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REVIEW ARTICLE

Wastewater Treatment Using Microbial Fuel Cells

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ABSTRACT: Environmental challenges related to water quality are not unique to impoverished nations, but are also among the most fundamental human demands worldwide. The need for clean water and power is growing by the day. Wastewater is seen as a source of both water and energy. Because of the high energy requirements and high cost, current wastewater treatment systems are associated with limitations. It is vital to create a technology that can produce viable alternatives to current energy resources. Microbial fuel cells (MFCs) are a cutting-edge technology, which have been developed and are now undergoing extensive research in order to treat wastewater sustainably. Showcasing a promising future as a sustainable method, microbial fuel cell (MFC) technology recovers energy and nutrients simultaneously to create bioelectricity, which uses the power of electro-genic microbes to oxidize organic contaminants found in wastewater. Sustainable MFC implementations may be a practical solution for carbon sequestration, biohydrogen synthesis, wastewater treatment, environmentally sustainable sewage treatment and green power production due to the constraints of traditional wastewater treatment. However, because to the challenge of balancing yield with total system upscaling, MFC electricity production remains a significant obstacle for practical applications. The advancements in MFC technologies are covered in this chapter, including modifications to their structural design, incorporation of various novel anode and cathode materials, diverse microbial community interactions and substrates to be utilized and the elimination of contaminants. Additionally, it concentrates on offering crucial insights and examining different applications and futuristic facets of MFCs connected to wastewater treatment and consequently, sustainable resource recovery. By the study we anticipate the industrialization of MFCs in the near future with proper planning and additional research, believing that this would result in cleaner fuels and a better environment for all people.

Keywords: Microbial fuel cell, Microbes, Microorganisms, Proton exchange membranes, Wastewater treatment

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1. INTRODUCTION

All living species, including plants, animals and humans, contain water. Water makes up around 70-90% of the organism's bodies [1]. Nobody can live without water for more than a week. Without water, all plants will perish. This would lead to the extinction of all organisms that rely on plants for nourishment [2]. Thus, life would cease to exist. Water covers approximately 71% of the earth's surface and distributed as underground and surface water. Surface water comes from the oceans, lakes, rivers, ice caps and glaciers. Freshwater resources include rainwater, lakes, rivers, streams and groundwater [1].

Due to the constant release of hazardous materials into water bodies brought on by the fast expansion of urbanization and industry, water contamination has been worsened and is now a global issue. In the next years, the world's population is expected to increase to more than 5 billion and if water pollution concerns are left uncontrolled, they would inevitably aggravate and put a negative impact on public health [2]. In order to safeguard our ecosystem and both human and the other living organism's health and growth, wastewater treatment is essential. If wastewater is not adequately handled, it may contaminate our water supplies, harm natural ecosystems and lead to life-threatening illnesses [3].

There are a numerous techniques used for treating wastewater. Adsorption, membrane filtration, coagulation/flocculation, oxidation, biological treatment and

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other techniques have been developed to reduce wastewater discharges and lessen the risks caused by pollutants [4]. Wastewater treatment usually entails significant expenses since it is necessary to efficiently eliminate the contaminants in the wastewater in order to produce clean and reusable water. Today's typical treatment techniques concentrate or degrade contaminants into a different phase rather than completely eliminating them [5].

Biological treatment using microbial fuel cells (MFCs) is one of the emerging technologies that provides a new prospect in a variety of ways [6]. Water systems with microbial fuel cells are based upon the catalytic activity of bacteria to oxidize organic or certain inorganic substrates found in agricultural, dairy, food, urban sewage and industrial wastewater to create power. Microbial fuel cells provide energy-efficient, environmentally friendly and low-cost wastewater treatment systems, but this requires significant innovation in a few crucial areas as well as system design. This chapter focuses on MFCs and their role in wastewater treatment and energy generation [7].

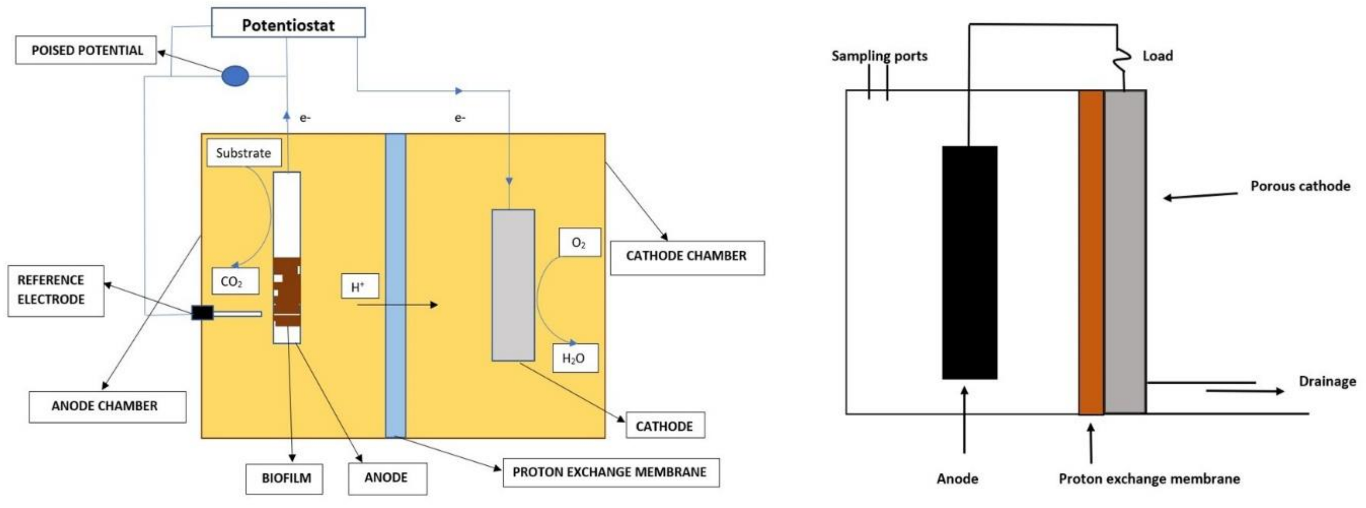
2. MICROBIAL FUEL CELLS (MFCs)

2.1. Construction of MFCs

A microbial fuel cell (MFC) uses microorganisms to transform chemical energy into electrical energy. As a sustainable treatment method, microbial fuel cells (MFCs) have been promising in eliminating heavy metals and persistent organic pollutants from various bodies present in the environment. Because MFCs use less energy and fewer chemicals than the other modern treatment technologies, they are preferred. In addition to requiring less energy, MFCs can provide enough bioenergy to address the energy crisis and open a greener threshold for producing renewable energy in order to promote sustainable development and environmental safety. Therefore, in green technology, MFC is essential for producing bioenergy while also treating wastewater [8].

The MFCs are made of a wide variety of components. These components are utilized in the reactor architecture, are packaged and organized. The MFC's design has a significant impact on the system's stability, coulombic efficiency and power production. A typical MFC is made up of an anodic chamber and a cathodic chamber that are divided by a proton exchange membrane (PEM). There are mainly two designs for microbial fuel cells, first is one chambered MFC (single chambered) and the second is a two chambered MFC (dual chambered) as shown in Figure 1. Each design can serve a certain function [9]. One of the most popular configurations is a two-chambered MFC (Figure 1A), consisting of an anode chamber and a cathode chamber, separated by a PEM. However, in one chambered MFC (Figure 1B) the cathode is directly exposed to air. As a result, there is no need for an additional cathode chamber [10].

To prevent the loss of electrons due to the mixing of electron acceptor and electron donor solutions, two chambered MFCs are preferred. By utilizing synthetic wastewater and a well-established laboratory bacterial culture, the functionality of the system is validated. For microorganisms to thrive copiously, artificial wastewater has to be standardized first. Anaerobically digested distillery wastewater can be used in place of the artificial wastewater after the design's functionality is confirmed. Standardizing wastewater improved bacterial growth, which in turn assists in the product-ion power [11].



1A **1B**

Fig. 1. Single (A) and dual (B) chambered microbial fuel cells.

In the anodic chamber, fuels are oxidized, releasing protons that flow through the membrane to reach the cathodic chamber. The cathodic chamber is provided with oxygen-saturated water, where the transported protons mix with the dissolved oxygen [12]. The two chambered MFC is shown in the Figure 1B.

The proton/cation exchange membrane is one of the most expensive components of the MFC. In commercial MFCs, Nafion and Ultrex are widely used as PEMs. However, their use is limited by some associated disadvantages. Due to the reason, these have been replaced by the nanoparticles-based materials. These materials include Fe_3O_4/polyether sulphone (PES), sulphonated poly ether ketone (SPEK), Polyvinylidene fluoride (PVDF), sulphonated polystyrene-ethylene-butylene-polystyrene (SPEBP), CNF/Nafion and activated carbon nano fibre (ACNF/Nafion) as nano-membranes. The mentioned PEM substitutes have been noted as the suitable alternatives to the commercial membranes that can be used in MFCs for wastewater treatment and power generation [13].

2.2. Microbes used in MFCs

A microbial fuel cell uses electrons from bacterially catalysed metabolic activities to generate electricity. In MFCs, a conductive substance transports the electrons that are liberated by bacteria during substrate oxidation from the negative terminal i.e., anode to the positive terminal i.e., cathode chamber. Protons diffuse through the cation exchange membrane at the cathode, where they mix with oxygen. A constant anode electron release and cathode electron consumption s required in MFCs.

MFCs, therefore, contain many microbes which help in electrons transportation from anode to the source through the metabolism of organic materials. These microorganisms can be found in abundance in freshwater sediments, soils, activated sludge, wastewater and marine sediments. A list of some microorganisms or microbes along with their substrates is shown in Figure 2.

2.3. Electron transfer in MFCs

Until recently, most of the studies on microbial fuel cells were limited to academic articles and publications that only looked at MFCs as an alternative energy source [14, 15]. Recent work on the cells has resulted in increased power output. In the future, research will focus on understanding electron transfer from bacteria to the anode's surface. The main aspect in understanding the theory underlying MFC operation is electron transport in the anode chamber [16].

The microorganisms, as discussed, act as biocatalysts in MFCs by consuming diverse substrates as a carbon source in the anode chamber and producing electrons and protons. Glucose, for example, may be employed as an electron donor in MFCs. The anodic and cathodic reactions occur at the anode and cathode, respectively [17].

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

$$6O_2 + 24e^- + 24H^+ \rightarrow 12H_2O$$

$$\text{Net reaction: } C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$

By completely oxidizing 1 mol of glucose under anaerobic conditions, 24 moles of electrons and protons are produced. The main question here is how the generated electrons move to the anode? The use of artificial electron mediators has improved the performance of several MFCs. Electron mediators are utilized to transport electrons from the broth to the anode's surface. Some of the used electron mediators are: Phenazines, phenothiazines, phenoxazines, quinones, benzylviologen-2,6-dichlorophenolindophenol, thionine and 2-hydroxy-1,4-naphthoquinone [18].

The primary electron transport method is direct transfer of created electrons via specific components known as nano wires. A nano wire is an electrical component that may carry the electron generated by the microorganisms to the surface of the electrode. A Scanning Tunnelling Microscope is generally used to examine the component's conductivity. There are various conditions which effect the electron transfer.

a) Conditions in anodic chamber

Anaerobic digestion of the substrate and electron generation are carried out by the bacteria in the biofilm on anode within the anodic chamber. Bio-electrodes have a major effect on MFC's performance because they can exchange electrons with electro-active biofilm. Numerous electrode materials with different surface areas, porosities and conductivities have been investigated. These factors influence how well microbes adhere to the surface to create biofilms. Electrode materials must have specific characteristics, such as high surface area, cheap cost, high surface porosity, biocompatibility and good electrical conductivity, in order to promote the adhesion of microorganisms and improve the production of electricity. The overall performance of MFCs is significantly impacted by each of these features. In MFCs, carbon electrodes, graphite/graphene materials, metal, metal oxides and natural waste materials are often used. Certain nanomaterials can also be used as anode in MFCs to increase their efficiency of which the carbon materials are the most oftenly used ones due to their low cost. These include carbon cloth, carbon fiber and carbon felt/brush. The other nanomaterials include graphene nanomaterials, GAC nanomaterials, metal nanomaterials like manganese dioxide, titanium oxide and tin oxide, gold nanoparticles and polymer nanomaterials [13].

Lately, research focus has shifted towards improving the efficiency of MFC's performance, many efforts are being made to strengthen anodic materials in order to promote bacterial adhesion and extracellular electron transfer, which could help increasing the electrogenic potential of MFC [19].

b) Proton exchange membrane (PEM)

MFC separators have traditionally employed cation exchange membranes. Because the reaction at the anode typically releases protons, which were assumed to be the species exchanged through the membranes, they are thus commonly referred to as proton exchange membranes (PEMs).To keep the current flowing in an MFC, a proton must be carried for each electron produced making PEM one of the most crucial elements in MFC.

PEM is the other critical variable influencing MFC's performance acting as the separator between the anode and cathode compartments. Because of its somewhat high conductivity to cations and low internal resistance as compared to other separators, PEM is the most often utilized separator in dual chamber MFCs [20].

The capacity of a PEM to transport created protons from the anode to the cathode is researched. An effective PEM should be leak proof, should possess high energy density, high electrical conductivity and thermal stability. Also, these must inhibit the movement of chemicals, oxygen and minerals from anode to the cathode chambers. However, little research has been done on how the kind of membrane, PEM or cation exchange membrane affects MFC's performance.

Besides acting as a major component in MFCs, PEMs have certain shortcomings as mentioned below;

1. One of the most well-known drawbacks of PEMs is their poor proton transferability, which persists despite differences in conductivity, internal resistance, and composition.
2. PEMs are costly. It has been observed that the approximate cost of a PEM is over 40% of the entire cost of a completed MFC.
3. Lower cathode cell performance can be caused by electrochemical processes in the cathode being prevented by a larger transfer ratio of cations to protons.
4. Chemical and biological fouling increases internal resistance, resulting in poorer efficiency and performance of MFCs.
5. Membrane fouling as a result of biofilm formation on the PEM can be considered for long-term operation. According to some experts, biofouling in dual-chamber MFCs has a negative impact on the MFCs' performance.

Of the various membranes (as mentioned in section 2.1) which can be employed for proton transport in MFCs, Nafion membranes are the most commonly used PEMs in MFCs.

c) Conditions in cathodic chamber

The cathode chamber in the MFCs functions to hold onto the electrons that are released from the anode. An electron acceptor molecule such as oxygen, ferricyanide, mercury, iron, copper and chromium are housed therein, along with a cathode electrode composed of porous material and a platinum catalyst. The reduction of oxygen in the surrounding air is aided by the cathode. Water is produced when protons and electrons unite during the reduction reaction. While oxygen is the most often occurring electron acceptor, additional electron acceptors include carbon dioxide, vanadium, uranium, permanganate, hydrogen peroxide, nitrogen species and triiodide.

Through PEM, the electrons that are emitted from the anodic chamber get into the cathodic chamber. At the cathode, the oxygen reduction reaction (ORR) occurs. It needs an ongoing oxygen supply in the cathodic chamber [21]. Various ways for increasing the quantity of oxygen in cathodic solution have been proposed. Using an air pump or an appropriate oxidant may successfully increase the amount of oxygen and hence the output power [22]. Further, the ORR is affected by the cathode selection.

A key element in maximizing the cost and performance of MFCs is the choice of cathode type and appropriate material. Cathodes are responsible for about half of MFC costs. The power density and electrochemical performance of MFCs are influenced by the cathode material. Air cathodes and aqueous air cathodes, with or without catalysts, are the two primary types of cathodes. The catalysts that are most frequently utilized are titanium and platinum. The biocathode is another type of cathode that can be utilized in MFCs and has recently attracted attention. The expensive cost of employing cathodes with catalysts is one of its disadvantages. However, this can be mitigated by using carbon-based materials that have a wide surface area and permit higher current densities.

Compared to abiotic cathode catalysts, MFC performance can be improved by using biocathodes involving aerobic bacteria [21]. Because algal biocathodes have the potential to increase oxygen supply in the cathode chamber, there is no need for any mechanical aeration device. In numerous researches, oxygen has been employed as the last electron acceptor at the cathode electrode's surface [23]. This transfer cycle is completed when electrons and protons interact with oxygen to generate water. Furthermore, the usage of biocathodes has been shown to lower the cathode's charge transfer resistance. It is observed that dissolved oxygen in an MFC with an algae-assisted cathode increased and as a result, electricity is created.

3. APPLICATIONS OF MFCs

The MFC is a revolutionary technology with several applications that may be categorized into four broad areas as shown below in Fig. 3.

3.1. Production of electricity

As previously said, the MFC is a unique technology that can create electricity and convert metabolic/chemical energy to electrical energy with the help of microorganisms. MFCs are a more practical method of producing energy since they use naturally occurring microbes for direct energy conversion. Potter made the initial discovery of microbia producing electric current in 1911, but the process gained popularity as a backup method of producing power in the 1990s. MFCs have the potential to be a substitute for traditional anaerobic digestion [24].

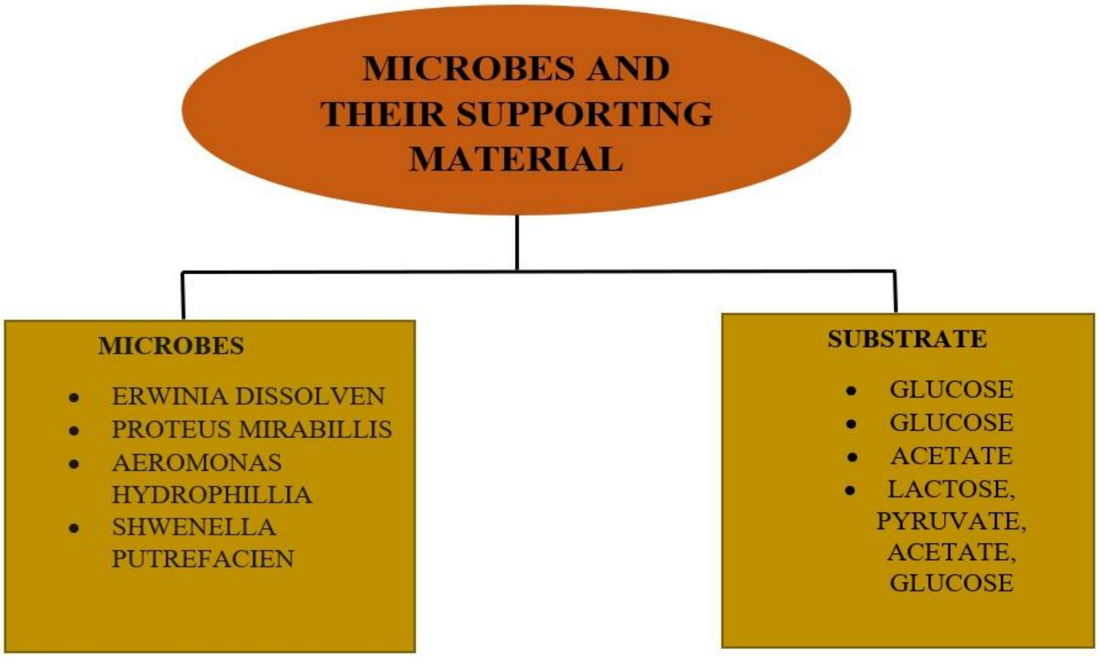


Fig. 2. Microbes and their supporting materials in MFCs

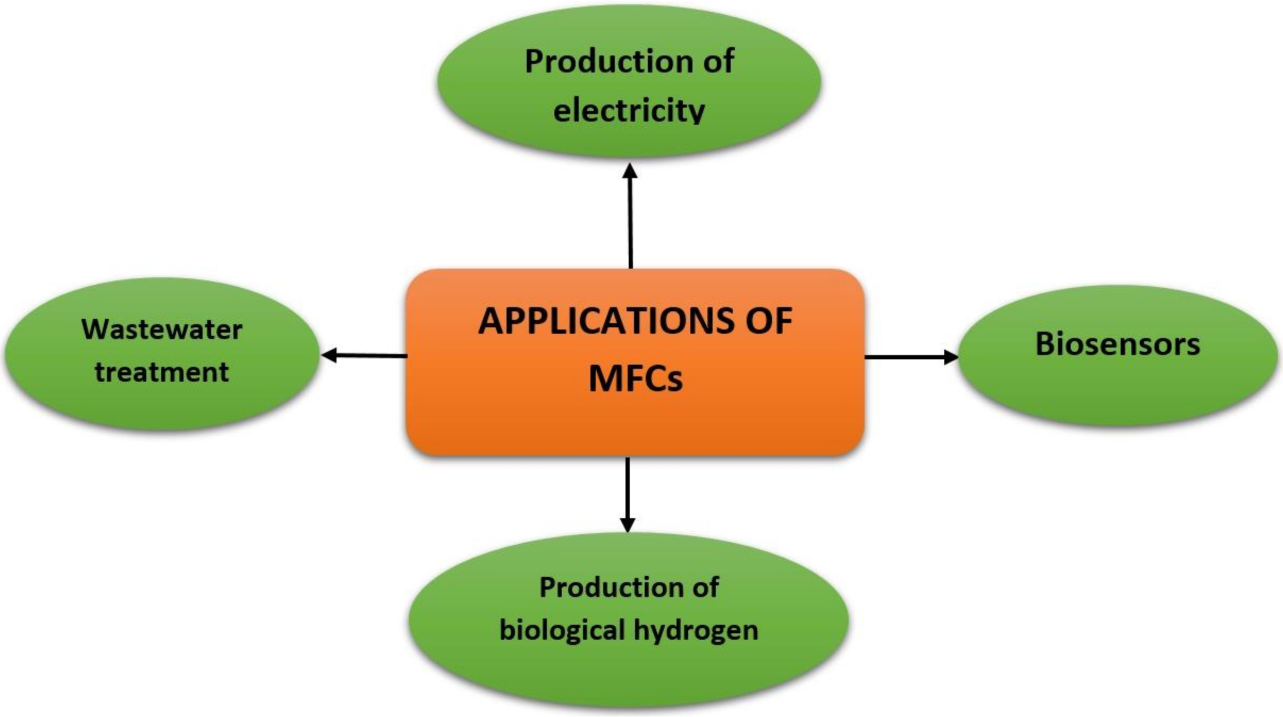


Fig. 3. Applications of MFCs.

MFCs have a reputation for being an excellent substitute for coal and other costly sources of energy since these can generate electricity while simultaneously cleaning wastewater. It has a high efficiency despite the fact that it does not obey the laws of Carnot cycle. However, because to the sluggish rate of electron transport, the electricity generated by MFCs is quite low. The created electrons may be saved in rechargeable devices and used as needed, which is a straightforward solution to this problem. MFCs are also appropriate for low-energy systems and sensors. The power generated by cells is extremely low, but it is possible to increase the voltage by connecting many MFCs in series or parallel [25]. A designed MFC might be employed in low-energy appliances, such as light-emitting diode lights and digital watches, successfully supplying the needed energy.

3.2. Production of biological hydrogen

Electrochemical, photochemical, thermochemical and biochemical processes are the best ways to create hydrogen gas. The two main methods for producing hydrogen from organic waste and wastewater are microbial fuel cells (MFCs) and microbial electrolysis cells (MECs). Vehicles using hydrogen gas have a great deal of potential as an environmentally responsible energy source. MFCs are a type of bio-electrochemical process that use microorganisms as catalysts to oxidize organic and inorganic materials and produce energy. On the other hand, MECs are a type of reactor that combine electrolysis with MFCs to produce bio-hydrogen. The most efficient, eco-friendly and clean methods for producing bio-hydrogen have been MEC and MFCs. The production of hydrogen using electrons and protons in the MFC chamber is a thermodynamically unfavorable process; therefore, external potential is required to enhance cathode potential and overcome this thermodynamic barrier. Normally, electrons and protons from the anode chamber combine with oxygen in the cathode to produce water. Compared to the fermentation of glucose, MFC's hydrogen production is a more environmentally benign process. Another study used a series-stacked MFC-ammonia electrolytic cell linked system to produce hydrogen utilizing ammonia-rich wastewater as a substrate. The catalyst used in this reaction was a Mo_2C/N-doped graphene nanocomposite hydrogen evolution reaction catalyst [26]. Another advantage of producing hydrogen in MFCs is the possibility to store gas and use it when required [27].

3.3. Biosensors

MFCs can also be used as biosensors. An MFC, hence, can also be referred to as a biosensor system since it may be used to gauge the solute concentration in waste water. As biosensors, MFCs have outperformed enzymes, the most popular biological sensing element, in terms of application. Microbes are an ideal biosensing element because of the ease with which MFCs can be regulated, hence opening up vast possibilities for enhancing the activity of an enzyme.

These can be used in biological oxygen demand (BOD) measurement sensors because of their high coulombic efficiency. Calculating the system's coulombic efficiency is an appropriate approach of assessing BOD in a fluid current. Several scholars have suggested that there is a linear connection between the solution's coulombic efficiency and BOD concentrations. *Shewanella sp*., as biobased catalytic systems, has been found to be appropriate for measuring the BOD of wastewater. It can also aid in the measurement of other materials. In diabetic patients, chemical sensors are employed to detect blood glucose and oxygen concentrations. The sensors have also been used to monitor vital indicators such as pulse, blood pressure and temperature. *Shewanella putrefaciens* has also been reported to use MFCs to quantify lactate [28].

The most commonly used MFC biosensors used are amperometric microbial biosensor, calorimetric biosensor, Conductometric biosensor and potentiometric microbial biosensor.

3.4. Wastewater treatment

One of the most well-known and practical use of MFCs is wastewater treatment. Since MFCs use anaerobic digestion to extract bioenergy from wastewater, they can be used in the water treatment process by harvesting energy. Pathogens are reduced and a large amount of wastewater may be handled by the method.

Traditional municipal wastewater treatment facilities are made up of several treatment units that are arranged in various ways, but the most essential factor in each configuration is attaining optimum efficiency. Numerous methods have been put forth for treating wastewater; yet, the primary barrier in the majority of these systems is either excessive time or expense. Additionally, the majority of therapeutic approaches need for a significant degree of operational procedures.

Clean water is a basic human right. Every year, a considerable volume of agricultural and industrial wastewater is produced. In the United States, for example, yearly animal manure output is roughly 580 million tons. Animal waste must be processed before being disposed off in the environment to avoid water contamination and odour control. It should also be noted that excessive nitrate and phosphate concentrations cause water contamination.

In general, wastewater is classified as organic or inorganic waste based on its constituents. MFCs provide a novel technique to generating power while simultaneously treating organic and inorganic waste. When microorganisms in wastewater oxidize the substrate, electrons are liberated and a steady source of power is created. Since 1991, the use of MFCs to treat wastewater has been the focus of interest. Urban wastewater contains an organic combination that may be utilized as fuel in MFCs. Furthermore, organic compounds like acetate, propionate and butyrate can be transformed to water and carbon dioxide. One of the desirable features of such cells is the ability to consume multiple waste kinds, including carbon dioxide and human waste [29].

In 1991, Habermann and Pomer began wastewater treatment with MFCs. Following it, studies were conducted in this field. Because of the richness of their organic content, sanitary waste, food processing wastewater and swine wastewater were recycled as biomass sources for MFCs [30].

MFCs are also utilized to treat inorganic waste. Some inorganic components were frequently found in wastewater. Sulphide is one of the most common and dangerous ions found in trash. Sulphide is produced in wastewater as a by-product of the reduction of sulphate in sewage and pipelines. This poisonous ion may create major difficulties such as odour, harm to human health and a corrosive environment for construction materials such as concrete. Sulphide may be oxidized to produce several sulphur compounds. Sulphur is the primary by-product of sulphide oxidation and cannot be oxidized again. Only microbial catalysts can oxidize the sulphur generated. A vast number of research experts have intensively examined the oxidation of sulphide and sulphur compounds in MFCs [31].

4. CONCLUSION

Microbial fuel cell devices have demonstrated encouraging results on a wide scale, particularly in bioenergy generation from wastewater treatment and off-grid power sources. Submergible and stackable MFCs or electrode modules have the potential for further research and development. Using membrane-less systems or low-cost membranes significantly reduces the cost of MFCs. There are numerous future opportunities for the broad use of MFC technology. The most significant application would be wastewater treatment. Submergible and stackable MFCs can be installed in any treatment tank of a wastewater treatment plant to further breakdown leftover organic matter and generate additional energy for plant operations. MFCs can also be used with an existing wastewater treatment facility, such as an anaerobic digester or primary clarifier, to reduce effluent to levels well below the discharge standard while producing additional power. When an external voltage is applied to MFCs, they can generate both bioenergy and hydrogen. Last but not least, MFCs are being extensively explored as remote sensors. In this period of increasing energy crises and environmental degradation, the generation of bioelectricity while controlling wastes has given this method increased relevance. Extensive future research on MFC is greatly required in order to obtain better efficiency, increased electrode potentials, work mechanism and potential field applications.

5. LIMITATIONS AND FUTURE PROSPECTS

In recent years, laboratory-scale MFC research has received a lot of interest; nevertheless, satisfactory commercial-scale applications have yet to be reported. Currently, simultaneous wastewater treatment and energy production is a widely investigated issue and a vast number of research studies have been done in this field [32]. However, significant constraints have hampered the general use of MFC technology in industrial-scale applications. These issues must be addressed in order to overcome the limited acceptance of this technology. MFC approaches have significant disadvantages, including expensive capital expenditure, limited power output, voltage instability, high internal resistance, mass transport loss and biofouling. In addition to cost and output yield restrictions, there are operational problems that must be addressed, including substrate properties, working circumstances, and long-term durability. Numerous researches have been undertaken to investigate and optimize operating parameters such as temperature, pH, organic loading rate, substrate salinity, conductivity, start-up and hydraulic retention time. Parametric and optimization studies, on the other hand, are typically focused on a certain substrate or substrate type. As a result, these studies must continue to be conducted on an individual basis [33].

To develop and use MFCs commercially, major improvements in several operational aspects of this technology are still required to create a stable system. However, given their existing capabilities, MFCs can be a beneficial solution for a wide range of applications in water and wastewater engineering. MFC applications for biosensing have attracted significant interest.

The limitations should be considered while planning and developing an MFC framework. Scaling up the technology is critical to realizing the eventual larger-scale use of MFCs. MFCs alone may turn out to be a viable technique to meet the future energy dilemma if adequate effort is made in overcoming current constraints [34].

CONFLICT OF INTEREST

The authors declare is no conflict of interests.

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