

Chapter 2

Energy Recovery with Microbial Fuel Cells: Bioremediation and Bioelectricity

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Abstract This chapter presents an overview on microbial fuel cells (MFCs) as a novel electrogenic reactor systems for simultaneous treatment of wastewater and generation of bioelectricity. MFCs work on the principle that organic matter present in wastewater serves as a primary substrate for the bacteria to consume and release electrons, facilitating the treatment of wastewater with simultaneous generation of power. Microbes in the anode chamber generate protons (H^+) and electrons (e^-) through reactions by decomposing the rich organics present in the wastewater and in the process treating the wastewater and producing a value added product which is bioelectricity. When these protons travel through the membrane and the circuit, respectively, power is generated from the system. Given the non-renewable aspect and polluting nature of fossil fuels, MFCs have generated interest among several research communities around the world. Following a historical approach toward this technology, the chapter discusses the various types of microbial fuel cells prevalent and compares the different MFC designs used. The role of proton exchange membrane separating the anodic and cathodic chambers is also explained. It focusses on the principle and working of an MFC and describes the instrumentation and procedure for reporting data. Additionally, the chapter presents benefits, drawbacks, and future scope of research in this field.

Keywords Microbial fuel cell · Energy generation · Nafion 117
Wastewater treatment · Substrate

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1 The Energy Economy and Energy Needs of Society

1.1 Historical Energy Consumption Trend

During 1700s, primary energy sources originated from water, wind, and firewood or manual labor. Before 1900, energy consumption per capita has not risen so much even with the expansion of coal energy, proposing that the early utilization of coal for the most part balances other fuel utilization. There has been a little increment in energy utilization per capita during World War I, however, between World War II and 1970; there was a tremendous increase in energy utilization per capita. There are reasons like European nations and Japan were reconstructed after World War II, oil industry needed to be created, to give occupations and assessment income to people, and between the periods of 1800–2000 the world population also expanded rapidly.

Around 1900, we started to bore for oil and petroleum gas. By 1950, these “non-renewable energy sources” had displaced the more seasoned energy sources with the exception of water energy sources. Figure 1 gives a brief idea for the same. We are utilizing non-renewable energy sources at a far more prominent rate than they are being made. After 1950, we started to utilize nuclear energy from uranium from its earliest stage. In the course of recent years, utilization of more established sustainable energy sources has expanded and utilization started new sustainable power sources too. Since fossil fuel-based economy will not keep going forever and that their utilization adds to ecological contamination. Sustainable power source which essentially originates from the solar energy gives chances to a boundless, reasonable energy supply with minimum damage to the ecosystem.

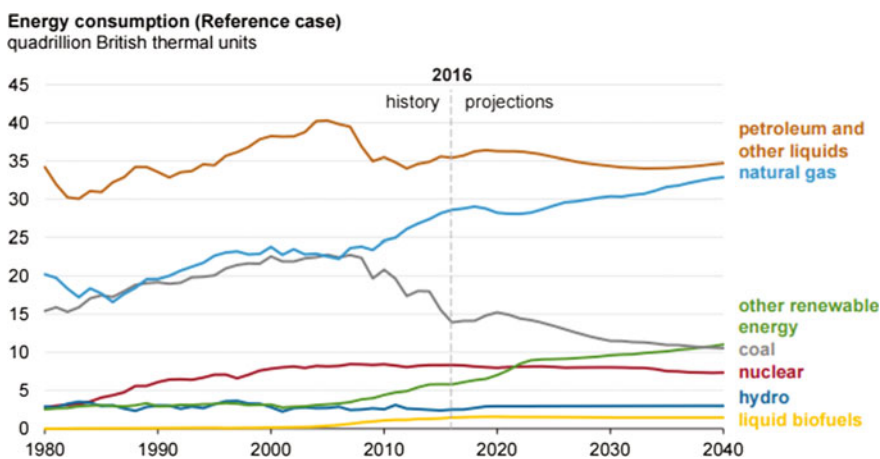


Fig. 1 History and projections of different energy forms (Aelterman et al. 2006)

1.2 *The Need for Renewable and Alternate Energy*

Renewable and sustainable power sources are those regenerated by natural processes at a rate independent of its utilization pattern. Such as:

Solar Energy: Energy from the Sun is utilized to deliver power, or for heating. In India, current solar energy generation is about 12.3 GW but there are challenges like more land requirement (40–60 MW per 1 km²), cost of installation which is needed to be overcome as time progresses toward more renewable energy. The program reached an ambitious Solar Alliance during the Paris Agreement of 2015.

Biomass Energy: Biomass as a fuel comprises of natural matter (cellulose, hemicellulose, and lignin) which is mostly agricultural residues; it is non-polluting in nature, and as plants capture CO₂ throughout their lives so such sources are considered carbon neutral. As a fuel, it might incorporate residues from wood, straw, sugarcane, and numerous other by-products of certain agricultural processes.

Biomass itself is a carbon neutral source that is CO₂ from atmosphere which is taken by plants during photosynthesis. This CO₂ is changed over into natural carbon and put away in woody biomass. Trees discharge the stored carbon when they die, rot, or are getting combusted. As the biomass discharges carbon as CO₂, the carbon cycle is maintained. Biomass energy can be extracted by either thermochemical (using heat) or by biochemical (using enzymes, bacteria). India currently generates about 6000 MW of energy from biomass.

Hydropower: Hydropower harbors one of the biggest sustainable power sources. Hydropower plants change over the energy of streaming water into power. This is for the most part done by making dams crosswise over waterways to make expansive repositories or reservoirs and after that discharging water through turbines to deliver power. Hydropower brings about no discharges of harmful gases into the air; however, the way toward making dams can make critical natural issues for water quality and for oceanic and untamed life environment.

Geothermal: Geothermal energy utilizes high temperatures of profound earth outside layer to deliver steam, which then powers turbines and produces power.

There are four major types of geothermal energy resources: hydrothermal, geopressurized brines, hot dry rocks, magma. The estimated potential for geothermal energy in India is about 10,000 MW, but due to the lack of infrastructure, India still not able to produce any amount of energy from earth's crust.

Wind Power: It has been the quickest developing energy source in the course of the most recent decade fundamentally because of exceptionally critical changes in wind energy (or vitality) innovation. Wind power is created by the wind turning streamlined sharp edges of the turbine blades mounted to a center point. The center point is associated with a pole that turns a generator.

Fuel Cells: Fuel cells are electrochemical devices which operate on hydrogen-rich sources as long as it has a supply of the fuel to produce clean energy. This energy can be used to feed power to the grid, automobiles, and even everyday electronics that we use. As of now, delivered power modules or fuel cells join hydrogen and oxygen without burning to create power. The oxygen can be utilized

Table 1 Fuel cell types and their configurations with estimated power output

Fuel cell type	Electrolyte	Operating temperature (°C)	Electrical efficiency	Fuel oxidant	Energy output (single stack)
Alkaline fuel cell	Potassium hydroxide	25–90	60–70%	H ₂ O ₂	300 W–5 kW
Proton exchange membrane fuel cell	Proton exchange membrane	25–80	40–60%	H ₂ O ₂	1 kW
Direct methanol fuel cell	Proton exchange membrane	25–130	20–30%	CH ₃ OH, O ₂ , air	1 kW
Phosphoric acid fuel cell	Phosphoric acid	160–200	50–55%	Natural gas, biogas, coal gas, H ₂ O ₂ , air	200 kW
Molten carbonate fuel cell	Molten mixture of alkali metal carbonates	620–660	55–65%	Natural gas, biogas, coal gas, H ₂ O ₂	2–100 MW
Solid oxide fuel cell	Ceramic-type membranes	800–1000	60–65 °C	Natural gas, biogas, coal gas, H ₂ O ₂	100 kW

from air itself, while the hydrogen can either be delivered from existing hydrogen infrastructure or renewable energy-based systems. Further, new power devices are being produced that can utilize petroleum products specifically in this context (Table 1).

The advancement of power devices has come about to improve new power device advances, and subsequently, the requirement for vitality and worries over energy security has brought about the improvement of microbial fuel cells (MFCs) advances. Globally, more than one billion people lack drinking water and more than two billion lack adequate sanitation. More than 38 billion of liquid wastewater is generated in urban areas of India; this does not include the industrial, rural, solid wastes, etc. The capacity of waste generated in USA is around 17 GW which is equivalent to energy produced by 17 nuclear plants. Hence, MFCs are developing at much faster rate for renewable energy generation.

1.3 Drive Toward Hydrogen Economy

Our universe comprises a blend of an unlimited cluster of components. Every component has an imperative part in the organization of the world. The most abundant elements in the universe include hydrogen, oxygen, and nitrogen. Hydrogen occupies up to 75% of the universe and has the potential to contribute to

environmentally benign energy infrastructure. Apart from assisting other distinctive living species in surviving, hydrogen can be used to generate energy as well. Hydrogen has often been stated as a future fuel in the energy economy trend line. Hydrogen is not found in its pure form on Earth; however, it can be produced from different compounds like biomass, natural gas, alcohols, or water. In all these cases, conversion of hydrogen to its pure form is energy intensive. As a result, hydrogen is used as an energy carrier or storage medium instead of an energy source in itself (Fig. 2).

As shown in Fig. 4, the expression “hydrogen economy” refers to the vision of utilizing hydrogen as a low-carbon energy source, for example, gas as a transport fuel or natural gas as a heating fuel. Hydrogen is appealing in light of the fact that whether it is burned to produce heat or reacted with air in a fuel cell to generate electricity, the by-product is water.

1.3.1 Some Advantages of Hydrogen Economy

1. Abundant energy source and clean form of energy.
2. Non-toxic does not cause any harm or destruction to human health.
3. Efficient energy source to convert a lot of energy for every pound of fuel. This means hydrogen vehicles will have more mileage as compared to an equivalent amount of gasoline.

These are issues that with the hydrogen infrastructure; however, with time, engineers and scientists are expected to resolve them, as with every technology.

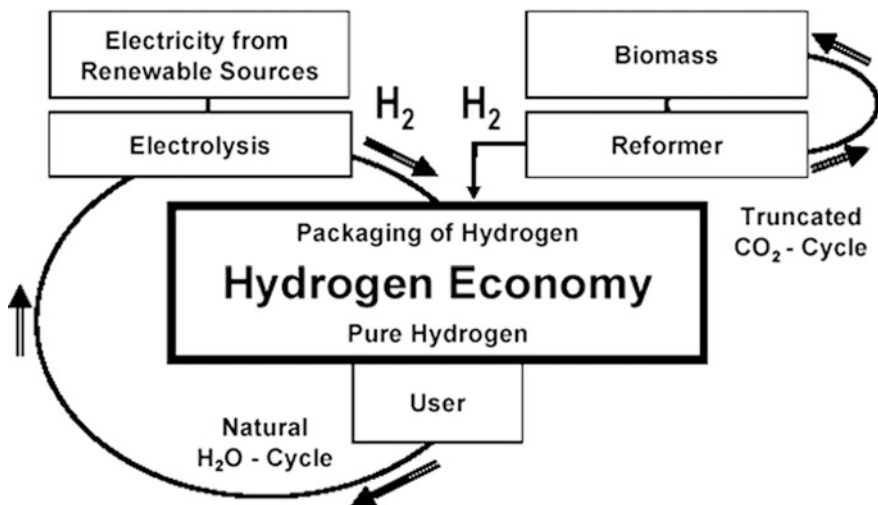


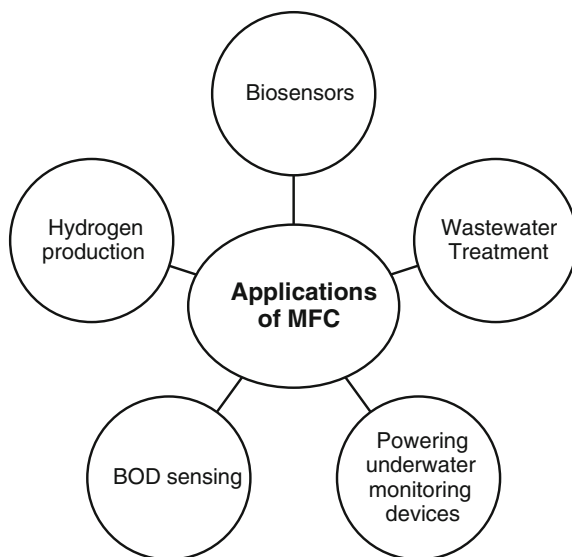
Fig. 2 Sustainable hydrogen production concept diagram (Bard et al. 1985)

Another type of fuel cell is the microbial fuel cell, these are devices where bacteria can grow on one electrode, break down organic matter, while releasing electrons from the organic matter, it is similar to how we get energy, we eat food, we oxidize it, we remove electrons, we send these electrons to the respiratory enzymes and then when we are done with them, we release them to oxygen. We eat and breathe to do this. So when bacteria releases this electron, it creates a potential of about 0.5 V; voltage time current is power, and that is how power is generated from the system. In concept, a real simple system, having two electrodes on either side of the container, bolted together, wastewater is added to the system and you generate electricity.

1.4 The Role of Microbial Fuel Cells as a Technology of Importance

MFCs have been depicted as bioreactors which are the newest approach for generating electricity by oxidation of organic matter present in the wastewater streams (Fig. 3).

Fig. 3 End use application for MFCs to serve bioremediation and bioelectricity generation



2 Microbial Fuel Cells

Optimizing energy recovery from wastewater is a sustainable approach for wastewater treatment and is also of interests to protect and improve the water environment everywhere. There is a large gap between generation and treatment of wastewater for domestic wastewater in developing nations and to facilitate such energy recovery processes microbial fuel cells can be used. The energy utilization research in microbial fuel cells is growing exponentially, but it suffers from established terminology and methodical framework to analyze system functionality. The sheer diversity in the process employed makes it intricate to compare experimental analysis with each other. Studies of such are interdisciplinary with concepts of microbiology, integrated with electrochemistry to serve as a component of environmental engineering (Table 2).

This chapter reports how the organic matter removal efficiency coupled with simultaneous bioelectricity production has been studied with pure and mixed microbial culture, which are naturally found or inoculated into wastewater streams. And how such alternate forms of energy harvesting by addressing and optimizing key parameters such as temperature, pH, and dissolved solutes can potentially contribute to energy security and economic stability across nations where a dire need of energy conversion crisis exist.

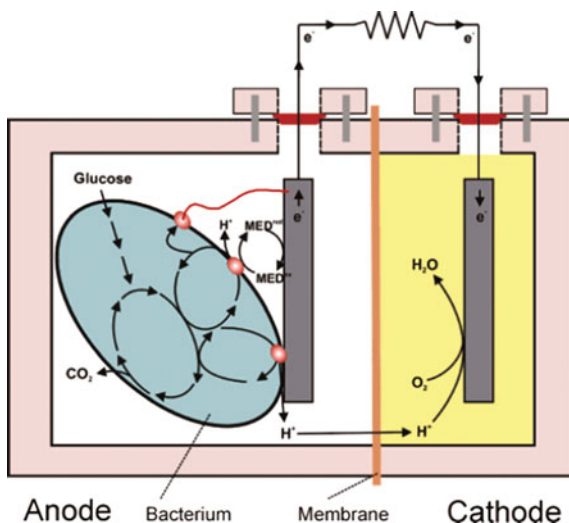
There is a large gap between generation and treatment of wastewater for domestic wastewater in India and to facilitate these renewable energy recovery process; microbial fuel cells can be used. MFCs can be used directly with wastewater or by inoculation with microbial species. Bacteria identified to produce bioelectricity in MFC are metal-reducing bacteria such as *Geobacter metallireducens*, *Geobacter sulfurreducens*, *Clostridium butyricum*, and *Shewanella putrefaciens*.

In microbial fuel cells, bacteria act as a catalyst and oxidize the organic matter and inorganic matter to produce electricity. These are an older invention than the battery. The electrons produced by the microbes from the substrate are transferred to the anode, which is the negative terminal and onto the cathode, which is the positive terminal. These are linked by conductive materials with a load (resistor). Electrons can be transferred by using electron mediators into the anode usage of

Table 2 List of some industries and the contaminants in its wastewater streams

Sources of industrial wastewater	Characterization of wastewater in the discharge stream
Coal-based thermal power plant	Significant levels of lead, mercury, cadmium, chromium, arsenic, and nitrous compounds
Food industry	High concentration of BOD and suspended solids
Iron and steel industry	Ammonia, cyanide, phenols, benzene, and other organics
Paper and pulp industry	High suspended solids (SS), BOD, chlorinated organic compounds
Petrochemical industry	Mineral oils, phenol, high COD and BOD, chromium

Fig. 4 Transfer of electrons by a bacterium in the anode chamber which then produces a three-phase reaction with electrons, protons, and oxygen at the cathode. Thereby, completing the circuit and producing power. Protons produced in the process migrate to cathode using cation exchange membrane (CEM) (Rabaey et al. 2004)



direct membrane electron transfer has also been shown in studies or by use of nanowires. It can be speculated that further undiscovered means can also facilitate such processes (Fig. 4).

2.1 Various Designs of Microbial Fuel Cells

Several configurations are possible with MFC systems, a commonly used and relatively cost-efficient design is the H-shaped two-chambered setup, having two chambers separated by a cation exchange membrane (CEM) such as Nafion (DuPont Co. USA) or a plain salt bridge made from mostly agar and saturated salts (acting as a CEM).

The efficiency in this design lies in selection of the CEM and the reaction chemistry at the cathode in terms of reduction reactions (typically for oxygen). As seen from Figure f, in such setups, the membrane is in the center of the tubes joining the bottle although the system is not restricted to using only tubes, if both the chambers are kept separate. Such systems despite being cost economic are plagued by high internal resistances, thus producing little power. However, such can be used to examine power production using new materials or compound-specific microbial activities.

Some studies have shown high power densities by using ferricyanide as electron acceptor at the cathode. These studies have shown the best fit model for bioelectricity production which is the use ferricyanide as an aqueous catholyte (Catal et al. 2008). However, use of ferricyanide is not sustainable in practice and it must be chemically regenerated. Some geometry of systems includes outer cylindrical reactor along with a concentric inner tube being the cathode as shown in Fig. 5d,

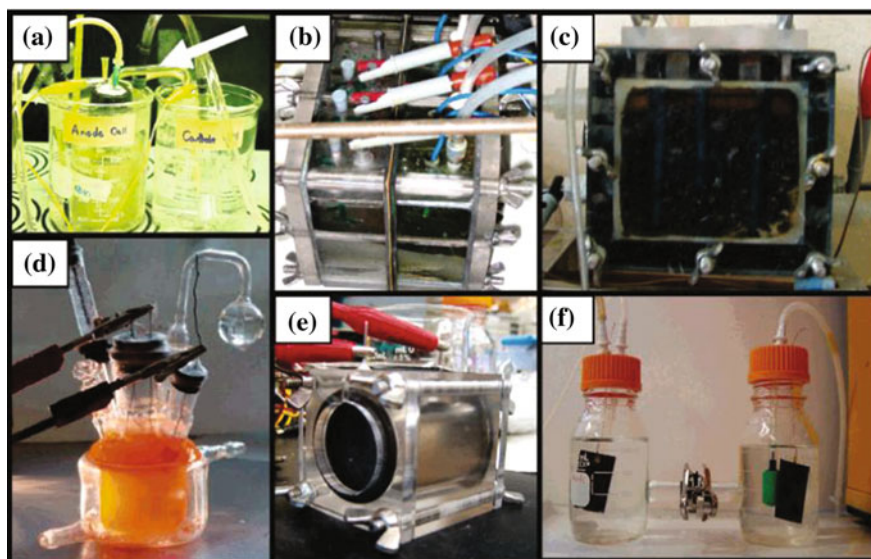


Fig. 5 Different MFC configurations: Setup **a** is a salt bridge MFC using regular glassware (Logan et al. 2006); setup **b** shows batch reactors where membrane separates the anode from the cathode, all bolted together (Rabaey et al. 2005); setup **c** is identical to **b** but has a continuous process as water is recirculated in anode chamber; setup **d** photoheterotrophic type MFC; setup **e** shows a single chambered air-cathode MFC system (Liu and Logan 2004); setup **f** is a two-chambered H-shaped system where gas sparging can be done (Logan et al. 2005)

and having an inner cylindrical reactor (granular media-based anode) with the cathode on the external surface as shown in Fig. 5a.

Another variation is shown in Fig. 5b, which is an up-flow fixed bed biofilm reactor, with continuous fluid flow through the porous anodes toward a membrane that separates the anode and cathode chambers. Some systems as shown in Fig. 5c has been made identical to resemble a hydrogen fuel cell, where the membrane is sandwiched between the cathode and the anode. To increase the current, MFCs can be stacked up and connected in series as shown in Fig. 5e.

Sediment MFCs was initially developed, and it demonstrated that power generation can be sustained by bacteria breaking down the organic matter in the sediment. Since then by developing proper materials, power output has been increased significantly. It is often viewed as an effective bioremediation tool, and it produces bioelectricity at the same time. Some studies used graphite disks platinum mesh electrodes while some have demonstrated its feasibility with modifications at the cathode by increasing the active surface area and using non-corrosive materials (Fig. 6).

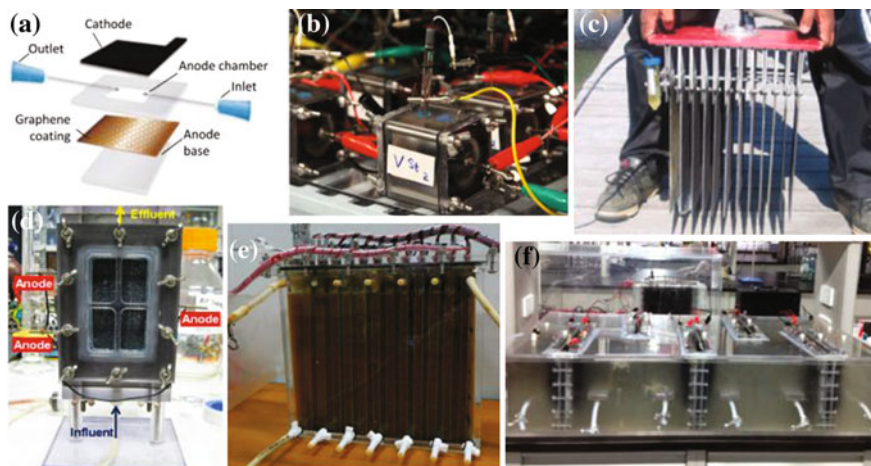


Fig. 6 Design improvement in MFC systems to account limiting factors: Setup **a** shows a micro MFC setup with anode capacity of 25 μ L; setup **b** uses an air-cathode system with low-cost brush anodes; setup **c** shows a sediment MFC exploiting benthic soil; setup **d** shows a three brush electrode setup for a continuous MFC reactor; setup **e** shows a 12 assembly stack system; and setup **f** shows a cassette arrangement for baffled MFCs (Logan et al. 2015)

Table 3 Different microbial electrochemical technologies which are either identical or an extension of MFCs

System names based on design	Mechanism	Notable work
Microbial electrolysis cell (MEC)	Production of hydrogen gas at the cathode, and metal reduction	16
Microbial electrosynthesis system (MES)	Produces soluble organics such as acetate	21
Microbial methanogenesis cell (MMC)	Production of methane at the cathode	13
Microbial reverse electro dialysis fuel cell (MRFC)	Power generation using a RED stack, yield is higher than a standard MFC	33
Sediment microbial fuel cell (s-MFC)	Power generation from marine sediments, soil, and mud	15

The above-mentioned systems with varying configurations with bipolar membranes can facilitate effective recovery of both acid and caustic solutions from the cathode and this has commercial value as well. Alternatively, these solutions can be complemented with minerals to allow for a carbon sequestration technology as shown in Table 3.

2.2 Construction Material for Electrodes

Anode: Material for anode construction should be cost-effective, having good electrical conductivity, and stable during operation. One study showed the utility of non-corrosive stainless steel. Copper-based materials are usually avoided, as it leads to toxic reactions with bacteria and leading corrosion current as well. Carbon emerges out to be the most versatile material, available as graphene, graphite rods, and plates or in the form of cloth, paper, and foam. In addition to that, suitable chemical mediators have also been employed, some of which are given in Table 4.

Graphite brushes are relatively inexpensive materials for anode construction, and also graphite felt electrodes as they are much larger surface area. One study found the relation between anodic materials in terms of reactivity in the order of carbon felt > carbon foam > graphite. Materials such as reticulated vitreous carbon (RVC) with different pore sizes have shown improved performance. It must be mentioned that the long-term effect of biofilm growth on anode surfaces has not been adequately examined.

Cathode: The reduction of oxygen is the primary reaction at the cathode and is associated with high cost because of the potential barrier when performed on graphite or carbon-based electrodes, implicating the need for catalysts such as platinum (Pt). In a MFC, activity loss for platinum can occur due to side reactions and other losses.

Some of the alternatives, however, are proposed, but different configuration can be possible. Some of the published literature shows that manganese oxides, iron phthalocyanine (FePc), polypyrrole (Ppy), cobalt tetramethoxyphenylporphyrin (CoTMPP), Fe³⁺ cathode made with ferric sulfate, cathodes based on high active surface area such as graphite-granule cathodes, and recent advancements have shown the favorable use of activated carbon because of its adsorption properties and ease of operation.

Table 4 Chemical mediators added to improve anode performance

Substrate	Microbes	Current density (mA/cm ²)	References
Fe (III) and Mn (IV) linked with neutral red	Mixed culture (anaerobes) from STP	0.175	HaoYu et al. (2007)
Sucrose	Anaerobic sludge from septic tank	0.190	Call et al. (2009)
Food industry wastes	Aerobic sludge	0.025	Rabaey et al. (2004)
Food waste	Anaerobic culture	0.045	Davis and Yarbrough (1962)
Beer brewery wastewater	Anaerobic mixed culture	0.18	Zhen et al. (2015)

Literature studies have shown that the above-employed cathodes have produced less power densities except activated carbon in comparison with platinum. As the above, materials are cost-effective and are easily available compared, this makes them a promising avenue to explore further MFC research.

2.3 Construction Material for Membranes

Membranes are primarily used in double-chambered MFCs, as a process to keep the anode and the cathode fluids separate. These membranes must be permeable in nature to facilitate movement of protons generated at the anode to migrate to the cathode. Membranes also serve as a barrier to avoid transfer of other species in the chamber. For example, these are effective in reducing unwanted substrate flux from anode to the cathode and oxygen from the cathode to the anode, having a positive influence on Coulombic efficiency of the system.

The most commonly used CEM is Nafion (Dupont Co., USA) while, Ultrex CMI-7000 (Membranes International Incorp. NJ, USA) has also been employed (Table 5).

2.4 Use of Wastewater/Xenobiotics for Bioremediation and Simultaneous Bioelectricity Generation

The working and proficiency of MFC to a great extent depend upon the kind of materials utilized for the metabolism of microorganisms. Researchers have revealed use of straightforward and complex natural/inorganic sources which introduced in wastewaters from various sources acting as a substrate for power generation. The utilization of wastewater as a medium for substrate is favorable; to start with, the electrical power is generated, and second, it drives treatment of wastewater. Broad research has demonstrated that these chemical substrates, for example, agro wastes are oxidized by various types of microorganisms and cause power generation. Here, we have talked about some pollutants, which are employed in MFC for power generation (Table 6).

3 Fundamentals of Bioremediation with MFC

3.1 Types of Substrates Used in MFCs

Microbial communities in MFCs can function as a tool for bioremediation. In addition, they also play a significant part in regulating the natural cycles of

Table 5 List of microbial fuel cell membranes, cation exchange membrane (CEM), anion exchange membrane (AEM), bipolar membranes (BPM), and other novel materials

Membrane type	Performance	References
Ultrex ^R AMI-7001 (AEM), Nafion ^R 117, Ultrex ^R CMI-7000 (CEM), Ultrafiltration membranes (UF-0.5 K, UF-1 K, UF-3 K)	<ul style="list-style-type: none"> • AEM has the best performance with the highest maximum power density (610 mW/m²) and CE (72%) compared to other membranes • All the membranes have almost the same internal resistance (1230 ± 744 Ω till 1308 ± 718 Ω) except UF-0.5 K (6009 ± 758 Ω) • Nafion has the highest oxygen mass transfer coefficients ($k_o = 1.3 \times 10^{-4}$ cm/s) 	Fornero et al. (2008)
Ultrex ^R AMI 7001, Nafion ^R 117, Ultrex ^R CMI 7000, Hyflon ^R , Zirfon ^R , Nylon meshes (NY 11, NY 20, NY 41, NY 6 H), Glass fiber filter (GFAPFF, GFAP40) J-cloth, Celgard ^R , SciMat ^R	<ul style="list-style-type: none"> • Ultrex^R AMI 7001, Celgard^R, Nylon meshes (NY 20, NY 41, NY 6 H), GFAP40 and J-cloth have the lowest pH splitting extent • Porous structured GFAP40 has the highest ionic conductivity • Nylon meshes (NY11, NY20, and NY41) and Hyflon^R have the lowest ionic conductivity 	Lee et al. (2010)
Fumasep ^R FAB (AEM), Nafion ^R 117 (CEM), Fumasep ^R FBM (BPM), Charge mosaic membrane (CMM)	<ul style="list-style-type: none"> • AEM has the highest current density among all the membranes. • The BPM with the highest protons/hydroxyl ions transport numbers has the lowest pH increase in cathode, followed by AEM, CMM and CEM 	Wang et al. (2008)
Ultrex ^R AMI-7001 (AEM) and Ultrex ^R CMI-7000 (CEM)	<ul style="list-style-type: none"> • AEM has higher performance compared to CEM with open circuit voltage and maximum power density at variations of air-cathode pressure 	Zhen et al. (2015)

ecosystem including the carbon cycle and water cycle. It is important for interactions in microbial communities so as to develop an effective design of microbial fuel cell. In microbial systems, there is a stronger interaction between the bacteria, due to the coupling of the electron signal with the energetic state of the cells via the electron transport chain. Thus, alternative strategies for analysis and optimization must be undertaken, which take into account the specificity of the interactions between cells in bacterial community. In turn, the relation between biofilm development and reactor operation is of interest to venture into.

In MFCs, substrate is often considered critical to obtain desired power densities. A great variety of substrates can be used in MFCs for power generation depending upon the culture of microbe; it can be pure organics to complex mixtures of organic effluents or introduced substrates for the wastewater. In these studies, the major objective has been the efficient COD removal from the wastewater and its safe

Table 6 Bioremediation studies with natural wastewater sources and power generation using MFCs

Wastes/pollutant	Source of wastewater	Concentration	Power density	References
Hexavalent chromium	Leather industry, metallurgy	39.2 mg/L	2.4 W/m ³	Wang et al. (2008)
Agro wastes (cyanide-rich streams)	Farming, poultry processing, slaughterhouses	1086 COD-mg/L	22.19 W/m ³	Prasertsung et al. (2012)
Cellulose	Wheat straw, rice mill, corn stover	0.5 g COD/l	70 mW/m ³	Clauwaert et al. (2008)
Selenite	Glass manufacturing, electronic industry	25 mg/L	2900 mW/m ²	Cai and Zheng (2013)
Nitrate and sulfite	Fertilizer industry, animal wastes	10.5 mg/L (nitrate) 60 mg/L (sulfite)	31.92 mW/m ²	Catal et al. (2009)

discharge to the environment and bioelectricity generation in the process. Diverse kinds of substrates including single substrate such as glucose, acetate or complex substrates used from the chemical industry, pharmaceutical waste, and from dairy or food wastewater, etc., have been tested as anolyte in MFCs for generation of electricity. With varying reactor configuration, active surface area, inconsistency of methods used, it is intricate to compare the data among each other for system characterization.

The current density is commonly used unit to measure the performance of a MFC. It can be described in terms of surface area of anode (mA/m²) or volume of the cell (current generate per unit volume, (mA/m³)).

Some commonly used substrates include the following:

Lignocellulosic Biomass: Lignocellulosic biomass serves as a promising feed-stock for cost-effective energy production in MFCs due to renewability and availability. However, cellulosic biomass cannot have direct utilization by the microbes. Conversion to monosaccharides or other compound with low molecular weight is needed.

Acetate: Acetate is a simple substrate commonly used in MFCs due to its inertness toward metabolic conversions (fermentations and methanogenesis) at a temperature. However, the use of acetate rules out the possibility of enriching a diverse microbial community and is not very practical as this contributes to energy costs.

Glucose: A major carbon source that can work as a nutrition source for diverse microbial community.

Dyes: Azo dyes are the most commonly used synthetic dye and are present in the dyes and textile-based industries. These dyes have colors which can lead to severe environmental problem and hence, their removal is of utmost importance. These dyes are not only having high toxicity but can also interrupt the interaction of light

Table 7 Performances of some commonly employed substrates in different MFC systems

Substrate	Concentration	Current density (mA/cm ²)	References
Cellulose	4 g/L	0.02	Nevin et al. (2010)
Acetate	1 g/L	0.8	Zhen et al. (2015)
Azo dye with glucose	300 mg/L	0.09	Han et al. (2017)
Glucose	6.7 mM	0.7	Catal et al. (2008)
Synthetic wastewater	16 g COD/day	0.017	Aldrovandi et al. (2009)

and oxygen with water bodies. Using these dyes as substrate is of interest among some researchers, as this can lead to color removal from the wastewater and simultaneously generate electricity.

Chemical Wastewater: Chemical wastewater can be used as a substrate, to conduct control experiments in terms of pH, conductivity, and organic loading rate. Several chemical compounds have been used for bacterial growth in wastewater contains reduced sulfur species and redox mediators (e.g., cysteine) that can serve as an abiotic electron donor, and power production can be increased. However, such systems are not practical as energy cost is increasing with the consistent use of these chemicals (Table 7).

3.2 Various Microorganisms Employed in MFC

MFCs are devices which utilize microorganisms and oxidizes organic matter present in substrates biologically, providing electrons to the electrode. A number of substrates having different cultures such as *Pseudomonas*, *Geobacter*, *Shewanella*, *Clostridium*, and *Desulfuromonas* can be used in a MFC for electricity generation and hence for other benefits. The composition of these bacterial communities that can be maintained in an MFC is an area of active research along with factors like their interactions in biofilms and growth kinetics (Table 8).

Aside from the bacterial species helped by mediators to exchange electrons, a few microorganisms can exchange the electrons oxidized from natural matter to anodes and cathodes without a mediator. Among the electrochemically active microscopic organisms are *Aeromonas hydrophila*, *Shewanella putrefaciens*, *Rhodospirillum rubrum*, and *Geobacter*. In MFCs, electrons can be exchanged by means of the surface of bacterial cells; microscopic organisms can exchange electrons through self-delivered mediators; electrons exchange is identified with nanowires created by microorganisms. Without nanowires, a few microorganisms create pili or nanowires on their outer film and hence can exchange their electrons. It is interesting to note

Table 8 MFC studies with pure bacteria cultures inoculated into wastewater streams with appropriate substrates

Microorganisms	Substrate	Power density (mW/m ²)	References
<i>Shewanella putrefaciens</i>	Glucose	355.5	Logan et al. (2006)
<i>Shewanella oneidensis</i>	Lactate	24	Ringeisen et al. (2006)
<i>Escherichia coli</i>	Complex substrate	600	Zhang et al. (2007)
<i>Pseudomonas</i> sp.	Peptone	979	Zhang et al. (2007)
<i>Nocardiopsis</i> sp. <i>KNU</i>	Carboxymethyl cellulose (CMC)	162	Ringeisen et al. (2006)

that nowadays so much research is going into nanomaterials while these microbes have been using nanowires for millions of years.

3.3 Various Wastewater Analysis Parameters and Its Effectiveness in the MFC

The industrial developments increase in population density and the absence of energy sources are the significant reasons which help in the development and hence improvement of renewable energy technologies in this energy era. Bioelectrochemical systems (BESs) are one of the rising practical advances which is able to generate energy from wastewater. The usage of BESs in the treatment of wastewater additionally helps to control contamination (or pollution) and hence economy of the treatment framework. Not only the electricity generation but also, bioremediation of waste, biosensing and the chemicals (hydrogen, methanol, etc.) generation are likewise significant uses of such BESs (Table 9).

Organic matter is the major component of wastewater, and its amount has been measured as BOD and COD traditionally. Some important parameters related to wastewater are mentioned below.

COD: The COD refers to the chemical oxygen demand, an analysis that measures chemical oxidation of the majority of organic matter present in the wastewater sample. COD measurements are needed for mass balances in wastewater treatment.

BOD: Refers to biochemical oxygen demand. The BOD analysis measures the oxygen used by microbes for oxidation part of the organic matter. The standard BOD analysis takes 5 days (BOD5), but alternatives used are BOD1 and BOD7, respectively. Starting with very high values of BOD and COD's of wastewater the values obtained after putting in a MFC has seen significant reduction even up to more than 60%.

Table 9 Wastewater parameters characteristics, testing these parameters before and after use from MFC gives the effectiveness of bioremediation (Pant et al. 2010)

General parameters		Solvents and alcohols (mg/L)	Volatile fatty acids (mg/L)
pH, TS (kg/m ³), TSS (kg/m ³)	Inorganic compounds	Acetone	Acetate
Conductivity (mS/cm)	Phosphorous (mg/L)	Methanol	Propionate
TCOD (kg/m ³)	Sulfate (mg/L)	Ethanol	Butyrate
SCOD (kg/m ³)	Nitrate (mg/L)	Propanol	–
BOD (kg/m ³)	Nitrogen Ammonia (mg/L)	Butanol	–

TSS: Total soluble solids or **TSS** is the amount of total suspended solids in the sample. In other words, the organic and inorganic materials are in the form of suspension in the wastewater. The TSS is generally not estimated while using a MFC, but it can become a factor to be evaluated as to see effectiveness of MFC's.

FOG: FOG stands for fats, oil, and grease and is used to determine the hydrocarbon components of the wastewater sample.

Bacteriological Analysis: This is done to characterize the bacteria present in the waste sample so as to get the virulent strain which is responsible for power generation. Generally, mixed cultures are more power generating than pure cultures. Such analysis can be done using real-time polymerase chain reaction (RT-PCR).

3.4 *Oxidizing and Reducing Agents in the Anode and Cathode*

In most of the MFCs, electrons reach the cathode and combine with proton which diffuses from the anode side through a salt bridge or membrane to cathode side and the oxygen is provided from air hence obtained product is water. Chemical oxidizers, for example ferricyanide or Mn (IV), can likewise be utilized despite the fact that these must be replaced or recovered. On account of metal particles, for example, Mn that is diminished from Mn (IV) to Mn (II), microscopic organisms can catalyze the re-oxidation of the metal utilizing dissolved oxygen.

Anode: The simplest materials for anode electrodes are graphite plates or rods, as they are relatively inexpensive, easy to handle and have a defined surface area. To increase the anode performance, different chemical and physical strategies have been followed. One study used fused Mn (IV) and Fe (III) and utilized covalently connected neutral red to intercede the electron exchange to the anode. Electrocatalytic materials, for example polyanilins/Pt composites, have likewise been appeared to enhance the present era through helping the immediate oxidation of microbial metabolites.

Cathode: Due to its good performance, ferricyanide ($K_3 [Fe (CN)_6]$) is very popular as an experimental electron acceptor in microbial fuel cells. The best advantage of ferricyanide is the low over-potential utilizing a plain carbon cathode, bringing about a cathode working potential near its open circuit potential. The best hindrance, in any case, is the inadequate re-oxidation by oxygen, which requires the catholyte to be consistently regenerated. Moreover, 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.

Oxygen is the most appropriate electron acceptor for a MFC because of its high oxidation potential, accessibility, ease (it is free), supportability, and the absence of a substance waste item (water is shaped as the main finished result).

4 Fundamentals of Bioelectricity Generation with MFC

4.1 Basics of Voltage Generation

Microbial power modules (MFCs) are gadgets that utilize microscopic organisms as the catalysts to oxidize natural and inorganic matters and produce current. Electrons created by the microscopic organisms from these substrates are exchanged to the anode (negative terminal) and stream to the cathode (positive terminal) connected by a conductive material containing a resistor, or worked under a load (i.e., creating power that runs a gadget). By tradition, positive current streams from the positive to the negative terminal, inverse to that of electron stream. Hence, voltage is generated by means of this transfer of electrons and protons.

4.2 Thermodynamics and Electromotive Force

Power is produced in a MFC just if the general response is thermodynamically great or favorable. The response can be assessed as far as Gibbs free energy communicated in units of Joules (J), which is a measure of the maximum work that can be obtained from the response or reaction is calculated as:

$$\Phi(G_r) = \Phi(G_r^0) + RT \ln(Q)$$

where

- $\Phi (G_r)$ is the Gibbs free energy for the specific given conditions.
- $\Phi (G_r^0)$ is the Gibbs free energy under standard conditions usually defined as 298.15.
- $K, 1$ bar pressure, and 1 M concentration for all species.
- $R (8.314 \text{ J mol}^{-1} \text{ K}^{-1})$ is the universal gas constant.

T (K) is the temperature in absolute scale, and
 Q (dimensionless) is the reaction quotient calculated as the activities of the products divided by those of the reactants.

The standard reaction Gibbs free energy is generally calculated from the energies of formation of organic compounds in water, available from many sources. For MFC computations, it is more advantageous to assess the response as far as the general cell electromotive force (emf), E_{emf} (V), characterized as the potential contrast between the cathode and anode. This is identified with the work, W (J), created by the cell as:

$$W = E_{\text{emf}}Q = -\Phi(G_r)$$

where $Q = nF$ is the charge transferred in the reaction, expressed in Coulomb (C), determined by the number of electrons transferred in the reaction, n is the number of electrons per reaction mol, and F is Faraday's constant (96,485.3 C/mol).

Even the use of Nernst equation is more effective compared to the above ones. The Nernst equation is

$$E_{\text{emf}} = E_{\text{emf}}^0 - (RT/nF)\ln(K)$$

4.3 Standard Electrode Potentials and Efficiencies

Standard Electrode Potentials: The responses happening in a MFC can be broken down as the half-cell responses, or the different responses happening at the anode and the cathode. As per the IUPAC convention, standard conditions (at 298 K, 1 bar, 1 M) are accounted for as a reduction potential, i.e., the response is composed as consuming electrons (Table 10).

For example, $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$, a reduction reaction hence will take place at cathode

Table 10 Half-cell potentials against SHE for MFCs

Electrode	Reaction	E_0 (V)	Conditions	E_{MFC} (V)
Anode	$2\text{HCO}_3^{3-} + 9\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_3\text{COO}^- + 4\text{H}_2\text{O}$	0.187 ^a	$\text{HCO}_3^{3-} = 5 \text{ mM}$, $\text{CH}_3\text{COO}^- = 5 \text{ mM}$, pH = 7	-0.296
Cathode	$\text{MnO}_2(\text{s}) + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$	1.23	$[\text{Mn}^{2+}] = 5 \text{ mM}$, pH = 7	0.47
	$\text{Fe}(\text{CN})_6^{3-} + \text{e}^- \rightarrow \text{Fe}(\text{CN})_6^{4-}$	0.31	$[\text{Fe}(\text{CN})_6^{3-}] = [\text{Fe}(\text{CN})_6^{4-}]$	0.361

Therefore,

$$E_{\text{cat}} = E_{\text{cat}}^{\text{O}} - (RT/4F) \ln \left\{ 1 / (p_{\text{O}_2}) * [\text{H}^+]^4 \right\}$$

The cell emf is calculated as

$$E_{\text{cell}} = E_{\text{cat}} - E_{\text{an}}$$

where the minus sign is a result of the meaning of the anode potential as reduction response (despite the fact that an oxidation response is happening). The power delivered by a MFC hence relies on upon the decision of the cathode, and this ought to be considered when looking at power densities accomplished by various MFCs. The conditions for the reaction at cathode and anode side should be same; otherwise, different levels of power output will be obtained.

Efficiencies: MFC efficiency depends on the material for electrodes, performance of the membrane, the ohmic and non-ohmic losses, and a favorable thermodynamic reaction. Some important parameters in this context are as follows:

Treatment Efficiency: MFCs have been proposed as a technique to treat wastewater, and along these lines, it is imperative to assess the general performance using biochemical oxygen demand (BOD), chemical oxygen demand (COD), or total organic carbon (TOC) removal. Different elements may likewise be imperative, for example, solvent versus particulate removal, and supplement, or nutrient removal. The choice of treating efficiency is arbitrary but mostly used is COD removal efficiency and can be found out by the ratio between the removed and influent COD. This parameter measures the amount of the accessible “fuel” that has been changed over in the MFC, either into electrical current (by means of the Coulombic efficiency) or biomass (by means of the development yield) or through reaction with electron acceptors (e.g., oxygen, nitrate, and sulfate).

Coulombic Efficiency: The Coulombic efficiency is defined as the ratio of total Coulombs actually transferred to the anode from the substrate to maximum possible Coulombs if all substrate removal produced current. The total Coulombs obtained (Logan et al. 2005) is as:

$$\varepsilon_{\text{Cb}} = \frac{M \int_0^{t_b} I dt}{F b v_{\text{an}} \Delta \text{COD}}$$

where $M = 32$, the molecular weight of oxygen, F is Faraday’s constant, $b = 4$ is the number of electrons exchanged per mole of oxygen, v_{an} is the volume of liquid in the anode compartment, and ΔCOD is the change in COD over time t_b .

For continuous flow through the system, the Coulombic efficiency is as follows:

$$\varepsilon_{\text{Cb}} = \frac{MI}{F b q \Delta \text{COD}}$$

where q is the volumetric influent flow rate, and ρCOD is the difference in the influent and effluent COD. Factors that reduce Coulombic efficiency are competitive processes and bacterial growth. Bacteria unable to utilize the electrode as electron acceptor are likely to use substrate for fermentation and/or methanogenesis.

4.4 Polarization Curves and Open Circuit Voltage

4.4.1 Polarization Curves

A polarization curve describes a relationship between voltage and current. A potentiometer is used to record polarization curve for anode, cathode, and for entire MFC using a potentiometer. Thus, voltage is measured and the current is calculated using the Ohm's law. The polarization curve can be categorically divided into three zones (Fig. 7):

Power Curves: A power curve (or power density curve) is a derivative of the polarization curve, as it is computed from the polarization curve. A power curve depicts power density as a function of current density. Power density for open circuit is zero. Maximum power point (MPP) is position where the power density and current reach the apex value. Beyond the MPP, the power drops due to increase in ohmic resistance and decrease in power production.

Open Circuit Voltage (OCV): Cell voltage that is measured in the absence of current or resistor is known as the open circuit voltage. Ideally, the OCV should approach the cell EMF (Fig. 8).

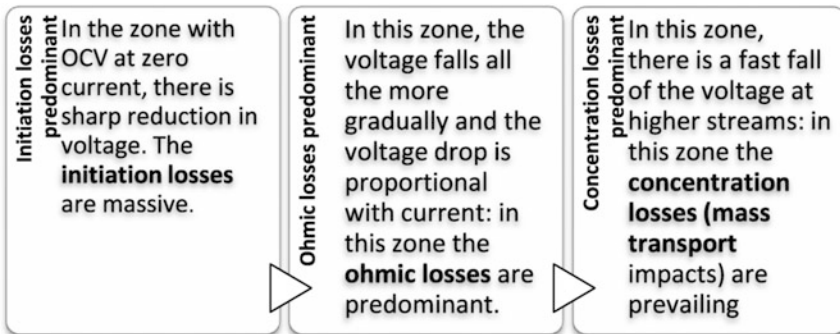


Fig. 7 Overview of losses associated with MFC systems

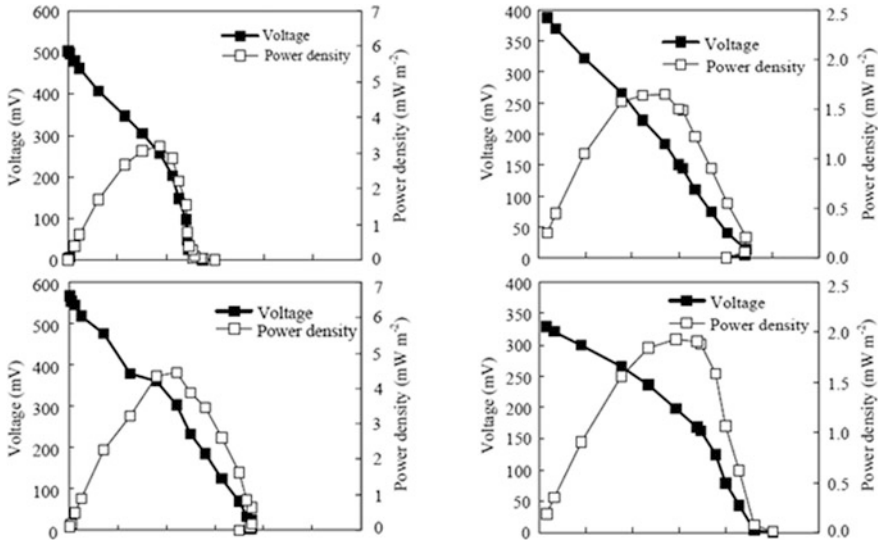


Fig. 8 Polarization and power curves for MFC performance (Lee et al. 2010)

4.5 Types of Losses in MFC

The maximum attainable MFC voltage (emf) is theoretically on the order of 1.1 V (see above). However, the measured MFC voltage is considerably lower due to a number of losses.

The difference between the measured cell voltage and the cell emf is known as overvoltage, and it is the sum of the over-potentials of the anode and the cathode and the ohmic loss of the system.

$$E_{\text{cell}} = E_{\text{emf}} - \left(\left| \sum \eta_a \right| + \left| \sum \eta_c \right| \right) + IR$$

- $\sum \eta_a$ = Over-potential of the anode
- $\sum \eta_c$ = Over-potential of the cathode
- IR = Sum of all ohmic resistances

The over-potentials of the electrodes in an MFC they can roughly be categorized as follows: (i) activation losses; (ii) bacterial metabolic losses; and (iii) mass transport or concentration losses. Some of the major losses in MFCs are described in the following page.

Ohmic Losses: The ohmic losses (or ohmic polarization) in an MFC occur due to the resistance to electron flow through the membrane electrode assembly (MEA) and the resistance to the flow of ions through the CEM. Ohmic losses can be lessened by limiting the electrode spacing, also by utilizing a membrane that has

low resistivity, checking altogether all contacts, and solution conductivity which are at the upper limit tolerated by the bacteria.

Activation Losses: Activation loss (also called activation polarization) occurs whenever a reaction occurs on the electrode surface. This energy loss is due to the activation energy required for an oxidation/reduction reaction to occur. Activation losses increase substantially at lower currents and gradually with increase in the current density. An effective way to lower these losses is to increase the electrode surface area and operating temperature.

Concentration Losses: Loss in concentration (or concentration polarization) happens when the rate of mass transport of a species to or from as far as possible limits current generation. Such happen for the most part at high current densities because of confined mass exchange of synthetic species by diffusion to the cathode surface while at anode, the concentration losses are brought on by constrained supply of diminished species toward the terminal or by restricted release of oxidized species from the cathode surface. This surges the proportion between the oxidized and the lessened species at the terminal surface which can deliver an expansion in the anode potential. At the cathode side, a drop in cathode potential may happen. Mass transport restrictions in the mass liquid can restrain the substrate flux to the biofilm, which is a different kind of concentration loss.

Microbial Losses: In a MFC, microscopic organisms transport electrons from a substrate at a low potential to the last electron acceptor at a higher potential through an outer circuit. In a MFC, the anode is the last electron acceptor and its potential decides the vitality pick up for the microscopic organisms. The more prominent is the distinction between the redox capability of the substrate and the anode potential, the higher is the metabolic vitality pick up for the microbes, yet the lower is the most extreme achievable MFC voltage. To boost the MFC voltage, the capability of the anode ought to be kept as low (negative) as could reasonably be expected. Be that as it may, if the anode potential turns out to be too low, electron transport will be repressed and maturation of the substrate (if conceivable) may give more prominent vitality to the microorganisms.

5 Conclusion

The success of any technology depends upon how it influences the energy market and the perception of the common public since MFCs can produce electricity while removing pollutants and other organic matter from wastewater streams, it can be speculated to offer advantages such as:

1. Low-cost electricity production from everyday waste materials.
2. Bioelectricity will be available all year around, as waste and xenobiotics are readily available.
3. Every household can produce a certain amount of electricity.

4. MFCs can be critical for nations in the African continent where in some places, the energy infrastructure has still not arrived.
5. Working with parallel with bioremediation and generate bioelectricity, making the process sustainable (Fig. 9).

Thus, MFCs represent powerful predictive tools, which will aid the design of systems exploiting bacterial capabilities. In MFC systems, chemicals are reduced at the cathode, and in some systems, it is possible to achieve chemical oxidation at the anode in situations when high concentration of biodegradable organics is present in the wastewater. For this to work, however, sufficient electron acceptors should be present at the cathode. For example, if a site is contaminated with petroleum or gasoline, the water can be channeled through consecutive hydraulic chambers similar to that used for zero-valent iron walls for treating chlorinated aliphatics in groundwater. First section should have the anode, with material of construction such as graphite granules, where the chemical will be oxidized (assuming anaerobic conditions) on the anode providing current to the cathode. The second section would contain a cathode, tube cathodes can be considered, and where oxygen will have the advantage of providing the additional electron acceptor into water to allow for either continued treatment or to increase the concentration of oxygen in the groundwater; this concept was explored with an air-cathode MFC for petroleum-contaminated groundwater. Power generation was 120 mW/m^2 which suggests MFC systems similar to this can be used to enhance bioremediation of petroleum-contaminated groundwater under anaerobic conditions (Fig. 10).

MFCs are being developed utilizing an assortment of materials in a continually expanding quality of designs. These frameworks are worked under a scope of conditions that incorporate contrasts in temperature, electron acceptor, anodic surface area, pH, operation time, and reactor sizing. In some cases, the operating conditions and even electrical components, such as internal resistance, power density, are missing, such has made it difficult to analyze and interpret results among similar systems. However, the list of accomplishments in our understanding of how electricity is produced in an MFC and how effective systems cost with increased power density are impressive. Precious metals, such as platinum, are no

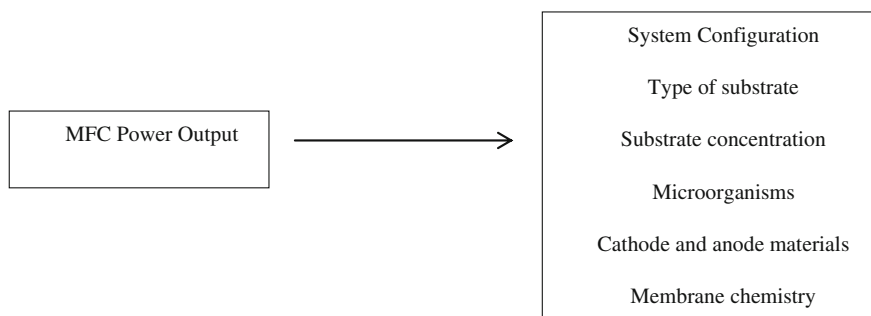


Fig. 9 Factors important for MFC performance and critical for commercial success

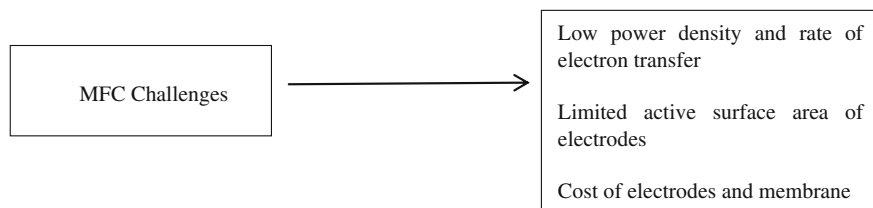


Fig. 10 Limitations associated with MFCs addressing which are a key to commercial success

longer needed on either electrodes, and use of non-precious metals such as cobalt, iron has produced similar power densities when coupled with suitable oxygen reducing agents.

The scope of MFC research is not just restricted to wastewater treatment as modified MFCs called BEAMRs can be used to achieve bio-hydrogen from any biodegradable matter, and such systems have shown potentials to cross the “fermentation barrier” with maximum possible conversion efficiency. For MFCs, the ultimate achievement will be when they can be solely used as a method of renewable energy production; right now, it might face challenges to grow in the shadow of large fossil fuel industries, but advances in power densities, reductions in material costs, and a global need to produce power from non-CO₂ sources will make MFCs practical for electricity production. The progress of such remains in the hands of researchers, who believe that MFC technologies are a part of the bright and promising future made on the foundation of a new generation of electrogenic reactor systems.

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