Review

An Overview of Microbial Fuel Cell Technology for Sustainable Electricity Production

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An Overview of Microbial Fuel Cell Technology for Sustainable Electricity Production

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Highlights

- Configurations and operations of microbial fuel cells are discussed.
- Bioelectrochemical system performance depends on the type of designs and electrode materials.
- Microbial fuel cells are feasible alternative for fuel production and wastewater treatment.
- Advances in electrode materials are summarized.
- Techno-economic and life cycle assessment of microbial fuel cells are highlighted.

Abstract: The overexploitation of fossil fuels and their negative environmental impact has attracted the attention of researchers worldwide to propose alternatives to produce bioenergy. Microbial fuel cells (MFCs) systems are sustainable biotechnologies that use bacterial activity to break down organic matter while generating bioelectricity. MFCs have bioelectricity from domestic wastewater (DWW), municipal wastewater (MWW), and potato and fruit waste, reducing environmental contamination and decreasing energy consumption and treatment cost. This review focuses on the recent advancements regarding the designs and configurations, the operation mode of MFCs, and their capacity to produce bioelectricity (e.g., 2203 mW/m^2) and fuels (i.e., H_2: 438.7 mL/g and CH_4: 358.7 mL/g, respectively). Besides, this review highlights practical applications, challenges, techno-economic, and life cycle assessments (LCA) of MFCs. Despite MFC's promising biotechnology, great efforts should be made to implement it in real-time and commercialization.

Keywords: bioelectrochemical system; bioenergy; fuel production; microbial fuel cell

1. Introduction to microbial fuel cell technology

Bioelectrochemical systems (BES) are a propitious biotechnology that have been implemented to replace energy sources from fossil fuels, i.e., petroleum, natural gas, and coal [1,2] and respond to the high-energy demand worldwide. BESs are classified into, i) microbial desalination cells (MDC) [3–5], ii) microbial electrosynthesis cells (MEC) [6], iii) enzymatic biofuel cells (EBC) [7], iv) electrolysis cells (EC) [8], v) microbial solar cells (MSCs) [9], vi) biobatteries [10,11], vii) constructed wetland microbial fuel cell (CW-MFC) [12], and viii) microbial fuel cells (MFCs). So far, within the types of BES, MFCs are the oldest and the first ones presented in 1911 [13]. The operation of an MFC is based on bacterial activity, so-called electrochemically active bacteria (EABs), which break down (oxidize) the organic matter (OM) to produce bio-electricity [14]. During the process, EABs use their metabolism pathway to transport electrons [15,16].

Besides, the components of an MFC are basically an anode compartment and a cathode compartment (Figure 1a), both separated internally by a membrane. The anode chamber is mainly responsible for the oxidation of OM (Eq.1) in the substrate (in presence of water) through microbial activity, producing electrons (e-), protons (H^+), and carbon dioxide (CO_2) [17]; then, e^- are transported toward the cathode chamber [14,18]. Subsequently, the protons are associated with oxygen (thanks to the PEM) (Eq.2) to form an essential compound in the reaction, i.e., the water molecule (H_2O). Eq.3

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indicates the complete chemical reaction in an MFC. Besides, the electron transfer mechanism at the anode surface of an MFC is presented in Figure 1b. The author referred to the following critical reviews to better understand this area [16,19].

$$\text{Anode: } C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^- \quad (1)$$

$$\text{Cathode: } O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (2)$$

$$\text{Overall reaction: } C_6H_{12}O_6 + 6H_2O + 6O_2 \rightarrow 6CO_2 + 12H_2O \quad (3)$$

Since the implementation of MFCs, wastewater has been used as excellent organic substrates in these systems to improve their efficiency in bioenergy generation and waste management [20–25]. Highest power density of 4.99 ± 0.02 W/m² was reached in a dual-chamber MFC inoculated with an excellent mixed culture [26]. This high performance was gained in a three-dimensional N-doped bio-anodes MFC fabricated with carbon felt as anode and cathode and was higher than the previous studies that used carbon-based. The MFC reactor had a working volume of 80 mL in each chamber. Probably, the system's performance was due to the electrode materials used. More recently, the highest power density of 1793 ± 77 mW/m² was achieved in an MFC operated with atomically dispersed Fe–N4 moieties as an excellent cathode catalyst [27]. The atomically dispersed Fe–N4 moieties were a perfect option to enhance MFCs performance.

Additionally, the performance of MFC systems depends mainly on the electrode materials, anolyte/catholyte, pH of the medium, bacterial communities [17], type of substrate, configuration, and operating conditions, as critically reviewed [28–30]. Furthermore, factors such as chemical oxygen demand (COD) and fuel concentrations, membrane thickness, and operating temperature also affect MFC performance [31,32]. Section 1.1 discusses the MFC designs, configuration, and operation since its implementation. MFC development could be an excellent alternative for low-income countries for being a cheap biotechnology compared to traditional energy sources. Even though MFCs faced significant challenges, they remain an ecological and economical option worldwide. This review is quite comprehensive compared to other studies; it presents the recent advances of MFC regarding the types of designs, operation, electrode materials, and substrates used. In addition, this review deeply discussed real-time applications and challenges, and techno-economic and life cycle assessments of MFCs.

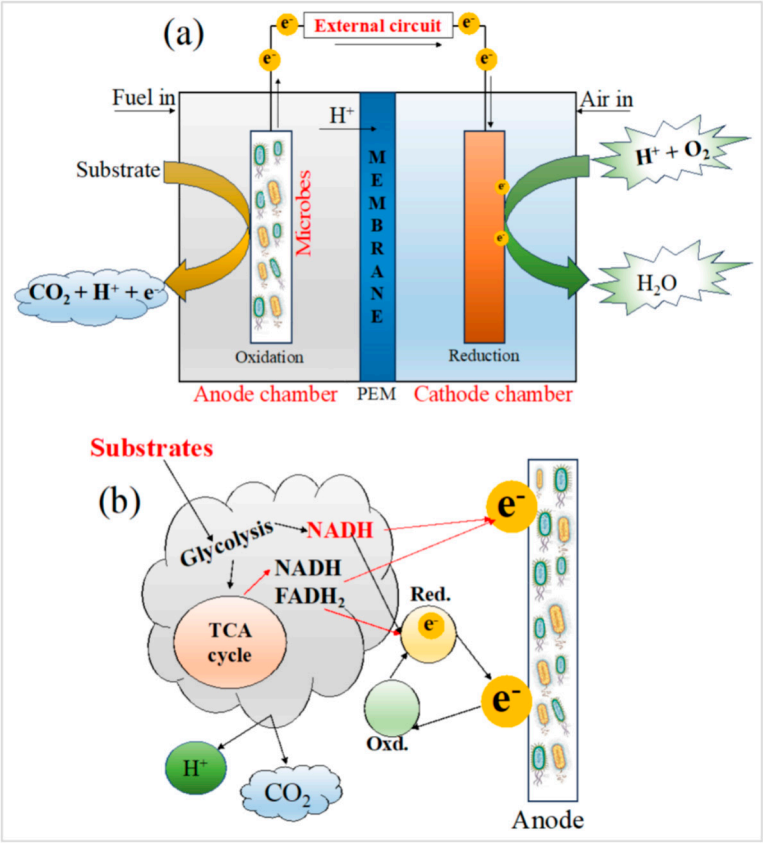

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Figure 1. (a) A typical diagram of an MFC with a PEM (Proton Exchange Membrane) and its bio-electrogenic process; and (b) the electron transport mechanism, adapted from [33]. During the process, there are three parameters to consider: the microorganism's structures to carry out the phenomenon, the type of microorganism, and the electrical conductivity of the anode material. So far, there are three methods of electron transfer through EAB activity. These include (i) electron transfer through redox-active protein molecules, (ii) use of shuttle electrons to transfer electrons, and (iii) direct electron transfer through conductive pili [34]. When the material is of high conductivity, it helps to improve the flow of electrons, exhibiting less resistance [35]. In addition, the mechanism of electrons transfer also involves natural mediators, director electron transfer, and synthetic mediators [36].

1.1. Designs, configurations, and operation

Since implementing MFCs, they have known different types of designs and configurations regarding improving their efficiencies. Among them are single-chamber MFCs (SC-MFCs) (Figure 2A), dual-chamber MFCs (DC-MFCs) (Figure 2B), triple-chamber MFCs (TC-MFCs) or more (Figure 2C), and stacked MFCs (Figure 2D). SC-MFCs and DC-MFCs are the most commonly used BESs in this field. However, stacking MFCs increases the voltage output significantly, as reported in a recent critical review [37].

Furthermore, much research concerning designs and configurations of MFCs has focused on improving these systems performance by modifying the anode surface area [38–42]. This process involves factors such as conductivity and the material to alter the electrode. Modifying the anode electrode is an excellent option to improve power generation and electron transfer, which is a crucial factor in the MFCs performance. The anode is the engine in a BES because it is the only region where the EABs act as biocatalysts and oxidation impellers to generate electricity.

Many studies on different types of MFC designs have been carried out in the last decade. According to the ScienceDirect database (so far, June 1st, 2023), a total of 9470 research articles have been published in different Elsevier journals, of which 4519 on SC-MFCs, 2546 on DC-MFCs, 2054 on Stacked-MFCs and 351 on TC-MFCs, respectively. Figure 3 represents different types of MFC configurations reported in previous studies. It can be seen that the number of research per year increased from 2014 to 2023. Much effort has been made to improve this technology's operation and performance. There were more studies on SC-MFCs than the other MFCs because they are cheaper systems to set up, are easy to use, have low internal resistance, have greater proton diffusion, and have high oxygen reduction in the cathode chamber [43], in comparison with the other MFCs systems. The following paragraph discusses the bioenergy production of the different types of MFC in terms of power density reported in recent studies.

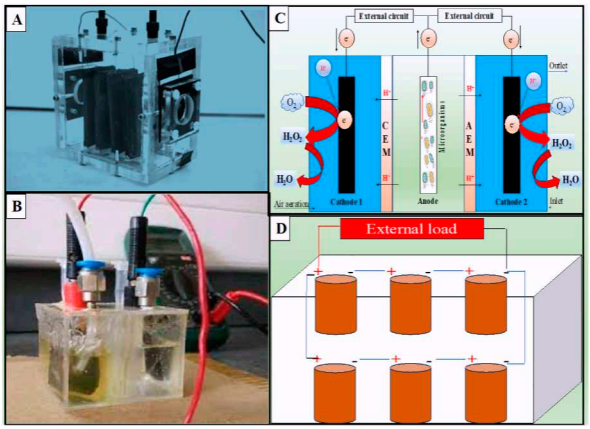

Figure 2. Designs, configurations, and schematic of MFCs previously used in Lab scale: (A) SC-MFC [44], (B) DC-MFC inoculated with Escherichia coli strain [45], (C) Triple chamber MFC, and (D) Stacked MFCs.

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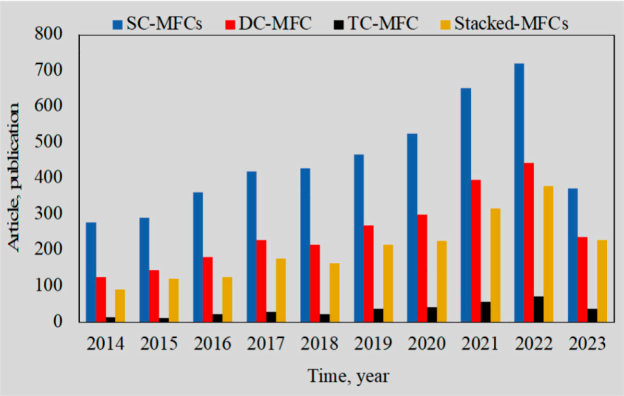

Figure 3. The number of articles on different designs and configurations of MFC from 2014 to 2023 (Source: ScienceDirect database, June 1st, 2023).

In one experiment by Choudhury et al. [46], two SC-MFCs with the same characteristics (identical) were designed and built with 300 mL of water (working volume). The anode and cathode were built with carbon cloth. The two chambers were dissociated with a Nafion 117 membrane. The anode and cathode had a distance of 157 μm, considered a crucial factor in the performance of the system. For the system's start-up, a pure strain was added to the MFCs and dairy wastewater as the primary source of inoculum. According to the authors, it was for the first time that the strain *Pseudomonas aeruginosa*-MTCC-7814 was applied in MFC with the same characteristics. The system was operated for 15 days and achieved highest power density of 105 mW/m^2 with a current of 313 mA/m^2. This performance was obtained when the SC-MFCs were connected in series producing a maximum voltage of 1025 mV. The above results were interesting; the authors' hypothesis that adding the pure strain *Pseudomonas aeruginosa* improve power production in the SC-MFC. However, when the structure of the MFC was changed, i.e., in terms of anode electrode material, a maximum power density of ~104 mW/m^2 was showed [47]. This result was statistically the same than that reported earlier [46]. So, the difference noted between the above studies is in the materials and type of configuration, and the systems' working. In the study by Chaturvedi et al., an SC-MFC with an air cathode was used. Furthermore, the anode and the cathode were separated with Nafion 212 as a membrane. In addition, when the SC-MFCs were inoculated with Anaerobic granular sludge [48] and *Shewanella putrefaciens* [49], the highest power density of 1190.9 and 1220 mW/m^2, respectively, were reached. These results were higher than that reported in the above-discussed studies. This achievement in the SC-MFCs was due to the anode electrode modification [50,51]. For a comprehensive review of this topic, the author has referred to the overview [52]. Section 1.1.1. discusses recent advancements in electrode materials and their modification for improving MFCs performance.

On the other hand, DC-MFCs, like other types of BES, have been implemented in wastewater treatment, elimination of contaminants in the soil, nutrient recovery for sustainable agriculture and bioelectricity generation. Researchers used different methods to improve these systems in terms power efficiencies, working hard to manufacture prototypes capable of continuously generating bioelectricity with high power. Table 1 compares different types of configurations of MFCs to improve their power generation performance. As can be seen, these systems have recently been used to treat various wastes, such as wastewater. High removal efficiencies (%) of uranium [U(VI)], nickel (Ni), COD, sulfide, and copper (Cu^{+2}), respectively, were achieved with the highest power density. Furthermore, in this comparative Table, the working volume and operating time of each reactor were considered.

An MFC with suitable electrode materials can power a digital clock, an LED [10], and biosensors [53] without any power or booster. These findings demonstrate tremendous advances that have been made in this field of research for the real-time application of this technology. In a recent study [54], metal oxides (CuO, MnO_2, and SnO_2) were applied in a DC-MFC as cathodic catalysts to recover

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phenolic compounds and generate bioelectricity in industrial wastewater. Apart from using these types of catalysts, the system was configured with carbon felt and carbon plate as anodic and cathodic electrode materials, respectively. Once the system configuration was finished, it was operated for 168 h. The findings of this exciting study demonstrated the feasibility and potential of DC-MFC to generate bioelectricity while removing phenolics in wastewater. It has been observed that parameters such as pH and temperature influenced the DC-MFC performance. For example, when the catholyte was pH 8 (alkaline), the system produced a maximum power density of 29.24 mW/m^2. In contrast, at pH 11, bioelectricity production decreased by 43.50%, i.e., 16.52 mW/m^2 [54]. This study has demonstrated that high alkalinity negative effect the performance of BES. However, further research on the influence of other factors on the performance of BES is suggested.

Furthermore, in another study [55], a DC-MFC with a new proton exchange membrane (polypropylene) was proposed, designed, and built. Graphite rods were used as anode and cathode electrode material. The system was operated for eight days and produced highest power density of 0.7 mW/m^2 which was 97.6% lower than the bioelectricity generation reported in the previous study [54]. Due to this low performance obtained in the DC-MFC with polypropylene membrane, it is recommended to do more studies using MFC with the same characteristics to improve its performance. A good recommendation would be to double the cathode surface area and modify electrode spacing to increase power generation yield [56].

Table 1. Recent developments of MFC in terms of designs and configurations. .

Configuration of BES	Working volume (mL)	Operation (days)	Type of electrolyte	Removal efficiency (%)	Maximum power generation	Ref.
DC-MFC	120	N/A	Uranium-containing wastewater	99.0 U(VI)	269.5 mW/m^2	[57]
SC-MFC	850	~ 30	Activated sludge	N/A	105 mW/m^2	[56]
DC-MFC	1000	N/A	Wastewater	92 (Ni); 87 (Cd)	722 mW/m^3	[58]
TC-MFC	28	~ 2 (50 h)	Synthetic municipal wastewater	80.0 (Iron); 22.1 (Sulfur)	576.6; 184.8 mW/m^2	[59]
SC-MFC	150	30	Synthetic wastewaters	89 (COD)	450.36 mW/m^2	[60]
Stacked MFC	37.5	~ 9	Barley–shochu waste	36.7 (COD)	15.7 mW/m2	[61]
Stacked MFC	28	N/A	Effluent	16.9 (COD)	1023; 1076 mW/m^2	[62]
Stacked MFC	N/A	N/A	Substrate	N/A	21111 W/m^3	[63]
Stacked MFC	N/A	~ 60	Wastewater	70.0 (Sulfide), 54.6 (COD)	3.29 mA	[64]
SC-MFC	80	N/A	Wastewater	83 (COD)	548 mW/m^2	[65]
DC-MFC	100-200	N/A	Wastewater	90 (COD); 40; 60 (orgN)	1.69 A/m^2	[66]
SC-MFC	N/A	18	Wastewater	81; 94 (COD)	989 mv	[67]
DC-MFC	118	30	Sewage sludge	99.08 (P)	~ 40 mV	[68]
DC-MFC	250	28	Wastewater	95.7; 94.7; 92.37 (COD)	1696.56 mW/m^2	[69]
SC-MFC	100	N/A	Wastewater	73.7 HCQ	241 – 280 mW/m^2	[70]
DC-MFC	300	30	Wastewater	70–88; 18–44 (COD)	2.2; 44.6; 86.9 mW/m^2	[71]
DC-MFC	125 (125 cm^3)	6 (144 h)	Wastewater	99.16 (Cu^{+2})	24.75 mW/m^2	[72]
TC-MFC	28	8	Wastewater	86.2 (Cu^{+2})	420 mW/m^2	[73]

SC-MFC – Single chamber MFCl; DC-MFC – Dual chamber MFC; TC-MFC – Triple chamber MFC; OrgN – Organic nitrogen; COD – Chemical oxygen demand; HCQ – Hydroxychloroquine.

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1.2. Electrode materials

A wide range variety of materials for electrodes have been used to assess the efficiency of MFCs. Finding efficient materials for the design of MFCs present great challenge for researchers working in this field. The operations and implementation of MFC technology have been limited by various factors, however the electrodes are the primely aspects of the MFC. Therefore, different electrode materials have previously been investigated and tested to enhance MFCs. Fortunately, the test results were encouraging as the materials showed potential to drive MFC technology forward. In this section the author provides an overview of the different electrode materials used most frequently because they are suitable materials. For an electrode material (anodic and cathodic) to be suitable, it must be of high conductivity, anticorrosive, biocompatible, chemically stable, and have high surface area and porosity as described [74]. Using similar electrode materials for anode and cathode increases the power density and improve electron transfer by microorganisms.

In addition, the appropriate material allows the formation of biofilms in the anode region, and the generated bacterial community remains to be in touch with the anode surface. However, if the anode material is not suitable, i.e., it is not biocompatible with the growth of the microbes, the electrons decrease considerably; this would also imply a decrease in bioenergy production, as comprehensively reviewed in reference [75]. Other crucial factors in electrode fabrication are the anode dimensions, as they influence in the performance of the MFC. With a large surface, there is a greater chance for microorganisms to grow and respire effectively on the anode surface. That will result in more electron transfer, increasing the potential of the MFC to generate bioelectricity. Another vital factor to consider is the type of membrane used in MFC systems.

The membrane is the essential component in the configuration of an MFC. Using a membrane in an MFC is inevitable since it avoids a mixture of reactions coming from the cathode and anode compartments; it also prevents the transport of oxygen [76]. In addition, the separator prevents the flow of any unfavorable compound in the reactor, improving the CE (Coulombic efficiency) of the MFC [77]. Depending on the variety of membrane, its properties and nature are the determining characteristics that increase or decrease MFC's internal load. When the MFC's internal load is high, it causes low performance of the MFC and limits its practical real-time application [78]. Despite significant advances in selecting MFC separators in recent years, finding a suitable and low-cost membrane remains a significant challenge for researchers.

A variety of separators (membranes) have been used in MFC systems so far (Figure 4). Nafion membrane is commonly used in MFCs because of its magnificent ionic conductivity [79]. Additionally, to replace the Nafion membrane, commercial membranes have been introduced, such as bipolar membranes [80,81], cation and anion exchange membranes (CEMs; AEMs) [82], nanoporous membranes [83] and microfiltration membranes [84]. However, several membranes have been investigated to overcome both the economic and environmental challenges [85], such as ceramic membranes [86], clay cups [87] and ceramic stick [10].

Yaqoob et al. [88] concluded that biocompatibility, conductivity, porosity, anode surface area, durability, stability, and cost of materials, are the essential properties that anode electrodes must possess in order to produce a good performance. In addition, the authors reported that surface treatment, composite, and coating are the main aspects of strategies for anode electrode modifications.

Additionally, Figure 5 shows various materials that were used in the MFC technology for years, which were considered the most common. However, each differs in porosity, biocompatibility and electrochemical stability, surface area, flexibility, and cost. Therefore, they are all equal in terms of high electrical conductivity. Although these materials have high electrical conductivity, they have disadvantages such as low resistance (graphite felt), high cost and low surface area (graphite rod and carbon paper), and low bioenergy production (stainless steel mesh). Among the electrode materials, graphite felt is the best material for configuring BES as described [89]. Besides considering the sustainability and environmental impact of BESs, it is also important to consider the practicality of using membranes and electrode reactors when trying to achieve increased economic viability.

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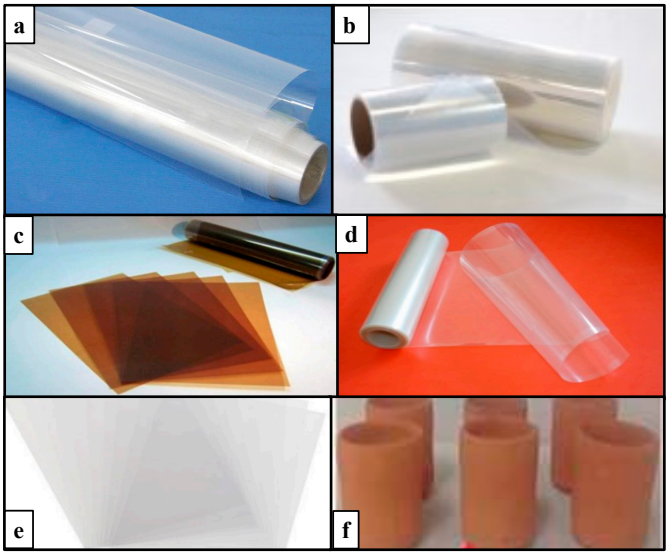

Figure 4. Types of membranes generally used MFC (**a**) Nafion 117 [83], (**b**) bipolar membrane [81], (**c**) AEM), (**d**) PEM, (**e**) CEM), and **(f**) clay cup membrane [87].

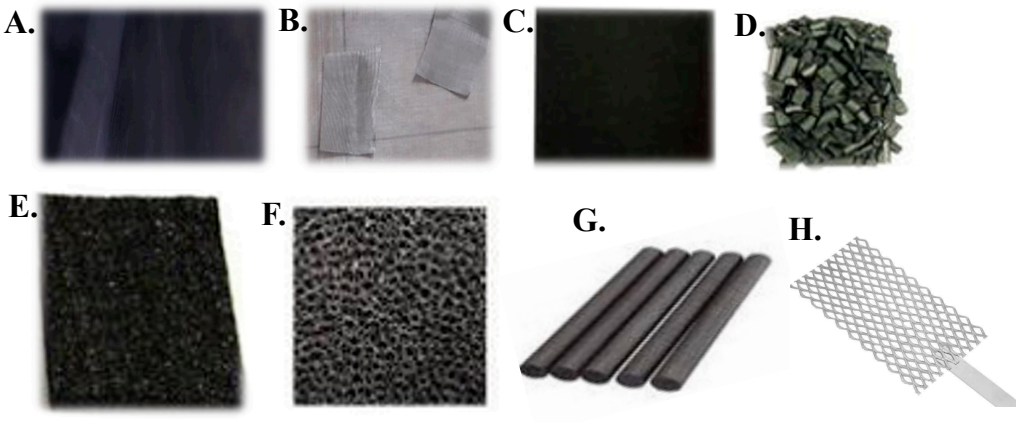

Figure 5. Electrode materials commonly used in bioelectrochemical systems: (**A**) graphite felt, (**B**) stainless steel mesh, (**C**) carbon paper, (**D**) graphite granules, (**E**) carbon felt, (**F**) vitrified carbon crosslinked, (**G**) graphite rod, and (**H**) platinum mesh. Adapted from reference Yaqoob et al. [88].

1.3. Influence of microorganisms

Microbes are drivers in the BES performance such as MFCs. The microbes are in charge of directly transporting the electrons through the substrate's oxidation. For successful electron transfer to occur, the electroactive microbes must be in touch with the anode surface via the extracellular membranes of the EABs; In addition, cytochrome proteins from the extracellular membrane are responsible for the process [90]. From a predictive point of view based on bioinformatic analysis, emphasis can be placed on the group of metal-reducing microorganisms such as *Geobacter* spp. (including *Geobacter sulphurreducens*), which have great potential. Due to their metabolic pathways, *Geobacter sulfurreducens* can produce high current densities in MFCs. Furthermore, *Proteobacteria*, *Pseudomonas*, and *Shewanella* are other group of microorganisms most investigated in mediator less MFC systems [91]; recently discussed in the reference [40]. To understand the electron transfer mechanism on the anode surface of MFCs, it is necessary to see the model proposed [92].

Mixed cultures of bacterial communities with biofilm formation (from wastewater) and pure cultures have been widely used in MFC to increase their work performance regarding power density [93]. However, previous studies have shown that mixed cultures are better because they significantly increase bioelectricity production in MFCs compared to pure biofilm cultures [94], critically reviewed

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in the reference [18]. Therefore, continuous bioelectricity production in an MFC using selective or specific microorganisms is a great challenge. Certain functions may be complex for it depending on the habitat of origin of the microorganism. Therefore, it is suggested to carry out laboratory studies through Molecular Biology to increase the potential of microorganisms to be used in MFC. Such studies should be done by genetic modification of the genome, which involves the targeted manipulation of bacterial DNA. The genes of importance in the process are the 16S fraction of the ribosomal RNA and the DNA of the plasmids. As a result, a strain with more significant bioelectricity generation potential will be obtained. Another alternative would be to use extremophile organisms that adapt to any operating condition without being affected by external and internal factors during the investigation. One of the advantages of using these organisms in MFCs is that they can produce bioenergy from any substrate.

2. Bioenergy production from MFCs

2.1. Bioelectricity production

MFC technologies have received much attention today because of their extraordinary capacity to produce bioenergy without harming the environment. Figure 6 illustrates the advances that were made to bring MFC technology to practical application. So far, more than 7,363 investigations have been conducted on using MFCs for low-cost electricity generation. In addition, over 3,216 review paper have been published on different aspects of MFC, followed by 2,530 book chapters, 388 conference abstracts, and 284 encyclopedias, respectively. It is worth mentioning that these data were taken only from ScienceDirect database because there are more publications on energy recovery using MFC systems in other preforms.

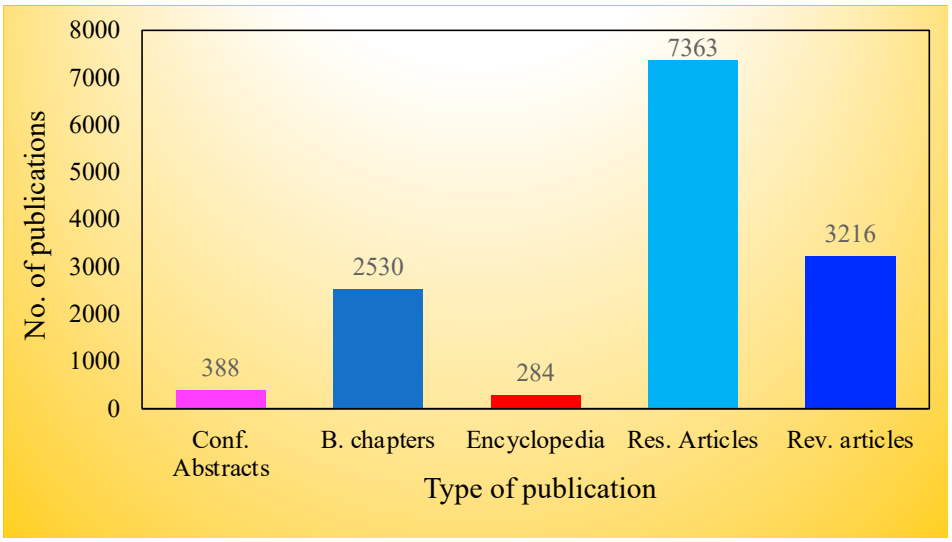

Figure 6. Publications on MFCs during the last decades (Source, ScienceDirect database, June 4th, 2023).

So far, great strides have been made in improving bioelectricity production at MFC. Many recent studies have reported high power generation efficiency using MFCs inoculated with different types of waste (wastewater, sludge, human urine, etc.). Table 2 shows the progress and advances of MFC technologies from 2022 to date. This table has selected some of the most promising studies on the configuration of MFCs and the critical parameters in the energy production process.

Highest power density of 2203 mW/m^2 was gained in an SC-MFC inoculated with anaerobic sludge as an excellent substrate [95]. The SC-MFC was built with a graphite brush as an anode, while modified materials, that is, graphite-based nanomaterials were utilized as cathode material. The performance achieved in the study could be referred to cathode modification and the operating conditions of the MFC. In contrast, Subran et al. [96] obtained highest power density of 590 mW/m^2

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in an SC-MFC made of carbon cloth as an anode and cathode and separated by Nafion 117 membrane. This value was almost four times lower than that reported [95]. In this study, the authors used rGOHI-AcOH (acetic acid) and rGO/Ni (reduced graphite oxide nickel nanoparticle composite) — two reduced graphene oxide hydrogen iodide graphite-based nanomaterials as catalysts [95]. The results were interesting as they showed that the rGOHI-AcOH-based on catalysts, as mentioned earlier, was feasible to drive the MFC system without interruption (in terms of power density). Therefore, the power output found [96] was 76.6% higher than the maximum power output (138 mW/m^2) reported in a tubular MFC (T-MFC) [97]. The T-MFC was fabricated using a graphite rod as an anode electrode, carbon cloth-coated Pt (200 cm^2) as a cathode electrode, and nanocomposite as a proton exchange membrane. The findings indicated that the best option to improve an MFC's performance is by modifying its electrode (i.e., synthesized and characterized nanocomposite membranes) and using suitable configuration materials. In the previous study by Bensaida et al. [98], the highest power density of 833.33 mW/m^2 was obtained in a prototype of MFC inoculated with $Mg(OH)_2$-coated iron nanoparticles. This value was 29.19 and 83.34% superior to that in agro-waste and synthetic wastewater, respectively. However, it was approximately three times inferior to that reported in anaerobic sludge [95].

On the other hand, in their quest to increase the amount of OM and keep bacterial populations active on the anode surface, researchers have investigated other types of substrates with great potentials, such as acetate, butyrate, glucose, cellulose, and sucrose, have been used in MFC to improve their output power as described in the reference [2]. The main idea of using these substrates in MFC is to improve the transport of protons from one compartment to another, in addition to forming good biofilms on the electrode and keeping the bacterial community active. Highest power densities between the range 305 and 506 mW/m^2 were recorded in an SC-MFC inoculated with butyrate (1000 mg/L) and acetate (800 mg/L), respectively [99]. It was noted that the SC-MFC-based acetate indicated better performance in comparison to that inoculated with butyrate. The difference between the reactor regarding the power density came from the concentrations of the substrates. Later, in an SC-MFC inoculated with glucose, highest power density of 52 mW/m^2 was reported, ~ 9 times and ~ 5 less than that found in butyrate and acetate, respectively [100]. Recently, Hashmi et al. [101] reported highest power density of 71.12 mW/m^2 in a DC-MFC when removing hazardous from wastewater. This yield in MFC was due to the addition of 350 µmol/L $C_6N_6FeK_3$ (potassium ferricyanide) in the cathode compartment. Concurrently, 180 µmol/L CH_2 (methylene) was applied to the anode compartment. As mentioned above, the concentration of the chemical compounds was an excellent option to increase MFC performance while treating wastewater.

According to the above results, the modified electrode is the best option to enhance the power density of the MFC compared to the commercial electrode. Therefore, the use of a conventional electrode increases the cost of configuration of MFC, which is a disadvantage for its extensive application and commercialization—furthermore, other alternatives to improve MFC efficiency organic substrates as excellent electrons donor. Finally, anaerobic sludge is reported to be one of the best substrates for improving power generation in MFCs and followed by $Mg(OH)_2$–coated iron nanoparticles, rGOHI-AcOH, and acetate as an excellent inoculant for MFC technologies. Also, algae have been reported to be a good substrate in enhancing MFC performance for the recovery of value-added products from wastewater [102,103], including biofuels [104], bioremediation and bioelectricity generation [105,106]. According to the literature, MFC-based algae have great potential for improving power efficiencies, nutrient removal, heavy metal recovery, and bioremediation of contaminants.

Additionally, Yaqoob et al. [107] recorded highest current density of 36.84 mA/m^2 (within 20 days of operation) using potato wastewater as an excellent electron donor for the biodegradation of pollutants in a benthic microbial fuel cell (BMFC). This MFC performance was 82.28% less than that previously reported in a DC-MFC operated with potato waste as substrate [108]. The study showed simultaneous effective removal of OM and COD up to 84%. OM concentrations and bacterial community played a critical role in improving MFC performance. In another investigation, a SC-MFCs was configurated by using a bamboo charcoal (BC) as anode electrode and a Pt-coated carbon

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cloth as cathode [109]. The working volume of the MFCs was 530, 530, and 500 mL, respectively. The MFCs were inoculated with potato-processing wastewater. In one MFC, a maximum current density of 1140 mA/m^2 was found. The current density achieved by Sato et al. [109] in potato waste-fed SC-MFC was higher than the other study cited in this paragraph. However, these findings indicated that potato waste, like other organic substrates, is potentially an excellent alternative to achieve enhanced MFC power generation and wastewater bioremediation performance. More investigations need to be done using potato wastewater in MFC technology development.

Table 2. Summary of production of bioelectricity using different MFC configurations.

Configuration type	Electrode materials		Membrane type	Substrate	Working volume (mL)	Operation (days)	Max. power generation	Ref.
	Anode	Cathode						
SC-MFC	Carbon felt (16 cm^2)	Carbon felt (31 cm^2)	Clayware	Synthetic wastewater	150	30	995.73 mW/m^3	[110]
DC-MFC	Carbon fiber	Carbon fiber	SPEEK-goethite	N/A	N/A	N/A	73.7 mW/m^2	[111]
T-MFC	Graphite rod	Carbon cloth coated Pt (200 cm^2)	Nanocomposite	Sewage wastewater	300	3 weeks	138 mW/m^2	[97]
DC-MFC	Graphite	Graphite	Nation 117	Activated strains	500	N/A	12.82 mW/m^2	[112]
SMFC	Carbon-polymer composite	Carbon cloth (3 × 3 cm^2)	N/A	Sediment from wastewater	100	30	1056.6 W/m^3	[113]
MFC	Carbon fiber brushes	Carbon fiber brushes	Nafion 117	Glucose, yeast, and MB	800	N/A	5.55 W/m^3	[114]
SC-MFC	Carbon brush	Lignin-derived activated carbon	N/A	Sludge	125	N/A	6.7 – 6.5 mW	[115]
C-MFC	Activated carbon coated carbon veil (30 mg/m^2)/ pressed over stainless steel mesh	Activated carbon coated carbon veil (30 mg/m^2)/ pressed over stainless steel mesh	Flat terracotta membrane (12.25 cm^2)	Human urine and sludge	12.5	N/A	492.85 μW	[32]
S-MFC	Graphite felt (7 × 7 × 0.4 cm)	Carbon cloth coated-Pt, plain carbon cloth, and graphite felt	N/A	Soil	N/A	~ 50	87.3 mW/m^2	[116]
DC-MFC	Graphite filter	Stainless steel mesh	Carbon-ceramic composite	Wastewater	5.3 (cm^3)	N/A	0.699 W/m^3	[117]
SC-MFC	Wired stainless steel 60 mesh	Wired stainless steel 60 mesh	Cylindrical terra-cotta pots	Textile effluent	N/A	N/A	21–42 mW/m^2	[118]

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SC-MFC	Graphite brush	graphite-based nanomaterials	N/A	Anaerobic mud	N/A	30	2203 mW/m^2	[95]
SC-SMFC	Unidirectional Carbon Fiber (total area 81 cm^2)	Unidirectional Carbon Fiber (total area 40.5 cm^2	N/A	Marine and fluvial sediments	2000	30	70 mW/cm^2	[119]
SC-MFC	Graphite felt (thickness 10 mm, diameter 80 mm)	Graphite felt (thickness 10 mm, diameter 80 mm)	N/A	Oily sludge	2000	~ 31	1277.90 mW m^3	[120]
SC-MFC	Carbon cloth	Carbon cloth	Nafion 117	Agro-waste	200	N/A	590 mW/m^2	[96]

T-MFC – Tubular MFC; MB – Methylene blue; C-MFC – Ceramic-based MFC; S-MFC – Soil MFC; SC-SMFC – Single chamber sediment MFC.

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2.2. Other types of energy production

2.2.1. Methane (CH_4) and Hydrogen (H_2)

In recent years, great strides have been made in using BES, such as MFCs, to treat wastewater and produce fuels simultaneously. This progress has been achieved by combining BES prototypes to improve their performance during processes. Thus, the use of MFCs for the production of both CH_4 and H_2 has captured the attention of researchers worldwide. Apart from the fact that this technology is environmentally friendly, it is also an excellent option for producing fuels while eliminating pollutants in wastewater. Furthermore, MFC technologies are less expensive compared to conventional methods. Figure 7 indicates the dark fermentation process for fuel production, such as H_2 and CH_4.

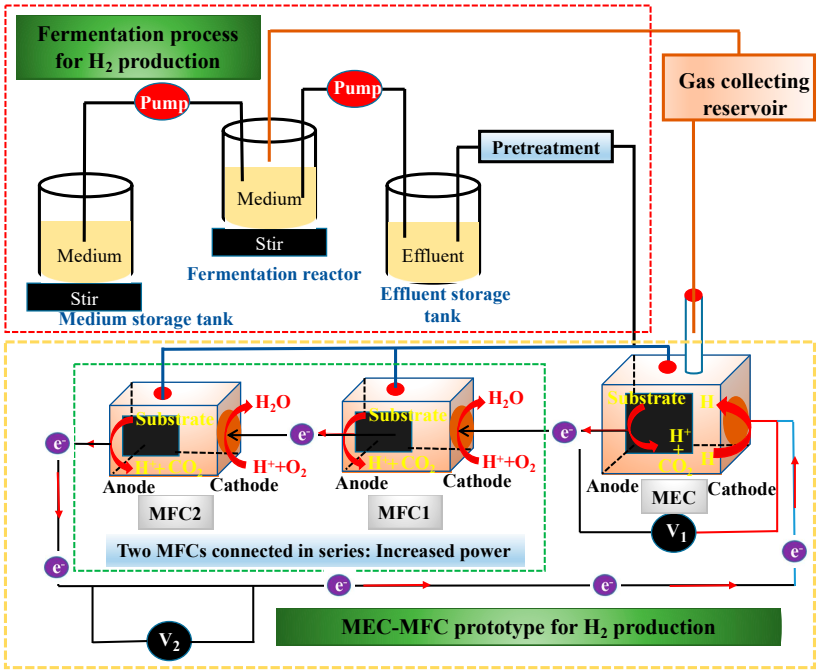

Figure 7. Diagram of the H_2 production through the dark fermentation process. As can be seen, a prototype MEC-MFC was coupled to improve the power generation during the process. Adapted from the combination of the references [29,121].

Recently, Hao et al. [122] constructed an SC-MFC (working volume of 2000 mL) coupled anaerobic membrane bioreactor (AnMBR) to enhance CH_4 production. So, 40 cm^2 of carbon felt was utilized as an anode, while the cathode was built from various materials (non-woven carbon cloth, platinum carbon, carbon black, etc.). Before assembly of the SCMFC-AnMBR, the carbon felt was sterilized using one mol/L concentration of HCl and NaOH, respectively. The SCMFC-AnMBR was inoculated with synthetic wastewater compared to the conventional one (C-AnMBR). The SCMFC-AnMBR indicated high recovery efficiencies of 38.89 mL·g/COD and 67.84 mL·g/COD CH_4, respectively, with a maximum voltage of 107 ± 14 mV. This study demonstrated that the SCMFC-AnMBR is better than the conventional system. While in the previous study [123]), a submersible MFC (SMFC) coupled anaerobic digestion (AD) was configured for the enhancement of CH_4 production. Hence, the prototype SMFC-AD was inoculated with glucose at different concentrations (2-4-10 g/L). The authors have compared the performance of the combined system and the single one (AD). The results showed that at a concentration of 2 g/L*glucose, the SMFC-AD reached higher CH_4 production of 320 mL/g.COD (0.32 L/g.COD) compared to other concentrations used in this study. The CH_4 production achieved [123] was 8 and 5 times higher than that reported in the SCMFC-AnMBR. According to this study's findings, it can be argued that the best glucose concentration to

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enhance CH_4 production is two g/L. Furthermore, high glucose concentrations negatively affect the reactor's performance in terms of fuel production.

Additionally, in one previous study by Nguyen et al. [124], single-chamber microbial electrolysis cells (MEC) by simultaneous dark fermentation (DF) process (Figure 7) were constructed. The DF was combined with MEC forming the so-called DF-MEC. Then the DFMEC was inoculated with a species of alga called *Saccharina japonica* (sDFMEC) to improve fuel production and accelerate the process. The sDFMEC recorded a maximum production of H_2 of 438.7 ± 13.3 mL/g-TS compared to other reactors. At the same time, the system (sDFMEC) reached maximum CH_4 production and COD removal of 63.1 ± 3.4 mL/g-TS and 75.6 ± 1.4%, respectively. Nonetheless, DF-MEC showed an efficient recovery of 32.2%, achieving maximum H_2 production of 403.4 mL/g-TS [124]. In contrast, the study by Gebreslassie et al. [125] reported maximum H_2 production of 110 mL/g-VS in a similar sDFMEC. This yield was 3.66 times inferior to the previous by Nguyen et al. Later, in an sDFMFC made of a surface-modified stainless steel mesh cathode, higher H_2 production of 408 mL/g-TS was gained [126]. The authors modified this to optimize the electrode performance during the DF process. The study revealed that anodization is the best alternative to improve fuel production using bioelectrochemical systems. These findings indicate that sDFMEC is more effective than the combination of SCMFC-AnMBR for fuel production. However, all these methods are feasible to improve CH_4 and H_2 production and bioremediation of contaminants in wastewater.

Other strategies to improve fuel production (i.e., H_2 and CH_4) are to use other types of the substrate such as biochar with performance of 118.5% H_2 and 14% CH_4, respectively [127], calcium-lignosulfonate-based biochar with increases of 50% H_2 [128], biochar-catalyst with increases of 51% H_2 [129], and electroactive cultures (EACs). More recently, a DC-MFC was built to evaluate the effect of the injection of CH_4 on anaerobic oxidation (AO) coupled MFCs (AO-MFCs) on power generation [130]. Two EAC (acetate and formate) were used in the AO-MFCs to improve the performance of the fabricated prototype. For the system start-up, 84.5 cm^2 (13 × 6.5 cm) of breathable cloth was used as an anode, while the cathode was made of 81 cm2 (9 x 9 cm) of carbon felt and separated by an ultrafiltration membrane. The anode chambers were inoculated with 40 mL (0.04 L) of anaerobic sludge. The study showed that specific EACs were responsible for converting CH_4 to CO_2 while producing bioelectricity.

Liu et al. [131] constructed a novel prototype MEC coupled AD (MEC-AD; working volume 400 mL) operated with few-layer Ti_3C_2TX MXene (FL-MXene), multilayer Ti_3C_2TX MXene, and MAX phase titanium aluminum carbide (MAX). Subsequently, the reactor was inoculated with cattle manure (CM) and sewage sludge (SS). Furthermore, graphite rods were used as an anode and cathode materials. The MEC-AD operated with 0.035 wt% of ML-MXene showed maximum CH_4 production of 358.7 mL/g VS. This result was superior to that reported in MEC (38.4 ± 1.7 mL/g TS) elsewhere [124]. The recorded difference was because both systems were configured and operated in different environmental conditions.

3. Applications and challenges of MFCs

MFCs have been explored for their real-time application, like other bioelectrochemical systems. The main idea of a researcher in this field is to be scaling up MFC toward its commercialization. MFCs play a fundamental role in the bioremediation of contaminants, such as azo dyes, heavy metals (e.g., Pb, Cr, Hg, Cd, etc.), sulfide and sulfate, nutrient removal (nitrate and phosphate), antibiotics, and petroleum removal, from wastewater and the soil [132–135]. This means that significant progresses have been made with respect MFC applications. Typically, MFCs have been designed at a laboratory scale to produce bioelectricity by using microbes in a bioreactor [13]. The results were encouraging, and from there, researchers began to investigate biological systems such as MFCs. However, implementing MFCs from laboratory scale to practical applications faced significant challenges worldwide [136].

Therefore, the challenges faced by MFC technologies are low power density, high-cost electrode materials, continuous electricity generation, low conductivity of electrode materials, and membrane fouling, as described in the reference [29]. Therefore, MFC is biotechnology with significant

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advantages (Figure 8). Literature reported that the low efficiency of MFCs should be due to their over-potential (internal resistance) depending on the system configuration [137,138]; in addition, this could limit the power generation in terms of power density [139]. It was previously suggested to modify electrode materials and reactor configurations and use suitable substrates to optimize MFCs performance, reducing its internal resistance [140]. In addition, the choice of microorganisms with great OM oxidation potential for electrons transfer mechanism is another aspect to consider during the configuration of the MFCs [138]. Furthermore, using catholyte or anyolite in the MFCs is an excellent inoculant to improve their power density. Recently, human urine [141–143], livestock urine (from sheep, goat, and cow) [16], and potato waste [144] have been used in MFCs as excellent feedstocks. The power densities were significantly increased after adding the above substrates to the MFCs. These feedstocks are suitable to enhance the problem of low power density in MFC technology for its possible real-time application. Recent studies have demonstrated the real-time applications of MFCs to power devices such as BOD biosensors [145], Internet of Things (IoT) [146], to charge cell phones [147], and digital clocks and LEDs [10]. Nevertheless, more studies are needed to carry out MFC toward real time application and commercialization.

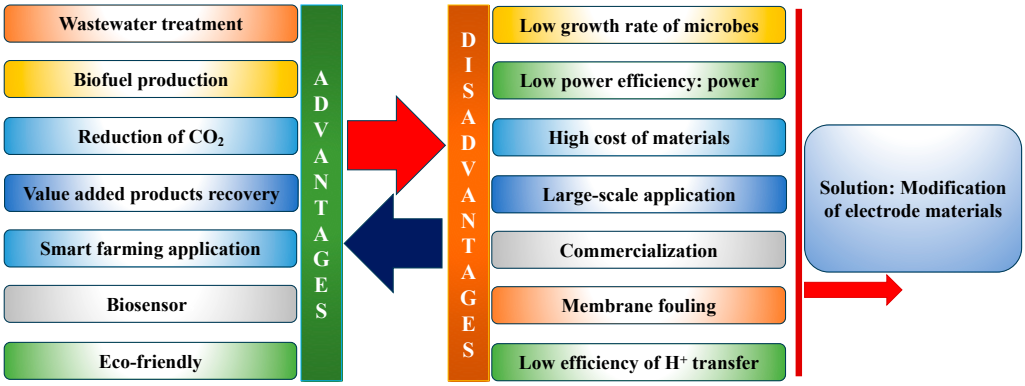

Figure 8. Pros and cons of MFC technologies.

4. Techno-economic and LCA of MFCs

Techno-economic assessment is used to determine the economic aspects of novel technologies (during their first stage of implementation) concerning their practical applications. BESs such as MFCs have been in sight of research regarding their commercialization worldwide due to the high global energy demand and accelerated population growth and industrialization. Literature has reported that 80% of the world's energy generation depends mainly on exploiting fossil fuels [148]. However, these energy sources produce high greenhouse gases (GHG) emissions [149], negatively affecting the environment. The use of MFCs to produce electricity is safer than conventional technology. Nevertheless, these systems require a depth evaluation of their environmental impact and tecno-economic feasibility before implementation. Therefore, more information about the topic is available in the reference [150].

Since MFCs are devices that recycle waste materials for energy generation (i.e., electricity, hydrogen) and improve water quality, they have great promise of becoming a feasible bio-economic system; however, wastewater substrates containing buffer salts (i.e., phosphates, carbonates) either in the anode or cathode of the system are not economically and environmentally practicable [151]. Additionally, besides considering the sustainability and environmental impact of BESs, it is also important to consider the practicality of using membranes and electrode reactors when trying to achieve increased economic viability.

Additionally, LCA is a well-known standardized technique that systematically and quantitatively evaluates the potential risks and impacts on a product or system's environment throughout its life cycle. According to the International Standards Organization (ISO 14040), LCA includes the following stages: (i) scope and goal definition, (ii) inventory analysis, (iii) impact assessment, and (v) interpretation of results [152].

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LCA is one of the emerging methods used to assess both bioenergy production and carbon sequestration through all the stages of a product's life cycle. Zhang et al. [153] developed LCA models to investigate the ecological impact of three different BESs, MEC, MFCs, and MDC. MEC was found to have the best performance and lowest negative environmental impact compared to the MFC and MDC systems. This is largely as a consequence of the production of H_2O_2 (hydrogen peroxide) in the MEC. Nevertheless, the low power generation of 10 W m^{-3} (volumetric power density) recorded in both MFC and MDC systems was correlated with negative environmental impacts as described [154]. Low levels of substrate remediation led to accidental leakage of high COD water, membrane fouling, and the release of unidentified microbes, etc.). Other work has also claimed a proportional relationship between the change in environmental impacts and the power density generated by BESs [153]. This research suggests that in order to achieve positive environmental impacts in MFCs and MDCs, higher power density production is needed.

An auto-circulating bio-electrochemical reactor (AutoCirBER) was designed to treat 8.4 L of DWW continuously, on a laboratory scale [155]. Experimental LCA was performed in the AutoCirBER system, demonstrating its environmental practicability in the long run (10 years); moreover, this system showed more than 90.4% COD removal and 59.55 W.h net annual energy recovery. For real-world application, it will be important to conduct further studies that include cost-benefit analysis, fluid dynamic analysis, etc. [155]. According to Pant et al. [156], for the implementation of BESs, i.e., MFCs on a commercial scale, it is essential to have a complete LCA including (i) choice of functional unit, (ii) appropriate system boundary, and (iii) co-products (Pant et al., 2011). Finally, LCA can provide significant insights to renewable energy policymakers and WWT stakeholders on the environmental impact of various MFCs systems [157].

5. Conclusions and future research direction

In this overview, recent studies and developments on microbial fuel cells are discussed. It is reported that MFCs are devices with great potential to convert chemical energy into bioelectricity by using electroactive microbes as biocatalysts. Nonetheless, these systems have faced significant challenges since their implementation. These include low efficiencies, the low growth rate of bacteria in the anode electrode, low conductivity of electrode materials, high cost for MFC configuration, membrane fouling, and large-scale applications in real-time. Despite these limitations, they are promising technology that efficiently treats wastewater and produces electricity simultaneously. Furthermore, MFCs have a significant advantage in reducing important greenhouse gas emissions like CO_2. Hence, it is necessary to perform the LCA of MFCs to avoid their environmental impact. Finally, this review discussed the practical applications of MFCs as promising biotechnology involving the bioremediation of pollutants.

Most of the techno-economic assessments were primarily based on data from small-scale laboratory works; the pilot and large-scale MFC applications are still limited so far. Due to scale effects, data based on laboratory-scale studies may not reflect natural system behavior in large-scale systems. Specifically, idealized design and operating conditions such as smaller electrodes, reactor volumes, and static conditions commonly used in laboratory-scale setups often result in better performance than in real-time large-scale application systems.

The study's findings discussed in this review paper indicate the complexity and need for caution in designing, choosing electrode materials, using suitable substrates, and extrapolating techno-economic data based on laboratory-scale studies for large-scale application of MFC systems. Therefore, further research on large-scale MFCs using modified electrode materials is unavoidable for commercialization.

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