

Advancements in Bioelectricity Generation Through Nanomaterial-Modified Anode Electrodes in Microbial Fuel Cells

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The use of nanotechnology in bioelectrochemical systems to recover bioelectricity and metals from waste appears to be a potentially appealing alternative to existing established procedures. This trend exactly characterizes the current renewable energy production technology. Hence, this review focuses on the improvement of the anode electrode by using different functional metal oxide-conducting polymer nanocomposites to enhance microbial fuel cell (MFC) performance. Enhancement of interfacial bioelectrocatalysis between electroactive microorganisms and hierarchical porous nanocomposite materials could enhance cost-effective bioanode materials with superior bioelectrocatalytic activity for MFCs. In this review, improvement in efficiency of MFCs by using iron oxide- and manganese oxide-based polypyrrole hybrid composites as model anode modifiers was discussed. The review also extended to discussing and covering the principles, components, power density, current density, and removal efficiencies of biofuel cell systems. In addition, this research review demonstrates the application of MFCs for renewable energy generation, wastewater treatment, and metal recovery. This is due to having their own unique working principle under mild conditions and using renewable biodegradable organic matter as a direct fuel source.

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1 INTRODUCTION

Producing a sustainable source of energy to reduce the need for fossil fuels has attracted a lot of attention in green energy generation technology. As a result, several initiatives to enhance the efficiency of renewable energy production through bio-electrochemical energy conversion systems have been launched. This is recommended due to the poor compatibility of precious metal anodes with microorganisms, which is attributable to the lack of surface roughness and can be enhanced by using a conductive polymer. Electronically conducting polymers are distinguished from other materials by their strong electronic conductivity and environmental resilience. Large-scale production of electrodes using flexible and conductive polymers provides a great opportunity to build practical devices for a variety of applications (Mounia and Renouvelables, 2016). Using carbon-free energy sources, particularly renewables, should be pursued aggressively. The current rate of growth in renewable energy production suggests that fossil fuels will not be completely displaced in the foreseeable future (Lueking and Cole, 2017). Better environmental performance is promoted through the reduction of waste and emissions at the source through more efficient use of energy and materials in the areas of nanotechnology and nanoscience (Sagastume Gutiérrez et al., 2018).



Today, light-based photocatalytic fuel cells (Zeng et al., 2018; Khan M. E. et al., 2018) and microorganism-based bioelectrochemical conversion device systems such as electromicrobiology (Ali et al., 2018) or microbial fuel cells (MFCs) have emerged as promising tools for the sustainability of renewable energy generation, simultaneous wastewater treatment, and water purification in the bioenergy sector (Mahrokh et al., 2017; Bakonyi et al., 2018). As a sustainable technology, biofuel cells (BFCs) have recently attracted a great deal of attention due to their unique ability to directly convert stored chemical energy from biodegradable substances to electricity, as shown in Figure 1 (Barelli et al., 2021). Parts of BFCs known as enzymatic biofuel cells (EBFCs) and microorganism-based biofuel cells (MFCs) are the two most important components of the BFC system for such conversion concepts, in which devices with renewable redox enzymes and/or microorganisms are used as catalysts to perform natural oxidation processes at the anode for the release of electrons and the generation of an electrical current (Zhao et al., 2017). Recently, green-synthesized nanocatalystmodified anode materials played an effective and value-added role in energy conversion systems (Dessie et al., 2021b). Hence, a biosynthesized nanocatalyst hybrid with a conductive polymer matrix-modified electrode has shown novel technological advances in renewable energy production simultaneously with wastewater treatment application (Dessie et al., 2021c).

In BFCs, the role of nanomaterials in treating waste or synthesizing the nanomaterial itself from various biowaste materials has been a qualified strategy for the conversion of waste into useful and reusable forms (Samaddar et al., 2018). As a result, improving the efficiency of MFCs using a nanocomposite nanomaterial electrode as a catalyst is critical for low-cost and efficient energy harvesting systems (Kodali et al., 2018). Such improvement has a strong contribution to the assembly of strong nanocomposite materials hybridized from renewable forestry waste (Chen et al., 2018), two dimensional layered nanomaterials (Cao et al., 2018), microscale and nanoscale electrode topography (Champigneux et al., 2018), their dimensional mesoporous electrodes (Bian et al., 2018), smart polymers (Yousefi et al., 2018), and conducting polymers with other nanomaterials as an electrode; in addition, membranes may offer performance improvement in MFC devices due to their synergistic effect (Di Palma et al., 2018; Mulijani et al., 2018). Among nanomaterials, conducting polymers from polyaniline (PANI) and polypyrrole (PPy) were chosen as the basic monomer material to prepare the nanocomposites because of their unique physical, chemical, structural, and optical capabilities. They are selected due to the nature of the nitrogen environment on the redox polymer backbone, which impacts an electrode material's performance for the MFC device setup (Dumitru et al., 2018).

According to the results of practical study, coating a single bacterial cell with a conjugated polymer/redox polymer results in a high-performance anode for MFC application (Song et al., 2017). These polymers due to their inexpensiveness, biocompatible nature (Singh et al., 2018), and flexibility in designing electrodes (Sushma and S, 2017) can increase efficiency in MFC devices. Stainless steel (SS) is one of the most obvious electrode materials in bioelectrocatalytic systems. However, its smooth surface decreases the deposition of the active bacterial community. In addition, its poor biocompatibility and low corrosion resistance have made it unusable indefinitely. To address these issues, a unique structural SS-based anode for highperformance MFCs was successfully modified by *in-situ* electrochemical deposition of PPy onto SS (Pu et al., 2018).

2 BIOELECTROCATALYSIS

Application of novel nanomaterials for pollutant degradation has been the recent advanced technology in nanoscience (Zheng et al., 2021). Such nanomaterials in microbial electrochemical technologies have oxidized various types of organic pollutants and can lead to chemical synthesis, bioremediation of polluted matrices, contaminant treatment, and electricity production. These technologies have been based on the presence of electroactive bacteria through metabolic activity in solid-state electrodes (Ramírez-Vargas et al., 2018). In MFCs, interfacial bioelectrocatalysis between electroactive bacteria and hierarchical porous composite materials could improve the cost-effectiveness of anode materials with superior bioelectrocatalytic activity of MFCs (Wu et al., 2018a). Therefore, the performance of MFCs is considerably improved as a result of this interaction (Jiang Q. et al., 2018). Within biological processes, nature has emerged as a roadmap for the creation of microbial electrochemical technologies. Ultimately, it is a consequent use from sustainable energy conversion to bioenvironmental and biosensor technologies (Schröder and Harnisch, 2017; Dessie and Tadesse, 2022). For implementing MFCs, it is critical to reduce the start-up time while also improving the energygenerating performance (Zhong et al., 2018).

2.1 Microbial Fuel Cell

Fuel cells have the potential to become an important energy tool for management, but their technical and economic practicality must be enhanced (Inamuddin et al., 2017). The increasing



energy demand and the negative environmental implications of power production from irreversible fossil fuel usage have sparked scientific interest in using biotechnology to harvest energy from various organic waste sources. Converting such renewable organic matter using MFCs has been widely regarded as the most promising source of renewable energy among other microbial technologies (Xia et al., 2018). The technology allows for direct electricity harvesting from organics via anodic microbial catalysis, as shown in Figure 2, and has been utilized to extract electrical energy from organic sewage (Zhao et al., 2017). Energy conversion using MFCs appeared to be a promising technique for the remediation of environmental toxins in terms of efficient removal of different organic chemicals and energy recovery (Zhang Q. et al., 2018). As a result, it is a viable long-term solution to the energy and environmental crises (Saravanan, 2018). Even from organic wastes beyond their bioelectricity production, it is also possible to produce different chemicals (e.g., methane and methanol) using novel microbes through fermentation reactions (Dhiman et al., 2018). Thus, to recover energy from methane, MFCs, on the other hand, can reduce dissolved methane emissions from anaerobic effluents (Chen and Smith, 2018). To fulfill such a requirement, researchers sometimes immobilize microbes on carbon nanotubes (CNTs) to improve the electrode/anodic performance because nanotubes have а long-term electrochemical property effect, which helps enhance power output (Zhang Y. et al., 2018). Other processes such as hydrolysis and acidogenesis can also improve wastewater treatment performance and power generation simultaneously in MFCs by reducing internal losses, i.e., by minimizing the internal resistance of the cell (López Zavala et al., 2018).

MFC technology has piqued the interest of scientists over the last half a century due to its ability to convert organic waste directly into electricity using microbially catalyzed anodic and microbial/enzymatic/abiotic cathodic electrochemical reactions under moderate conditions (Santoro et al., 2017). Using bacterial metabolism, the cell device can produce alternating energy from a wide variety of organic substrates under these conditions (Liu et al., 2017). The generated current is mostly created by the metabolic activities of microorganisms. It would be beneficial to learn more about microbial systems' ability to optimize energy extraction methods in MFCs. The most likely use of this technology appears to be large-scale coupling of such a device with treating wastewater (Krieg et al., 2017). As a result, MFCs have risen to prominence in recent years as a novel technique for converting chemical energy, especially from carbon-rich organic matter, into power generation through a sequence of energy metabolisms mediated electrochemically by active microorganisms (Chandrasekhar and Ahn, 2017). The anodic chamber is effluents in the digested by microorganisms, generating electrons (e-), which are received by the anode and transmitted to the cathode via load resistance in a standard MFC principle and setup, as shown in Figure 3. At the same time, the released protons (H⁺) created during the metabolism reach the cathode via proton exchange membranes, which are H⁺ exchangers. An electron acceptor accepts e⁻ and H⁺ at the cathode, completing the circuit and providing electricity (Capodaglio et al., 2013; Deval et al., 2017). membranes—either cation or Ion anion exchange membranes-are widely used in microbial fuel cells (Jiang S. et al., 2018). Nafion is a commercially available fuel cell ion exchange membrane; however, it has drawbacks such as low conductivity at low humidity and low-stability at high temperatures (Peo-nio-liclo, 2010). In addition to reduced cost, the advancements of electroactive-based carbon nanotube membranes are reviewed in detail (Liu et al., 2020).

For example, the bacterial microorganism Chlorella vulgaris (Huarachi-Olivera et al., 2018), which is a chlorophyte microalga, has been used to cleanse wastewater and create oxygen at the cathode of MFCs, accumulating algal biomass and creating power in bioindustrial settings. In addition to anolytes, the bioelectrochemical performance of MFCs was examined using various catholytes, such as phosphate buffer and anode effluents, in the presence or absence of *C. vulgaris* (Commault et al., 2017). The presence of exoelectrogenic microorganisms increases the performance of MFCs, which can be further improved by using a nanocomposite cathode catalyst (Kodali et al., 2018). Since ancient times, biomass, a sustainable fuel derived from biological materials, including plant and animal waste, has been utilized as the major energy source (Hoa et al., 2017). Due to enhanced efficiency levels in terms of energy and catholyte production, the use of ceramics as low-cost membrane materials for MFCs is gaining traction. Water or hydrogen peroxide creation from the oxygen reduction reaction in the cathode, water diffusion, and electroosmotic drag through the ion exchange membrane contribute to catholyte production in ceramic MFCs, as shown in Figure 4 (Gajda et al., 2020). Thus, the ceramic membrane's efficient performance shows its appropriateness as a feasible and economical choice for speeding up the scale-up process and expanding the use of MFC technology.

There is currently a scarcity of data on the elements that influence the power generation of MFCs that use soil organic matter, sewage sludge, marine sediment, garden compost, industrial and home waste, and animal waste as fuel sources (Abbas et al., 2018; On et al., 2017). Integrating all elemental





issues in the bioprocesses may be able to boost the overall yield and efficiency of the process. Especially, using an integrated system, energy recovery from water hyacinth can be improved even today (Varanasi et al., 2018). Furthermore, municipal solid waste is employed as a valuable power generator for global energy recovery (Abdel-Shafy and Mansour, 2018). Conversion of environmentally friendly municipal solid wastes into fuels and chemicals is also beneficial to the society (Matsakas et al., 2017). However, enhancing power generation in low-light settings and efficiently collecting electrons from photosynthetic bacteria on the electrode are also key difficulties in the development of a functional photosynthetic microbial fuel cell (PMFC). To address these issues, an anode was developed in a dual-chambered PMFC with an abiotic cathode by casting a nanocomposite matrix that assisted biofilm development of the photo-catalyst *Synechococcus* sp., surging the bacterial photosystems (PS I and PS II) with suitable light ($\lambda_{650-750 \text{ nm}}$) at a broad excitation spectrum ($\lambda_{350-644}$ nm) through fluorescence resonance energy transfer (Kaushik et al., 2017). Researchers have established that an adequate microbial population structure and metabolic activity of the electrode biofilm communities are required for satisfying the performance of microbial electrochemical cells using this conversion technology (Liu et al., 2017).

In air-cathode single-chamber MFCs, electrode improvement and optimization are also ongoing (Wang Y. et al., 2018). Extracellular electron transfer of surface active microbes (Li F. et al., 2018) as well as precise electron carriers events of electron rich microbial species for electron transport functionality (e.g., biofilm formation, electron shuttles, swarming motility, dye decolorization, and bioelectricity generation) to MFCs aids in

TABLE 1 | Power density performances using different electrodes in an MFC system.

Substrate	Anode	Power density (mW m ⁻²)	References
Marine water	Graphite plate	450.5	Abbas et al. (2018)
Acetate	Graphite fiber	3006 mW/m3	Ali et al. (2019)
Acetate	Copper/carbon cloth	6.45 ± 0.5	Bian et al. (2018)
Methane	Carbon brushes	62.0	Chen and Smith (2018)
Seawater	PPy/MnO ₂ /carbon felt	562.7 ± 10	Chen et al. (2017c)
Acetate	Carbon paper	9.59 ± 1.18	Di Palma et al. (2018)
Acetate	PANI-CNT/carbon cloth	202.3	Dumitru et al. (2018)
Starch	Stainless steel	660	Eyiuche et al. (2017)
Paddy field soil	Graphite fiber felt	77.62 μW	Fakhirruddin et al. (2018)
Brown sugar	Fe ₃ O ₄ -PPy/carbon felt	0.170 A/m2	Fan and Xi (2021)
Acetate	Iron aminoantipyrine/carbon veil fiber	1300	Gajda et al. (2018)
Dairy wastewater	Ceramic/carbon veil fiber	724.4	Gajda et al. (2020)
Glucose	α -MnO ₂ /PANI/pencil graphite	820.02 ± 7.86	Dessie et al. (2022)



the generation of more stable and reliable power (Ng et al., 2017). Due to such benefits, MFCs have a lot of practical applications. Some of them are bioremediation and wastewater treatment, removal and recovery of heavy metals, constructed wasteland management, water desalination, biophotovoltaics, biosensors as alternate power tools, and biochemical production *via* microbial electrosynthesis (Mounia and Renouvelables, 2016). The detailed comparison of MFC performances from previous works using different anodes is clearly summarized and shown in **Table 1**.

2.1.1 Bioelectricity Generation

A biofilm developed from electron-releasing microorganisms facilitates renewable bioelectricity generation as well as organic carbon removal from waste matter simultaneously, as shown in **Figure 5** (Angelaalincy et al., 2018). MFCs are a notable source of sustainable energy due to the degradation in antibiotics and changes in their toxicity (Wang J. et al., 2018) followed by the conversion to power (bioelectricity production) via a biological process. MFCs have been studied for bioelectricity production through organic wastewater degradation by a microbial consortium. For example, methanogenesis/methane (Yamasaki

et al., 2018), photosynthesis (Chandra et al., 2017), soil (Li et al., 2019), ceramic (Santoro et al., 2018a), sediment-rich benthos (González-Gamboa et al., 2018), marine benthos (Chen et al., 2017b), novel earthen pot-plants (Regmi et al., 2018a), and xylose-fed mesophiles and thermophiles (Dessì et al., 2018) help plant-assisted MFCs turn solar energy into bioelectricity due to their unique plant-microbe association at the rhizosphere zone of a plant (Regmi et al., 2018b), which are interesting modification devices of MFCs, and they demonstrate how alternative electrodes can be used to boost efficiency. PMFCs are different from regular MFCs, where they produce bioelectricity and biomass in-house rather than relying on external substrates (Nitisoravut and Regmi, 2017). Using a dual chamber, electricity can be generated from the empty fruit bunches of palm oil trees. MFCs are also a typical device system (Ghazali et al., 2017), and they are gaining popularity due to their ability to generate power from a range of substrates by recycling organic wastes. As a result, using animal excrement and leaf mold as a bioelectricity-producing substrate has a lot of promise (Gazali and Moqsud, 2017).

MFC technology is developing as an appealing approach for mitigating pollution in water bodies by combining electricity

generation and waste degradation. In this device system, biodegradation of hazardous chemicals using a nanocomposite polymer-coated nanocomposite-based anode can improve dye degradation and power output (Sarma et al., 2018; Dessie et al., 2021a). For example, algae are well-known organisms whose characteristics are prominent in biofuel production and wastewater remediation (Vo Hoang Nhat et al., 2018). cyanobacteria Integration of algae and in MFC bioelectrochemical systems (BESs) can boost energy recovery and nutrient remediation in wastewater treatment dramatically. Algae can contribute to the BES function as an organic feedstock to support bacterial growth by supporting anode bacteria in generating electricity, delivering oxygen through photosynthesis as a cathode electron acceptor, and eliminating nitrogen and phosphorus from effluent water (Luo et al., 2017). It can be concluded that high specific surface area, low cost, strong electrical conductivity, and biocompatibility of anodic materials enhance performance efficiency of MFC systems.

2.1.2 Wastewater Treatment

Because of their high organic matter and nutrient content, wastes from concentrated animal feeding facilities, such as domestic wastes (Han et al., 2018a), plastic waste (Saleem et al., 2018), food waste (Salihoglu et al., 2018; Kibler et al., 2018; Dahiya et al., 2018), agricultural waste (Dai et al., 2018), poultry droppings waste (Oyiwona et al., 2018), fruit waste (Han et al., 2018b), and medical waste (Hong et al., 2018), are difficult to manage. Traditional swine waste treatment methods, such as exposed anaerobic lagoons, produce poor effluent quality and emit greenhouse gases, while modern treatment comes at a significant cost (Amini et al., 2017). Thermal, mechanical, chemical, and biological treatments of asbestos-containing wastes do not completely address the difficulties associated with asbestos fiber release, and they are incompatible with the concepts of sustainable land use, recycling, and material cycle closure (Spasiano and Pirozzi, 2017). Strategies for encouraging the conversion of food waste into bioenergy by anaerobic digestion, in addition to MFCs, may be an additional treatment option (De Clercq et al., 2017).

One of the most prevalent approaches is to use rumen fluid in the production of energy from market waste (such as avocado fruit and tomato wastes) utilizing MFC technology (JM et al., 2018). As a result, MFCs have emerged as a promising technology for self-powered, real-time, on-site wastewater treatment plants in large-scale applications. MFCs, on the other hand, can become a significant instrument for water quality monitoring if their manufacturing costs are drastically reduced, making them accessible even in the poorest and most distant parts of the world (Chouler et al., 2017). Today, platinum group metal-free catalysts (Santoro et al., 2018b), particularly from manganese (Mn), iron (Fe), cobalt (Co), and nickel (Ni), as well as their integration into an air-breathing cathode (Gajda et al., 2018), are used as bio-electrochemical catalysts to treat wastewater and generate electricity (Kodali et al., 2017). In addition to using metal free-catalysts, electrode materials have a huge effect on the performance and cost of MFCs (Zhang Y. et al., 2017). As a result,

a unique electrode fabrication using low-cost, stable, and biocompatible metals aids in improving power generation in MFCs (Yamashita and Yokoyama 2018). In the power generation system, active microorganisms can transmit electrons to the anode in wastewater treatment mechanisms in three ways: using exogenous mediators, using mediators created by bacteria, or by directly transferring electrons from respiratory enzymes (i.e., cytochromes) to the electrodes (see **Figure 6**) (Hassan et al., 2021). In brief, two alternative and simple electrodes, one for each stacked MFC, were used to prove this mechanism: granular graphite and stainless steel mesh. In biocathodes, organic matter was oxidized, ammonium was oxidized to nitrate in an external aerated reactor, and nitrate was reduced to dinitrogen gas (Vilajeliu-Pons et al., 2017).

BESs have been hailed as a ground-breaking method in pollutant management that is both sustainable and costeffective (Srikanth et al., 2018). MFCs are one sort of technology that has recently demonstrated renewable energy positive-treated wastewater at a pilot scale. Despite these accomplishments, nothing is known about whether all wastewaters contain significant amounts of energy and, if so, whether MFCs can collect enough energy to counteract electrical power requirements in the wastewater treatment process (Stoll et al., 2018). Hence, to eliminate such limitations, especially wastewater from organo-chlorinated aromatic compounds (Khan N. et al., 2018), chicken processing plants (Gomes et al., 2018), and heavy metal (Zhang et al., 2018a), integration treatment by MFC-coupled wetland construction is a recent and an attractive strategy to treat wastewater (e.g., nitrobenzenecontaining one) and generate electricity simultaneously. This inherent relationship between substrate degradation and electricity generation was evaluated by the electronic characteristics of the fabricated electrode materials (Xie et al., 2018). Hence, bioanodes, which are highly rich in conducting biofilms, enhance the degradation of complex wastes. As a result, these electrodes are highly efficient in treating waste water.

2.1.3 Metal Recovery

Heavy metals have emerged as a major inorganic contaminant and hazard to the environment and the human health in recent decades. Only by removing them from metal-laden wastewater before dumping them into aquatic streams can the environment and human health be protected (Saini et al., 2018). Most heavy metals must be considered as highly valued recyclable resources due to their rapid industrialization and long-term sustainability. Advanced oxidation processes, such as photocatalytic degradation, have been evaluated for the effective removal of ions for this purpose. In a revolutionary metal photoelectrochemical cell (PEC), the feasibility of recovering heavy metals from wastewater (e.g., acid mining and electroplating) while also producing electricity is common. However, as BESs point out, its restoration and electricity output are insufficient (Wang D. et al., 2017). To address this issue, a new method combining PECs and MFCs was designed and utilized to effectively remove refractory organic contaminants (such as phenol and aniline) from wastewater while recovering energy for in situ use (Zhang et al., 2019).



FIGURE 6 | Extracellular electron transport in microbial electrochemical systems is depicted. The creation of a conductive layer at the microbial cell wall or the growth of nanowires (I) permits direct microbial electro transfer (DET) (III). The naturally released mediators (II) or chemically used electron redox-shuttles were used in the mediated transfer of electrons (MET) (IV) (Hassan et al., 2021).

For example, Pophali et al. (2021) reported reducing Cr(VI) in wastewater by impregnating activated carbon fiber (ACF) photoanodes and photocathodes with cerium oxide (CeO₂) and cuprous oxide (Cu₂O) nanoparticles and then growing carbon nanofibers (CNFs) on the ACF substrate using catalytic chemical vapor deposition (CVD), as shown in **Figure 7**. As a result, the constructed MFC reduced COD and Cr (VI) by approximately 94 and 97%, respectively, when operated under visible light irradiation, with a current density of 6,918 mA/m² and a power density of 1107 mW/m², and the MFC produced a lot of bioelectricity (Pophali et al., 2021).

MFCs also play an important role in the recovery of valuable metals such as silver from wastewater in the form of nanoflakes, which have anti-biofouling properties in a variety of industrial and environmental processes. Maximum power and current densities of 3006 mW/m³ and 34,100 mA/m³, respectively, were found during this recovery, as shown in **Figure 8** (Ali et al., 2019). As a result, MFCs are regarded as a revolutionary self-powered wastewater electrolyzer for heavy metal electrocoagulation (Gajda et al., 2017). Hence, MFCs are part

of a new technology for producing green energy and reducing the effects of pollutants on the environment (Wang Z. et al., 2017). Cu^{2+} reduction to copper at the cathode with the anode improved by the rGO/polypyrrole electrode with a COD removal efficiency of 94.5% is also achieved (Rikame et al., 2018).

Removal of inorganic heavy metal contaminants such as arsenic (Hernández-Flores et al., 2018), lead (Saini et al., 2018), excessive selenium (He et al., 2018), Cd, Cu, and Cr from various industries provides a very sustainable solution for better living due to their toxicity, harmfulness, and carcinogenicity to human beings (Ahmad and Mirza, 2017). On the other hand, the effect of a new nanocomposite material beyond heavy metal contaminants is a means for waste water treatment from organic dye contaminants; due to this, nanocomposites are considered as key and common to trigger catalytic performance (Arshad et al., 2017). In the subject of environmental engineering, reduction and recovery of precious metals are research hotspots. The transformation and distribution of platinum in MFCs provided a possible strategy to retrieve platinum (Pt) from wastewater with less than 16.88 mg/L



platinum by charring biofilms in MFCs and generating the Pt/C catalyst in this field as a support (Liu et al., 2019).

2.2 Bioremediation

Specific combinatorial biobased remediation, including bioremediation, and other approaches are highly effective for

sustainable power generation from waste and reduction of heavy metal loads (ROY et al., 2018). Several possible enzymes have been found from various microorganisms that degrade complex chemicals by biodegradation, biostimulation, or bioaugmentation processes, according to recent advances in the environmental remediation of environmental contaminants and their



environmental effects (Gaur et al., 2018). As a result, significant progress has been achieved in optimizing MFC performance for both renewable bioenergy generation and environmental remediation. As a result, a concentrated effort has been made to improve MFC performance by improving the reactor structure and electrode architecture, the addition of redox-active electrondonating mediators, biofilm acclimation, feed nutrient correction, and other parameters (Li M. et al., 2018). Significant effort has been taken for the remediation of organically polluted soil, leading to the development of numerous remediation technologies, including physical, bioremediation, and chemical remediation (Zhang H. et al., 2017). Organic-metal cocontamination is also evolving as a major environmental concern worldwide. Such contamination is more difficult to treat than individual contamination because of its great difference in chemical courses and the remediation mechanism of organic and metal pollutants (Chen F. et al., 2017).

The use of heterogeneous catalysts to promote the efficiency (Yuan et al., 2016; Khater et al., 2022) and sustainability of reactions using water as a solvent and the use of solid support (metal nanomaterials and bimetallic and polymetallic nanoparticles; Nascimento et al., 2018) have shown increased stability, reactivity, selectivity, and reusability. An electron-rich polypyrrole hybrid with mercaptoacetic acid (PPy-MAA) composite, which is known to be a very efficient adsorbent in Ag⁺ removal from an aqueous environment in the cleanup of metal-contaminated water sources, was used for this purpose. In the absence of an additional reducing agent, in situ reduction of Ag⁺ cations to Ag⁰ nanoparticles (NPs) was achieved, as well as the silver nanocomposites (AgNCs), which were studied using several optical and electron spectroscopic techniques (Giri et al., 2017). Catalytic reduction of organic pollutants was also achieved using a biosynthesized Ag/C/Fe₃O₄ nanocomposite made from red water and Caesalpinia gilliesii flower extract (Rostami-Vartooni et al., 2018). In addition to silver nanomaterials,

biogenic gold nanoparticles can also modify the anode electrode in the presence of the microbial community for enhanced MFC performance (Wu et al., 2018b). However, both silver and gold are too expensive. Hence, they are not recommended for use as a common electrode for MFC devices at the larger scale. Therefore, this review highlights and discusses the behavior and the way of synthesis of some inexpensive nanocomposite electrode materials.

Nanomaterial-based technologies are gaining traction as a viable approach for removing toxins and completing the environmental cleanup (Wang D. et al., 2018). Synthesizing multifunctional, stable, and regeneratable composite material for cleanup is always seen as a long-term solution for contaminant degradation (Farooq et al., 2018). Such technical aspects have environmental advantages over lignocellulose-based carbon materials (Suganya and Senthil Kumar, 2018). Conventional waste treatment from acid black liquor using the electro-fenton process (Buftia et al., 2018) and an alternative sorbent (activated carbon from kraft lignin) from anthracite (AC_{COAL}) or coconut (AC_{BIO}) was evaluated using black liquor in the paper pulp industrial process for in situ contaminated sediment remediation (Gustafsson et al., 2017). However, the remediation is not much effective using the sorption method in the presence of active carbon materials. Hence, in this review, we briefly visualize that the listed metal-polymer combinations differ from carbon and its composites for their application.

3 METAL OXIDE-CONDUCTING POLYMER NANOCOMPOSITES

Metal oxide-based electrodes alone in bioelectrochemical conversion device systems as electrodes/anodes are not employed commonly due to their low electrical output





(Eyiuche et al., 2017). Analyzing polymers' fast and reversible redox cycling feature allows them to reversibly transfer electrons and protons, improving the overall electrode functionality (Dessie and Admassie, 2013). As a result, they have a wide range of applications, including those as supercapacitors, mediators for biological processes, and catalysts for electrochemical reactions (Wang and Feng, 2017). Carbon-based polymer nanocomposites (Jafary et al., 2018; Plekhanova et al., 2018) and other semiconductor materials are widely used in environmental remediation applications due to their prominent catalytic applications (Praveen et al., 2018). Therefore, in this review, the role of PPy in iron oxide and manganese oxide as nanocomposites and their scientific relevance will be discussed.

3.1 Iron Oxide/Polypyrrole

One of the most significant obstacles in MFC technology for fullscale application is power output limitation (Gajda et al., 2018). Colloidal magnetic nanocomposite-based iron oxide (Fe₃O₄, γ - Fe_2O_3) (Natarov et al., 2018) and its composites (Fe_2O_3 -in-CNT) (Guo et al., 2021) have attracted considerable attention due to a wide range of their applications. Biofilm formation and enrichment of exoelectrogenic bacteria are influenced by iron and iron-doped metal oxide nanoparticle coatings in the anode to boost current production of microbial electrochemical cells. This type of coating has high hydrophilicity and a unique electric characteristic (Muthukumar et al., 2019). For example, bacteria isolated from the soil of rice paddy fields can generate renewable energy (electricity) due to their exoelectrogenic nature (Fakhirruddin et al., 2018). The reaction of microbial populations in anode biofilms to increase concentrations of ferrous iron was more sensitive, according to principal component analysis.

The bulk of the anode biofilm communities of MFCs belongs to *Geobacter*, which was not the case for the cathode biofilm populations (Liu et al., 2017). A liquid-catalyzed fuel cell is a redox flow fuel cell that converts carbohydrates straight to power. Ferric chloride (FeCl₃) was employed as the major catalyst to boost efficiency (Xu et al., 2017).

Anode modification using Fe₃O₄-PPy composite-modified anodes is most attractive and cost-effective to increase MFC performance. Fe₃O₄-PPy composite-modified carbon felt anodes, according to the paper, may effectively improve the power production capacity and sewage treatment efficiency of MFCs. Compared to the unmodified anode, the steady-state current density and chemical oxygen demand removal rate were increased by 59.5 and 95.3%, respectively (Fan and Xi, 2021). When this composite was transformed with the addition of MnO₂, however, the surface of the anode was altered, resulting in kinetic activities. Because of their large surface area and abundance of electron-donating functional groups and heteroatoms, they have a high surface area. As a result, the PPy-encapsulated MnO₂, Fe_2O_3 , and MnO₂-Fe₂O₃ nanocomposite materials act as promising MFC anode electrodes with good electrochemical operations and power densities, according to the findings (Prakash et al., 2020).

In general, immobilization of metal or metal oxide catalysts on the surface of a pure polymer or a functionalized polymer could result in conducting polymer-based nanohybrids (CPNHs) with better catalytic performance and durability. Metal oxides have a lot of surface area and/or porous architectures; hence, they have a lot of synergistic effects with conducting polymers. As a result, CPNHs can provide a stable, environmentally acceptable bio/ electro-catalyst with improved catalytic activity and electrontransfer rate. Therefore, blending or direct deposition between CPNHs and metal or metal oxide nanomaterials as anode/ cathode and membrane applications in fuel cells (either in direct alcohol fuel cells or microbials) is common today, as shown in **Figure 9**. The detailed understanding of the electrode materials' features, changes, and performances is thoroughly reviewed (Ghosh et al., 2020).

3.2 Manganese Oxide/Polypyrrole

It is vital to use catalysts on the cathode in order to improve MFC performance in real wastewater. Potential electrochemical catalysts for MFCs have to be widely available and should be low-cost materials. Manganese dioxide (MnO₂) was also thought to be one of the most effective materials for MFC catalysts because of its inexpensive cost, nontoxic and ecologically benign nature, excellent chemical stability, and catalytic activity (Jiang et al., 2017; Dessie et al., 2020). To enhance electrochemical activities in MFCs, MnO₂ electrodeposition on PPy-coated SS presents a promising technology for bioelectricity generation and wastewater treatment (Phonsa et al., 2018). As a result, using in situ chemical polymerization processes to sandwich MnO₂ in PPy provides an alternate viable solution for high performance cells, as shown in Figure 10B. This is due to the acquisition of higher electron-storage capacity property of MnO2/PPy composite-modified electrodes, which is clearly shown in Figure 10A. The electron transfer mechanism on MnO₂/PPy composite-modified anodes is also shown in Figure 10C. As a result of sandwiching MnO₂ in PPy by in situ chemical polymerization, the MnO₂/PPy composite-modified anode surface has more microorganisms, according to the results.

Manganese ions play an intermediary role in electron transfer and transfers electrons from bacteria to the anode in this case. As a result, the "mosaic" structure causes electrons to reach the anode more efficiently in the redox process due to 1) increased electronic transmission channels between microbes and the anode due to microstructure improvement, 2) manganese ions acting as an electron transfer intermediary to accelerate the electron transfer rate, and 3) the composites' pseudocapacitance property, which improves the anode antipolarization performance.

4 FUTURE OUTLOOKS AND CHALLENGES

Significant advancements have been made on anode modification to increase the performance of MFCs. To succeed in this, various forms of modification techniques and architectural designs are frequently used. However, there are many challenges that need to be addressed in order to modify effective bioelectricity generation in MFC. The type and nature of electrodes, bioreactor design, shape and size, and the types of active electro microorganisms decides performance in MFC applications. However, noble-based nanomaterials are effective in producing electricity even in small device applications of MFCs. However, anodes modified by such nanomaterials are not cost effective in scaling up MFC devices. Hence, to reduce use of such costly nanomaterials, novel, lowcost, biocompatible, and environmentally friendly nanocomposites are used. Although power generation by using nanocomposite-modified anodes yields low power production, factors governing MFC performance will be optimized in the future to advance effective anode materials. Among these factors, electroactive microorganisms/biocatalysts, the type and concentration of fuels (substrates), and pH are critical. In the future, all listed parameters should be optimized to reduce polarization loss, activation losses, concentration losses, and ohmic losses. All the losses will be minimized by fabricating a functional nanocomposite through low-cost metal oxidepolymer integration. conducting As а result. thermodynamically stable, kinetically fast, and bioelectrochemically active nanocomposite-modified anodes can be designed, improving the performance of MFCs with respect to bioelectricity, wastewater treatment, metal recovery, and so forth.

5 CONCLUSION

Bioelectricity production in microbial fuel cell technology can be achieved in a variety of ways with purposes ranging from energy production to metal recovery (precious noble to heavy metals) and bioremediation. Bioelectricity production from diverse waste discharges via active microorganisms acting on anode electrodes modified with low-cost and suitable nanocomposites can very well operate as a sustainable source of energy, reducing the need for fossil fuels and resulting in green energy. Anaerobic digestion strategies that promote the conversion of various waste sources to bioenergy require an additional treatment procedure and are not cost-effective. Anaerobic digestion of waste products, contaminants, and chemicals in microbial fuel cell systems can be considered a good approach to keep the environment clean while also producing sustainable energy. Generally, promising or renewable energy generation simultaneous with wastewater treatment using MFCs from various waste discharges is intensified and attracts a lot of attention. However, enough power generation has not yet been carried out at the commercial level. Hence, MFCs still need to undergo additional research to scale-up devices in the near future.

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AUTHORS CONTRIBUTIONS

YD designed the research, wrote the manuscript, and revised the final draft of the manuscript. ST supervised the whole research and reviewed the manuscript.

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