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Review

Microbial Fuel Cell and Associated Novel Derived Systems as Bifunctional Technologies to Produce Green Energy and Pollutant-Free Water

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Abstract

Global energy security and water scarcity are currently two major challenges facing society. Many new strategies and technologies have been developed to address these issues; however, most can only partially solve a single one. Therefore, microbial fuel cells (MFCs) and associated novel technologies have emerged as sustainable, bifunctional solutions for treating various wastewater streams while generating renewable electrical energy through the biochemical oxidation of organic substrates. The basic configuration of an MFC comprises anodic and cathodic chambers, an external electrical circuit, ion-exchange membranes, organic substrates, and electrogenic bacteria. Biological fuel cells are inherently multidisciplinary systems whose performance depends on several biotic and abiotic parameters, with bacterial electrogenic metabolism as the driving force. In this review paper, the most important factors affecting MFC performance and the common equations employed to determine bioelectrochemical efficiency are described. A major highlight is the analysis and comparison of recently proposed MFC-derived hybrid technologies: microbial electrolysis cells (MECs), microbial desalination cells (MDCs), plant microbial fuel cells (PMFCs), and constructed wetland MFCs (CW-MFCs) for treating wastewater and soil pollutants while enhancing the recovery of green energy. Novel configurations, basic biochemistry, and a brief history of bioelectrochemistry are also reported. In addition, this review aims to compare the applications, fundamentals, basic configuration, and limitations of each biological fuel cell. Based on a comprehensive analysis, the challenges, opportunities, economics, and scaling-up possibilities of each MFC-derived technology are reported. Since biological oxidation in the anodic chamber and reduction at the cathode surface are the basis of all fuel cells, there are characteristic challenges that must be addressed: enhancing power output, increasing pollutant degradation and scalability, reducing construction and operational costs, and ensuring long-term stabilization. MFCs and the associated derived systems appear suitable for converting residual organic matter into green energy, even at a pilot scale; however, to improve scalability and reduce power costs, further research is still needed.

Keywords: bioelectric energy sources; biofuels; microbial fuel cells; wastewater; water purification

1. Introduction

The microbial fuel cell (MFC) is a consolidated technology that dates back to the mid-1980s. Since this electrochemical device uses a bacterial microbiome as a biocatalyst, the MFC has also been called a biotic or biological fuel cell. In the early years, MFCs were primarily used to generate energy by oxidizing simple substrates such as glucose, fructose, other monomeric sugars, acetates, and low-molecular-weight carbohydrates. More recently, MFCs have been employed as an alternative method to remove organic loads and complex pollutants, such as petroleum-derived hydrocarbons, dyes, pharmaceuticals, and leachates, from wastewater. This application has positioned MFCs as a bifunctional, sustainable technology capable of generating clean energy while simultaneously treating wastewater streams [1].

A conventional MFC consists of two essential compartments: an anodic and a cathodic chamber. The anodic chamber serves as a digester, where anaerobic microorganisms metabolize organic matter, producing free electrons, protons, and carbon dioxide. Electrons are then collected at the anode and transferred from the anodic to the cathodic chamber via an external circuit, where they combine with oxygen (atmospheric air) to produce green energy and water molecules [2]. In the cathodic chamber, reduction reactions occur at the cathode surface; oxidation reactions occur in the anodic chamber. The electrochemical performance of an MFC depends on several factors, including the bacterial consortia, electrode type, organic residue, pH, temperature, and reactor configuration [3]. The common reactions occurring inside MFCs are as follows:

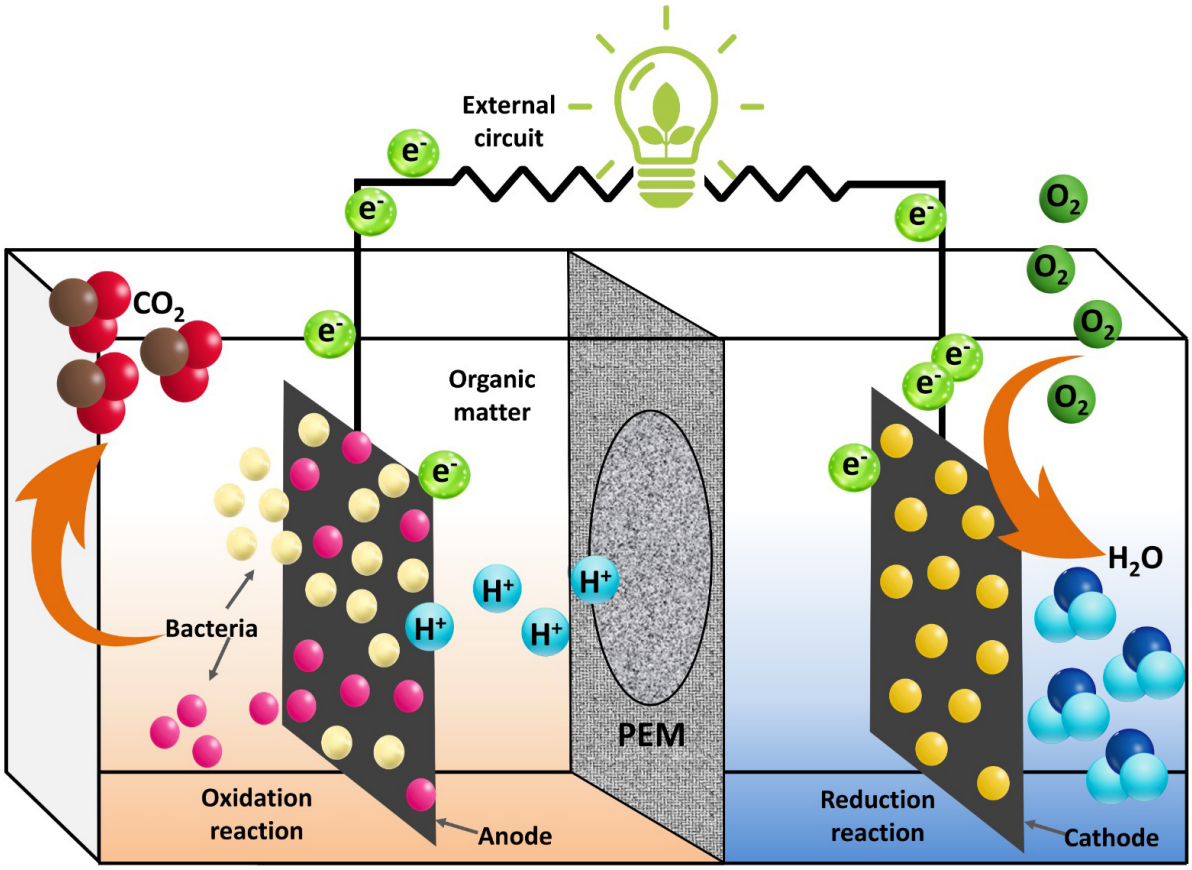

Fig. 1. Conventional structure of a basic MFC. Electrogenic bacteria metabolize organic substrates in the anodic chamber to produce protons and free electrons; these electrons pass through an external circuit to the cathode, where the electrons generate electrical energy and water. The separator maintains charge balance within the anodic chamber. MFC, microbial fuel cell.

Anodic chamber

$$CH_3COO^- + 3H_2O \rightarrow CO_2 + HCO_3^- + 8H^+ + 8e^- \quad (1)$$

$$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^- \quad (2)$$

$$C_{10}H_{19}O_3N + 18H_2O \rightarrow 9CO_2 + NH_4^+ + HCO_3^- + 50H^+ + 50e^- \quad (3)$$

Cathodic chamber

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (4)$$

As shown in Eqns. 1,2,3, free electrons and protons are generated during the oxidation of organic matter; the number of free electrons is directly related to the nature of the organic matter sources. The maximum number of electrons is derived from the chemical oxygen demand (COD) in domestic wastewater (Eqn. 3); notably, other organic-rich wastewater streams can also be used as substrates in MFC; however, heavy metals and other organic compounds could inhibit the metabolic activity of bacteria, diminishing electron generation and the subsequent MFC performance. In the cathodic chamber, the reduction reaction occurs at the electrode surface, generating water. Between the anodic and cathodic chambers is an ionic exchange membrane called a proton exchange membrane (PEM), whose main functions are to (i) maintain charge balance by allowing protons to move from the anodic to the cathodic chamber, (ii) reduce oxygen back-diffusion to the anodic compartment, and (iii) ensure an adequate and efficient cell operation [4]. The basic configuration of an MFC is shown in Fig. 1.

The MFC is considered the basic and pioneering bioelectrochemical system (BES), from which different hybrid technologies have been developed, including plant MFCs (PMFCs) [5], constructed wetland MFCs (CW-MFCs) [6], microbial electrolysis cells (MECs) [7], microbial desalination cells (MDCs) [8], among others. These BESs produce green energy via either gaseous biofuels or direct current generation, while also yielding pollutant-free water. BESs rely on bacterial metabolism as the driving force for biochemical reactions. Nowadays, the significant impact of BES technologies on wastewater treatment is well known; however, despite efforts to optimize bacterial cell technologies for cleaning residual water, some challenges

and drawbacks remain that must be addressed before profitable, large-scale applications can be realized. The aforementioned hybrid technologies are employed for different purposes and offer many advantages over others; however, these systems share common limitations such as high construction and operating costs, ohmic losses, biotic and abiotic interactions, low energy output, and electrode fouling. These parameters have received considerable attention to address the impracticality of BES technologies at the pilot scale.

This review paper focuses on the fundamentals, limitations, applications, trends, and common configurations of MFCs and the associated hybrid-derived electrochemical cells. The main objective is to compare the fundamentals and applications of these derived BESs as novel technologies for producing green energy while enhancing pollutant treatment. The economic feasibility and scalability of each derived system are also discussed in depth, with a focus on potential large-scale applications. In addition, common novel strategies, drawbacks, and future scopes are reported. An interesting highlight of this paper is the comparative assessment of the different derived systems, which shows the wide range of applications, pollutant treatment capabilities, power costs, and electrochemical efficiencies that each cell can achieve. Such comprehensive comparisons have been reported only sparsely in the existing literature.

2. Brief History of Bioelectrochemistry

The term "bioelectrochemistry" refers to electrochemical reactions carried out by biological organisms, such as plants, algae, and bacteria. Luigi Galvani is regarded [6] as the father of bioelectrochemistry for the discovery of the "animal electricity" phenomenon, observed as the contraction of dead frog muscles induced by an external electrical impulse [9]. Subsequently, in 1911, Potter observed [6], for the first time, electricity generation by a living bacterium (*E. coli*) in a bio-based cell composed of a liquid medium and platinum electrodes. Cohen then confirmed this observation in 1931 by connecting biological fuel cells in series to achieve up to 35 V and 0.2 mA [6]. MFCs gained more attention in the mid-19 60s when the National Aeronautics and Space Administration (NASA) employed this technology as an energy source for space missions, transforming the chemical energy enclosed in urine and human waste into electricity [10]. Later, pioneering research on long-term MFC operation was conducted by Habermann and Pommer in 1991 [11], who continuously treated municipal wastewater for approximately 5 years using extracellular mediators, carbon-based anodes doped with nickel hydroxide, titanium cathodes, and sulfate-reducing bacteria as the inoculum. This research demonstrated, for the first time, the potential of MFCs to remove organic pollutants from wastewater; however, this work also showed the limitation of MFCs in producing high current densities compared with conventional fuel cells. Bond and co-workers [12] studied energy harvesting from marine sediments by placing a graphite electrode at the bottom of the anoxic zone and using an air cathode.

An interesting finding was the identification of *Geobacteraceae* microorganisms on the anode surface, which were responsible for completely oxidizing organic compounds in the sediment and for transporting free electrons to the final acceptor (the carbon anode). This marked a turning point in the history of BES. Since then, hybrid technologies, alternative configurations, and engineering strategies have been developed to enhance biological metabolism, energy recovery, and waste treatment, thereby improving the performance of MFCs and BESs. From MFCs, other novel technologies have recently emerged; for example, MEC technology was first reported in 2005 as a promising alternative for producing green hydrogen in an electrochemically biocatalyzed reactor [13]. Subsequently, Strik and co-workers [14] demonstrated, for the first time, energy recovery from living plants (*Glyceria maxima*) in a PMFC operated with graphite electrodes and a cation-exchange membrane placed at the surface of the anode compartment. The authors reported promising results, including a power output of 67 mW m^{-2} and the feasibility of using living plants *in situ* to produce green energy without damaging the plants [14]. The use of wetland plants in BES led to the development of a new hybrid technology, the CW-MFC, first reported by Yadav and co-workers in 2010 [15]. Meanwhile, Cao and co-workers [16] modified the conventional MFC by adding a new compartment between the anodic and cathodic chambers to remove ions from the aqueous phase; the authors named this electrochemical device the MDC. Sediment microbial fuel cells (SMFCs) are another MFC-derived system, consisting of an anodic compartment in the sediment zone and an air cathode. This technology, proposed by Reimers et al. in 2001 [17], has been proven to be an alternative method for generating electricity and removing pollutants from sediments. Finally, MFC technology has evolved significantly in recent years; an interesting highlight of this electrochemical device was reported by Walter et al. [18], who employed a stack of four membraneless MFCs to power a microcomputer without any external electronic system. A schematic timeline of the history of bioelectrochemistry is shown in Fig. 2.

3. Conventional Microbial Fuel Cell

The conventional configuration of an MFC is known as a dual-chamber MFC and includes the following compartments: anodic and cathodic chambers, a PEM, and an external electrical circuit (Fig. 1). The oxidation reaction catalyzed by anaerobic bacteria occurs in the anodic chamber; during this process, free electrons are generated and transferred to the final electron acceptor (the anode) and then transported to the cathodic chamber through the external electrical circuit. To maintain charge balance, protons are also produced during bacterial oxidation; protons

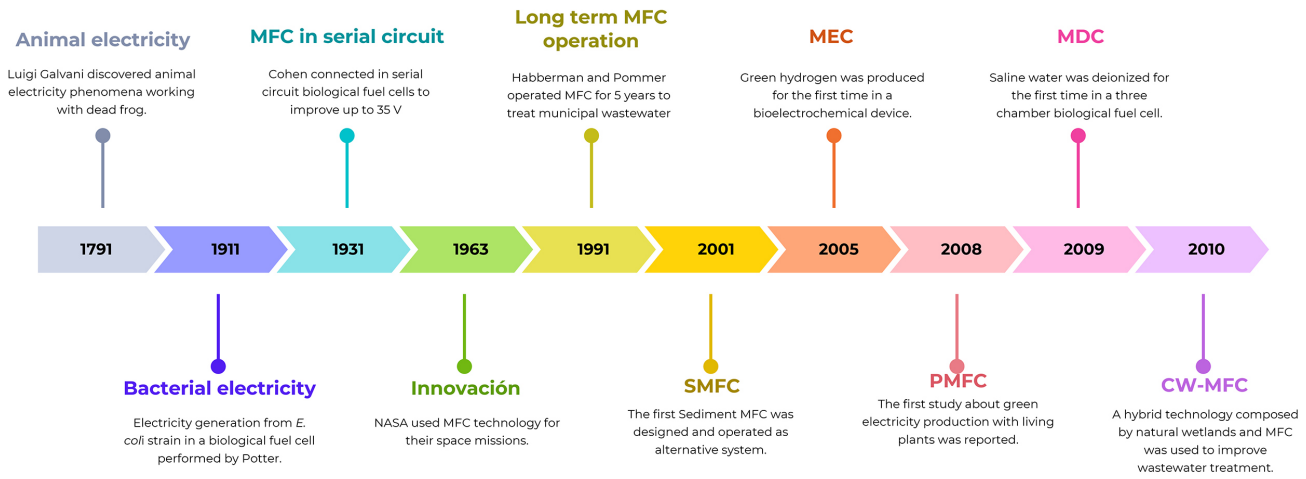

Fig. 2. Timeline of bioelectrochemistry history. The starting point of the history of bioelectrochemistry is the discovery of animal and bacterial electricity by Luigi Galvani and Potter. Since then, this technology has evolved considerably, culminating in the novel and promising designs of hybrid biological fuel cells. MEC, Microbial Electrolysis Cell; MDC, Microbial Desalination Cell; SMFC, Sediment-MFC; PMFC, Plant Microbial Fuel Cell; CW-MFC, Constructed Wetland MFC.

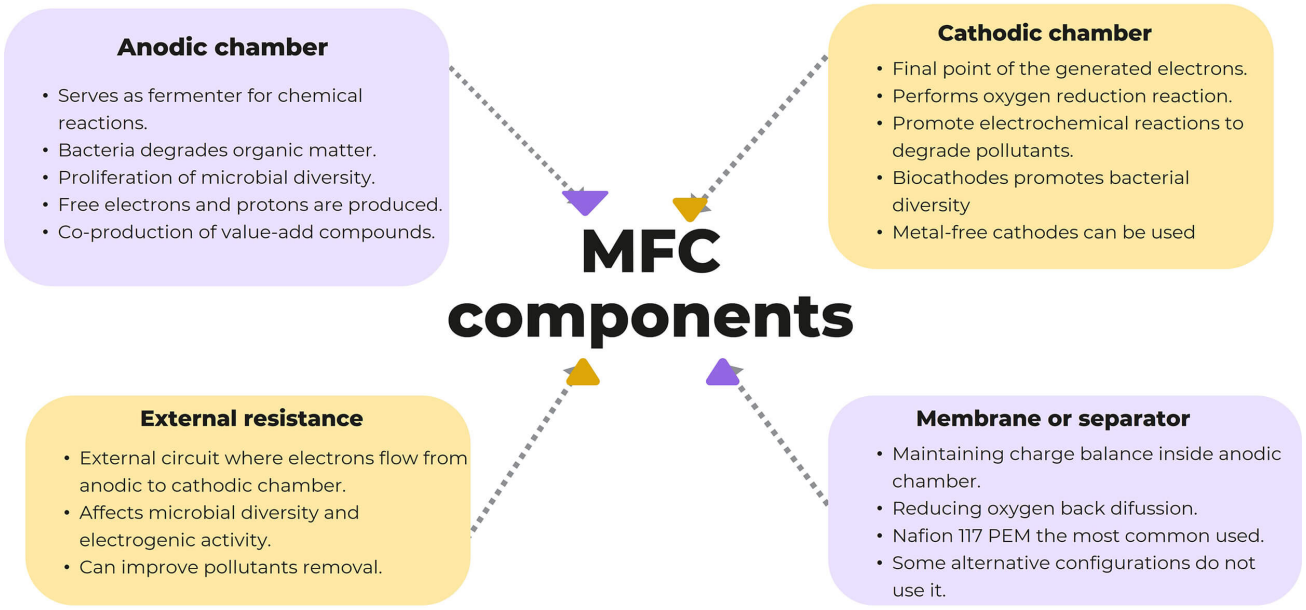

Fig. 3. Main features of the MFC basic components. This diagram shows the basic components of the MFC, along with the associated main characteristics and functions. The anodic chamber is the bioreactor where bacterial oxidation is performed. Electrochemical reduction is performed in the cathodic chamber. Membrane and external resistance are physical tools through which ions and electrons flow.

permeate into the cathodic chamber via the PEM and react with atmospheric oxygen, producing water [9]. Several studies have considered the anodic chamber the "heart" of the MFC, due to the wide range of processes that occur within it: wastewater treatment, COD reduction, production of free electrons, biomass growth, co-product generation (such as biofuels), and reduction in organic load [19,20]. The cathodic chamber has different functions; the chamber serves as the final destination for the electrons generated in the anodic chamber, where the electrons combine with oxygen and protons to produce usable energy and water. Moreover, the chamber boosts power energy by reducing energy losses and can degrade pollutants through biochemical and electrochemical reactions [21]. The use of biocathodes as an alternative to conventional metal-based cathodes has demonstrated strong applicability, a favorable cost–benefit ratio, and promising potential for the recovery of heavy metals and nutrients [22]. Fig. 3 summarizes the main characteristics of the MFC components.

The external electrical circuit plays a crucial role in MFC performance; the circuit provides the pathway through which electrons pass from the anodic to the ca-

thodic chamber. External resistance has been shown to exert a great impact on power density and pollutant removal as reported by Zhang et al. [23], who showed that reducing external resistance to 50 Ω increased the generated power density up to 2.61 W m^{-2}. Years later, the relationship between external resistance loading, electrochemical activity, and pollutant removal efficiency was confirmed [24]. The PEM is another critical element of the MFC structure; the main purpose of the PEM is to transport free protons from the anodic to the cathodic chamber. The most widely used membrane is Nafion 117; however, despite the associated high performance in proton permeation and avoidance of oxygen back-diffusion, the large-scale use of Nafion 117 is not feasible due to the associated unfavorable cost-effectiveness. Thus, alternative materials such as agar [25], clay–ceramic [26], cellulose [27], chondroitin sulfate-based membranes [28], and composite polymers [29], as well as other configurations such as single-chamber MFCs, have been proposed to reduce operational costs and improve practicality at the pilot scale.

3.1 Common Configurations

Four main configurations of MFC technology have been reported in the literature: continuous-flow, single-chamber, dual-chamber, and stacked-cell modules [30]. The basic MFC refers to a dual-chamber configuration as was described in the previous section. Three main categories of dual-chamber MFCs have been identified: H-type, saline-bridge, and cube-type. A distinctive characteristic of H-type fuel cells is the associated geometric shape, which resembles the letter "H". In this configuration, the anodic and cathodic chambers are connected through a glass tube and separated by a PEM, agar, or a saline bridge. In practice, H-type MFCs have been constructed from glass, plastic, or acrylic materials, and have demonstrated high COD removal yields (approximately 70%) and the ability to bleach organic dyes [31], treat organic loads [32], and treat wastewater [33]. The double-chamber cube-type MFC comprises two cubes separated by a PEM, which serve as independent chambers for electrochemical reactions. The use of cube-type fuel cells has demonstrated remarkable potential to produce green energy from synthetic and domestic wastewater in an easy-to-operate system [2,34]. A notable advantage of this design is the reduced energy loss due to the shorter electrode spacing; however, the main disadvantages include non-homogeneous stirring at the bottom of the cell and low efficiency when extracellular mediators are used to transport free electrons [35]. Moreover, previous studies have revealed that ohmic losses are dominant in cube-type cells [36]. Despite these limitations, this configuration is often preferred for large-scale applications.

An alternative system derived from conventional dual-chamber MFC is the single-chamber MFC, whose main advantages include the elimination of a PEM, reduced reactor volume and construction materials, and the absence of a separate cathodic chamber or catholyte solution, as well as being easy to operate [37]. This simple configuration emerged in response to the common use of the expensive Nafion 117 PEM in conventional designs, which accounts for most of the MFC cost. In agreement with Yadav and Afzal [38], the single-chamber MFC achieved higher energy recovery and COD removal efficiency than the conventional dual-chamber design employing dairy effluents as the organic source [38]. However, a recent critical review by Apollon et al. [1] suggests that dual-chamber MFCs could be more efficient for energy recovery than single-chamber MFCs when complex and non-conventional substrates are used as electron donors; the maximum power densities achieved by these configurations are 88,990 mW m^{-2} and 50,570 mW m^{-2}, respectively. Similar to the double-chamber MFC, the single-chamber MFC has different categories based on the geometry and arrangement; the most common are cube-type, flat-plane, and cylindrical. The cube-type was studied in the early years of single-chamber MFCs; the cube-type has some advantages, such as simple design, easy assembly, and low construction cost. Moreover, the cube-type has demonstrated interesting potential for removing COD from synthetic wastewater [39], polyalcohols [40], domestic organic waste [41], organic loads from simulated potato-processing wastewater [42], and ions from saline water under mesophilic and low-temperature conditions [43]. Conversely, flat-plate air-cathode single-chamber MFCs have recently been studied for continuous electricity generation. For example, Song and co-workers [44] operated a flat-plate MFC to remove organic matter from both synthetic and real wastewater. Using an ultra-low voltage customized DC–DC booster circuit operated in continuous mode, the authors increased the recovered voltage from 0.5 to 3.3 V, achieving a power density of 8.16 W m^{-3} [44]. An important disadvantage of this configuration is the need for a PEM separator to optimize power output, as previously reported for treating ethanol-containing synthetic wastewater with a passive air-breathing cathode [45].

For a cylindrical single-chamber MFC, Liu et al. [46] constructed and evaluated a novel bioelectroreactor composed of eight anodes and an air cathode to treat local wastewater while producing green energy. This system achieved a maximum power output of 26 mW m^{-2} and a COD removal efficiency of almost 80%. Subsequent optimization of the cylindrical configuration reduced the electrode spacing to 2 cm, further improving green energy recovery and achieving a favorable cost–benefit balance for the reactor [47]. Further studies demonstrated that the cylindrical air–cathode fuel cell configuration significantly reduces internal resistance and considerably increases COD removal during sewage treatment, when *P. aeruginosa* is used as the inoculum, compared with the air-cathode cubic design [48]. These findings highlight the critical impact of reactor geometry on the bioelectrochemical efficiency and pollutants removal yield. The potential of single-chamber

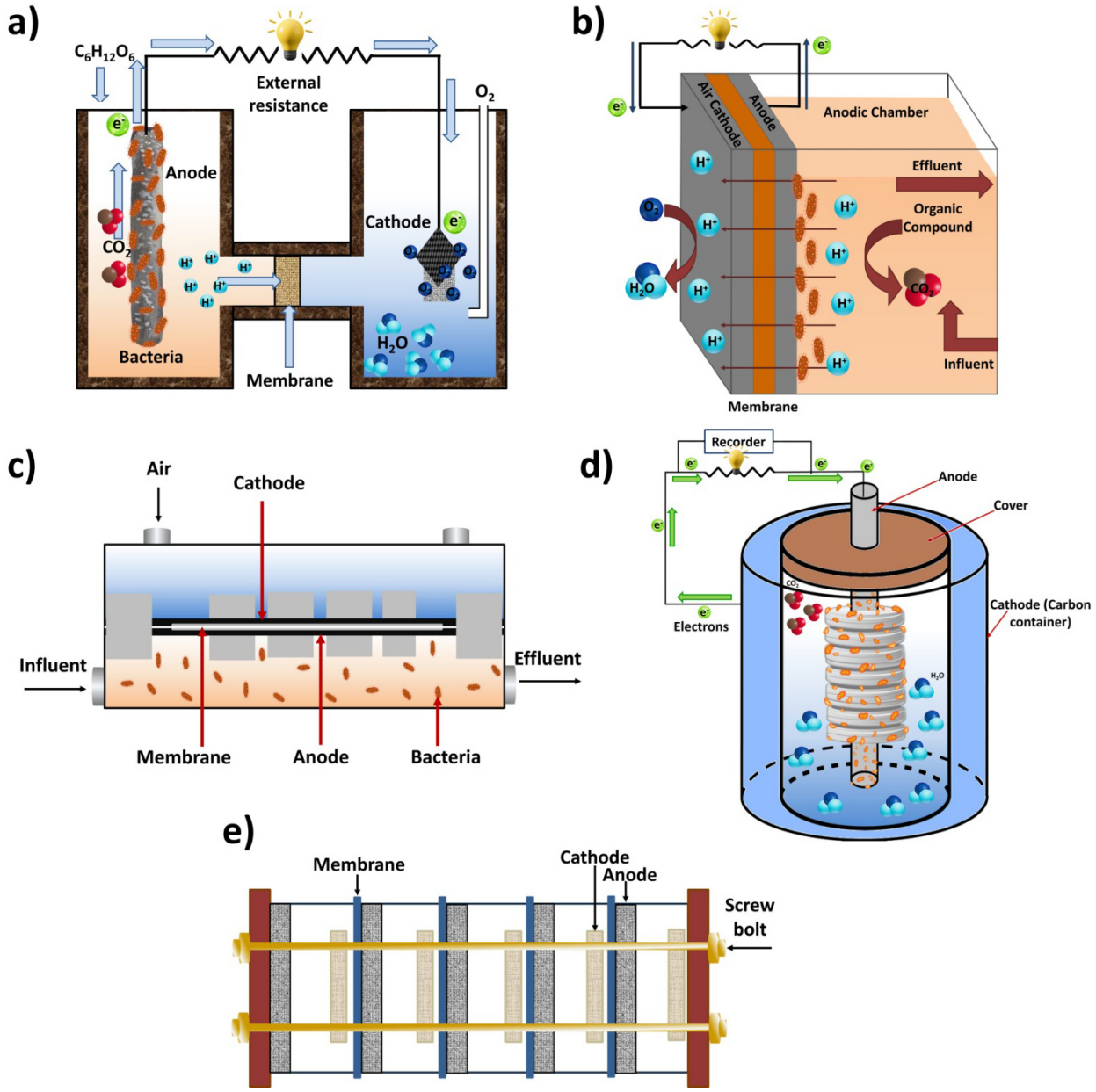

Fig. 4. Basic diagram of different MFC configurations. (a) H-type double-chamber. The geometry is quite similar to the letter H; in most cases, the chamber employs a saline bridge or agar as a PEM separator. (b) Cube-type single chamber. Commonly, the single chamber does not use a PEM, although if a membrane is required, the membrane is placed next to the cathode. (c) A flat-plate single-chamber is used in continuous mode. (d) Cylindrical one-chamber arrangement employs more than one anode in continuous mode, and (e) the stacked fuel cell comprises several single MFCs connected in parallel or series circuits.

MFCs for municipal wastewater treatment at the pilot scale has also been demonstrated. In a previous report, a 45 L bioelectroreactor was installed at a wastewater treatment plant after the primary clarifier. The pilot-scale MFC operated for around 9 months and exhibited a stable power output even at low COD loading, with continuous removal of organic matter and elimination of nitrogen and total suspended solids [49].

Finally, the stacked configuration is assembled with individual MFCs connected in series or parallel to optimize power output and energy generation; *i.e.*, power output is multiplied by the number of single cells connected. One of the first proposals for a stacked MFC system was made by Aelterman et al. [50], who connected six individual MFCs and achieved a maximum volumetric power output of 258 W m^{-3}, employing hexacyanoferrate as the catholyte and a granular graphite anode. An interesting proposal the authors make is the use of bipolar plates between electrodes, which promoted high power output and adequate mass transfer between chambers. The use of H-type MFCs to assemble a stacked biological fuel cell was also tested, achieving a maximum power of 0.405 W with

three individual MFCs connected in series. This system was operated in batch mode for approximately 30 days using carbon paper electrodes, glucose as the substrate, and hexacyanoferrate as the catholyte [51]. More recently, stacked fuel cells have been successfully implemented for wastewater treatment at the pilot scale [52,53]. Fig. 4 shows the configuration of some MFCs reported in the literature. (More information about this topic is found in specialized literature [35,54]).

3.2 Factors Affecting Cell Performance

Since MFC technology spans several areas, including engineering, electrochemistry, microbiology, fluid dynamics, and biochemistry, various physical, biological, and chemical factors affect the efficiency of power generation and pollutant degradation. Several studies have examined how different biotic and abiotic parameters affect the electrochemical performance and power output of MFCs, highlighting the complexity of this technology and the co-dependence of these factors in optimizing energy recovery [55,56,57].

The most important biological parameter is the bacterial population. Inoculum selection is critical for MFC performance and operational strategies, owing to differences in metabolic pathways and electron transfer mechanisms among the bacterial community. In many cases, pure cultures such as *Geobacter* [58,59], *Clostridium* [2,60], *Shewanella* [61,62], and *Pseudomonas* [63,64] are used for bioelectrochemical applications, demonstrating a high capacity to generate energy with or without mediators. The application of these mediators depends on the electrogenic mechanisms in the bacteria of each pure culture and on the ability of the bacteria to produce natural mediators. Conversely, co-cultures and bacterial consortia have demonstrated strong performance in real-world applications. This may be due to the higher stress resistance, nutrient adaptability, and diverse metabolic pathways, which enhance the oxidation of organic matter and the subsequent production and transport of free electrons [65]. Accordingly, mixed cultures obtained from sources such as wastewater, sediments, and activated sludge are often preferred over pure cultures due to avoiding inoculum pretreatment, micronutrient supplementation, and intensive maintenance of the anodic chamber [66]. Moreover, previous studies have reported that mixed cultures generate more power than pure cultures [67,68]. In general, mixed cultures are used to optimize power output, whereas pure cultures are used to determine the biochemical pathways and mechanisms employed by bacteria.

Organic source (substrate) is another biological factor that affects the electrochemical performance of biological fuel cells. In the early stages of MFC development, simple substrates such as monosaccharides, organic acids, and low-molecular-weight carbohydrates were used to produce energy; however, over time, other sources, including various wastewater streams, complex carbohydrates, and even petroleum-derived wastes, have proven to be effective carbon sources [1]. As described in Section 1, substrate composition directly affects free-electron generation and can, therefore, enhance or reduce energy recovery. Current trends indicate that the residual complex organic matter oxidized within the anodic chamber is not limited to corncob flour [69], wheat–bran-extracted cellulose [70], sugarcane industry wastewater [71], landfill leachate [72], and petroleum refinery wastewater [73].

Alternatively, the most frequently evaluated physical factors are: electrode materials and spacing; the membrane or separator; reactor configuration; external resistance loading; anolyte and catholyte composition; operational parameters such as solution pH, salinity, hydraulic retention time, and temperature. The anode is a crucial component in MFCs, playing an important role in receiving the generated electrons and providing microorganisms with an adequate environment for proper growth. The ideal anode must be biocompatible, durable, have high surface area and porosity, be inexpensive, and exhibit a high electron-transfer rate [74]. Conventional anodes are classified as carbon-based and metal electrodes. For carbon-based anodes, single materials such as felt [75], fiber [76], foams [77], brush [78], graphite [79], and activated carbon [80], as well as carbon composites [81] and carbon nanometric anodes [82,83], have been employed, while the most common metal-based anodes involve the use of Cu, Au, Ag, Pt, and stainless steel [84]. Recently, it has been reported that a three-dimensional (3D) open microarray anode based on carbon cloth promotes bacterial enrichment and delivers high power generation with fast startup [59]. This report highlights the importance of porosity and surface area as key parameters for optimizing electrochemical performance. Notably, extensive information about anode materials, properties, configurations, advancements, limitations, and trends can be found in the existing literature [81,85].

The cathode is the electrode responsible for the reduction reaction involving free electrons, protons, and oxygen (Eqn. 4); its properties are quite similar to those of the anode. Similar to the anode, the cathode plays a crucial role in MFC bioelectrochemical performance; thus, the correct selection of cathode material can increase the potential gradient and improve power output. Since the oxygen reduction reaction (ORR) occurs at the cathode surface, it is necessary to improve cathode efficiency by introducing electrocatalysts into the cathode or by adding a catholyte solution to the cathodic chamber [86]. Mass transport limitations, oxygen diffusion, and OH^- transport must also be considered, as previous studies have reported that OH^- accumulation raises solution pH and reduces power output [87]. Over the last decade, the use of biocathodes has become established as a feasible alternative to enhance cathodic reactions and power density, as well as to remove nutrients from wastewater over the long term [88,89]. Moreover, the use of mixed-bacteria biocathodes further enhances power output [90].

Another important factor is the presence of a membrane or separator, whose main functions are to transport ions from the anodic to the cathodic chamber and to separate the two chambers. As mentioned above, the most common membrane is Nafion 117; however, due to the associated high cost and impracticality at large scale, other materials have recently been employed. In some cases, the PEM is replaced by an anion exchange membrane (AEM) to transfer OH^- ions to the cathodic chamber, thereby avoiding cation transport (Na^+, Mg^{2+}, and protons), salt precipitation, and MFC instability [91]. In agreement with Rossi et al. [92], ORR in the cathode chamber is favored at neutral or alkaline pH, so transporting OH^- to this chamber improves MFC operation, reduces activation losses, and increases power output. Recently, a novel AEM composed of an ionic liquid coupled to polyvinyl alcohol was synthesized to boost energy recovery [93]. Finally, laminate membranes composed of an AEM and PEM have been demonstrated to be a suitable option not only for energy production but also for the removal of heavy metals from wastewater [94].

The electrode spacing and distance are other elements to consider in MFC designs. A short electrode distance between electrodes is generally associated with lower internal resistance and optimal bioelectrochemical performance; however, if the distance is too short, oxygen can diffuse back to the anode, thereby reducing bacterial activity [92]. In contrast, another study reported that increasing electrode spacing enhanced power density in a small cube-type single-chamber MFC [95]. In that system, the optimal electrode was 6 mm, yielding a maximum power density of 400 mW m^{-2}. Similar trends were previously reported during domestic wastewater treatment in an air-cathode MFC [96]. Overall, electrode configuration and spacing should align with the main goal of the MFC; a closer arrangement is suitable for achieving high power density, whereas a spaced arrangement is recommended when short-term wastewater treatment optimization is required [97].

Operational parameters such as solution pH, salinity, and temperature also significantly impact MFC performance. For example, a previous report examined the effects of solution pH and salt loading in the anolyte of an H-type fuel cell and found that a NaCl concentration of 6 g/L at pH 8 maximized the volumetric power density to 1188 mW m^{-3} [98]. This improvement in power density could be explained by the presence of inorganic salts, which can mediate electron transfer and serve as micronutrients for the growth of mixed cultures of bacteria (*Clostridium*, *Tetrahymena*, and *Desulfovibrio*). The positive effect of an alkaline pH in the anolyte solution was also demonstrated in a cylindrical MFC treating synthetic wastewater, where the maximum power density achieved in this paper was 108.32 mW m^{-2} at pH 9, with a 1:2 anolyte recirculation ratio [99]. Similar values for anolyte pH have been reported as optimal for generating power in an H-type MFC [100], a double-chamber MFC [101], and with marine consortia [102].

Salinity, which is related to the ionic strength of the solution, affects bioelectrochemical performance by reducing internal resistances and improving proton transport and electron transfer to the anode. Moderate saline environments can raise power output to a certain point; high salt loading negatively affects electrogenic bacteria, *i.e.*, the tolerance of bacteria to a given salt concentration limits the ionic strength of the anolyte. The impact of temperature is explained by microbial growth kinetics and proton transport rate. Most of the bacteria employed in MFCs are cultured at mesophilic conditions (25–40 °C). At lower temperatures, oxidation reactions proceed very slowly, requiring longer times. Conversely, higher temperatures (>40 °C) could inhibit metabolic activity. Tremouli and co-workers [103] evaluated a dual-chamber MFC, observing that the maximum power density was obtained at 4.1 g KCl/L at pH 9 and a mesophilic regime (35 °C). Similar behavior was observed during petroleum biodegradation, where the maximum energy was recovered at 30 °C and a 1.5% w/v NaCl concentration. An interesting highlight is the negative effect of salt addition: at concentrations above 1.5% w/v and under thermophilic conditions, electrochemical efficiency was reduced by 35-fold [104]. A summary of the most important parameters that affect the bioelectrochemical performance of MFCs is presented in Fig. 5.

3.3 Electrochemical Efficiency

Commonly, electrochemical efficiency is measured by either power output per unit anode surface area (mW m^{-2}) or volumetric power output (mW per anodic chamber volume, m^{-3}). These measurements have usually been used to compare electrochemical performance and power generation in MFCs operated under different configurations, operational parameters, and substrates, and to measure the energy directly recovered from substrates. Most papers report power output as the primary metric for MFC performance.

Previously, Ge et al. [105] introduced a term called normalized energy recovery (NER), defined as the total power generated by the MFC during operation per total volume of wastewater treated (Eqn. 5). In some cases, this term can be adapted to incorporate the degraded COD, a modification is usually used when additional organic substrates are present in the anolyte (Eqn. 6).

$$\begin{aligned} ER &= \frac{power * time}{wastewater\ volume\ (treated\ within\ time)} \\ &= \frac{power}{wastewater\ flow\ rate} \\ &= \frac{kW\ h}{m^3} \end{aligned} \tag{5}$$

$$NER = \frac{power * time}{COD\ (removed\ within\ time)} = \frac{power}{wastewater\ flow\ rate * \Delta COD} = \frac{kW\ h}{kg\ COD} \quad (6)$$

NER does not depend on the size or configuration of the bioelectroreactor. Instead, the NER includes additional information, such as wastewater flow rate, organic loading, and organic matter removal efficiency, making NER suitable for standardizing energy-efficiency calculations across different configurations and as a preliminary tool for energy balance in MFC systems [106]. Moreover, NER is an adequate parameter for scaling up BESs such as PMFC, MDC, MEC, and MFC [107].

Coulombic efficiency (CE) is another metric used to evaluate bioelectrochemical performance in MFC technology. CE is defined as the ratio of the total Coulombs transferred from the substrate to the anode to the maximum possible Coulombs that could be obtained if all of the substrate were converted to current [108]. In fed-batch and continuous operation modes, CE can be calculated using Eqns. 7,8, respectively.

$$CE = \frac{M \int_0^t I\ dt}{F\ b\ V\ \Delta COD} \times 100 \quad (7)$$

$$CE = \frac{M\ I}{F\ b\ Q\ \Delta COD} \times 100 \quad (8)$$

where M is the molecular weight of oxygen (32 g mol^{-1}), t is the operation time in seconds, I is the current provided by the cell in amperes, F the Faraday constant (96,485 C mol^{-1}), b is the number of electrons exchanged per mole of oxygen (4), V is the volume of the anodic chamber and Q is the inlet anodic flow rate, and ΔCOD is the decrease in COD during cell operation.

The calculation of CE has been reported previously for different MFC configurations and operating conditions [109,110,111]; however, despite the widespread use of this metric, CE does not directly measure the maximum energy recovered and is limited to the highest current density achieved. This limitation arises from the nature of the CE calculation, which is based on electron recovery relative to the maximum hypothetical electron production [112].

In the literature, several papers report MFC efficiencies using various configurations, electrode materials, and substrates; some of these are summarized in Table 1 (Ref. [23,26,31,33,34,39,40,42,48,51]).

4. Novel Technologies Derived From MFCs

The MFC is the basic BES from which several novel technologies have been derived in recent years; the most important include the PMFC, MEC, MDC, CW-MFC, and sediment MFC (SMFC). Fig. 6 shows schematic diagrams of these BES. Similar to the MFC, these derived biological fuel cells are based on electrogenic bacterial metabolism, electron transport, ion permeation, organic matter oxidation in the anode chamber, and chemical interactions and reactions in the cathodic zone, *i.e.*, there is a wide range of factors affecting bioelectrochemical performance, with bacterial metabolism as the driving force. Despite these shared features, each derived system has its own characteristics, limitations, and applications; these are described in the following paragraphs.

4.1 Microbial Electrolysis Cell

MECs are one of the most studied MFC-derived systems. The basic conformation of this cell is quite similar to the conventional two-chambered MFC design, where the cell comprises an anaerobic anodic chamber, a PEM, an external electrical circuit, and a cathode chamber (Fig. 6). The main difference between MFCs and MECs is the atmosphere in the cathodic chamber, which must be anoxic for MECs to perform the proton reduction reaction and the production of high-purity hydrogen as the main product. Thermodynamically, hydrogen production in MECs requires energy from an external source; reported energy inputs range from approximately 0.2 to 0.8 V, which is low compared with the energy required to break water molecules in conventional electrolysis [113,114]. MECs were first reported in 2005 by two independent research groups at Penn State University and Wageningen University [13]. Since then, significant efforts have been made to adapt this technology for large-scale applications.

The great impact of MEC technology lies in the ability of the cell to produce the most powerful known fuel: hydrogen, with a caloric power of 140 MJ kg^{-1}. Moreover, hydrogen, as an alternative biofuel, has distinctive characteristics, including being environmentally friendly; combustion produces water as the main byproduct; no greenhouse gas emissions; the ability to be used in electrochemical cells to produce electrical energy; universality. Consequently, hydrogen has great potential to promote the partial replacement of conventional fossil-based fuels [115].

Hydrogen gas is produced via various biological processes, including dark fermentation, photofermentation, photolysis (direct/indirect), and MEC. Among these, MEC offers significant advantages over the others due to the high purity and yield of the hydrogen produced. As reported by Kadier et al. [114], the reactions occurring in the anode and cathode chambers are as follows (note that acetate is considered the reference substrate):

Table 1. Comparison of different MFC efficiencies reported in the literature.

Substrate	Configuration	Operational conditions	Power density (mW m^{-2})	CE (%)	COD removal (%)	Reference
Medium solution containing sodium acetate	Cube-type double chamber	Carbon cloth electrodes, PEM membrane, 25 °C, anaerobic mixed consortium, and a mineral buffer solution as the anolyte.	2610	-	-	[23]
Synthetic wastewater containing sucrose as the carbon source	Cube-type double chamber	Graphite felt electrodes, a ceramic membrane, anaerobic sludge bacteria, pH 8, and room temperature.	112.81	23.74	87.7	[26]
Ravot medium	Cube-type double chamber	Graphite felt electrodes, a CIM-7000 membrane, 30 °C, and *Clostridium* bacteria.	214.2	64	-	[34]
Reactive black 5 azo dye	H-type double-chamber	Carbon cloth electrodes, 100 ppm substrate, 21 days, and sludge bacteria consortia.	474.06	-	70 ± 2.9	[31]
5 mM sodium benzoate	H-type double-chamber	Salt-bridge membrane, 30 days, and *Corynebacterium vitaeruminis* bacteria.	18.15	-	81.81	[33]
Phosphate buffer nutrient solution	Cube-type single-chamber	Wastewater treatment plant bacteria, a low temperature (4 °C), and carbon electrodes containing Pt.	425	31	-	[39]
Sodium acetate coupled to ribitol (polyalcohol)	Cube-type single-chamber	Mesophilic regime (32 °C), carbon cloth electrodes, and a Nafion membrane.	2350	28	92	[40]
Simulated potato-processing wastewater	Cube-type single-chamber	Mesophilic regime (30 °C), pH 7, four bamboo charcoal anodes, and an air carbon cloth cathode.	576	-	-	[42]
Medium solution containing 1 g L^{-1} glucose	Cylindrical one chamber	Carbon-based electrodes connected by a titanium wire, pH 7, 30 °C, and inoculated with *P. aeruginosa.*	3322	-	85	[48]
Nutrient mineral buffer containing 0.2 g L^{-1} glucose	Stackable H-type double chamber	Carbon paper electrodes, a PEM membrane, pH 7, room temperature, and a mixed culture.	135	-	-	[51]

Cylindrical and cubic one-chamber MFCs have the highest power densities and COD removal efficiencies compared to other designs; however, a direct comparison between all configurations must be carefully considered due to the differences in operating conditions, organic sources, bacteria consortia, and physical tools such as electrode materials and pre-activation treatments, PEM material, external resistance, and nutrient–mineral solution.

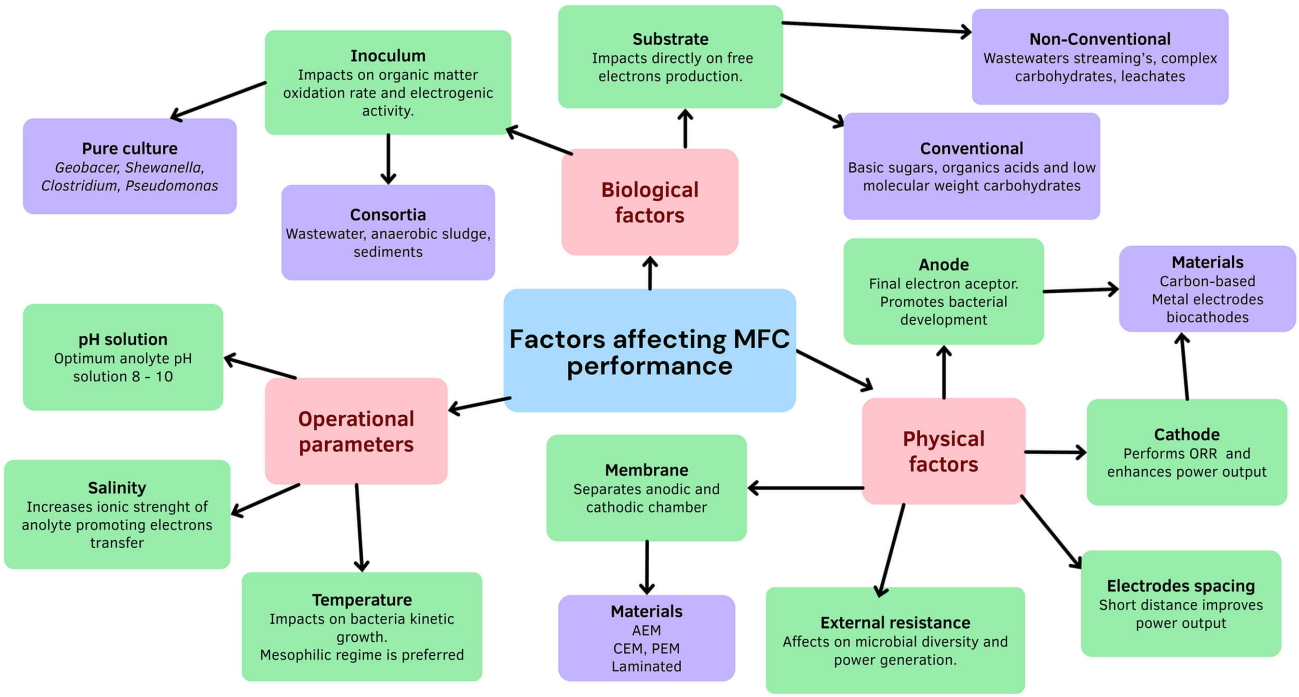

Fig. 5. Factors that affect MFC bioelectrochemical performance. The most important factors that affect MFC performance are categorized into biological, physical, and operational parameters. Biological factors have a critical impact on anodic chamber biochemical reactions, while physical and operational parameters play an important role in the overall performance.

$$C_2H_4O_2 + 2H_2O \rightarrow 2CO_2 + 8e^- + 8H^+ \quad (9)$$

$$8H^+ + 8e^- \rightarrow 4H_2 \quad (10)$$

The maximum hydrogen yield is 4 moles per mole of acetate, which is identical to the hypothetical maximum hydrogen yield reported for dark fermentation [116]. However, it is important to note that during fermentation, other by-products, such as H_2S, organic acids (propionic and butyric), CO_2, and even CH_4, are produced, thereby reducing hydrogen yield. This drawback is addressed in MEC technology, which produces high-purity hydrogen gas in the cathodic chamber. Under optimized conditions, hydrogen yields of up to 12 moles of hydrogen per mole of glucose can be achieved [117]. Despite efforts to improve hydrogen production, this hypothetical limit has not yet been reached due to operational limitations and catalytic capacity; thus, more research is still needed. Previous studies have reported high hydrogen production and yields: 8.4 mol H_2 mol^{-1} glucose in a double-anode single-chamber MEC [118], 3.9 mol H_2 mol^{-1} glycerol in a single-chamber membrane-less MEC [119], 7.72 mol H_2 mol^{-1} glucose in a single-chamber MEC operated under alkaline conditions with an applied voltage of 1.6 V [120], and 974 mL H_2 g^{-1} acetate in a double-chamber MEC equipped with a polyvinyl alcohol–chitosan membrane [121]. An interesting alternative for further increasing hydrogen yield is to couple MEC technology with conventional dark fermentation. This strategy has been shown to enhance hydrogen yield from not only simple sugars but also complex substrates such as cornstalk hydrolysate [122], sugar beet juice [123], cellobiose [124], and cheese wastewater [125], achieving maximum yields of 129.8 mL H_2 g^{-1}, 6 mol H_2 mol^{-1} glucose, 900 mL g^{-1} COD, and 95.1 mL H_2 g^{-1} COD, respectively.

The large-scale application of MEC has recently been proven; a previous study reported a hydrogen production rate of 3.48 LH_2 $L_{reactor}{}^{-1}$ d^{-1} in a continuous two-step cascade process comprising anaerobic digestion and the MEC, using fruit waste as carbon source. The cascade configuration improved hydrogen recovery by 96% and carbohydrate oxidation by 4-fold [126]. Previously, a 100 L MEC was operated at ambient temperature to treat domestic wastewater for approximately 12 months, achieving an average hydrogen production of 0.6 L per day and a negative energy balance, as energy output was lower than energy input [127]. Estrada-Arriaga et al. [128] transformed a septic tank into a 50 L MEC reactor to simultaneously treat household wastewater, and produce green hydrogen at a rate of 0.072 L d^{-1} coupled with high COD and ammonium removal efficiencies of 84% and 98%, respectively. The highest large-scale hydrogen production rate reported to date was obtained by Guerrero-Sodric et al. [129] in a 135 L bioelectroreactor operated with synthetic wastewater and an external voltage of 0.8–1.1 V for 6 months; the

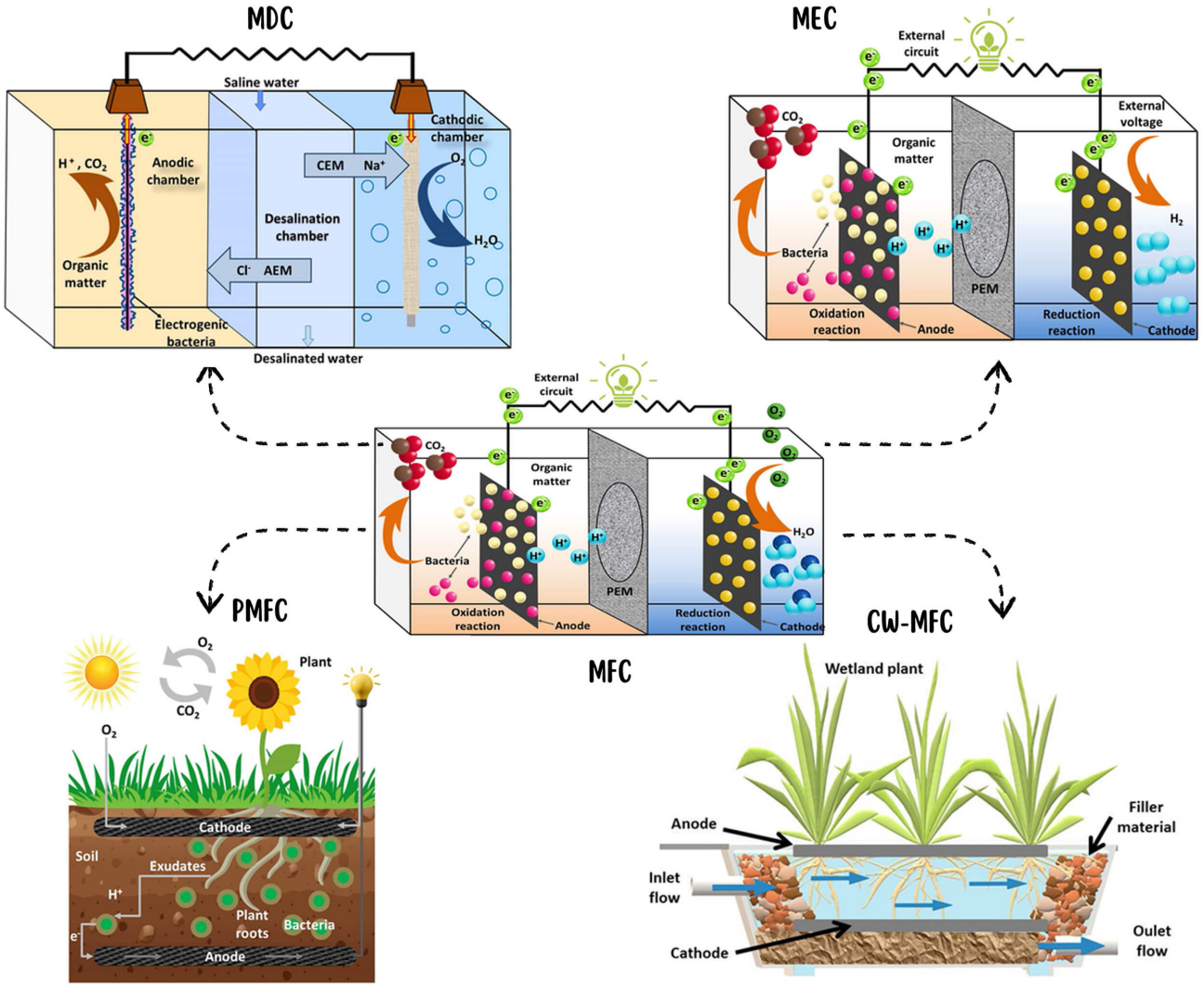

Fig. 6. Schematic diagrams of the MFC and the associated main derived BES. The conformation of the MEC is quite similar to the MFC; the only difference between these cells is the atmosphere of the cathodic chamber. MDC incorporates a middle chamber and an anionic membrane for water desalination. PMFC and CW-MFC exploit the metabolism of living plants to recover energy from the associated exudates and remove pollutants through phytoremediation. MDC, microbial desalination cell; PMFC, plant microbial fuel cell; CW-MFC, constructed wetland MFC.

hydrogen production rate was enhanced up to 0.1 m^3 d^{-1}, with a corresponding CE of 27%.

Biomethane production in the cathodic chamber is another promising MEC technology. In a pilot-scale tubular bioelectroreactor, 64 mL methane L^{-1} d^{-1} was obtained with nitrogen recovery of around 270 mg L^{-1} d^{-1} [130]. More recently, MEC technology has been implemented in a CW-MFC, demonstrating high energy recovery potential and significantly higher ammonium removal compared with standalone technologies [131]. Further information on MEC technology can be found in other sources [113,115].

4.2 Microbial Desalination Cell

As shown in Fig. 6, the MDC comprises three chambers: anodic, cathodic, and middle. The anodic chamber serves the same function as in MFCs and MECs, *i.e.*, electrogenic bacteria metabolize organic matter to produce free electrons, protons, and CO_2; these electrons are collected at the anode and transported to the cathode via an external circuit. The cathodic chamber can operate under aerobic or anaerobic conditions, as previously described, although the initial designs were operated under an aerated atmosphere. The middle chamber serves as the desalination chamber, in which cations are transferred to the cathodic chamber through a PEM, and anions are permeated to the anodic chamber through AEM [132]. In some studies, MDCs have been used as a pre-desalination process before other technologies such as reverse osmosis, enhancing total dissolved solids (TDSs) removal and boosting power output by 58% [133], and forward osmosis, diminishing COD (94%) and conductivity (99%) [134]. Collectively, these reports highlight that coupling MDCs with other desalination processes

can enhance ion removal by up to 2-fold compared with standalone bioelectrochemical cells.

MDC spans several areas, from electrochemistry to microbiology and surface phenomena; thus, a wide range of parameters affects desalination efficiency, pollutant removal, and energy recovery. Similar to other BESs, such as MFCs and MECs, the implementation of biocathodes has shown promise for optimizing power output. *Chlorella vulgaris* microalgae were cultivated on the cathode surface to treat saline water at two salt loadings: 15 and 35 g L^{-1}. Higher salt concentrations increased both power density and algal growth, with the most significant effect on desalination efficiency, which improved 1.5-fold at higher salt loading [135]. In conventional MDCs, high removals of sulfate (72%) and COD (88%) were also observed. Bacterial community analysis revealed that *Desulfobulbus*, *Geobacter*, and *Desulfovibrio* were the main species contributing to the desalination of synthetic saline water at 35 g L^{-1} [136]. Temperature is another key parameter that plays an important role in MDC performance. A study reported that increasing the temperature (up to 45 °C) resulted in maximum salt removal and current density (22.7% and 402 mA m^{-2}); however, at this temperature, the highest COD removal and CE were not achieved [137]. The impact of external resistance loading on desalination performance has also been investigated. Rahman et al. [138] demonstrated that at high external resistances, the desalination rate was quite slow (2.52 mg h^{-1}), whereas reducing the external loading to 1–67 Ω considerably increased the desalination rate to 8.59–10.41 mg h^{-1}. An interesting and promising alternative for boosting ion removal while enhancing power output in an MDC is to add ozone as an electron acceptor in the cathodic chamber. The addition of ozone gas resulted in maximum Cr(VI) and Pb(II) removals of 99.2% and 98.4%, respectively, with high power densities of 354 and 232 mW m^{-2}, respectively; these values were higher than those obtained in the conventional aerated cathodic chamber MDC [139]. More recently, a conventional MDC operated with ferricyanide as the catholyte and low external resistance showed high current efficiencies (80–100%) and an interesting freshwater production rate of 10.6 L m^{-2} h^{-1} from different saline water sources. This study demonstrated the strong potential of MDCs to desalinate water while simultaneously producing green energy [140].

Integrated technologies comprising MDCs and other electrochemical devices have been reported as alternative approaches to improve bioelectrochemical performance and salt-removal efficiency. For example, an MDC was coupled to an MEC to treat industrial wastewater and saline water simultaneously; the findings revealed a positive energy balance, with a maximum volumetric power generation of 0.0267 kW h m^{-3}, and the removal of almost 100% of the nitrogen and lead from the industrial wastewater [141]. In another study, the desalination process and copper removal via chemical precipitation were demonstrated in an integrated system composed of a set of five-chamber MDC and an electrodialysis system, which achieved the maximum removal rates of 5.07, 53.6, and 1.84 kg m^{-3} d^{-1} for copper, salt, and COD, respectively, with an optimal power density of 737.3 mW m^{-2} [142]. These results suggest that this integrated alternative could be applied on a large scale to real wastewater treatment in a suitable manner. Novel configurations, such as quadruple MDC [143] and triple enclosed cuboid chambers [144], have also been employed to achieve high desalination rates. For more information on MDCs, please review the specialized literature [8,132,145].

4.3 Plant Microbial Fuel Cell

Strik et al. [14] used a *Glyceria maxima* plant in the anodic chamber of an MFC to evaluate electricity generation from a living plant; this experiment led to what is now known as PMFC. The premise of this system is to use organic matter in the ground, plant roots, and the rhizosphere as the main carbon source for electrogenic bacteria in plant-associated soil. In this system, the anode is placed under the plant in direct contact with the rhizosphere and natural microbiome, while an air cathode is usually placed above the soil surface. Both electrodes are interconnected by an external electrical circuit (Fig. 6). In a PMFC, the soil not only serves as a medium to promote plant growth but also to facilitate ion transport, maintaining charge balance and avoiding pH gradients and the use of the high-cost PEM; this is an important advantage of PMFCs over other BESs [146].

The energy flow in a PMFC is as follows: (i) solar energy is captured by the plant through the photosynthesis process and transformed into saccharide molecules, (ii) these saccharide molecules represent the chemical potential of the plant and support normal plant growth, (iii) part of this chemical potential is released via rhizodeposition, liberating exudates into the surrounding soil, and (iv) electrogenic bacteria metabolize organic matter from the plant to produce free electrons and electrical energy. Thus, in a PMFC, solar energy is converted into electrical energy [147]. PMFCs have gained significant attention in recent years as a promising technology for powering low-energy-demand devices using low-cost materials, natural resources, and plants. Moreover, PMFCs can be applied almost anywhere, with no competition for food resources, no need for harvesting or plant damage, and potential for long-term operation [148]. In fact, any plant can be used to generate energy in a PMFC.

In addition to the factors described in Section 3.2, the used plant species plays a primary role in PMFC performance. Notably, plants are classified by the associated photosynthetic pathway as C3, C4, or CAM; among these, C4 has demonstrated higher photosynthetic efficiency and, thus, higher power output than the other pathways [146,149]. In literature, a wide range of plants have been commonly employed in PMFCs. Representative C3 species include *Glyceria maxima* [14], *Oryza sativa*

[150], *Phragmites australis* [151], and *Typha angustifolia* [152]. C4 includes *Cyperus papyrus* [153], *Amaranthus viridis* [154], *Eichhornia crassipes* [155], and *Agapanthus africanus* [156]. CAM plants include *Agave potatorum* [149], *Sedum hybridum* [157], and *Opuntia joconostle* [158]. Overall, the variety of plants comprises ornamental [156,159,160] trees [161], and even crops [162,163].

Recently, PMFCs have also been investigated for the co-production of hydrogen [164] and the elimination of dye in industrial wastewater [165]. A promising trend in this technology is the integration of food plants such as vegetables and culinary plants, hydroponic systems, and novel energy systems into PMFC configurations to provide high power density while producing sustainable food [166,167]. More information regarding PMFC technology can be found in other sources [146,168].

4.4 Constructed Wetland Microbial Fuel Cell

CW-MFC, also known as an electroactive wetland, is a novel hybrid technology that combines a conventional MFC with natural wetlands, with a focus on producing green energy; meanwhile, a wide range of pollutants are degraded by the natural bacterial–plant symbiosis and the electrochemical contribution. This hybrid BES combines the MFC with natural wetland principles to enhance energy recovery, water treatment capacity, and effluent water quality in long-term processes using low-cost materials [6]. Moreover, since CW-MFCs build on MFCs and natural wetlands, these cells inherit the limitations and challenges from each, such as low energy recovery and pollutant degradation rates. It has been reported that some wetland plants, such as macrophytes, can create an enriched environment for the proper growth and development of electroactive bacteria, thereby promoting energy recovery and pollutant degradation in wastewater [169]. This effect is attributed to the wide range of organic materials that bacteria can use as carbon sources, including sediments, exudates, organic matter, nutrients in wastewater, plant roots, and biomass. In addition, CW-MFCs involve several depuration processes, such as phytoremediation, adsorption, chemical precipitation, electrochemical reduction, and biological degradation, among others, that improve water remediation [5,170]. Consequently, this technology is efficient at treating wastewater, and the amount of green energy produced is higher than that of standalone MFCs and constructed wetlands, as supported by various studies [6,171]. Moreover, in agreement with Ebrahimi et al. [172], the construction and operational costs of CW-MFCs are lower than those required for conventional MFCs but higher than those of standalone CW; however, the economic balance could be improved depending on the energy recovered and the decontamination rate. Since most CW-MFCs do not use a PEM separator, the associated construction cost is reduced by almost 1.5 times compared with a single MFC; this, coupled with the large volume of water treated, suggests that CW-MFCs are a more sustainable option than both constructed wetlands and MFCs [173].

Similar to PMFCs, plants positively affect the bioelectrochemical performance of CW-MFCs. Several studies have demonstrated that planted systems can enhance pollutant degradation and energy recovery by up to 2-fold [174], which is mainly attributed to phytoremediation processes coupled with the wide range of bacterial populations in the rhizosphere. The major advantage of CW-MFCs lies in the associated capability to effectively remove a wide range of pollutants, from synthetic wastewater composed of low-molecular-weight organic molecules to heavy metals [175], drugs [176], aromatic compounds [177], organic dyes [178], and polyfluoroalkyl substances [179]. This versatility highlights the need to adapt CW-MFC technology in real, large-scale, and in-field applications. However, some issues remain unresolved; thus, more research is needed on electrode materials, electrochemical arrangements, pollutant degradation mechanisms, filler materials, electroreactor configurations, ohmic losses, and long-term stability. Future trends must be directed toward metabolic engineering to improve bacterial–plant symbiosis, the fabrication of novel, efficient, low-cost, and biocompatible electrodes, the removal of other complex pollutants, scaling-up strategies, and long-term operation and stability of CW-MFCs under field conditions.

5. Current Trends and Limitations

Electrogenic bacterial metabolism is one of the key parameters that impact the bioelectrochemical performance of the aforementioned BES; this means that the activity of the bacterial community is the driving force in any bacterial fuel cell. Once the oxidation reaction has started in the anodic chamber, free electrons flow to the anode and then move toward the cathode via an external circuit, generating electricity; this is a common phenomenon in MFC and MFC-derived systems. The differences among biological fuel cells are observed in the cathodic chamber, reactor configuration, and the nature of the organic substrates employed. PMFC and planted CW-MFC use plant roots and exudates as substrates and usually employ an air cathode. Meanwhile, MFC, MEC, and MDC employ wastewater streams, leachates, and dissolved organic matter as organic sources for electrogenic bacteria. MDC is the only BES reported here that simultaneously uses AEM and CEM separators and a middle desalination chamber; thus, the configuration of this cell is more complex than that of other single- or dual-chambered fuel cells. The cathodic chambers in MEC and MDC operate under an anoxic atmosphere, enabling the production of high-purity hydrogen that could serve as a universal alternative fuel. PMFC can produce green energy from food plants without causing plant damage or requiring harvest, making this technology suitable for applications in rural areas, greenhouses, and gardens. In contrast, CW-MFC addresses the drawbacks of standalone MFC and CW by handling large wastewater volumes, re-

moving a wide range of pollutants, and increasing power output; however, CW-MFC requires long flow paths and novel configurations.

Each BES has distinct functions, limitations, and potential for real-world applications; some of these are summarized in Table 2.

In addition to those described in Table 2, there are some common limitations shared by all BESs that must be addressed before real-world applications; these are as follows:

(i) Low power output: Most of the BESs reported in the literature show low power output attributed to internal resistances and low catalyst activity at the cathode. Bacterial competition during the consumption of organic matter can also reduce the conversion of chemical potential into electrical energy. Reactor configuration, the composition of the organic source, the bacterial community, electrode materials, and the electrochemical arrangement all play crucial roles in bioelectrochemical performance.

(ii) Scaling-up challenges: Electrode fouling undermines the bioelectrochemical potential of BESs during long-term operation. Moreover, high power output is often achievable only with carbon-based electrodes doped with precious metals, thereby making BESs unsuitable for pilot-scale operation. Research focused on novel low-cost electrodes, ohmic losses, and electrode spacing and arrangement is needed to reduce operational costs.

(iii) Long-term operation: Electrode fouling reduces the bioelectrochemical performance of any fuel cell. For adequate long-term operation, maintaining electrode efficiency and proper bacterial activity in changing environments are major challenges. In PMFCs and planted CW-MFCs, filler material plays a crucial role in decontamination through processes such as adsorption and absorption; thus, the associated efficiency may decline over the long term. Biomass accumulation on membrane surfaces and biofouling limit the bioelectrochemical potential of MFCs, MECs, and MDCs.

(iv) Real wastewater stream treatment: Although several studies have reported high pollutant degradation efficiencies and rates when using synthetic wastewater in most BESs, the use of real wastewater streams remains almost unexplored; this highlights the urgent necessity to understand pollutant removal behavior under real wastewater conditions. Enhancing the removal of emergent and recalcitrant toxic pollutants, such as heavy metals, drugs, azo dyes, and petroleum-derived compounds, is also necessary.

The future trends of biological fuel cells must be directed, but not limited to the following areas: bacteria–plant metabolic engineering strategies, novel bioelectroreactor configurations and designs, electrode arrangement and spacing, low-cost and efficient ion-exchange membranes, continuous-flow operation and parameter stability, enhanced pollutant degradation capabilities, increased bioelectrochemical depuration of pollutants, biosensing applications, and genomic–metabolic issues.

6. Economics of MFC and the Associated Derived Technologies

Currently, MFC technology has not been widely implemented at a large scale due to the associated unfavorable cost–benefit ratio and low energy output from bacterial oxidation. These limitations make this technology unprofitable for large-scale and in-field applications. Among the basic components in the MFC common structure, the PEM and electrodes are the most expensive. In fact, it has been reported that ion-exchange membranes usually account for almost 63% of the total capital cost in MFC, MEC, and MDC construction [6]. Regarding anodes, graphene oxide has shown promise for enhancing power generation in recent years. However, the synthesized material is more expensive than natural carbon-based materials, such as biomass-derived anodes. Therefore, using inexpensive materials, such as carbonized residual biomass, could help reduce the power cost of the MFC [74]. Eliminating separators in certain configurations is another strategy to further lower power costs in MFC-derived technologies. Recently, Biswas and Chakraborty [173] compared the cost–benefit balance of MFC, CW, and CW-MFC, demonstrating that CW-MFC technology is the most profitable option due to the associated lower construction costs compared with MFC, and greater treatment capabilities of CW-MFC for major pollutants relative to a single constructed wetland. The authors concluded that the economic viability of CW-MFC stems from the high energy recovery and power output achievable over large areas [173]. Moreover, since CW-MFC employs inexpensive filler materials as membranes, the construction and operating costs are considerably lower than those of other MFC-derived technologies, such as MEC and MDC. This positive feature is also observed in PMFCs, where plant soil and clays serve as separators [180,181]. In a previous study, Xu and co-workers [182] demonstrated that, among different BES, CW-MFC was the most suitable option for practical, large-scale applications based on a cost–benefit analysis.

The large-scale implementation of MFCs depends on integrating this technology into pilot wastewater treatment plants. A recent study revealed that, considering technology readiness level and system readiness level, large-scale MFC implementation can be economically viable for wastewater treatment while simultaneously producing green energy [183]. In addition, the use of non-platinum cathodes for the reduction reactions lowers power costs, thereby enhancing process economics [184].

MEC and MDC are the most complex derived technologies, employing high-cost cathodes and membrane separators. For MEC, a techno-economic analysis based on the cost of external electricity consumption and the hydrogen production rate demonstrated a positive balance for this technology at a large scale, even with financial subsidies [185]. More recently, it has been shown that coupling MEC technology with anaerobic digesters not only improves the

Table 2. Applications and limitations of MFCs and MFC-derived technologies.

BES technology	Applications	Limitations	Future trends
MFC	Produce electrical energy from organic matter in wastewater. Biosensors application and resources recovery.	Low power output and requires a high-cost PEM. Challenges for scaling up to large-scale applications.	Novel configurations. Low-cost electrodes and separator materials. Hybrid systems composed of MFCs and other technologies, such as dark fermentation, MEC, and photofermentation.
MEC	High-purity hydrogen production from organic wastes. Biosynthesis of chemical compounds. High-rate hydrogen production.	Requires an external energy source. Subject to ohmic losses and high internal resistances. Prone to undesirable side reactions.	Adaptation of MEC to other technologies to enhance hydrogen yield. Development of novel and low-cost catalysts for the reduction reaction. An alternative low-cost PEM. Novel configurations.
MDC	Three-functional technology capable of degrading organic wastes, generating electricity, and desalinating saline water. Resource recovery. Hydrogen and chemical compounds production.	High construction and operation costs. Low power output and desalination rate. Bacterial growth inhibition due to Cl^- ions. Membrane fouling and ohmic losses.	Improves desalination rates and eliminates membrane biofouling. Solves scale-up challenges. Integrates MDC into a wastewater treatment train.
PMFC	Production of electrical energy from plant roots and exudates. Food plants are sown while green energy is generated.	Application on land crops. Low power output. Electrode contamination by external agents such as soil. Bacterial competition during exudate consumption.	Implementation in land-based crops and food plants. Metabolic engineering to enhance natural bacterial–plant symbiosis. Long-term operation across a wide range of environments.
CW-MFC	Enhances power output and increases the volume of wastewater treated compared to CW and MFC systems. Facilitates the degradation of conventional and emerging recalcitrant pollutants. Serves as carbon capture technology.	Requires a large land area. Higher operational and construction costs compared to conventional CWs. Some wetland plants may die depending on pollutant type and loading. Electrode fouling, biofilm formation, and ohmic losses. Use of proper filler materials to enhance pollutant degradation.	Expands pollutant removal capabilities. Implementation of CW-MFC technology as biosensors. Optimization of operational conditions; biotic and abiotic. Novel designs to avoid biofouling and electrodes deactivation. Long-term stability and reliability.

treatment of waste-activated sludge but also provides an investment return of nearly 13% [186]. According to Hosseinzadeh and co-workers [187], the estimated cost per grame of hydrogen produced by anaerobic digestion coupled with MEC is around USD 2.8 g^{-1}, which is lower than that of the standalone technologies. These findings demonstrate the potential of MEC for pilot-scale applications. Finally, among the BES compared in this paper, MDC is the least discussed in the literature. A previous review concluded that producing 1 m^3 of desalinated water in an MDC had a negative net present value of around USD 28,281, indicating that the MDC is currently unprofitable for treating saline water. Despite this negative economic balance, MDC appears to be a promising technology for removing a wide range of pollutants, while simultaneously purifying saline water and producing green electricity [8].

7. Conclusions

In addition to conventional MFCs, various novel hybrid technologies have been developed for different purposes. MECs can produce green, high-purity hydrogen in an anoxic cathodic chamber. MDCs are known as a trifunctional technology that degrades organic pollutants in the anodic chamber, produces electricity, and simultaneously desalinates saline water in the middle chamber. In contrast, PMFCs and CW-MFCs avoid using PEM separators, instead employing low-cost filler materials such as ceramics and clays to remove pollutants via physicochemical processes during green energy production. A major advantage of these BESs is the elimination of a wide range of conventional pollutants (COD, nitrogen, and phosphorus) as well as hard-to-eliminate pollutants (heavy metals, dyes, and aromatic compounds), while generating electrical potential and value-added by-products. However, further effort is required to improve the applicability of these systems at a large scale and in long-term operational processes. In practice, several parameters play a crucial role in pollutant degradation efficiency and energy recovery potential, and must be optimized to achieve a positive cost–benefit balance: electrode materials, separators, electrical resistance, the bacterial community, and reactor configuration. Techno-economic analyses suggest that MFCs and the associated derived hybrid systems are suitable for pilot-scale application, with CW-MFCs representing the most beneficial option due to the associated low construction and maintenance costs, coupled with high pollutant treatment capabilities and high power generation. Nevertheless, scalability, treatment of real wastewater streams, long-term operation, and electrode fouling remain common challenges that require attention.

Author Contributions

JCGH and JHSG, designed the original version of the manuscript, performed data analysis, compared and synthetized literature information. JHSG, contributed to the editorial changes, language improvements and manuscript structure. KAHH, designed figures and collaborated in article original structure. All authors contributed to editorial changes in the manuscript. All authors read and approved the final manuscript. All authors have participated sufficiently in the work and agreed to be accountable for all aspects of the work.

Ethics Approval and Consent to Participate

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Conflicts of Interest

The authors declare no conflicts of interest.

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