# Green approach for energy production by waste stabilization

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In recent times, there has been a gap between the demand and supply of energy and there needs to be a reduction of the carbon footprint. Also, the depletion of non-renewable sources of energy has led to the intensification of research in the area of renewable sources of energy, since the reliance on fossil fuels is unsustainable. One of the most promising technologies in this area is the microbial fuel cell (MFC), which is not just a sustainable, eco-friendly and self-sustaining source of energy, but also an effective method for the treatment of wastewater. In MFCs, electrochemically active bacteria convert the organic substrate directly into energy from eco-friendly reduced compounds. These cells can not only use carbohydrates as the substrate but also certain complex substrates present in wastewater. In this review paper, various designs of the MFC, its characterization and performance have been presented. The performance of an MFC depends on a number of different factors such as the material of the anode and cathode used, the choice of anode microbial catalyst and cathodic electron acceptor, and the amount and type of substrate available in the anaerobic anodic chamber. The recent updates in the research of MFCs are also presented in this paper and it addresses the different configurations of the cell, their effect on its performance, and ways to improve its performance in order to make it economical.

Keywords: Microbial fuel cells; Wastewater; Bioelectrochemical system

#### INTRODUCTION

The energy crisis has increased a great deal in the past few years and it is evident that we need an alternative source of energy to make up for it. Also, it is highly unlikely that a single source of energy will be in a position to replace the use of fossil fuels [1]. Therefore, we require several alternatives to be used under different situations. One of these is the MFC which has recently received a lot of attention since it can be used to generate electricity by converting the energy stored in organic compounds without causing any pollution to the environment, with no net carbon emission, and can also be used in wastewater treatment. Unlike most fuel cells, MFCs don't require metal catalysts at the anode [2]. Biocatalysts (microorganisms) are used, which biologically oxidize organic substrate and transfer electrons to the anode, which travel externally to the cathode, producing electricity. The organic matter used here is versatile, ranging from simple molecules, to complex mixtures of organic wastes [3], making it an ideal source of renewable bioenergy.

Taking glucose as a substrate, the reactions occurring in the anodic and cathodic chamber, respectively, are:

• Anodic reaction  $C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24e^- + 24H^+$ 

- Cathodic reaction
- $O_2 + 4e^- + 4H^+ \rightarrow H_2O$

In order to make the use of MFCs economical, research is going on to increase its power output, which may depend on the available organic substrate and its particle size. Some MFCs are currently in use and certain applications of the MFCs are being worked upon. This review highlights the important parameters of the MFC, its design, mechanism and its applications.

The concept of MFCs is not new. The earliest hypothesis was demonstrated in 1910 [4], but it didn't gather much attention, due to low current density, low power output, and the use of electron mediators, to carry electrons from the cell to the anode. Research in the area of MFCs intensified after a major breakthrough in this field, which suggested that there exist certain microbes which can transfer electrons directly to the anode. Shewanella putrefaciens is one of the biochemically active bacteria which transfer electrons from the interior of the cell membrane to the anode. A bacterial strain. by the name of Geobacter sulfurreducens KN400, is said to be capable of higher current production, about eight times more efficient as compared to other strains [5].

The bacteria used to oxidize organic substrates in mediator MFCs include *Pseudomonas aeruginosa*, *Proteus mirabilis*, *Actinobacillus succinogenes*, *Streptococcus lactis*, *Erwinia dissolvens*, etc. [6]. These bacteria oxidise organic matter and do not pass on the electrons during metabolic activity

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directly to the anode. Instead, they transfer these electrons to external mediators, such as thionine, methyl viologen, humic acid [7], which act as carriers for electrons from bacterial cells to the anode. The efficiency of these types of MFCs is very low and the mediators used are expensive and toxic, so the current research is focused on mediatorless MFCs only.

In mediatorless MFCs, the microbes used belong to the class of exoelectrogens like *Geobacter metallireducens*, *Geobacter sulfurreducens*, *Rhodoferax ferrireducens*, *Shewanella putrefaciens*, etc. [8]. The exoelectrogenic bacteria come in direct association with the anode and transfer electrons produced during oxidation to it either through protein carriers located in the cell membrane like porin-cytochrome complexes or through special cell membrane projections, like pilli, which act as microbial nanowires [4, 9].

One of the recent researches in MFC development involves the infusion of silver atoms in bacterial cells. This research is based on experiments which were carried out on the bacterial species, Shewanella oneidensis. These bacteria create a biofilm around the electrode in the anodic chamber and oxidise the substrate into smaller molecules, producing electrons as a by-product. The electrons are then carried outside the cell through the cell membrane, where they are received by the anode and transferred to the cathode through an outer circuit in order to generate an output current. But the rate at which the electrons diffuse outside the cell through the cell membrane, is very low, due to which only a small output current or power density is obtained. In one of the experiments, the nanoparticles of silver were added to the anode. These nanoparticles released silver ions, which were reduced by electrons released in the metabolic activity of microbes, into silver and were incorporated inside these bacterial cells, wherein these silver atoms worked as transmission wires for capturing and carrying the electrons, produced during metabolic activity, at very high rates, through the membrane to the anode. This infusion of silver atoms inside microbes increased the current density by many folds.

# Design of the MFC

A prototypical MFC has two chambers: a cathodic chamber and an anodic chamber. These chambers are interconnected either by a salt bridge or a proton exchange membrane.

Oxidation of substrate occurs inside the anodic chamber, which results in the release of electrons and protons [10, 11]. In order to avoid the transfer of electrons directly to a final electron acceptor, i.e., 70 oxygen, the anodic chamber is made anaerobic (deprived of oxygen). Also, the microbes used in the MFCs are mainly anaerobic in nature, therefore, the presence of oxygen will not affect their metabolism. Anaerobic conditions can be created by the purging technique. In this technique, a vacuum is created inside the anodic chamber and this vacuum pressure is released by nitrogen. The performance of an MFC depends on several factors, out of which the material of the electrode is an important one [4, 12]. The electrode, or anode, used in the anodic chamber, must possess certain qualities like high conductivity, resistance to corrosion, biocompatibility, high surface area and should be chemically stable [9, 13, 14]. In most MFCs, the electrodes used as anodes are made up of carbon like graphite rods.

The cathodic chamber involves the reduction of the final electron acceptor that may be oxygen or any other oxidizing agent. In case the final electron acceptor is oxygen, water is the by-product. The electrode used as the cathode is generally made of copper or graphite, due to its low-cost and high performance [9] The reduction of oxygen on electrodes made of carbon is very slow which generates low current density. Therefore, the use of carbon electrodes is a limiting factor in MFCs where oxygen acts the final oxidising agent. This limitation is overcome by replacing the final electron acceptor, i.e., oxygen with hexacyanoferrate, permanganate, nitrate, etc. Catalysts like platinum are also used to enhance its performance.

Two-chambered MFC can take up a number of different practical shapes, some of which are shown in Fig 1 (a) cylindrical shape, (b) rectangular shape, (c) miniature shape, (d) upflow oriented MFCs, and many others.

Currently, the cylindrical MFCs find practical use only in the laboratories, and although they can be operated in both batch and continuous mode, they are mostly run only in batch mode, with glucose or acetate solution [4] as a medium in order to generate electricity. Miniature ones find use in less accessible regions and for long operations. MFCs with upflow orientation are easier to scale up; and they are used extensively for wastewater treatment, rather than for electricity generation, because pumping fluid in these MFCs is costlier in terms of energy usage, as compared to the power output that they deliver.

MFCs do not necessarily have to be twochambered. Single-compartment MFCs have also been developed since the cost is reduced in this case and also because they offer a much simpler design. These MFCs typically do not require a cathodic chamber. Cathode lies in the open air, the available oxygen in the air behaves as the final electron



Fig. 1. Schematics of two-compartment MFCs in various shapes.

acceptor, while the anode lies in the anodic chamber. Fig 2 shows the schematics of different shapes of a single-compartment MFC, where (a) shows an MFC with the anode in the rectangular anodic chamber which contains the permeable air cathode lying outside the chamber; (b) shows MFC with the anode in the cylindrical anodic chamber and cathode lying outside; (c) shows a tubular one-compartment MFC with a granular anode, made of graphite, lying inside and cathode lying outside.



Fig. 2. Schematics of single-compartment MFCs in various shapes

In order to elevate the power output delivered by the MFC, several MFCs can be arranged together in parallel, or in series. This also helps to examine the performance of the microbial fuel cell. It has been observed that higher current output is achievable by stacking MFCs together. Fig. 3 shows five individual MFC units stacked together.





### MECHANISM AND MICROORGANISMS USED

Since all living organisms require energy for their survival, this energy is obtained by performing certain metabolic activities like digestion, respiration, etc. Respiration is the main metabolic activity involved in releasing energy from different substrates like glucose, acetate, etc.



Scheme 1. Conversion of glucose to acetyl CoA by glycolysis

Microorganisms too use this metabolic process, i.e., respiration or more specifically, cellular respiration for the synthesis of ATP (energy-rich compounds). These microbes break down the organic molecules and produce electrons and protons through three respiratory pathways, namely glycolysis/EMP pathway, Krebs cycle and electron transport chain (ETC). In glycolysis, different organic compounds like carbohydrates, lipids, proteins, etc. are converted into acetyl coenzyme A (CoA).

This process can be explained by taking the example of glucose (a carbohydrate), the overall reaction of which is shown in Scheme 1:

 $\checkmark$  The glucose molecule is first phosphorylated to glucose-6-phosphate. In this reaction, ADP is converted to ATP (enzyme used: hexokinase).

✓ Glucose-6-phosphate (an aldose) is isomerised to fructose-6-phosphate (enzyme used: phosphohexose isomerase).

✓ Fructose-6-phosphate is then phosphorylated to fructose 1,6-bisphosphate by combining with another phosphoryl group (enzyme used: phosphofructokinase).

✓ Fructose 1,6-bisphosphate breaks down to form two different triose phosphates, dihydroxyacetone phosphate (DHAP) and glyceraldehyde-3-phosphate (GAP). Only one of the two isomers can directly continue the process of glycolysis.

✓ DHAP is rapidly converted to GAP (enzyme used: phosphotriose isomerase).

✓ GAP is oxidised to form 1,3biphosphoglycerate (by combining with a phosphate group) (enzyme used: glyceraldehyde 3-phosphate dehydrogenase). NAD<sup>+</sup> is reduced to NADH and H<sup>+</sup> in the process.

✓ The phosphate group on 1,3biphosphoglycerate is donated to ADP, converting it to ATP and turning 1,3-biphosphoglycerate into 3phosphoglycerate.

✓ 3-Phosphoglycerate is isomerised to 2phosphoglycerate (enzyme used: phosphoglycerate mutase). ✓ 2-Phosphoglycerate gets dehydrated, loses a molecule of water, and becomes phosphoenolpyruvate (PEP), an unstable molecule.

 $\checkmark$  A phosphate group from PEP is donated to ADP, making the second molecule of ATP. PEP itself gets converted to pyruvate. Pyruvate undergoes oxidative decarboxylation to form 2 molecules of acetyl coenzyme A.

This acetyl CoA is processed in Krebs cycle where it is first oxidised and the electrons released reduce NAD<sup>+</sup> to NADH. In order to maintain the continuity of metabolic processes, the NADH must get oxidised back to NAD<sup>+</sup> which is achieved by electron transport chain (ETC), wherein the reduced molecule, i.e., NADH is carried to the cell membrane where special membrane-embedded proteins oxidize it back to NAD<sup>+</sup> and shuttle the electrons and protons outside the cell membrane [15]. The shuttled electrons are then harvested by the anode and transmitted to the cathode *via* an outer circuit as shown in Fig. 4.

In MFCs, the microbes used are mostly anaerobic bacteria, as they do not directly transfer electrons to the final electron acceptor. These bacteria are capable of extracellularly transmitting the electrons produced while oxidizing the substrate to the anode, either indirectly (in mediated MFCs), or directly (mediatorless MFCs).

Complete oxidation of glucose by a bacterium, for example *R. ferrireducens* yields 900 Coulombs (amperes\*seconds), the calculation of which goes as follows:

1 mol of electrons = 96,500 C;

1 mol of glucose =  $96,500 \times 24$  C or 1 µmol of glucose = 2.316 C;

Therefore, 389  $\mu$ mol of glucose = 2.316  $\times$  389 = 900 C.

The recent MFC technology uses microbes that belong to the class of exoelectrogens like *Shewanella putrefaciens*, *Geobacter*, *Rhodoferax*, as they directly transfer electrons to the anode and generate relatively high power densities.

# PROTON INHIBITION

While oxidizing the substrate, protons are also generated in the anodic chamber along with the

electrons. The electrons, as discussed earlier, are mediated by anode to the cathode through an outer circuit. It is essential to remove the protons from the anodic chamber in order to maintain electrical neutrality. Moreover, the increasing concentration of protons inside the anodic chamber will inhibit the metabolism of microbes. So, for this purpose, the anodic and the cathodic chambers are interconnected by a cation exchange membrane, like a polymeric electrolyte membrane, or salt bridge [8, 16] The polymeric electrolyte membrane or salt bridge facilitates the movement of protons from the anodic chamber to the cathodic chamber and therefore, inhibits the agglomeration of protons in the anodic chamber [17, 18]





# FACTORS AFFECTING THE PERFORMANCE OF MFCs

The performance of an MFC depends on a number of different parameters, which could be physical (material of the cathode and anode used [12], configuration of the MFC reactor), biological (inoculum type, which could be pure or mixed, substrate concentration) or operational (substrate type, external resistance, effect of temperature and pH) [19]. Table 1 shows the power output delivered by the MFC when different wastewater samples are used as substrate.

Experiments conducted on MFCs show that their performance depends on their configuration and materials used in their design, rather than just the microbes present in the wastewater, although they have a huge role to play.

For example, a membrane electrode assembly MFC, MFCs stacked in series and MFCs stacked in parallels delivered a maximum coulombic efficiency (% based on COD) of 0.9 [20], 12.4 [21] and 77.8 [21], respectively. Similarly, when brewery wastewater was used as the substrate, the coulombic efficiency (CE) delivered by a baffled MFC and serpentine type MFC has been found to be 19.1 [22] and 7.6 [23] respectively. The mixture of domestic wastewater and textile wastewater delivered a CE of 36 [24] in a membrane-less cross-linked MFC and thermo-chemically pretreated dairy wastewater

activated sludge, when used as substrate in a twochambered MFC delivered a CE of 9 [25].

The material used for electrodes has to be selected with the utmost care since there is a high chance of corrosion. Materials like copper, stainless steel, graphite, platinum and many others have been used, and each one seems to have its pros and cons. For example, it has been observed that MFC deliver higher power densities when copper was used as an electrode. This is due to galvanic corrosion [26]. But it was found out that copper shows antibacterial properties. Likewise, stainless steel has been used as electrode material, but it was found out that its use depends upon the amount of chromium present in the alloy [26]. Furthermore, the active surface of the electrode, its conductivity, the nature of its surface, its biocompatibility, are some other parameters that govern the performance of an MFC.

Several attempts have been made to upgrade the performance of an MFC, one of which was the usage of carbon cloth as anode material, treated with phosphate buffer and ammonia gas. This attempt gave an increase in power production by 98% as compared to the MFC without this treatment.

Materials used as electrodes could typically be the same for anode and cathode but properties such as high conductivity and mechanical strength along with effective catalytic nature can make up a potential cathode. In the past few decades, there has been substantial research in this area to develop and design MFCs such that the performance is enhanced. The problem still lies with commercialisation and scale-up which is being worked upon, to find permanent solutions. The temperature, at which bacteria grow and perform their metabolic activities, ranges from 0°C to 40°C. Below 0°C, the bacteria cease to grow and their metabolic activities also stop but they don't die. Above 40°C, proteins denature and protoplasm starts to coagulate, which ultimately leads to the death of the bacterial cell. In some species of bacteria, the temperature range is  $-5^{\circ}$ C -40°C. Thus, an MFC, in this case, can produce electricity in the temperature range of  $-5^{\circ}$ C -  $40^{\circ}$ C, while the relatively higher amount of electricity produced at a particular temperature in this range depends upon the bacteria used and is determined experimentally. Table 2 shows the performance of MFC with different electrode materials; when different types of bacteria use the same substrate (glucose) for metabolism.

# APPLICATIONS

## Electricity generation

MFCs are different from other electricityproducing devices like heat engines in a way that they directly produce electricity without the generation of heat, heat being a low-grade energy. Microbial fuel cells convert chemical energy into electrical energy with the help of microorganisms, hence, they are environmentally friendly. Therefore, microbial fuel cells serve a dual benefit by generating electricity and waste management. The rate of power generation is still low in MFCs. Hence, they can be used for power generation in small systems where low power input is required.

There are various factors responsible for the power output of the MFCs such as operating conditions (temperature, pH), the material of the electrode, and the proton exchange membrane. The rate of power production was high when the anode material used was biofilm-converted graphite.

Substrate	Anode material used	Cathode material used	Power output	Ref.
Domestic wastewater	Graphite rod	Carbon cloth	0.17 Wm <sup>-3</sup>	[27]
Brewery wastewater	Carbon brush with titanium core	Activated carbon	0.097 kWhm <sup>-2</sup>	[28]
Distillery wastewater	Graphite sheet	Platinized carbon powder	4.6 Wm <sup>-3</sup>	[29]
Swine wastewater	Carbon felt	Activated carbon	0.750 W m <sup>-2</sup>	[30]
Sewage sludge	Graphite with Neutral Red	Graphite coated with a 1mm thick porcelain septum	0.091 W m <sup>-2</sup>	[31]
Anaerobic sludge	Carbon cloth	Carbon felt	0.468 W m <sup>-2</sup>	[32]
Anaerobic sludge with glucose	Carbon paper	Carbon paper	0.182 W m <sup>-2</sup>	[33]
Marine sediment in acetate	Graphite	Carbon paper coated with Pt/C or nitrogen	14 mWm <sup>-2</sup>	[34]

**Table 1.** Power output delivered by MFCs using different substrates

Table 2. P	erformance of	MFCs based	on the	same substrate	consumed by	different cu	iltures of	microorgan	isms
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Substrate	Electrode type	Culture used	Power density (mW m <sup>-2</sup> )	Ref.
Glucose	Glazed carbon	Proteus vulgaris	4.5	[35]
Glucose	Woven graphite	Erwina dissolvens	0.27	[36]
Glucose	Graphite	Rhodoferax ferrireducens	8	[37]
	Woven graphite		17	[37]
	Graphite foam		33	[37]
Glucose	Graphite	Pseudomonas aeruginosa	88	[9]
Glucose	Graphite	Mixed consortium, batch	3600	[3]
Glucose	Graphite	Mixed consortium, continuous	18	[38]
Glucose	Graphite	E. coli Geobacter	760	[39]
Glucose	Carbon paper	Geobacter	40.3	[8]
Glucose	Graphite plate	Saccharomyces cerevisiae	16	[40]
Glucose	Carbon cloth	P. aeruginosa	52.5	[41]

The MFCs also work at a small scale, in which electrodes can be 6-8  $\mu$ m thick and 2-4 cm long, hence, they can easily replace the batteries. As they provide an energy form that is renewable, batteries need not be recharged.

## Wastewater treatment

MFCs can utilize wastewater as fuel and can treat this wastewater by using wastes such as sewage water, municipal solid waste, human wastes, etc., as these wastes possess a large quantity of organic matter. Owing to the drawbacks of the conventional methods for wastewater treatment, such as high slug production, high treatment and high management cost, the microbial fuel cells provide a great alternative by minimizing the drawbacks of existing conventional methods. The stability of these MFCs is quite good for wastewater treatment. Some microbes used in the MFCs remove the sulfur content from wastewater and give the desired result.

MFCs are used to decrease the chemical oxygen demand (COD) of wastewater before it is liberated into the environment. Table 3 depicts the %COD removal in various types of wastewaters using MFCs. MFCs have proven to reduce the COD of wastewater by 98% [45]. The COD of the wastewaters can be further increased by optimizing the conditions such as maintaining moderate temperature, i.e., neither too hot, nor too cold. Usually, the optimum temperature is around 20-50°C.

 Table 3. % COD removal using MFCs in various types

 of wastewater

Wastewater	%COD	Ref.
	removal	
Domestic wastewater	88	[42]
Urban wastewater	70	[17]
Chemical wastewater	63	[43]
Cyanide wastewater	88	[44]

#### Hydrogen production

One of the other important roles that the MFC can serve us is in the production of hydrogen. For this to occur, the MFCs are modified to biochemically assisted reactors. In biochemically assisted reactors, the conditions applied are anaerobic in the cathodic chamber, hence the protons get reduced to hydrogen on the cathode and get the desired result. The electrical requirement needed for this reduction is greater than 0.3 volts [46]. Hydrogen can easily be stored in the MFCs, and hence, subsequently be used for electricity production. The type of substrate affects hydrogen production. For example, it has been found out that using 1 mole of glucose as substrate produced 10-12 moles of hydrogen [46].

### Biosensors

MFCs can also be used as sensors for pollution analysis. Biosensors have a measuring system with a

receptor in it. The MFCs-based biosensors can help us measure the biological oxygen demand (BOD) of the wastewater. The charge developed in typical MFCs is directly proportional to the wastewater strength, hence it can be used for BOD sensing. Biosensors can be operated for a period of five years, without maintenance [45]. Hence, they are stable and reliable.



**Fig. 5.** Increase in the number of publications in MFC research over time.

### CONCLUSION

Although the MFC is a low-power producing system when compared to other renewable sources of energy because of its thermodynamic limitations, we can see that MFCs can help a great deal in transitioning from conventional sources of energy to more renewable ones.

There are a number of challenges to be faced and overcome in order to commercialize the use of MFC, two of them being the higher power output and inexpensive electrode and PEM material. There are certainly other problems associated with MFCs like internal resistance, diffusion of the substrate and protons. In order to increase the power output, we need new microbes to be used as catalysts, which could increase the electron transport rate from the biofilm to the anode. It has been reported that if Geobacter transports electrons to the anode from the biofilm at the same rate at which it transports electrons to ferric iron, it could increase the current flow in an MFC by 4 orders. It is also possible to increase power output by metal catalysts like platinum but its scale-up would be impossible because of unendurable costs.





Fig. 6. Country-wise contribution made to MFC research field.

Carbon-based electrode materials can compete with expensive catalysts when it comes to power generation.

Research is being carried out in order to increase MFC performance by treating low-cost materials under different conditions, accompanied by minimum expenditure. Further exploring will widen its applications. We have mentioned the potential applications of MFCs in the previous section. MFCs, when used for wastewater treatment, need a larger surface area for the anode, since the biofilm builds on it. Therefore, we need to use a material for anode that doesn't deteriorate easily. Newer areas of application of MFCs are being developed. One of them is to power implanted medical devices for which blood would provide oxygen and glucose. Certain enzymatic catalysts are known which operate fuel cells, but their use is yet to be made feasible. The use of human white blood cells as a source of electrons has also been an area of interest lately.

In order to increase the efficiency of the MFCs, a number of various techniques are underway. The doping of catalysts on the electrode, the use of a more suitable oxidant in the cathode, increasing the area of the anode by replacing the use of the anode electrode with a mesh or foam, increasing the distance between the anode and the cathode are some of the efforts being put into increasing the efficiency and subsequently the power output generation of a microbial fuel cell.

This review presented a brief overview of MFC technology in general, its various designs, applications and limitations. To make further progress, we need to be able to understand the microbiology of the current-producing process.

Although research has been increasing in this field over the past few years, and various countries from different parts of the world have been contributing to its research, in order to use MFC commercially in the industry and society, further progress in this field is expected in terms of scale-up for large-scale applications.

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