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# Microbial Fuel Cells, a Sustainable Technology for Bio-energy Harvesting: A Mini Review

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#### **Abstract**

A microbial Fuel Cell (MFC) is a type of bio-electrochemical systems that utilizes the metabolic activities of microorganisms to directly transform organic substrates into electrical energy. Based on the overlap of microbiology, electrochemistry, and environmental engineering, MFCs utilize electrochemically active bacteria to oxidize organic substances, releasing electrons that move through an external circuit to generate electricity. These systems are considered a sustainable approach to energy production, particularly from wastewater and other organic-rich waste streams, simultaneously achieving waste treatment and energy recovery. Recent advancements focus on enhancing power output, scalability, and costeffectiveness through the use of novel electrode materials, optimized reactor designs, and the genetic engineering of microbial consortia. MFCs hold promise for decentralized energy generation and environmental remediation, though challenges remain in commercialization and large-scale implementation. Several strategies have been investigated to overcome the problem of low power density generation in microbial fuel cells, with nanotechnology being the most promising technique due to its distinct effect on the reactions that happen inside the cell.

Keywords: Microbial fuel cell, Green energy, Wastewater, Electrodes, Bioelectricity

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## 1. Introduction

Water is the most essential compound for the presence of all living organisms on Earth, as it plays a crucial role in nearly every biological process. Moreover, it's one of the most critical elements in so many human activities and industries (Attanandana, 2000). Water pollution and the energy crisis are currently among the most threatening problems in the world. Billions of people around the globe lack the supply to safe water and adequate sanitation. These crises are more intense in

rural and non-urban areas (Boonsook, 2003). World Health Organization (WHO) estimated in 2022 that out of 8.2 billion people around the world, 2.2 billion didn't have direct access to safely managed drinking water services, and out of which 411 million people directly used water from unprotected wells and springs and contaminated surface water bodies like lakes, ponds, rivers and streams (Unigwe, 2023).

Wastewater is a waste product generated by all human activities, whether domestic or industrial, and it contains a wide range of organic compounds (both particulate and dissolved), microorganisms (bacteria, fungi, algae, protozoa, and viruses), and various non-organic compounds (Nishat, 2023). The presence of so many organic and inorganic compounds in wastewater makes it a very rich source of energy, important nutrients, and valuable minerals. In domestic wastewater, human excreta contain a very high concentration of carbonaceous compounds. They are considered the main source of chemical oxygen demand, with values around 50-70 grams of COD per capita of human waste generated (Green, 1996). Additionally, the amount of energy stored in mixed wastewater (comprising grey and black wastewater) has been reported to be approximately 14.7 kJ per gram of COD, which is estimated to be around 4-10 folds of the energy required to treat wastewater (Masunaga, 2003). Theoretically, the amount of power stored in the waste generated per capita per day is approximately 25 watts, which is sufficient to run a compact fluorescent light bulb (Zamri, 2023).

Bio-electrochemical technology provides a reliable and sustainable solution for addressing water and energy challenges in rural areas and small industrial facilities. Microbial electrochemical cells are green and innovative bio-electrochemical systems that use extracellular electroactive microorganisms to catalyze the oxidation of biodegradable organic and inorganic compounds in wastewater in the absence of oxygen (anaerobic conditions) and convert the chemical energy stored in wastewater into usable energy in the form of biogas (hydrogen gas or methane gas) in a system called microbial electrolysis cell, or in the form of electric current in a system known as microbial fuel cells (Sato, 2002). The incorporation of biological activities of electroactive microorganisms along with electrochemical reactions makes microbial electrochemical systems more complex than other electrochemical systems such as batteries, conventional fuel cells, and supercapacitors. However, microbial fuel cells have many advantages over conventional fuel cells (direct methanol fuel cells and proton exchange membrane fuel cells) such as the ability to operate at room temperature, precious metals as catalysts at the anode are replaced by extracellular electroactive microorganisms capable of simultaneously treat wastewater and harvest the energy stored in it (Sato, 2005). Moreover, the most commonly used method for harvesting energy stored in wastewater and solid waste is anaerobic digestion, which produces methane gas that can be used as fuel in the combustion process. Other forms of energy extracted from wastewater include hydrogen, which has a significantly higher combustion enthalpy than methane (142 kJ/g for hydrogen vs. 55.5 kJ/g) (Wu, 2011).

This study examines recent advancements in the field of microbial fuel cells and their future prospects for enhanced performance.

### 2. Overview of Microbial Fuel Cells and Their Drawbacks

The main components of an MFC are the anolyte (often referred to as the substrate), the catholyte, the anode, the cathode, the proton exchange membrane, and the external resistance. Typically, organic and inorganic pollutants present in the anolyte are oxidized by electro active microorganisms attached to the surface of the anode (also called anode-respiring microorganisms), electrons are transferred from the microorganisms' cells into the anode directly or through mediators;

whereas, when mixed microorganisms community is present on the anode, fermentative microorganisms oxidize complex organic electron donners in the anolyte then anode-respiring organisms oxidize the by-products of the fermentation process which are simpler organic compounds, electrons then flow through the external resistance to the cathode while protons migrate in the anolyte and pass through the proton exchange membrane till they reach the cathode to combine with electron acceptors present at the catholyte (e.g. potassium ferricyanide). However, the catholyte is removed in the single chamber microbial fuel cell configuration, and the electron acceptor is replaced with oxygen present in the air (Deng, 2016). There are several other architectures for MFCs, such as stacked MFC, which is a group of microbial fuel cells arranged in a parallel configuration and capable of producing higher current densities than the conventional double-chamber microbial fuel cell configuration. Benthic or sedimentary microbial fuel cells are another architecture of MFCs, in which the anode is immersed in aquatic sediment. At the same time, the cathode is placed above the overhanging water column, facing the air with one of its sides. Another crucial application of microbial fuel cells is microbial desalination cells, in which 2 ion exchange membranes are sandwiched between the anode and the cathode chambers. Plant microbial fuel cells and algal microbial fuel cells are forms of microbial fuel cells in which photosynthetic organisms are used to improve the efficiency of power generation (Boguniewicz, 2017).

Several factors significantly impact the performance of microbial fuel cells. Among these factors are cell configuration and assembly, the physical and chemical structure of the electrodes, the distance between the electrodes, the characteristics of the proton exchange membrane, the type and chemical composition of the substrate, and the bacterial consortia present in the anolyte (Liang, 2021). Despite the advantages microbial fuel cells have over conventional anaerobic treatment techniques, they haven't been practically applied on a large scale due to the low power density generated and the high price of their components. Among the most critical problems that microbial fuel cells face are the limited number of electro active microorganisms attached to the surface of the anode and the efficiency or extracellular electron transfer from the cell of the bacteria to the anode, this leads to hindering power production and limiting the performance of the cell which makes microbial fuel cells undesirable (Zhang, 2009). Some microorganisms can transfer electrons directly into insoluble electron acceptors. For instance, Geobacter species can grow filaments that are known to have conductivity similar to that of metals. These pili play a crucial role in the electron transfer process, as well as in biofilm formation. Additionally, it was observed that using a consortium of mixed microorganisms distinctly improves both power density and wastewater treatment efficiency in microbial fuel cells, and consequently enhancing the overall efficiency of the cell (Massoud, 2009).

The anode is a crucial component of any microbial fuel cell, as it provides electroactive microorganisms with the required surface for attachment and biofilm formation. It's also responsible for collecting electrons generated by microorganisms present on its surface (Heidrich, 2011). Therefore, many studies have focused on synthesizing anodes with well-engineered materials that have superior characteristics or modifying the currently used anode materials to enhance their properties and increase the overall efficiency of the microbial fuel cell. A good anode should possess certain properties, such as high biocompatibility, good electrical conductivity, good bioaffinity, Chemical stability, good physical properties, a high surface area with macro pores, and a low cost (Frijns, 2013).

## 3. Microbial Fuel Cells' Structural Configuration

Microbial fuel cells can take multiple forms and configurations, each with its advantages and disadvantages. The most famous configurations of microbial fuel cells are single-chamber and double-chamber microbial fuel cells. In a double-

chamber microbial fuel cell, the anodic and cathodic chambers are separated by a proton exchange membrane that facilitates proton movement from the anolyte to the catholyte, while preventing negatively charged ions and electron acceptors from passing.

Microbial fuel cells can also be operated in continuous mode or batch mode. On the other hand, single chamber microbial fuel cells consist of an anodic compartment only. The anode is completely immersed in the anolyte, while the cathode has one side facing the anolyte and the other side facing the air (hence called air cathode microbial fuel cell). They can operate with the presence of a proton exchange membrane (membrane single chamber microbial fuel cells) or without it (membraneless single chamber microbial fuel cells) (Duarah, 2022). The compartments' structural design can alternate between conventional rectangular compartments, cylindrical-shaped compartments, Up-flow microbial fuel cells, and flat plate microbial fuel cells.

Additionally, the distance between the electrodes is a very important aspect that affects power generation in MFCs; smaller distances between the electrodes increase power density, as they make charged species movement easier and lower the internal resistance of the MFC. Single-chamber microbial fuel cells (or air cathode microbial fuel cells) are more attractive than double-chamber microbial fuel cells. They are more suitable for biosensor applications, easier to scale up, and can be employed in practical applications. They are more cost-effective since they don't require aerators or the addition of expensive electron acceptors, as the oxygen present in free air serves as an electron acceptor (Kumar, 2015). As for the up-flow microbial fuel cell design, it's similar to the design of double-chamber microbial fuel cells, with the cathode chamber placed on top of or inside the anode chamber. Another adopted design of microbial fuel cells is the single-chamber tubular microbial fuel cells. In this design, the anode is in a tube shape while the cathode is integrated at the outer circumference of the anode (Palmore, 2004).

#### 3.1. Electrodes

In MFCs, the anode and cathode share some required characteristics, as they are both electrodes that carry charges; however, they also exhibit some differences due to the distinct electrochemical reactions that occur on their surfaces. For the anode, a well-performing anode should have high electrical conductivity, a very high surface area, high porosity with a large pore size to facilitate ion diffusion into the inner layers of the electrode, chemical and physical stability, be biocompatible, eco-friendly, and easy to fabricate (Massoud, 2009). Several materials have been experimented with as anode materials in microbial fuel cells, including carbon-based materials, hydrogels, aerogels, metals, and composites. When comparing the electrical conductivity of these materials, metals rank at the top, exhibiting excellent electrical conductivity. However, metals aren't biocompatible, which leads to very poor bacterial attachment to their surface.

Additionally, most metal electrodes can suffer from corrosion due to the electrochemical reactions inside the cell, with stainless steel and titanium being exceptions. Therefore, many strategies have been investigated to mitigate that effect, such as coating metal electrodes with conductive biocompatible materials like carbon and polyaniline, grafting with different chemical mediators, surface hydrophilization, and heat treatment. The most attractive material proposed for microbial fuel cells is carbon. Carbon electrodes are biocompatible, chemically and physically stable, electrically conductive, offer a very high surface area with sufficient pore size for bacterial attachment and biofilm formation, and are cost-effective. These characteristics make them the most suitable for microbial fuel cells. The most commonly used carbon electrodes are carbon felt, carbon paper, graphite rods, carbon cloth, carbon brushes, and granular activated carbon. Among commercial carbon electrodes, carbon brushes demonstrate the best performance because they consist of graphite fibers connected to a conductive

metal core, such as stainless steel or titanium, which provides them with a remarkably higher active surface area than other carbon electrodes. Generally, 3D anodes demonstrate much better electrochemical performance in microbial fuel cells since they offer much higher surface area for bacterial attachment and biofilm formation than 2D anodes. Consequently, carbonization of natural and synthetic carbon-based materials has emerged as a sustainable, cost-effective, and efficient technique for simultaneously producing carbonaceous electrodes and managing solid waste (Ahammad, 2016). Carbonization of carbon-based materials results in self-doped materials, as heteroatoms (such as nitrogen, phosphorus, silicon, and sodium) present in the structure of the original material serve as useful dopants. These dopants have the potential to enhance the bioactivity of the fabricated anode (Svardal, 2011). However, it was found that doping carbon electrodes with high concentrations of metals results in a toxic environment for microorganisms on the anode, which hinders power density in microbial fuel cells. On the other hand, aluminum is a non-toxic metal that can be incorporated with carbon by various methods (Crini, 2019).

(Yang, 2024) Turned cellulose sponge into high performing 3D anode through direct carbonization at different temperatures (600°C, 700°C, 800°C, 900°C, 1000°C and 1100°C). Raising the carbonization temperature significantly increased the specific surface area, electrical conductivity, capacitance, and maximum power density, while lowering the charge transfer resistance. The highest recorded power density in that study was 4.1 W.m<sup>-2</sup> by the cell assembled with the cellulose sponge carbonized at 1100 °C. Moreover, this study investigated the potential of modifying the anode using conductive polymers, such as polypyrrole and polyaniline. The results show that adding conductive polymers didn't make significant changes in power generation and charge capacitance.

(Barakat, 2023) Synthesized a 3D carbon-based anode through the direct graphitization of corncob and investigated it in a single-chamber microbial fuel cell. The proposed anode was found to be decorated by a micro-porous layer array composed of SiO<sub>2</sub>-incorporated graphite. Corncob graphitized at 1100°C demonstrated the best electrochemical performance, with a maximum power density of 2010 mW/m², which was approximately 15 times the power density generated by carbon cloth (135 mW/m²). Furthermore, the effect of adding sodium acetates to wastewater (5 g/L) was investigated; it was found that adding sodium acetates increased power density from 475 mW/m² to 1963 mW/m².

(Wang, 2024) Prepared urchin-like porous structural gel beads as three-dimensional (3D) packed anode materials using the chemical coprecipitation method. The resulting reduced graphene/chitosan/Fe3O4 gel beads contained Fe<sub>3</sub>O<sub>4</sub> nanoparticles with a diameter of 13 nm. The maximum open-circuit voltage and power density obtained from the cell assembled with the gel beads were 759 mV and 17.823 mW/m³, respectively. Modified beads demonstrated 2.3 times the voltage and 23.21 times the power density compared to the control cell (327 mV and 0.768 mW/m³). The significant increase in power generation was attributed to the urchin-like canal structure of the beads, which offered electroactive microorganisms a very high surface area and micro/macro pores that were beneficial for biofilm formation.

(Liu, 2023) prepared self-bonding spherical biochar particles through carbonization of pretreated corncob powder at different temperatures (400°C, 500°C, 600°C, 700°C, 800°C, 900°C) and used them in a dual-chamber microbial fuel cell. The packed-bed bioanode exhibited good electrochemical performance, with a maximum output voltage of 743 mV and a maximum power density of 2066.7 mW/m³. Moreover, bacterial analysis revealed the abundance of certain electroactive bacterial strains, including Bacteroides, Geobacter, norank\_PHOSHE36, and Clostridium sensu stricto 10, on the surface of the bioanode.

(Radeef, 2023) Used a mixture of multi-walled carbon nanotubes (MWCNTs), polyvinyl alcohol, and natural wastes (date seeds powder and banana peel powder) to coat metallic anode electrodes and used them in a continuous flow microbial fuel cell fed with car wash wastewater. The maximum power densities recorded for the microbial fuel cells were 1072 mW/m³ and 730 mW/m³, while the maximum COD removal efficiency was 99.4%.

(Singh, 2015) Created a multiscale web of carbon nanofibers incorporated with alpha alumina and nickel nanoparticles and used it as an anode in a mediatorless microbial fuel cell. The electrode material was made by impregnating a substrate of active carbon fibers with aluminum/nickel metal salts, followed by calcination, hydrogen reduction, and chemical vapor deposition. Microbial fuel cells assembled with the proposed material exhibited a maximum open-circuit voltage of 900 mV and a maximum power density of 1,780 mW/m<sup>2</sup>.

On the other hand, the cathode compartment is the part of the MFC that contains the catholyte and the cathode, where the reduction half-reaction occurs. The most commonly used material as a cathode in MFCs is carbon cloth. However, since the reduction reaction (typically an oxygen reduction reaction) depends on the presence of ORR catalysts, the surface of the carbon cloth is modified with catalysts. The most commonly used catalysts for reduction reactions at the cathode in fuel cells are platinum-based catalysts. However, platinum is a very expensive metal, and it can be contaminated by the presence of other anions in wastewater, which causes it to lose its activity. Therefore, researchers have been looking for economic replacements for Pt-based catalysts. Among the proposed alternatives for Pt-based catalysts is activated carbon, which has been proven to be an effective catalyst for reduction reactions at low potential values. Moreover, transition metal-nitrogencarbon networks and metal-organic composite catalysts have demonstrated a good ability to catalyze the oxygen reduction reaction, making them a promising replacement for Pt-based catalysts in MFCs (Schäfer, 2013).

(Liang, 2021) explored the potential of mixing activated carbon with carbon black using different techniques and using the mixture as a cathode catalyst in an air-cathode microbial fuel cell configuration. Results showed a satisfactory increase in the values of maximum open-circuit voltage and maximum power density, which encourages the use of an activated carbon-carbon black mixture as a cathode for single-chamber microbial fuel cells.

(Boguniewicz, 2017) Used a mixture of activated carbon, carbon nanotubes, and PVDF to modify the surface of carbon cloth and used it as a cathode in an air-cathode microbial fuel cell driven with sugarcane wastewater.

## 3.2 Proton exchange membrane

The proton exchange membrane (PEM) is a crucial part of any microbial fuel cell, as it prevents negatively charged species from passing directly to the cathode (short circuit) and prevents electron acceptors present at the catholyte from reaching the anode, which can lead to operational failure. Polymeric membranes based on perfluorinated sulfonic acid, developed by Dupont, are the most widely used membranes in microbial fuel cells, with Nafion being the most commonly used one among them. These membranes have very high proton conductivity and excellent mechanical properties. However, they are perfectly proton-selective, which causes oxygen crossover from the cathode to the anode and also allows the movement of undesirable ions from the substrate to the cathode, resulting in the deposition of these ions on the surface of the cathode and ruining its catalytic activity, as well as changing the pH of the catholyte. Additionally, Nafion is very expensive, which makes it undesirable in microbial fuel cells (Boonsook, 2003). Therefore, researchers have been testing a very wide range of alternatives to replace Nafion as a proton exchange membrane. Among these alternatives are cation exchange membranes, such as CMI-

7000 from Ultrex, and agar salt bridges, as well as sulfonated polyimides, polyethylene and its derivatives, styrene and its derivatives, chitosan, ionic liquids, j-cloth, nylon fibers, glass fibers, ceramics, and biodegradable shopping bags, and unconventional materials like natural rubber or laboratory gloves. Some of these alternatives have demonstrated interesting performance that outperforms Nafion's performance in long-term operation (Sato, 2005).

#### 3.3 electroactive microorganisms and substrates

Based on recent studies, it's expected that there are over 1 trillion microbial species living on Earth. The most common types of microorganisms are bacteria, fungi, and viruses. In microbial fuel cells, bacteria and fungi are of particular interest since they have the ability to degrade complex organic molecules and generate an electric current through their respiratory processes. However, not all microorganisms can send electrons directly to the electrode; therefore, there are certain electrogenic microorganisms that are favored in microbial fuel cells, such as *Rhodoferax ferrireducens, Clostridium butyricum, Geobacter spp., Shewanella spp., and Aeromonas hydrophila* (Masunaga, 2003). These microorganisms can donate electrons to the electrode through 2 mechanisms, the first is direct electron transfer (by the means of cytochromes or pili/nanowires) and the second is mediated electron transfer mechanism (through anchoring electrons on soluble chemical compounds that act as mediators whether they are produced by the microorganisms or added to the substrate). Direct electron transfer occurs when microorganisms make a biofilm on the anode's surface, which helps attach bacterial cells to the anode and facilitates the electron transfer process. Some microorganisms can form thick biofilms (up to 50 μm), such as *Geobacter sulfurreducens*. Some studies have investigated various methods to enhance the thickness of biofilms through bacterial stimulation to increase electron conductivity. One of these methods is the addition of metal nanoparticles, which could increase power generation by up to 40% (Cronk, 1996).

Recently, yeast-based microbial fuel cells have received considerable attention, as they were previously overlooked in the early days of microbial fuel cells due to the yeast's limited extracellular electron transfer activity, resulting from their poor ability to form thick layers of biofilm and the complexity of eukaryotic cells. Consequently, most reported studies have focused on improving yeast's ability to form biofilm. In a recent study, a carbon felt electrode was modified using polyethyleneimine to promote the biofilm formation and attachment of the yeast Saccharomyces cerevisiae on the surface of the carbon felt, thereby stimulating direct extracellular electron transfer. The study's results showed that the yeast's biofilm layers were evenly distributed on the surface of the treated carbon felt. Additionally, the microbial fuel cell demonstrated a maximum power density of  $256.3 \pm 11.5 \text{ mW/m}^2$ . Yeasts offer a superior advantage over bacterial species in MFCs, as they can grow faster and have the ability to degrade complex organic molecules that are difficult for most bacterial species to break down (Masunaga, 2003).

Substrates used in microbial fuel cells can range from simple synthetic solutions to complex wastewater, which contains a wide variety of organic substances. For synthetic solutions, it's easy to control the composition of the anolyte to be compatible with the microorganisms used in the cell. Some examples of organic substances used as carbon sources in microbial fuel cells are acetate, lactate, and glucose. On the other hand, complex substrates are utilized when microbial fuel cells are employed for specific applications beyond electricity generation. Complex substrates include different types of wastewaters (domestic, industrial, or agricultural), marine sediments, soil, and leachates. Typically, activated sludge or marine sediments are added to the anolyte in microbial fuel cells to provide it with a rich culture of electroactive bacteria. Complex substrates are easier and more practical to scale up as substrates in microbial fuel cells than simple synthetic solutions. The following figure

demonstrates a comparison of the energy stored in different types of organic molecules. Cellulosic substances store the most energy of all. However, acetate compounds are easier for most microorganisms to degrade and produce higher power densities in MFCs (Sato, 2005).

#### 4. Conclusion

MFCs are a sustainable and promising technology that can be utilized for harvesting bioenergy from various types of wastewater. They have several advantages over other conventional types of fuel cells, which make them more favorable. This review gives a brief definition of an MFC, their components, and the mechanism by which they work. Additionally, it demonstrates how previous literature studied different techniques to improve power generation in microbial fuel cells. The most crucial components of microbial fuel cells are the anode, the cathode, and the proton exchange membrane. Additionally, it's essential to improve all components to ensure optimal performance from the MFC. The most commonly used technique for electrode modification involves the use of nanoparticles, such as transition metals, carbon nanotubes, and graphene oxide. It's also mentioned that the most expensive part of the microbial fuel cell is the proton exchange membrane due to its distinct chemical structure. Moreover, a very wide range of organic substances can be used as fuel in MFCs, with cellulose-based substances being the most efficient substrate to use.

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