows that maximum power obtains for pH 8, which was 680.625 µW, where pH 10 gives higher power than pH 6.

Table 4.3 and 4.4 represents COD removal percentages and the total generated output of microbial fuel cell for various pH. In fifteen days operation pH electrolytic solution generated 13577 mV, 7061 µA and 6664.358 µW, on the other hand all these values was 12497 mV, 5867 µA, 5145.886 µW and 11455mV, 6890µA, 5469.385µW respectively for pH 6 and pH 10 of electrolyte. In every case COD removal was over 88%, 86% and 82% for the electrolyte having pH 8, pH 10 and pH 6 respectively.

Table 4.3 COD removal percentage for various combinations of pH

pH	COD Removal (%)
pH 6	82%
pH 8	88%
pH 10	86%

Table 4.4 Total yield obtained for various combinations of pH

Operation	MFC running process	Measurement	Total value
pH	pH 6	Voltage	12497 mV
		Current	5867µA
		Power	5145.886µW
	pH 8	Voltage	13577mV
		Current	7061µA
		Power	6664.358µW
	pH 10	Voltage	11455mV
		Current	6890µA
		Power	5469.385µW

4.4 Effects of local waste water on power generation

The focus of this experiment was to compare the energy content of local waste (Bhairab River, hospital, municipal) water available in Jashore, Bangladesh. The experiment was done at room temperature and Zn-Cu was used as electrode materials, where the electrolyte pH 8 and electrode spacing 7 cm. All operating conditions were same only variable was the sources of electrolyte.

In Figure 4.7 for hospital waste water, at first day obtained voltage was 998mV, and then it decreased till day 4. But in day 5 it ascends to 864mV which then reduce gradually to 772mV at 9th day. This scenario is quite similar for other two cases, maximum voltage for river water was 1003mV and municipal waste water was 980mV. Figure 4.8 shows that, for hospital waste water maximum generated current was 3.16mA, where the maximum current for river water was 5.89mA and for municipal waste water was 2.14mA. Figure 4.9 show that, the maximum generated power from hospital waste water was 3.153mW, where the maximum power was 5.907mW and 2.097mW from river and municipal waste water respectively.

In case of river water obtained voltage in Figure 4.7 was 1003mV at the initial day, which decreased from 920 to 795mV from day 2 to 9 in a step wise manner. In Figure 4.8 found current was highest in river water comparison with both municipal and hospital waste water. It's known that flow of current is the flow of electrons or ions.

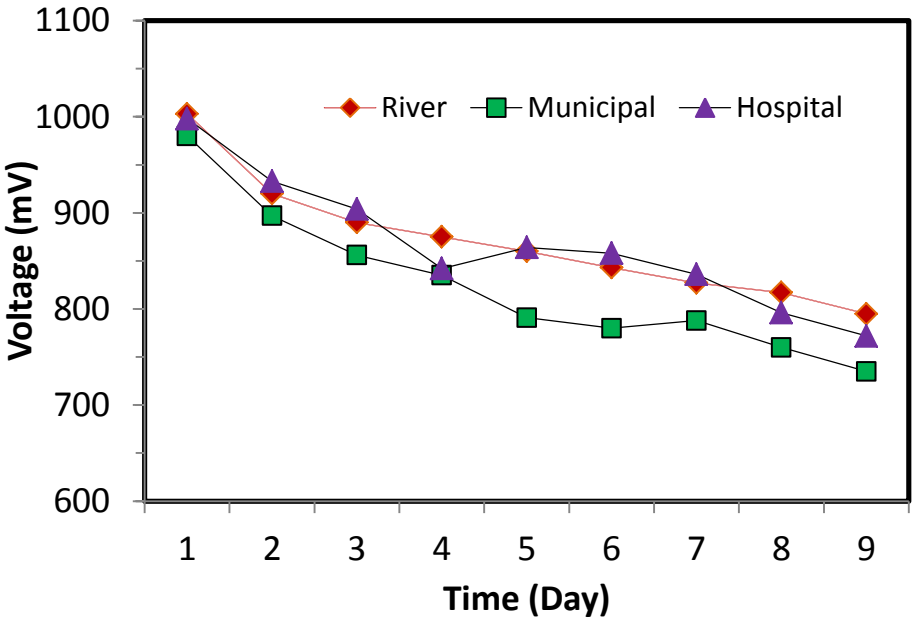


Figure 4.7 Effect of waste waters on generated voltage

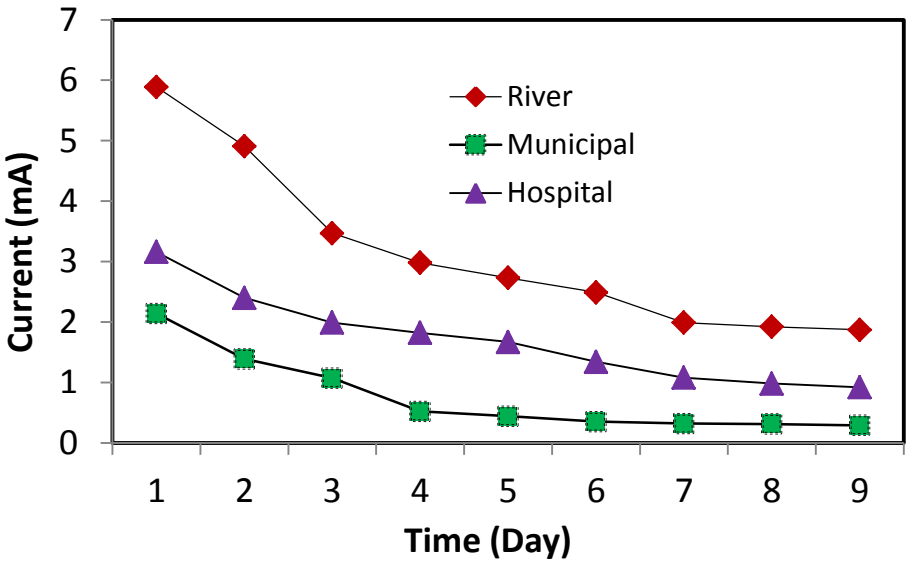


Figure 4.8 Effect of waste waters on generated current

River waste water contains more salt which dissociated and produced large amount of anions and cations; those were responsible for increasing current flow. Figure 4.9 shows power vs days of operation. Here calculated power was the highest for river waste water. At first day it was 5.907mW for river water, after that it reduced. For day 1 to 4 power descended linearly, at day 5

the power was 2.266mW for river water. Then power value reduced from day 6 to 9 softly. In this case found lowest power was 1.437mW.

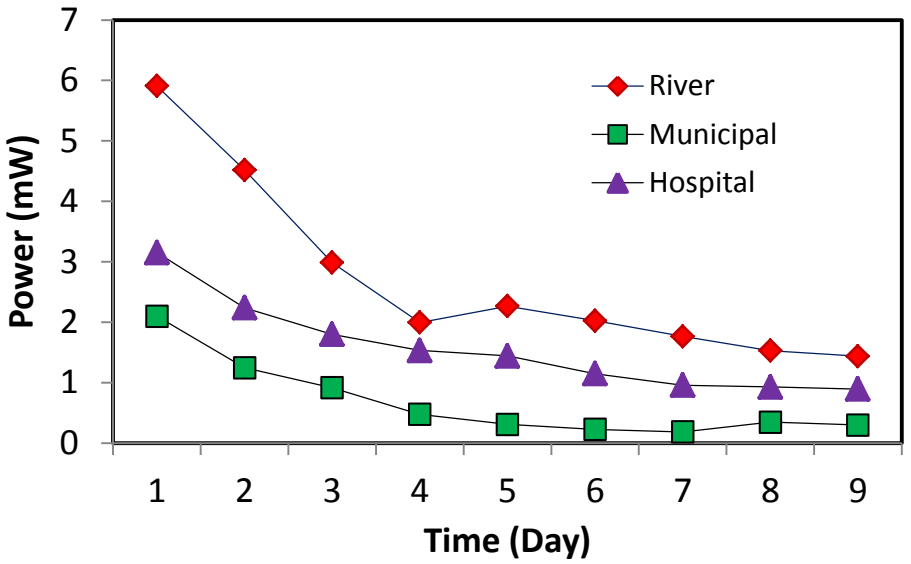


Figure 4.9 Effect of waste waters on generated power

Table 4.5 and 4.6 represents the total generated output and COD removal percentages of microbial fuel cell for different waste water. In nine days operation Bhairab river waste water gives higher voltage (7830mV), current (28.25mA) and power (24.424mW) than municipal and hospital waste water. COD removes in Bhairab river water was 88%, which was 6% higher than municipal waste water and 4% higher than hospital waste water.

Table 4.5 Total result generated from different waste water

Operation	MFC running process	Measurement	Total value
Various waste	Bhairab River waste water	Voltage	7830mV
		Current	28.25mA
		Power	24.424mW
	Municipal waste water	Voltage	7422mV
		Current	6.83mA
		Power	6.095mW
	Sador (Jashore) Hospital waste water	Voltage	7803mV
		Current	15.36mA
		Power	14.092mW

Table 4.6 COD removal percentage from waste water

Various waste	COD Removal (%)
Bhairab River waste water	88%
Municipal waste water	82%
Sador (Jashore) Hospital waste water	84%

4.5 Effect of additives on power generation

The goal of this experiment was to identify the role of various additives such as urine and fish waste on power generation of MFC. The operating conditions of this experiment were Zinc-Cu as electrode materials, pH of electrolyte was 8 and electrode spacing was 7 cm and room temperature.

MFC was constructed using 10 (w/v) % concentrations of urine, fish waste and raw waste water respectively and then MFC's voltage, current, power were investigated. Figure 4.10, indicates voltage versus days of operation, where at the beginning 1005mV, 970mV and 895mV were the voltages for urine mixture, fish waste mixture and raw waste water respectively.

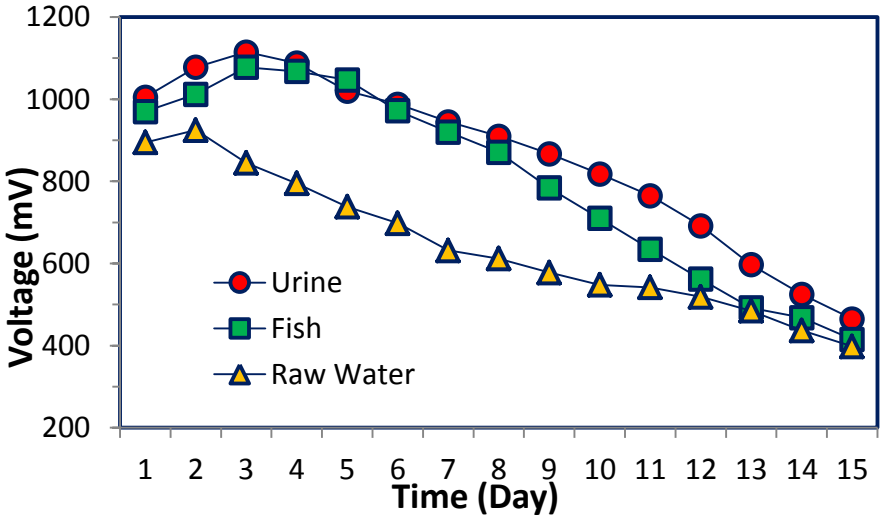


Figure 4.10 Effect of additives on generated voltage

Figure 4.10 shows that the maximum voltage was 1115mV, 1078mV and 925mV for urine mixed waste water, fish waste mixed waste water and raw waste water respectively at day 3. After that, in every case the obtained voltage decreased gradually. Here we can see that raw waste water gives the lower voltage than the other two. In operation of fifteen days urine mixed

waste water produced 12878mV whereas, fish mixed waste water produced 12004mV and raw waste water produced 9647mV.

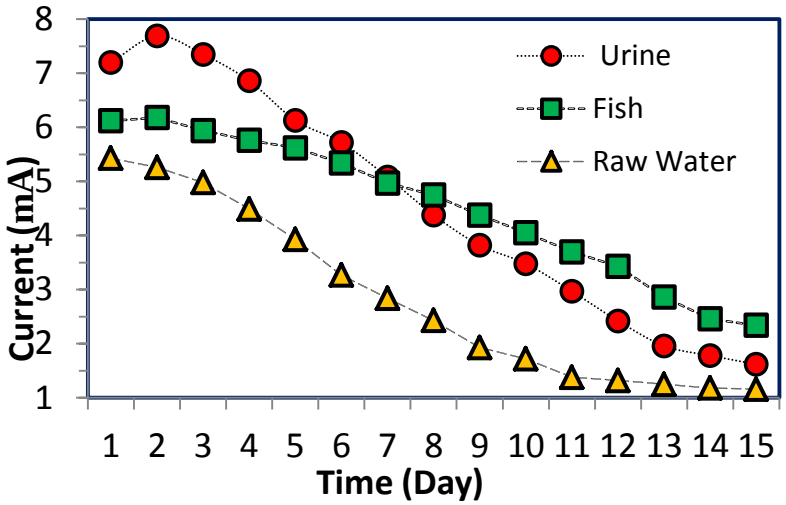


Figure 4.11 Effect of additives on generated current

Figure 4.12 shows that the obtained current was highest (7.69mA) in urine mixed waste water and lowest in raw waste water (1.62 mA), on the other hand maximum current for fish waste mixed waste water was 5.43mA.

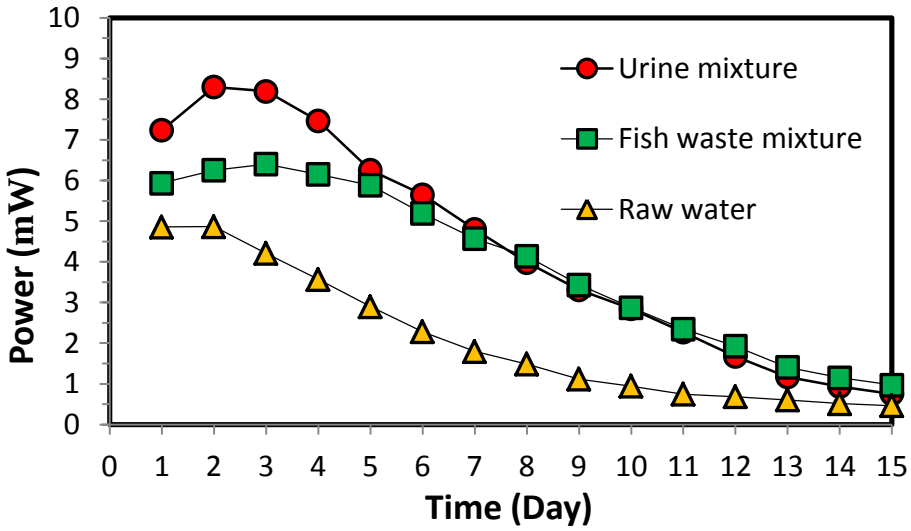


Figure 4.12 Effect of additives on generated power

As voltage and current the highest value was obtained for power from urine mixed waste water shown in Figure 4.11, whereas the maximum values were 8.299 mW, 6.403 mW, 4.865 mW and minimum values were 0.754 mW, 0.971 mW, and 0.462 mW for the above indicated samples

respectively. Parkash, [104] where he used cow dung as electrolyte and got voltage 825 mV and current 0.0113 µA, which is lower than this experiment.

Figure 4.10, 4.11 and 4.12 shows that, in all cases the obtained values were initially increased then got maximum, after that decreased. The main reason behind that, growth of microorganisms is very important factor in MFC. So, incubation is very important for the proper growth of microorganism. Here, the microorganism took around three days for their proper growth, that why the output values from MFC increased initially, after the maximum growth of microorganism, then the growth rate is decreased so reaction rate is also decreased. Table 4.7 and 4.8 represents the total generated output and COD removal percentages of microbial fuel cell for different additives with waste water. In fifteen days operation urine mixed waste water gives higher voltage, current and power than raw waste water and fish waste mixed waste water. Maximum 89% COD removes for fish waste mixed waste water.

Table 4.7 Total output obtained for various additives used in waste water

Operation	MFC running process	Measurement	Total value
additives used in waste	Raw waste water	Voltage	9647mV
		Current	42.57mA
		Power	31.038 mW
	Urine mixed waste water	Voltage	12878mV
		Current	68.46mA
		Power	64.85mW
	Fish waste mixed waste water	Voltage	12004mV
		Current	67.9mA
		Power	58.641mW

Table 4.8 COD removal percentage for various additives used in waste water

Various waste	COD Removal (%)
Raw waste water	72%
Urine mixed waste water	85%
Fish waste mixed waste water	89%

4.7 Effects of urine concentration on the output of MFC

Cow's urine contain some vitamins, minerals, and ions such as Na, N, Mg, Fe, Si, Cl, Mg, P, K, S, citric, succinic acid, lactose, calcium salts, enzymes, carbolic acid, etc. [105]. Cow's urine is considered as a valuable resource for N, P and energy recovery for its high concentration of nutrients [106]. Nitrogen is present in cow's urine in the form of urea. Around 2 (w%) urea present in urine, four atoms of hydrogen contain in each molecule of urea, which have low binding energy than the hydrogen atom in water.

Figure 4.13 represents the variation of urine percentage on voltage generation in microbial fuel cell. From here it's seen that the maximum voltage were 989 mV, 1146 mV and 1081 mV for 5%, 10% and 15% urine respectively in first three days, then decline in a regular manner for every case. In all the cases around the operation was run 15 days finally the voltage (261 mV, 328 mV and 340 mV) were reached for (5%, 10%, 15%) urine respectively, with time the voltage is decreased for the formation of biofilm on the anode surface. This finding is much higher than Simeon and Raji [107], where they got 731 mV by using urine in soil based MFC. Here the maximum voltage is obtained for 10% urine mixed waste water.

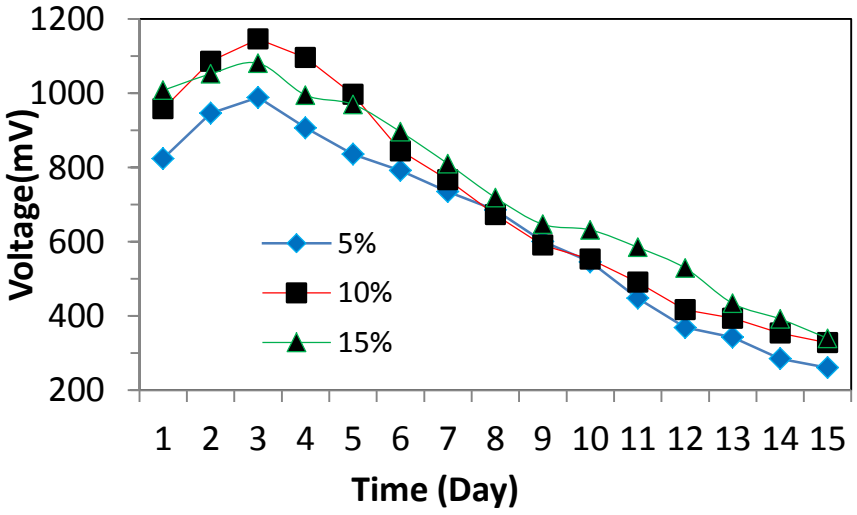


Figure 4.13 Effect of urine concentration on generated voltage

In Figure 4.14 the maximum (350.81mA/m^2) current density obtained from 15% (v/v) urine mixed waste water in second day. From third day to fifth day the obtained value approximately

the same for all cases. After that, current density for 15% (v/v) urine concentration goes higher than other two. The content of urea presents in urine mainly affects the current density. In operation of fifteen days total current density was obtained 2312.86mA/m^2, 2452.23mA/m^2 and 2892.52mA/m^2 for 5%, 10% and 15% urine concentration respectively.

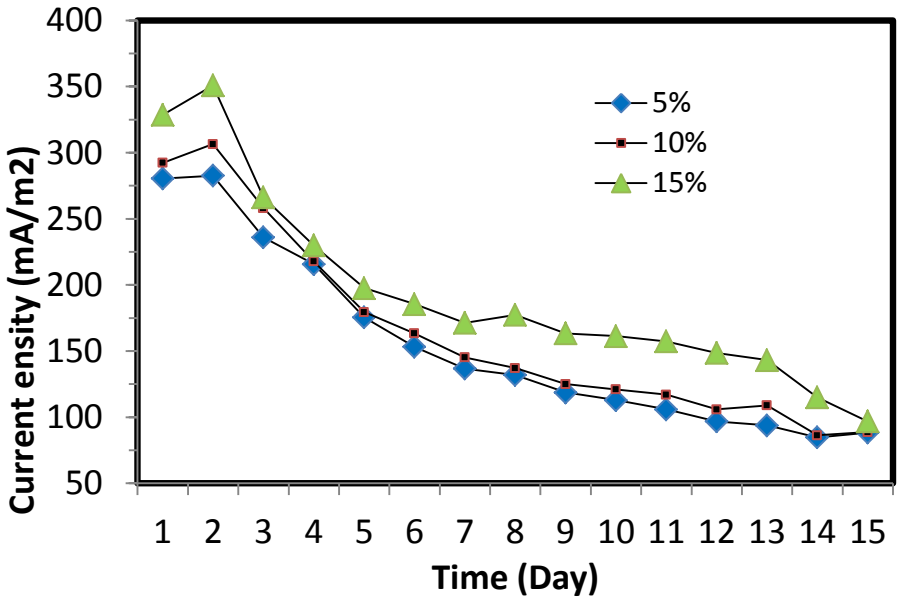


Figure 4.14 Effect of urine concentration on generated current density

Figure 4.15 shows the changes of power density (mW/m^2) with time (day) for different urine concentration. The graph shows the maximum (369.052mW/m^2) power density obtained from 15% (v/v) urine mixed waste water in second day. From third day to fifteen day the obtained value declined, at the final stage the outputs from all three cells are around same. Power is directly linked with voltage and current. In operation of fifteen days total current density obtained 1681.786mW/m^2, 2012.609mW/m^2 and 2359.16mW/m^2 for 5%, 10% and 15% urine concentration respectively.

Table 4.9 shows the total output generated in this experiment for 5%, 10% and 15% urine concentration used as additives. Maximum voltage 11090mV, current density 2892.52mA/m^2 and power density 2359.16mW/m^2 generated for 15% urine concentration. In fifteen days operation maximum 92% COD removed for 15% urine concentration.

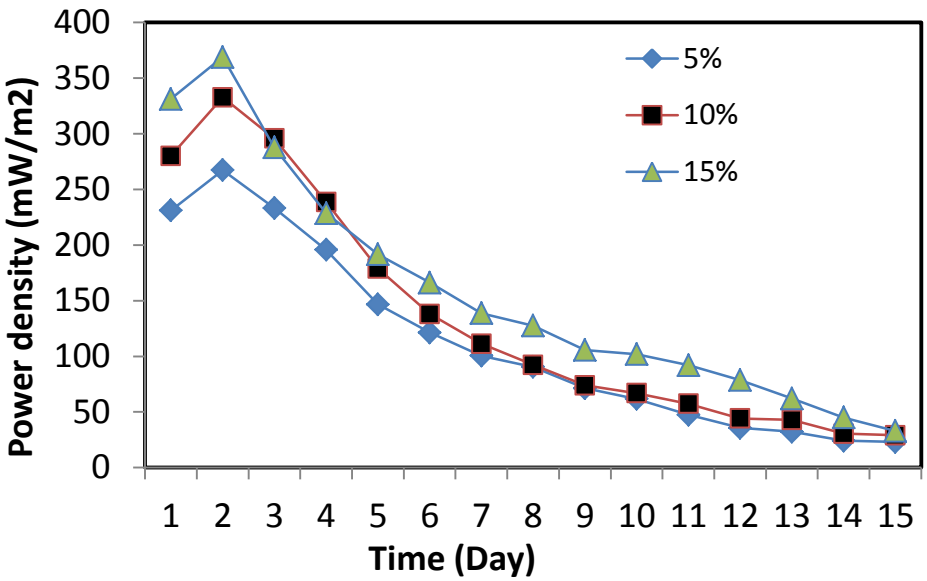


Figure 4.15 Effect of urine concentration on generated power density

Table 4.9 Total yield obtained for various urine percentages (v/v)

Operation	MFC running process	Measurement	Total value
Urine percentages (v/v)	5%	Voltage	9568 mV
		Current density	$2312.86 mA/m^2$
		Power density	$1681.786 mW/m^2$
	10%	Voltage	10696mV
		Current density	$2452.23 mA/m^2$
		Power density	$2012.609 mW/m^2$
	15%	Voltage	11090mV
		Current density	$2892.52 mA/m^2$
		Power density	$2359.16 mW/m^2$

Table 4.10 COD removal percentage for various urine percentages (v/v)

Urine percentages (v/v)	COD Removal (%)
5%	87%
10%	90%
15%	92%

CHAPTER V

CONCLUSIONS

5.1 Conclusions

A microbial fuel cell is designed in this work and several MFCs were constructed using locally available materials. The effects of electrode materials, pH of electrolyte, sources of electrolyte, concentration and type of additives were investigated. Following conclusion can be drawn from this investigation:

(i) Zinc-copper electrode combination generated higher power than carbon felt-copper and carbon rod-copper electrode combinations. Maximum power density obtained from zinc-copper electrode combination was 65.02mW/m^2, which were more than carbon felt-copper electrode combination (47.31mW/m^2) and carbon rod-copper electrode combination (26.46mW/m^2).

(ii) The reaction rate of microorganism on organic substrate is highly dependent on substrate pH condition. To investigate the effect of pH, this research found that pH 8 can generate higher power than pH 6 and pH 10. The maximum power for pH 8 was 680.625 µW whereas, pH 6 generated 537.675 µW and pH 10 the value was 560.625 µW.

(iii) Local waste water obtained in Jashore is a good source of electricity. The energy content of Bhairab River, hospital waste water and municipal waste water obtained in Jashore were investigated. In nine days operation 24.424mW was obtained from Bhairab River water, whereas, 14.092mW from Sador (Jashore) Hospital waste water and 6.095mW from Municipal waste water. So, the energy content of Bhairab river water is higher than municipal and hospital waste water.

(iv) Additives increase the reaction rate of microorganism, which increase generated power. Here effect of locally available additives (urine, fish waste) on generated power was investigated. It was identified that urine is better than fish waste as additives for

microbial fuel cell. Power content of urine mixed waste water was 9.58% higher than fish waste mixed waste water.

(v) The concentration of additive affects the generation of power. In this experiment the concentrations (v/v) of urine were investigated. In fifteen days of running total power density generated 1681.786milli W⁄m^2, 2012.609milli W⁄m^2 and 2359.16milli W⁄m^2 from 5%, 10% and 15% urine concentration respectively.

5.2 **Recommendations for future work**

To improve the performance of MFC following recommendations are suggested for future work.

i. Platinum based composite electrode can be used instead of single electrode which will give better yield.
ii. Can be used filtration process to concentrate electrolyte.
iii. Perform continuous flow of electrolyte for getting continuous power.
iv. Step-up transformer can be used for getting higher voltage.
v. Storage device (capacitor) can be attached to storage current and practical apply.

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