ELECTRICITY GENERATION AND WASTEWATER TREATMENT THROUGH MICROBIAL FUEL CELL

By Ajay Singh and Vaishali

MICROBIAL FUEL CELLS ARE POTENTIAL AND MULTI-BENEFICIAL SOURCE OF PRODUCING ELECTRICITY.

Introduction

While approaching towards a sustainable evolution, humans should incorporate even the tiniest organism present on Earth, to invest their efforts in such a collaborative mission. MFC, which is bio-chemical fuel cell based on the microbial action of certain bacteria to generate electricity when fed on the organic matter is an apt example of such a collaboration.

Considering the waste produced every day, imagine the possibility of harnessing energy from it and the benefits it will possibly create for us. The motto of 'wealth from waste' could be realized through such a technology.

What is MFC?

Microbial Fuel Cells are basically biofuel cells which use biocatalysts for the conversion of chemical energy to electrical energy. It is a device that directly converts the energy produced by the microbial metabolism or enzyme catalysis into electricity by using conventional electrochemical technology.

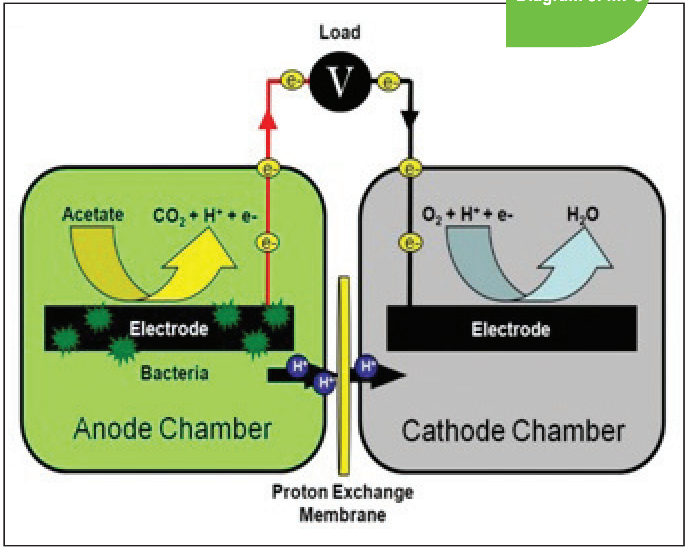


Figure 1: Schematic Diagram of MFC

Principle of MFC

Generally, a typical MFC consists of anodic and cathodic chambers to facilitate the redox reactions of the microbial activity.

"The organic matter is kept as an anolyte which is oxidized by microorganisms and they generate CO2, electrons, and protons. The electrons so produced are transported to the cathode chamber through an external circuit whereas the protons are transferred to the cathode through a membrane, hence generating electricity."

In order to maintain the reactions working, anaerobic conditions are maintained in the anode chamber and aerobic in the cathode chamber with a regular supply of oxygen.

MFC is an effective methodology in order to generate electricity through the sludge entering in the sewage treatment plant. Moreover, it reduces the COD of the organic substrate due to the production of CO2. The quantity of CO2 so released is relatively very less and it can be captured by surrounding plantations.

Reactions occurring at:
Anode: $C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24e^- + 24H^+$
Cathode: $6O_2 + 24H^+ + 24e^- \rightarrow 12H_2O$

Mediator Less MFC

It has recently been shown that certain metal-reducing bacteria, belonging primarily to the family Geobacteraceae can directly transfer electrons to electrodes using electrochemically active redox enzymes, (Ghanghrekar et al) such as cytochromes on their outer membrane. These microbial fuel cells does not need mediator for electron transfer to electrodes and are called as mediator less MFCs. Mediator less MFCs are considered to have more commercial application potential, because mediators used in Biofuel cells are expensive and can be toxic to the microorganisms.

Bacterial Metabolism

A bacterial cell is able to extract energy out of the organic compounds and to store and use this energy to grow and multiply its colony. These energy transformations must follow the basic laws of thermodynamics.

According to the Ist law of thermodynamics, 'energy can neither be created nor destroyed', as for bacteria the energy in the matter is only available for use. And according to the second law, in closed irreversible systems, entropy will always increase. The energy available in a system can be broken up into useable energy and unavailable energy, the unavailable energy goes to increasing the entropy of a system. Bacteria combine both of these types of reactions into a system to operate cell functions. Intermediate reactants that temporarily store energy help join energy releasing and consuming reactions so that it is possible to synthesize compounds that could otherwise not be created (Chapelle 2001).

An electron acceptor is an inorganic compound that accepts electrons from bacteria and completes the oxidation of an organic substrate (Chapelle 2001). Depending on the terminal electron acceptor (TEA) present, two metabolic pathways can be used by the bacteria; fermentation and respiration (Schroder 2007).

Fermentation is an important anaerobic mechanism for degrading organic matter; however it is not a process that creates electricity in MFCs. Many electrons remain within fermentation products, not readily reacting with electrodes. Respiration is a combination of the reduction of a TEA and the oxidation of an organic compound where the electrons are transferred through an electron transport chain to the final TEA. The higher the potential of the TEA, the higher the energy gain for the organism, thus the more favorable the reaction.

Materials for Construction

Anode: Anodic materials must be conductive, biocompatible, and chemically

Figure 2: Lab Scale MFC

Figure 3: Carbon Graphite Electrode

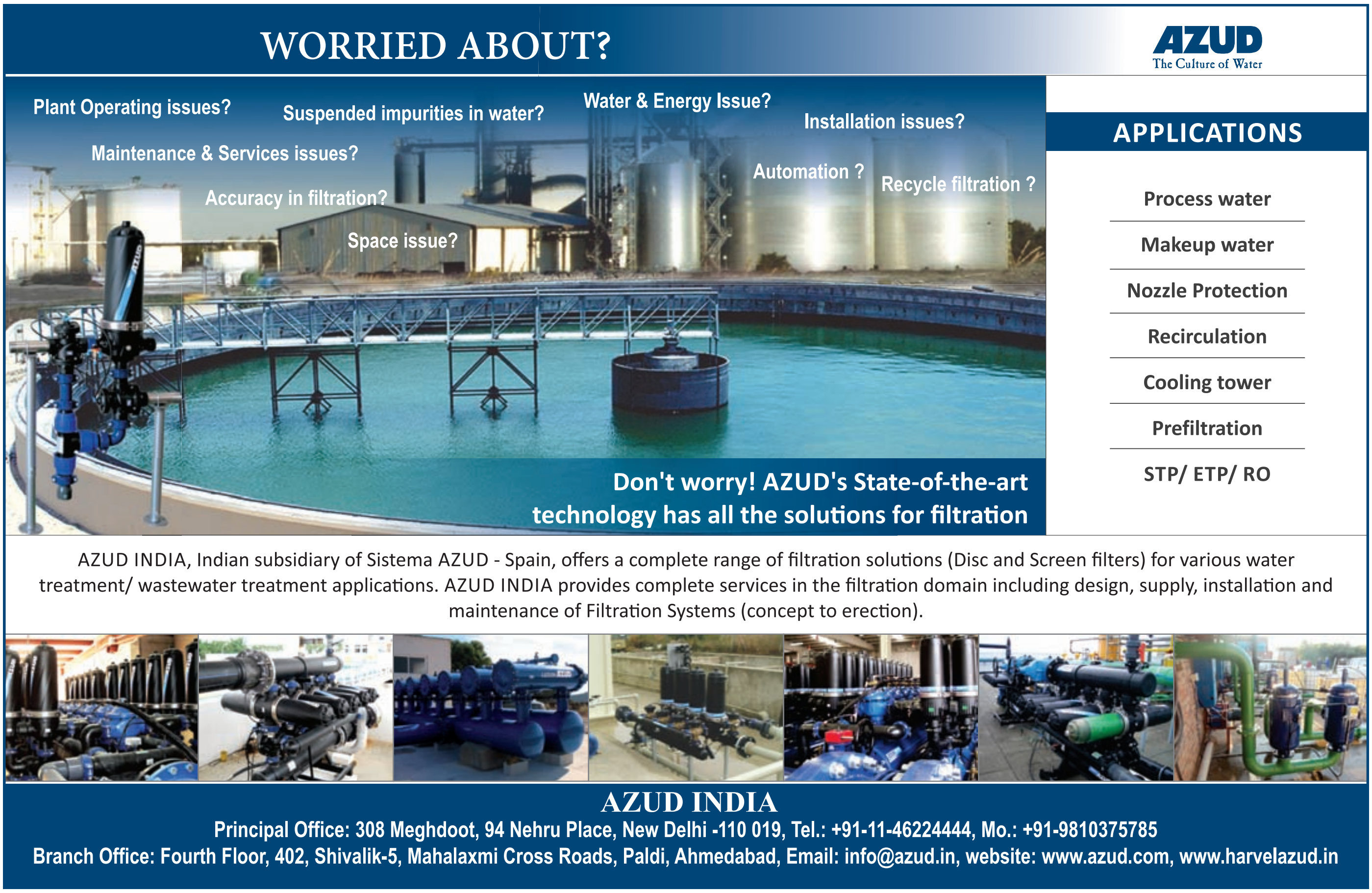
Figure 4: Nafion Membrane

Figure 5: Lab Scale H Shaped MFC

stable (Logan, 2006) in the reactor solution. Metal anodes consisting of noncorrosive stainless steel mesh can be utilized, but copper is not useful due to the toxicity of even trace copper ions to bacteria. The most versatile electrode material is carbon, available as compact graphite plates, rods, or granules, as fibrous material.

It has been shown that current increases with overall internal surface area, which can be achieved by using reticulated vitreous carbon, is available in various pore sizes. Maintaining high porosity is important to prevent clogging. The long term effect of biofilm growth or particles in the flow on any of the above surfaces has not been adequately examined. The electrolyte stays as the substrate which is discussed in further section.

Cathode: Due to its good performance, ferricyanide (K3[Fe(CN)6]) is very popular as an experimental electron acceptor. The greatest advantage of ferricyanide is that it has low over potential achieved by using a plain carbon cathode, resulting in a cathode working potential close to its open circuit potential. The greatest disadvantage, however, is the insufficient re-oxidation by oxygen, which requires the catholyte to be regularly replaced. In addition, the long term performance of the system can be affected by diffusion of



ferricyanide across the cation exchange membrane (CEM) and into the anode chamber.

Membrane: Often the MFC designs require the separation of the anode and the cathode compartments by a CEM. Exceptions are naturally separated systems such as sediment MFCs or any particularly designed single-compartment MFCs.

The most commonly used CEM is Nafion. Substitutes to Nafion, like Ultrex CMI-7000 are also feasible for MFC applications and are significantly more cost-effective than Nafion. More methodical studies are needed to evaluate the effect of the membrane on performance and long-term stability.

Design of Lab Scale Mfc & Power Generation in Mfc

Most often, an inexpensive design of a two chamber MFC built in a traditional H shape is used, in which two bottles are connected by a tube containing a separator which is usually a cation exchange membrane such as Nafion or Ultrex, or generally a plain salt bridge. The crucial aspect to this design is choosing a membrane that allows protons to pass between the chambers (the CEM is also called a proton exchange membrane, PEM), but it doesn't allow the substrate or electron acceptor in the cathode chamber (generally oxygen). In such a configuration, the membrane is held in the center of the chambers connecting the bottle. As long as the two chambers are kept separated, they can be pressed up onto either side of the membrane and clamped together to form a large surface.

An economical manner to join these bottles is to use a glass tube that is heated and bent into a U-shape, filled with agar and salt, and put in through the lid of each chamber. The salt bridge MFC, however, produces little power due the high internal resistance observed.

H-shape arrangement are viable for basic parameter research, such as examining power generation while using different materials, or types of microbial communities that ascend during the degradation of compounds, but they typically produce low power densities. The amount of power that is generated in these systems is affected by the surface area of the cathode relative to that of the anode and the surface of the membrane.

In the cathodic chamber, ferricyanide is used as the electron acceptor which significantly increases the power density due to the availability of a good electron acceptor at high concentrations. It increases power by 1.5 to 1.8 times when compared to a Pt-catalyst cathode. The highest power densities so far testified have been with low internal resistance systems with ferricyanide at the cathode.

It is not essential to place the cathode in water or in a separate chamber when using oxygen at the cathode. The cathode can be placed in direct contact with air.

For MFC calculations, it is more convenient to evaluate the reaction in terms of the overall cell electromotive force (emf), defined as the potential difference between the cathode and anode. This is related to the work, W(J),produced by the cell, or

$W= EemfQ= -\Delta Gr$

where Q=nF is the charge transferred in the reaction, expressed in Coulomb (C), determined by the number of electrons exchanged in the reaction, n is the number of electrons per reaction mol, and F is Faraday's constant (9.64853x104 C/mol).
Combining these two equations, we have:

$E_{emf} = E_{emf}^{0} - RTln(\pi)/nF$, $\pi=1$ for ideal conditions.

Also $E_{emf}=E_{cat}-E_{anode}$

Power: The overall performance of an MFC is evaluated in many ways, but principally through power output and Columbic efficiency. Power is calculated as:

$P=IE_{cell}$
Normally, the voltage is measured across a fixed external resistor (Rext) and the current is calculated by Ohm's Law. Thus, usually power is calculated as:

$P = E^{2}_{cell} / R_{ext}$

Power Density: Power is often normalized to some characteristic of the reactor in order to make it possible to compare power output of different systems. The choice of the parameter that is used for normalization depends on application, as many systems are not optimized for power production.

The power output is usually normalized to the projected anode surface area because the anode is where the biological reaction occurs. The power density (W/m^{2}) is therefore calculated on the basis of the area of the anode (AAn).

$P = E^{2}_{cell} / (A_{An} \times R_{ext})$

Sometimes the anode consists of a material which can be difficult to express in terms of surface area (i.e., granular material). In such cases, the area of the cathode can alternatively be used to obtain a power density.

To perform engineering calculations for size and costing of reactors, and as a useful comparison to chemical fuel cells, the power is normalized to the reactor volume,

$P_{v} = E^{2}_{cell} / (v.R_{ext})$

Where, Pv is the volumetric power (W/m^{3}) and v is the total reactor volume.

In an experiment performed by Liliana Alzate-Gaviria (CICY, Mexico), the power density generated by the MFC was determined by the volumetric power and the power equation was used for calculations. While using a resistance of 1000Ω, the maximum power density generated was 4.41 W/m^3 with a voltage of 1.05V. Whereas, when a resistance of 600Ω was applied, a maximum power density of 6.53 W/m^3 was obtained with 0.99V and also the organic matter removal expressed in COD was 65% and 82%, with 1000 and 600Ω respectively.

Following table depicts the comparison among various variable parameters of MFC.

Substrate	Mixed Culture	Electrode Type	Redox Mediator	Current Efficiency (%)	P (W/m^3)	References
Glucose	Mixed Consortium	Plain Graphite	Ferricyanide	89	216	Rabaey, 2003
Acetate	Sewage Sludge	Plain Graphite	Ferricyanide	-	32	Park, 2003
Wastewater	Bacteria Present in Wastewater	Plain Graphite	None	12	1.6	Liu, 2004
Wastewater	Activated Sludge	Plain Graphite	None	-	1.7	Kim, 2004
Glucose	Bacteria Present in Wastewater	Woven Graphite	None	40	13	Liu, 2005
Synthetic Wastewater	Anaerobic and Aerobic Sludge	Granular Graphite	Hexacyanoferrate	-	258	Aelterman, 2006
Acetate	Microbial Fuel Cell	Granular Graphite	Cathode Exposed to Air	90	65	Clauwaert, 2006
Wastewater	Bacteria Present in Wastewater	Graphite Brush Anodes	None	23	2.3	Logan, 2007
Sucrose	Anaerobic Sludge Collected from septic Tank	Stainless Steel	None	7.29	36.72	Behera, 2009

Open Circuit Voltage (OCV) is that cell voltage that can be measured after some time in the absence of current. Theoretically, the OCV should approach the cell emf, however, in practice, it is lower than the cell emf, due to various potential losses.

For example, a typical measured potential of a cathode using oxygen at pH 7 is about 0.2 V, which is clearly lower than the expected value of 0.805 V, signifying the huge energy loss happening at the cathode. This energy loss is stated as 'over potential', or the difference between the potential under equilibrium conditions and the actual potential, which for this case is 0.605 V (0.805 V - 0.2 V). This explains that the main application of thermodynamic calculations is to recognize the size and nature of energy losses.

Substrates Used in MFC

There is a wide range of varieties of substrate which are potentially viable in order to produce electricity.

Substrate	Description	Power(mW/m^2)
Complex	Anaerobic Sediments	16
	Starch Wastewater	19
	Starch Wastewater	20
	Domestic Wastewater	24
	Anaerobic Sediments	28
	Domestic Wastewater, CE-PEM	28
Defined	Lactate	0.6-15
	Lactate, Peptone, and Yeast Extract	788
	Acetate(saltBridge)	0.3
	Acetate	14-49
	Glucose	33-3600
	Glucose - CE-PEM	262

Factors Affecting Performance of Microbial Fuel Cell

Effect of Temperature on MFC Performance

Bacterial activities are well-known to be affected by temperature, anaerobic digestion requires 30°C-50°C for optimal operation but MFCs are known to operate well. In an experiment, an MFC operated at a mesophilic temperature of 30 ± 5°C during the first 102 days. During this period the maximum power density reached was (4.41 W/m^3) 1000Ω at 32°C.

Effect of Electrode Spacing

Columbic efficiency and energy recovery improves by decreasing the electrode spacing when the low ionic strength solution is used (100 milimolar). However, the Columbic efficiency and energy recovery does not get affected when using the higher ionic strength solution (400 milimolar).

Effect of Ionic Strength

Energy recovery is directly proportional to ionic concentration of the sludge. Adding ionic solvents may increase the current density. Graph depicts that 400 milimolar concentration produces higher power density when compared to 100 milimolar.

Influence of pH

An acidic pH in the anode chamber reduces electricity production. Low pH (pH 5 and 6) also results in decrease in power density. The lower pH in the MFC inhibits the activity of electrogenic bacteria. The highest power densities occurred at pH values near neutral.

Effect of Dissolved Oxygen

With increase in aeration in cathode compartment, the current increases sharply while DO increases at a slow rate. But when the aeration was stopped the current decreased, whilst the decrease in DO was less significant.

Applications of Microbial Fuel Cell Technology

Wastewater Treatment and Electricity Generation

The membrane less MFC can be used effectively for synthetic wastewater treatment with COD removal up to 90%. The combination of wastewater treatment along with electricity production may help in saving millions of rupees as cost of wastewater treatment at present.

Powering Underwater Monitoring Devices

Data on the natural environment can be helpful in understanding and modeling ecosystem responses, but sensors distributed in the natural environment require power for operation. MFCs can possibly be used to power such devices, particularly in river and deep-water environments where it is difficult to routinely access the system to replace batteries. Sediment fuel cells are being developed to monitor environmental systems such as creeks, rivers, and oceans.

Power Supply to Remote Sensors

Typically, batteries are used to power chemical sensors and telemetry systems, but in some applications, replacing batteries on a regular basis can be costly, time-consuming, and impractical. A possible solution to this problem is to use self-renewable power supplies, such as MFCs, which can operate for a long time using local resources.

BOD Sensing

The proportional correlation between the Columbic yield of MFCs and the concentration of assimilable organic contaminants in wastewater make MFCs possible usable as BOD sensors. MFC technology can be used as a sensor for pollutant analysis and in situ process monitoring and control.

Hydrogen Production

The generated current in MFC can be used to produce hydrogen gas. Since waste flows are often variable, a temporary storage of the energy in the form of hydrogen, as a buffer, can be desirable. For hydrogen production, the cathode is vacuum-packed to remove air entering the chamber and a voltage is applied to it. This energy input is required since hydrogen production from acetate or other substrates is not a spontaneous reaction.

Advantages of Microbial Fuel Cells

Generation of Energy Out of Biowaste/ Organic Matter

This feature is certainly the most 'green' aspect of microbial fuel cells. Electricity is being generated in a direct way from bio-wastes and organic matter. This energy can be used for operation of the waste treatment plant, or sold to the energy market.

Sludge Production

In an aerobic bioconversion process, the growth yield is generally estimated to be about 0.4 g Cell Dry Weight/ g COD removed. Due to the harvesting of electrical energy, the bacterial growth yield in a MFC is considerably lower than the yield of an aerobic process.

Omission of Gas Treatment

Generally, off-gases of anaerobic processes contain high concentrations of N2 gas, H2S, and CO2 next to the desired hydrogen or methane gas. They have no economic value as gas generated by the anode compartment that can hence be discharged, provided that no large quantities of H2S or other odorous compounds are present in the gas.

No Aeration Required

The cathode can be installed as a 'membrane electrode assembly', in which the cathode is precipitated on top of the proton exchange membrane or conductive support, and is exposed to the open air. This omits the necessity for aeration, thereby largely decreasing electricity costs.

Direct Conversion of Substrate Energy to Electricity

A microbial fuel cell has no substantial intermediary processes. This means that if the efficiency of the MFC equals at best, it is the most efficient biological electricity producing process at this moment. In MFC, the organic material in wastewater is directly converted into bio-electricity.

Conclusion

It can be inferred very well that PEM microbial fuel cell can generate electricity and cleanse wastewater as well, which marks it practicable for in situ treatments or for the modification of current sewage treatment plants. Changing from aerobic to anaerobic wastewater treatment would cut energy intake by avoiding the need to aerate the sludge. However, current anaerobic treatments are often believed of as being slow, need concentrated waste and high temperatures to operate reliably, the effluent often needs additional treatment before it can be discharged and sludge disposal is still essential.

MFCs perform at lower temperatures and produce less biomass. Improvement in future studies is to increase the anode area to recompense for the losses due to death and space occupied by other non-electricity generating bacteria in the biofilm. It was shown that as is the case with an external electron acceptor, the presence of conductivity is imminent in the anolyte of the MFC.

About the Authors

Ajay Singh is pursuing Bachelor's degree in technology in the field of Environmental Engineering from the esteemed institution Delhi Technology University (Formerly DCE), Delhi. **Vaishali** is also an aspiring engineering student in Environmental Engineering from the same university. Vaishali and Ajay both are certified in Water Harvesting Technology and Management and possess sound knowledge in Green Building & Practices.

To know more about the authors, you can write to us. Your feedback is welcome and should be sent at: mayur@eawater.com. Published letters in each issue will get a one-year complimentary subscription of EverythingAboutWater Magazine.