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Review

Electro-Microbiology: A Green Approach for Energy and Environment Sustainability

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Abstract: Energy scarcity and environmental degradation have developed into major worldwide challenges. Electro-microbiology has the potential to turn trash into environmentally friendly and sustainable resources. Low power density MFCs remain a viable option for disposing of organic waste, as they are more cost-effective than previous methods. Coordination between researchers with diverse backgrounds is required to issues look at the new gates in waste to energy issues. Biocathodes are necessary for electrosynthesis because they require microorganisms to function as an electron source and then catalyze chemical synthesis. Organic compounds may be synthesized using discarded CO_2 as a carbon source, reducing the requirement for considerable quantities of arable land. Additionally, the proposed approach can be sustainable and carbon neutral when a renewable energy source is explored. An additional benefit of microbial-assisted chemical synthesis with MECs is that it enables the production of valuable chemicals from wastewater while producing electricity. This study examines the sustainable approaches for green energy by discussing bioelectrochemical and electrochemical resources and technologies.

Keywords: biogreen energy; organic resources energy; electrochemical energy; bioelectrochemical energy; carbon neutrality; electrochemistry; microbial electrochemical technology (MXCs); microbial fuel cells (MFCs)

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1. Introduction

Electromicrobiology is concerned with the interplay of microbes with electronic equipment and the electrical characteristics of microorganisms. Without the need for artificial electron shuttles, various microorganisms may contribute electrons to or absorb electrons from electrodes. However, the electron transfer processes between microbes and electrodes have been extensively explored in just a few microbes. *Shewanella oneidensis* communicates primarily with electrodes via flavins, which operate as soluble electron shuttles. *Geobacter sulfurreducens* establish direct electrical connection with electrodes via c-type cytochromes on the outer surface. Additionally, *G. sulfurreducens* can conduct long-distance electron transport through pili, termed microbial nanowires, that show metallic-like conductivity comparable to that previously discovered in synthetic conducting polymers. Conductivity is conferred to *G. sulfurreducens* biofilms via pili networks, which act as a conducting polymer with supercapacitor and transistor functions. Conductive microbes and/or their nanowires offer a lot of possible practical uses, but further introductory study is necessary to optimize them rationally.

The microbial world is incredibly diverse in terms of morphology, biochemistry, and metabolism. Microbes do remarkable accomplishments, whether they are living in harsh habitats, adapting to stressful situations, or transforming the geography of our world. Microbes' metabolic diversity enables them to utilize various substances as energy sources. Certain bacteria are even capable of generating energy. Electricigens, exoelectrogens, electroactive bacteria, and anode-respiring bacteria are all terms used to describe these microorganisms. The principles underlying this extraordinary capacity are anchored in electrochemistry, which comprises the passage of electrons between molecules and is required for all living species to breathe. Electrogenic bacteria have a unique redox circuitry that extends outside the cell and can transport electrons to solid, conducting surfaces, like electrodes, and produce current.

The recent literature on the subject covered electro-microbiology from different perspectives, using various approaches. Authors in [1] discussed the impact of microbial electrochemical technologies, focusing on their applications in wastewater treatment plants to enhance environmental sustainability. This study opened a narrow window toward environmental sustainability within the concept of electro-microbiology applications and its distinguished technologies. Authors in [2] elaborated microbial fuel cells and microbial electrolysis in terms of oxidation of organic and inorganic materials for electric power production. This study used the biocathode method using electricity and wastewater as the primary resources in electrochemistry technologies applications. This study deals with a comprehensive analysis and review of electrochemistry topics in the field with an in-depth focus on comparing different techniques within environmentally friendly applications and greenhouse gas mitigation. In view of the previous studies, it seemed essential to discuss electro-microbiology as a focused and separate topic with its potential application with a high yield of environmental advantages, which is not addressed in the previous studies. Therefore, this study covers electro-microbiology with an exhaustive review of the concept, importance, and future outlook that can be a good source for researchers and practitioners in the field.

2. Purpose and Objective of Research

The discipline of electro-microbiology is making significant advances in the generation of biofuels and renewable resources to answer the 21st century's challenges, which are being explored by experts seeking green energy resources. Fossil fuels are a nonrenewable energy source with significant environmental repercussions due to their limited supply. As a result, it is vital to create new technologies for producing alternative and renewable energy. It is critical to develop breakthrough technologies capable of simultaneously increasing energy output and transferring it to biochemical pathways for synthesizing important substances. Electro-microbiological systems, such as biological energy systems (BESs), can help immensely overcome these obstacles by developing a diverse range of fuels and chemicals with a variety of applications within a wide range of scope as shown in Figure 1.

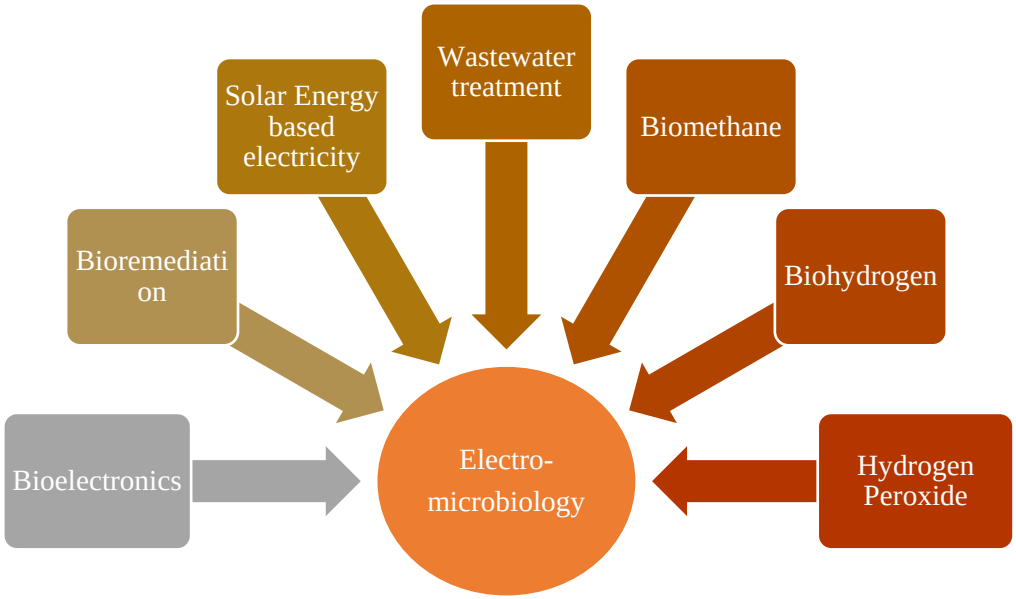

Figure 1. Diagrammatic depiction demonstrates the scope of electromicrobiology's applicability.

3. Bioelectrochemical Systems

Bioelectrochemical systems are those in which an organism provides electrons [3]. Bioelectrochemical systems are pretty similar to electrochemical systems in their fundamentals. Electrochemical systems generally use electricity to begin a chemical reaction or create power via a chemical reaction [4]. Fuel cells are considered a subcategory of the latter category of electrochemical devices. The first fuel cell of its kind was designed in the nineteenth century by Sir William Grove to conserve electrical energy [5]. Before that, the Bagdad battery is claimed to be one of the earliest known fuel cell systems [6]. A fuel cell is an enclosed device that converts energy generated by chemical processes to electrical energy. An anode, a cathode, a fuel supply, and an energy acceptor make up a fuel cell. The anode and cathode are coupled to facilitate electron passage. The anode chemically degrades the fuel by contributing an electron, which travels to the cathode and is absorbed by an acceptor undergoing a chemical process. For instance, hydrogen gas might be utilized as a fuel in which the anode chemically breaks down hydrogen gas to H+ ions, which are then coupled with oxygen that has been chemically split after the cathode accepts the hydrogen ions. Fuel cells are typically classified according to the electrolytes utilized, the temperature at which the reaction occurs, and the kind of fuel employed. Alkaline cells, for example, are placed beneath low-temperature cells, whereas molten carbonate cells are placed beneath high-temperature cells.

On the other hand, Electrochemical cells are more adaptable than fuel cells since they may generate or consume electricity. The potential governs the mechanism of action and whether it is generated externally or by the cell's own reaction. The difference in cell potential between the two electrodes determines the direction of the response within the cell. This point is defined in contrast to a standard hydrogen electrode and equals 0 volts. A salt bridge measures the link between two half cells, tanks with electrolytes, and an electrode so that ions can enter and exit each half cell separately without mingling, as well as linking the electrodes with each other and evaluating the cell potential between the electrodes.

3.1. Mechanism of Bioelectrochemical System of Microbial Fuel Cell

Bioelectrochemical systems utilize microorganisms' electroactive characteristics to create power from organic materials. These devices operate similarly to batteries but are powered by bacteria. Initially, this technique was primarily employed to construct microbial fuel cells as wastewater treatment reactors, as bacteria can utilize organic substances found

in wastewater to produce electricity. However, as the diversity of electroactive bacteria became clear, fundamental study into the nature of electroactivity accelerated. Various microbial electrochemical cells are already in use, including microbial fuel cells, microbial three-electrode cells, microbial electrolysis cells, microbial electrosynthesis cells, and even microbial solar cells. These devices, mainly presented as microbial electrochemical technologies (MXCs), where X specifies the reactor's functionality, have advanced rapidly in several environmental, technical, and medicinal applications. Microbial fuel cells (MFCs) based on mediators are critical for instructional reasons and the examination of the processes underlying the electron transfer activities of microorganisms. However, the diminished outcome of the fuel cell (current density is typically 50 mA cm^{-2}) and the high cost and environmental concerns associated with using artificial mediators render mediator-based MFCs technologically impracticable and economically impracticable unviable, which is why this strategy was later discarded. The last several years have seen the discovery and application of a variety of electron transport approaches that do not rely on artificial redox mediators to power MFCs. The term "mediatorless" is frequently used to describe these fuel cells, even though inlying electron commuting molecules are frequently engaged in the current generation process. These latest proposals propose to leverage anaerobic microbes' naturally developed pathways and mechanisms for disposing of electrons generated during their metabolic operations.

To characterize electron transfer processes, it is crucial to distinguish between those in which soluble entities assist in electron transfer from the cell membrane to the electrode and those that do not. Electron transfer processes are classified into direct electron transfer (DET) and mediated electron transfer (MET).

3.1.1. Direct Electron Transfer (DET)

A DET is an electron transfer from the biocatalyst to the fuel cell anode that takes place in the absence of any intermediary entity other than the bacteria. It has relied on physical interaction between the membrane of a bacterial cell or a membrane organelle and the anode of a fuel cell. Authors in [7] define an indirect biofuel cell as one in which the biological reaction generates a secondary fuel for the electrode. In contrast, direct biofuel cells involve either electron-shuttling reversible mediators or direct electron transfer between the biological component and the electrode. Because the great majority of microbes are electrically non-conducting, such transmission processes were deemed impossible for a long time. The existence of membrane-bound electron transport proteins like cytochromes, which allow electrons to travel from the inside of the cell to its outside, is required for direct electron transport from microbial cells to the anode of a fuel cell. These membrane characteristics have been particularly adapted by sediment-dwelling metal reducing bacteria such as *Shewanella*, *Rhodoferax*, and *Geobacter,* which employ solid iron (III) oxides as final electron acceptors. In this circumstance, the fuel cell's anode may immediately reinstate its job as an electron acceptor. Fuel cell anode-to-bacterial-cell contact (adherence) is required for direct electron transfer; as a result, only bacteria within the first monolayer exhibit electrochemical activity. Thus, the MFC's productivity is constrained by the maximal cell density in the bacterial monolayer. For example, an MFC powered by *Rhodoferax ferrireducens* can generate an optimum current density of 3 mA cm^{-2}.

Because of recent evolution, certain *Shewanella* and *Geobacter* strains now possess molecular pili (nanowires) that conduct electricity, enabling them to access and utilize remote solid electron acceptors. As an additional benefit, these pili allow the microbes to accept electrons from an electrode that is not directly in touch with the cell. The pili are associated with membrane-bound cytochromes, which are vital for electron transport outside the cell. The fabrication of such nanowires permits the development of denser electrochemically active biofilms, increasing anode performance. To date, a growing number of microorganisms have been discovered that are capable of effectively transporting electrons to an electrode. However, many of these species cannot generate energy from complicated substrates. Thus, *Geobacter* species, for example, are limited to low molecular

weight substrates, e.g., acetate or butyrate, and must rely on the availability of fermenting species to disintegrate complex organic materials.

3.1.2. Mediated Electron Transfer (MET)

Another successful method of connecting microbial metabolism to an electrode is by mediated electron transfer. Three main transmission pathways are well recognized–all dependent on microbial production of reduced metabolic intermediates, which are then released by microbial cells. These compounds are classified as primary and secondary metabolites based on their function in microbial metabolism. Primary metabolites are substances fundamentally involved in the metabolic processes of microorganisms (substrate decomposition) and are frequently significant metabolic byproducts. Secondary metabolites are generally unrelated to basic metabolic activities. Microorganisms, on the other hand, can produce them to aid in the disposal of electrons, e.g., to a remote solid electron acceptor. *Pseudomonas aeruginosa* and *Shewanella oenidensis* produce bacterial phenazines and quinine, respectively, in the presence of a positively polarized electrode or a solid electron acceptor such as iron (III) oxide and the absence of competing soluble electron acceptors. These electron shuttle chemicals may be oxidized at solid electron acceptors like electrodes, allowing many redox cycles between cells and acceptors. Compared to secondary metabolite biosynthesis, diminished primary metabolite exudation is strictly related to substrate oxidation. Evidently, the total number of reduction counterparts produced must equal the total amount of oxidized metabolites. A metabolite must fulfill specified conditions to be advantageous as a reductant in anodic oxidation. Its redox potential should be as minimal as possible and must be oxidizable electrochemically under MFC parameters. Fermentation and anaerobic respiration are the two basic anaerobic metabolic pathways from which vital reduced metabolites can be generated. The utilization of fermentation for MFC functioning has attracted more attention than anaerobic respiration. Numerous fermentative and photoheterotrophic activities generate energy-dense reduced metabolites, such as ethanol, hydrogen, and formate. These substances can be oxidized in the microbiological medium if electrocatalytic anodes are utilized to help the oxidation reaction.

The catalyst must meet several parameters that drastically restrict the spectrum of electrocatalytic materials accessible. It must be (1) biocompatible (non-toxic to microorganisms), (2) be extremely active in electrocatalytic oxidation of a variety of metabolites, (3) have strong electrocatalytic activity in the pH range of 5–7 and at relatively low temperature (10–40 °C), (4) stable in terms of both chemical and electrochemical stability and biofouling resistance, and (5) invulnerable to biological product poisoning. This classification imposes severe constraints on the selection of acceptable catalyst systems. Thus, nickel, copper, and cobalt-based metal oxide and transition metal catalysts must be ruled out due to their low consistency at the appropriate pH and antibacterial properties (nickel, cobalt, copper, silver, and others). Authors in [8] published the first investigation on the direct creation of power through the use of these metabolites, using immobilized hydrogen-producing cultures as biocatalysts and platinum as an electrocatalyst for hydrogen oxidation. Due to the platinum electrodes' susceptibility to poisoning and deactivation, the claimed power densities were somewhat low.

Authors in [9] made significant progress by developing platinum sandwich electrodes shielded from poisoning reactions by applying conductive polymers such as polyaniline or its fluorinated derivatives. These electrodes significantly enhanced the efficiency of MFCs with current densities as high as 1.5 mA cm^{-2}. Additionally, they enabled the use of an extensive range of microorganisms that are heterotrophic, photoheterotrophic, or even photosynthetic, as well as the availability of complex polysaccharides such as cellulose and starch for production process in MFCs. The costly noble metal electrocatalyst was also switched with tungsten carbide (WC). A very affordable but highly effective and resilient electrocatalyst. However, tungsten carbide looks to be a potential anodic electrocatalyst for MFCs. It has a high level of electrocatalytic oxidation performance at a low cost. Additionally, unlike platinum, the poisonous platinum poisons hydrogen

sulphide and carbon monoxide did not affect tungsten carbide. In terms of current MFC technology, the greatest 3 mA cm^{-2} current density and 586 mW cm^{-2} optimum power density is the greatest ever achieved.

4. Applications of Electromicrobiology

Electromicrobiology investigation has accelerated significantly throughout the preceding decade. This has been sparked by a variety of factors, including a rise in research into alternative energy sources, as well as advances in waste management, reclaimed water, and sensors. Recently, new efforts have been made to understand how extraneous electron transfer happens in microorganisms and how it might facilitate bacteria' behaviors in the surrounding environment, even at relatively long distances. While these techniques will undoubtedly impact the advancement of the technologies mentioned above, an additional field of electromicrobiology may rely on extrinsic electron transfer: microbial electron synthesis of valuable fuels and chemicals. Biocathodes are crucial to electrosynthesis because they need bacteria to act as an electron source and catalyze chemical production. Using carbon dioxide waste as a carbon source in organic molecule synthesis reduces the demand for arable land. If a sustainable energy source is employed, it is carbon neutral.

4.1. Bioelectronics

Electrically active microbes might make significant enhancements in the expanding field of bioelectronics. For instance, microbes' capacity to monitor various substances and environmental circumstances indicates several opportunities to create biosensors and biocomputers [10]. Biological oxygen demand (BOD) and toxicity may be detected in water using biosensors. These metrics can be coupled to bacterial metabolic activity measurement. Using living materials to grow or build electronics has potential advantages, as they can be obtained from less expensive feedstocks, resulting in less waste and avoiding using harmful substances. Self-repair and replication are possible if the electronic application incorporates microbes and their subassemblies. There are several varieties of bioelectrical gadgets, but one of the most common is the so-called mud battery, which comprises an electrode embedded in organic-rich silt and linked to a cathode submerged in aerobic water. When bacteria capable of respiration in the presence of EET instantly start respiring when the electrode is introduced, this decomposes the organic matter in the sediment, creating current. This is an eye-opening experiment for research scientists, and it marks the start of our knowledge of sediment batteries, equipment capable of generating very low currents, which can power sensor devices or other limited power gadgets on the darker sea bottom or in other regions where sunshine or wind are scarce [11,12].

4.2. Bioremediation

Bioelectrochemical processes represent a new technology platform for the treatment of wastewater contamination. The application of microbes as a catalyst in fuel cells for power generation was discovered 40 years ago [13]. During aerobic conditions, bacteria create carbon dioxide and water; in anaerobic conditions, they release carbon dioxide, protons, and electrons. Since organic matter is utilized to "fuel" the Microbial Fuel Cell (MFC), MFCs are recommended for wastewater treatment plants [14]. Sludge from the water would be consumed by bacteria and provide extra electricity for the plant while utilizing inorganic intermediates to access the cellular electron transport chain and obtain the electrons generated. This procedure must be indulged in fuel cells, which are comprised of organisms with the ability to generate electrical current. These organisms are referred to as Exoelectrogens. The bioremediation technique utilizes Geobacter's capacity to oxidize organic materials to remove hydrocarbon pollutants from soil and water. Metals are easily oxidized or reduced, which is one of their distinctive features: Mn^{4+} oxides are solids that undergo reduction to form soluble Mn^{2+} salts (e.g., $MnCl_2$). At the same time, oxidized versions of U or Cr are harmful partly because they are very soluble and reduce to insoluble metal hydroxides. As a result, if an S-BED unit is built with this in account and contains

the proper microorganisms, such devices might convert soluble uranium or chromium to insoluble forms, collecting them in a cathode chamber and collecting them erasing them effectively [15].

4.3. Generation of Electricity from Solar Energy

A new approach for converting solar power into electricity has emerged with microbial fuel cell technology advancement. Photosynthetic MFCs are a new kind of energy harvesting device that uses the sun's irradiation to generate electricity 24 h a day, seven days a week. Under day-night cycles, photosynthetic MFCs may produce power constantly from the respiratory and photosynthetic activities of microorganisms. When it comes to small-scale biological fuel cells, they have a lot more energy per unit size than bigger ones do [16]. Shrinkage of photosynthetic MFCs automatically creates ideal circumstances for increased power density through reduced internal resistance and improved mass transfer. Additionally, small-scale photosynthetic MFCs enable the scaling up of MFCs by using numerous units in a stack arrangement.

In MFCs, organic materials are delivered into the anode chamber. The electrode is tuned to an appropriate voltage for bacteria to use as an electron acceptor. The aerobic cathode compartment receives electrons via a conductive cable, in which they produce water by combining with distributing protons and molecules of oxygen. Well-established methods for producing energy from organic materials, such as sewage or agricultural or industrial runoff, have been employed in the past. Because they are used to digest organic material and create little waste and no methane, they are considered sustainable and environmentally benign energy sources. While this is correct, power densities and current efficiencies are poor, and the total energy expenditure per unit of energy produced is high. Unless you reside in a place where very little or no light is available, and wind energy cannot be generated due to a lack of sufficient air movement, the notion of these gadgets affecting the energy aspect of sustainability is entirely speculative in this era of wind and solar power dominance. There are such areas, and notwithstanding what has been said so far, if applications for bio-electrochemical devices can be developed, they might be both ecologically friendly and self-sufficient. These devices may have considerable environmental and/or human health advantages, particularly in locations where electricity infrastructures are lacking or insecure.

4.4. Wastewater Reclamation

The utilization of bio-electrochemical systems for wastewater treatment has advanced significantly since the initial demonstration of MFCs [17]. These advancements entail a shift away from moving from pure cultures to mixed ones of microorganisms that are more resistant to variations in the substrate supply [18] and hence provide greater power outputs than pure cultures. When an aerial cathode is used despite a submerged cathode, the increased oxygen level enables a quicker reaction and a larger energy output. If, on the other hand, a water cathode is employed, the clean water generated in the cathode compartment is stored for possible reuse. There have been no large-scale demonstrations of these systems using industrial or municipal waste streams. The latter example demonstrated excellent BOD and COD removal with minimal or no sludge buildup in the sewage system [19]. Expanding the lab-scale technologies to the municipal scale remains a 'work in progress.' These systems are significant for human health because they might enable water reclamation in areas where electricity networks do not exist, displacing harmful sewage disposal methods. In this case, a low power yield might result in a significant sustainability dividend in terms of energy, water, and waste (i.e., environmental quality). Enhancing inorganic nitrogen removal is critical for the sustainable growth of the mariculture business due to the low carbon to nitrogen (C/N) ratio of effluent and rigorous discharge standards. Authors in [20] demonstrated the effective treatment of simulated mariculture wastewater (high salinity, low COD/N ratio of 0.5–1.0) using an integrated self-biased bio-electrochemical system with a catalyst (TiO_2/Co-WO_3/SiC) on the cathode and naturally growing algae in the

cathode chamber. The synergy of bacteria, algae, and cathode enhanced pollutant removal and increased the system's sustainability and efficiency in treating mariculture effluent.

5. Biosynthesis Prospects of Electro-Microbiology

To confront the mysteries of the 21st century, and in response to researchers' hunt for renewable resources, electro-microbiology is making a big difference in biofuel production and renewable resources. It is critical to generate new technologies capable of simultaneously increasing power output and transferring them to biosynthetic pathways for creating valuable molecules. By creating a variety of fuels and chemicals, electro-microbiological systems such as BESs may significantly address these difficulties. Additionally, microbial aided chemical synthesis using MECs is a fascinating and new method for manufacturing valuable compounds from wastewater and generating power.

5.1. Biomethane

BESs can generate methane gas from nonrenewable resources like diesel and petrol. Methane is a critical inherent in manufacturing liquid methane rocket fuel and liquefied natural gas. The capacity of electroactive bacteria to perform under normal circumstances, without aeration, with reduced sludge generation, and a high methane yield makes MECs-based bio-methane production from organic wastes more sustainable and cost-effective than other traditional procedures [21]. Numerous investigations have demonstrated that beer effluent, glucose, paddy soil, acetate, and pre-treated sludge in alkaline medium may generate power and methane. Initially, it was assumed that methane generation would affect the EABc in the anode portion; however, authors in [22] described that glucose could be used to produce hydrogen and methane concurrently in an immobilized mixed-culture reactor. As a result, the high efficiency with which BESs synthesize biomethane is demonstrated.

Environmental issues are addressed, and the new area of carbon acquisition and utility for greenhouse gas emission reductions is promoted via methane creation from CO_2 and hydrogen. Efforts to maximize biomethane synthesis from CO_2 and to reap all of its benefits must be prioritized above chemical techniques. This process might be more financially viable with the proper supply of CO_2 and effective power use in BESs. Additional research examined the combined BESs-AD system for higher methane generation than AD at 0.90 V (vs. Ag/AgCl) poised cathode potential [23]. Under the specific poised potential, bio-electrochemical devices may convert CO_2 to methane. Numerous in-situ approaches are used to increase the quality of biomethane produced during anaerobic digestion, including elution of CO_2, the inclusion of H2, pressurized reactors, and electro-methanogenesis. As a result, biocathode-based electro-methanogenesis is a potential method for converting dark fermentation effluents to methane [24]. By combining BESs with anaerobic digesters, the expenditure of biogas cleansing and revamping is significantly reduced.

In comparison, A new study stated the utilization of methane as a means of direct energy conversion by retrogressing methanogenesis in MFCs using synthetic consortia [25]. The authors assert that this technique will reduce leakage (distribution, transportation, and storage) and capital costs. To summarize, selecting optimal EAB strains from MECs can be critical for developing a methane generation system that is both efficient and sustainable. Additionally, adjusting other aspects, such as the kind of reactor, the layout of the electrodes, material composition, and microbial community composition, will affect methane generation. However, because most of the outcomes gained up to now are built on laboratory-size investigations, further steps are necessary to extrapolate existing understanding regarding biomethane synthesis at vast scales. In the future, cost-effective and sustainable methane production solutions will be accomplished without transportation and significant leakage.

5.2. Biohydrogen

Hydrogen gas is a frequently used launching fuel in various industrial processes. Hydrogen may potentially be used as a renewable source of power. Hydrogen generation is in great demand due to its numerous industrial applications and natural scarcity. Aside from occasionally employing electrical techniques, the initial generation of substantial hydrogen was derived via exhaustible resources such as natural gas, coal, and naphthalene distillates [23]. As a result, alternative and environmentally benign sources of hydrogen are required. In this context, authors in [26] pioneered using an MFC in conjunction with water electrolysis. Bacteria break down organic molecules into carbon dioxide, electrons, and protons. An anode receives the electrons; with the help of these electrons, the external voltage is generated, and electrons react with protons at the cathode, resulting in further hydrogen production. Hydrogen (H_2) generation and wastewater treatment (WWT) in MECs may open up new avenues for recuperation of resources. Electro-hydrogenesis [27] is a process that generates hydrogen from organic wastes using MFCs. It is a beneficial, eco-friendly, and cost-effective source of hydrogen. However, low yields and thermodynamic restrictions due to microbial metabolism act as bottlenecks in fermentation-based systems. Pretreatment, metabolic engineering, reducing hydrogen partial pressure, and parameter manipulation are only some methods used to increase dark fermentation's hydrogen output. To boost hydrogen production, researchers have recently combined dark fermentation with bioelectrochemical technologies (BESs, MECs) [28]. The MESs is an exciting and novel technique for increasing hydrogen generation by reusing dark fermentation liquid and avoiding the use of high-energy inputs. Additionally, MESs has higher conversion efficiency [29,30] and a broader substrate range than traditional water electrolysis.

The combination of MECs and dark fermenters, as well as the subsequent usage of DF-effluents (VFA) in the anode, may cause a pH range to be disturbed, indicating the pH-dependent nature of anode respiring biofilms. pH window adjustment through buffering solutions will be difficult in large-scale applications. Consequently, acid-resistant EAB must be developed for uninterrupted and expanded one-step hydrogen production. More research is needed to determine the impact of several abiotic and biotic variables, like influent composition, bacterial community category, reactor layout, and electrode material, on the final hydrogen generating capability. At the cathode, hydrogen production must theoretically overcome an endothermic impediment of −0.414 V vs. SHE by supplying energy to the MEC from an external entity (0.14 V) and the residual voltage (0.279 V) handled by EAB via oxidation of waste by anodic means. Carbon cathodes, on the other hand, create hydrogen at a slow pace which can be accelerated with the use of metal-based catalysts, such as titanium (Ti), platinum (Pt), or nickel (Ni). Nowadays, biocathodes have emerged as a viable alternative to abiotic cathodes since they are an eco-sustainable and justifiable catalyst that is both regenerative and long-lasting for productive electro-hydrogenises in MECs. Authors in [29] have published correlative research on biocathode buildup for hydrogen generation in MECs. Researchers offer an efficient strategy for developing biocathodes from sulfate-reducing microorganisms to boost the pace of hydrogen production. However, further research is needed to examine the effects of mixed and pure consortia on hydrogen production and methane biosynthesis in MECs. While bio-hydrogen generation using BESs-associated technology is still nascent, it is often regarded as the most environmentally benign and imperishable means of producing biofuels. Scientists should concentrate on researching and developing materials of exceptional performance and Catalysts adept in ramping up and optimizing H2 synthesis in MECs to solve upcoming energy issues responsibly. Electro-microbiological processes have benefited from converting CO_2 to multicarbon molecules such as acetate and other hydrocarbon-based liquid fuels.

Conversely, energy from wastewater treatment is collected and stashed via C–C bonds. Additionally, acetate can be employed as a precursor compound in producing various other biochemicals. Although the rate of acetate generation was initially low, it was increased in subsequent tests. A laboratory setup produced roughly 89.9% acetic acid, far higher than is typically attained with aerated fermentation (75.8%). Microbial electrosynthesis of acetate

and ox butyrate has been proposed for the first time using the acetogen *Sporomusa ovum*, which uses electrons generated by graphite cathodes to reduce CO_2 [30]. Since then, MECs have utilized a varied assortment of microbes to convert CO_2 to acetate.

Researchers have recently been interested in biocathode-driven MECs that produce acetate. According to a previous study, biocathode-based CO_2 reduction is a balanced and sustainable method for producing liquid fuels [31]. The lengthy performance of biocathode MECs in a semi-batch operation established the economic viability of microbial electrosynthesis methods. MECs produce a large amount of acetate, which can be maintained by physiologically produced hydrogen at the cathode. Acetate production requires sustained microbial colonization and using the right electron acceptors to maximize metabolic activity at the biocathode. To effectively reduce MEC, an imparted voltage of 280 mV vs. SHE must be supplied to surpass the thermodynamic obstacle of a biological process [32]. However, a lower voltage is required to overcome this excess potential due to microbial energy consumption and mass/charge transmission resistances in bio-electrochemical systems [33]. While microbial electrosynthesis is a promising method for CO_2 capture and the production of multicarbon compounds that act as a source of intermittent energy and are the forerunners of complex compounds, improved acetogenic communities are still required in MECs to maximize acetate output while minimizing methanogenesis. We employed judicious enrichment to develop a steady environment capable of constant CO_2 to acetate transformation. This enables the instantaneous establishment of electrosynthesis operations and minimizes thermodynamic losses. Besides the above-stated characteristics, various other base elements, such as electron transfer intermediaries and electron transfer mechanisms in cathode and electrode materials used in certain reactor blueprints, might affect efficacy in all aspects. MEC technology is still in its formative stages; future research should focus on developing innovative electro-microbiology techniques.

5.3. Hydrogen Peroxide

Hydrogen peroxide (H_2O_2) is a commonly used industrial reagent in the water and wastewater sectors to perform advanced oxidation on developing pollutants and composite organic molecules. Currently, anthraquinone oxidation is used to commercially create 95% of all H_2O_2, a dangerous and energy-intensive process. Electro-microbiology-based approaches may yield a low-cost and straightforward way of generating hydrogen peroxide at a cathode [34]. Numerous investigations have led to the sustained generation of H_2O_2 in BESs using a variety of substrates. Similarly, sulfate-reducing bacteria can break down chlorinated pollutants in MECs while producing electricity and H_2O_2. This demonstrates that MECs can be employed in waste treatment and H_2O_2 generation, which can subsequently be utilized in enhanced oxidation procedures for pharmaceutical effluent treatment. Specifically, the two-electron route for oxygen reduction reaction (ORR) is intimately tied to peroxide formation. The slow rate of oxygen reduction (ORR) at the cathode, along with the excessively high cost of catalytic materials, is one of the fundamental limitations of MFCs in large-scale applications. Additionally, inorganic ORR catalysts exhibit large overpotentials, mostly due to the complicated structure of the ORR process [35].

When pH is neutral, the overpotentials of enzyme catalysts such as laccases and bilirubin oxidases are drastically decreased. Unfortunately, their scalability is limited by their significant expense, limited resilience, and incompetency in real-world wastewater. As a result, various low-cost catalysts that are both environmentally benign and financially effective must be created to improve the efficacy of MFCs and the generation of H_2O_2.

It is possible to insert key functional groups such as nitrogen by electrode modification and pretreatment with an acidic solution, enhancing H_2O_2 generation and power densities [36]. Functional groups may also reduce starting time, improving the productivity of MECs and MFCs. It was postulated that two-electron routes for oxygen reduction might be modulated by applying a spectrographically pure graphite (SPG) electrode in wastewater treatment [37]. Authors in [38] presented a comparable configuration for producing H_2O_2 and producing electricity in MFCs using a graphite cathode doped with nitrogen. Although

carbon-based cathodes altered with various metal nanocomposites have been extensively utilized as cathode materials due to their huge active surface area and inexpensive cost, more advancement is needed to enhance their performance further. To further examine the underlying biotic mechanisms behind H_2O_2 generation, it is necessary to investigate the influence of various operational aspects on the effectiveness of microbial peroxide producing cells in the future. In general, further study is required to optimize H_2O_2 production and production of power using wastewater treatment techniques. The cathode's sluggish reaction kinetics act as a constraint on greater H_2O_2 production. As a result, it is advised that effective cathodic catalysts be developed to enhance H_2O_2 generation via two electron-based routes. To sustainably enhance peroxide production, bottlenecks associated with sluggish reaction kinetics and other limiting variables should be spotted and resolved. Additionally, MECs and photoelectrochemical systems coupled with in-situ electro Fenton procedures might provide new opportunities for enhanced treatment in various scenarios.

5.4. Biomass

Microalgae are more efficient in removing nutrients than other microbes, owing to the presence of multiple critical nutrients (ammonia, nitrate, phosphate, urea, and trace elements) in diverse wastewaters [39]. Thus, the endless supply of CO_2 might be used to grow algae while simultaneously generating electricity [40,41]. Microalgae have been proposed as a viable alternative to traditional fuels that might bring an eco-friendlier renewable energy source. Scientists in renewable energy have moved their emphasis to photosynthetic MFC technology in recent years, as evidenced by research literature. However, plant-based MFCs have been used to generate both biomass and power concurrently; their sluggish development and low biomass limit their implementation on a broad scale. Authors in [42] have shown energy and biomass generation in the MFC based on bacteria-Chlorella through wastewater treatment. Microalgae may generate infinite oxygen at the cathode by exploiting ambient CO_2 and biomass generated in photosynthetic MFCs. In addition to acting as a sustainable electron acceptor, microalgae can interact with biocathodic communities to improve catalytic processes. The literature has extensively studied the many growth factors impacting algal biomass growth in photosynthetic-MFCs, such as light duration and aeration time [43]. Using biochar to purify sewage wastewater before it is used to irrigate agricultural areas can be improved by combining it with another sorbent material, such as chitosan. As a result, environmental contamination will have a long-term cure even though biomass augmentation is considered an untapped field of study. At the cathode, photosynthetic MFCs use microalgae to produce oxygen, which is a readily available electron acceptor.

6. Green Technology and Future Prospects

The bulk of bio-electrochemical fuel cells is still many years away from commercialization and technological use. Historically, considerable study has focused on the interactions between the electrode, the biocatalyst, and the substrate. It is still a matter of time until we see significant advancements in electron transfer rates and efficiency, as well as in fuel cell architectures, and novel strategies associated with genetic or molecular engineering must yet demonstrate their ability to improve the functionality of bio-electrochemical fuel cell systems.

Both EFCs and MFCs have extremely young design methodologies. They take pretty different pathways due to the fundamentally different features of their separate biocatalysts. Thus, although most efforts in EFC research are directed toward shrinking, the development of MFCs significantly favors scaling up. Numerous MFC configurations have been proposed, spanning from H-shaped cells for foundational research to standard flat cells to 3-D (e.g., tubular or packed bed) cell configurations for wastewater treatment.

MFCs are categorized into two categories according to their basic configuration: traditional two-chamber fuel cells, which are usually divided by a cation or proton-exchange layer between the anode and cathode chambers– and single-chamber fuel cells, which com-

bine an anode compartment with an open-air cathode. At the moment, predicting which cell designs will triumph is challenging. An MFC's basic layout is presumably similar to an environmental or benthic fuel cell. An anode of graphite buried in anoxic sediments and a cathode of oxygen-saturated seawater make up these fuel cells. The water–sediment interface naturally separates the anodic and cathodic chambers. Current is generated at the anode by microbial decomposition of organic compounds found in sediments.

For enzymatic fuel cells, there is no need to adhere to a standard fuel cell design approach. Due to the probable omission of a dividing membrane, various cell designs are available, depending on the intended use. Thus, a membrane-free fuel cell relying on enzyme-coated micrometer-diameter carbon fibers has been postulated for use in animal or human tissue transplantation. This gadget can only provide extremely low currents by nature, sufficient for monitoring things like blood sugar levels. Using bigger tubular fuel cells that can be implanted into larger vessels, such as blood vessels, is a real possibility in the future. Dispensable devices relying on enzyme-modified, ink-printed microelectrodes are also being designed for use as biosensors in conjunction with enzyme-based fuel cells. These are only a few examples of the many designs and uses available. Biofuel cells are not intended to be a substitute for chemical fuel cells due to their significantly lower power densities. The advent of this novel automation will instead concentrate on specialized functions that are now inaccessible by traditional fuel cell technology. MFCs have found a variety of useful uses in recent years. The sole objective and usage are emphasized in the treatment of wastewater. MFCs enable this application's compelling combination of water treatment and energy generation. For example, it is estimated that 0.5–1 kWh of electricity is needed to treat 1 m^3 of municipal sewage aerobically. In comparison, it is predicted that approximately 1 kilowatt-hour (kWh) of electrical energy may be extracted utilizing MFC technology, resulting in a significant reduction in the energy needed for the treatment of polluted water and, thus, a decline in greenhouse gas emissions.

Benthic fuel cells, on the other hand, are relatively advanced. Even though the power density provided by these fuel cells is relatively low, it is sufficient for power devices, such as maritime sensors. A well-known example of this type of application is the unattended benthic generator (BUG). MFCs are being considered for further applications, including biosensors and robotics (independent self-powered machines). EFCs' prospective domains of application are substantially different from MFCs'. Because enzymes have a relatively short shelf-life outside live creatures, and an enzyme's optimal functionality is generated in physiological conditions, EFCs are most intuitively used in healthcare and implantable equipment. As a result, the first implantable glucose/oxygen fuel cell is now commercially accessible, allowing them to be implanted into the bloodstream for use in powering medicine delivery devices or a biomedical monitoring system. The enhancement of the often-restricted lifespan of EFCs constitutes a significant research challenge that is sometimes overlooked in favor of developing short-lived fuel cells, such as those used in disposable biosensor devices.

7. Conclusions

Microorganisms' unrivaled capacity to produce energy necessitates a complete understanding of their processes. *Shewanella oneidensis* and *G. sulfurreducens* are two of the well-studied electricigens. Direct electron transfer, in which the microbe lowers a terminal electron acceptor directly, or mediated electron transfer, in which soluble redox shuttles are used, might increase extracellular electron transmission in these bacteria (and other electricigens). Multiheme cytochromes on the outer membrane help direct electron transmission by making contact with the terminal electron acceptor and assisting further electron transfer. Soluble electron carriers such as flavins, phenazines, and quinones promote electron transfer via mediation. These mediators are often redox compounds that bacteria create and release to assist in extracellular electron transport. Once the microbe has given off electrons, they move them to the electrode and restart the electron transfer process. Bacteria such as *Shewanella* can transmit electrons by direct and mediated electron transfer. Electro-

microbiology has a plethora of intriguing future research directions. We still have limited knowledge of how microorganisms give electrons to electrodes and much less about how electrons are transmitted from electrodes to cells. Electromicrobiology offers the potential to address some of society's core pressing issues. Although many early experiments in electromicrobiology are driven by the objective of further refining microbial fuel cells for energy harvesting, various other possible interactions between microbes and electrodes have emerged recently, and more are likely to be envisioned. Electromicrobiology's underlying processes must be constantly studied to develop any of these technologies in a meaningful manner.

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