Study on the Synergistic Mechanism of Simultaneous Wastewater Degradation and Power Generation in Modified Biochar-Based Microbial Fuel Cells

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Abstract: Conventional wastewater treatment suffers from high energy consumption and significant carbon emissions. Microbial fuel cells (MFCs) coupled with biochar electrodes can simultaneously remove pollutants and generate electricity. This paper summarizes research progress on biochar in MFCs. Addressing limitations such as poor conductivity and insufficient active sites, it proposes strategies including physical modification, chemical modification, biological modification, and composite modification to enhance power density and pollutant removal efficiency. Finally, it discusses challenges for large-scale implementation and explores potential technical pathways for low-carbon wastewater treatment.

Keywords: Microbial Fuel Cell; Biochar; Wastewater Treatment; Electrode Modification

1. Background and Challenges

Currently, industrial enterprises represent one of the primary sources of wastewater, with approximately 330 billion m^3 of organic wastewater generated globally each year. Traditional treatment processes consume roughly 3% of the world's electricity [1-2]. Simultaneously, persistently rising nitrogen and phosphorus concentrations in water bodies pose a global eutrophication crisis. Traditional wastewater treatment methods, such as nitrification/denitrification aeration, account for over 60% of total electricity consumption in wastewater treatment plants [3]. In recent years, annual publications on microbial electrochemistry (MET, including MFC) have surged from fewer than 50 in 2005 to over 700 in 2023. The innovative approach of treating waste with waste while simultaneously generating energy aligns more closely with future technological development.

The activated sludge process (ASP) remains the most widely adopted and mature biological treatment technology, with energy consumption scaling proportionally with treatment capacity. Based on COD removal, energy consumption typically ranges from 0.3–0.6 kWh kg^{-1} COD [4]. When measured by volumetric load, energy consumption is 0.6–1.2 kWh m^{-3}, with aeration constituting the primary energy-consuming component. High energy consumption leads to significantly increased carbon emissions, with each cubic meter of treated wastewater contributing approximately 0.9 kg CO_2-eq of direct and indirect greenhouse gas emissions from the process chain [5]. Traditional treatment methods have reached saturation in terms of both treatment capacity and energy consumption. Additionally, the demand for treating and discharging nitrogen, phosphorus, and emerging pollutants adds technical and economic pressures [6].

Conventional nitrification–denitrification processes require external carbon sources and involve substantial chemical dosing, increasing operational costs and posing risks of secondary pollution. Efficient treatment methods are lacking for specific wastewater streams; for instance, conventional adsorption or coagulation processes struggle to completely remove antibiotic residues [7]. Waste treatment byproducts also pose significant challenges. In China, municipal sludge production reached 6.5×10^7 tons in 2020 and is projected to exceed 9.0×10^7 tons by 2025 [8]. Traditional disposal methods like landfilling or incineration require temperatures above 850 °C and consume substantial energy. Jiang's research demonstrates that low-temperature pyrolysis at 300 °C can simultaneously achieve Cu(II) removal and carbon sequestration in biochar, indicating a potential future development direction [9].

To address the energy consumption bottleneck of traditional processes, coupling microbial fuel cells (MFCs) with low-cost biochar electrodes or functional reactors enables simultaneous pollution treatment, electricity generation, and partial resource recovery. Research demonstrates that integrated constructed wetland-MFC systems can achieve 100% tetracycline removal at a peak power density of 7.90 mW m^{-2} [4]. Tian Yu's work shows that eggplant-based biochar anodes enable simultaneous pollutant degradation and biomass resource recovery during MFC operation under overload conditions, enhancing system energy recovery rates [10]. Regarding cathode improvements, Xu's research demonstrated that algal carbon-driven systems exhibit highly efficient and relatively sustainable activity for removing recalcitrant organic pollutants like nitrobenzene [11]. The Anammox-MFC coupled system, by incorporating porous biochar, shortens Anammox start-up time by 17–50% and increases total nitrogen removal rates by 10–15% [3]. Zhang and Jiang demonstrated that anodes using microwave-pyrolyzed biochar (400–800 W, 300–700 °C) can increase power density by 2–3 times compared to conventional carbon-based anodes [12].

Single-chamber air cathode MFCs treating municipal wastewater achieved a net electrical energy output of 28 kWh m^{-3} [5]. For phenol-containing wastewater, banana peel biochar cathodes achieved 93.8% COD removal at a power density of 142.2 mW m^{-2}, with a cost only 1/65th that of Pt/C [13]. A bagasse biochar cathode achieved 98.1% isopropanol removal at a high power density of 2,316 mW m^{-2} [14]. These cases demonstrate that the MFC-biochar coupling system is a complex platform capable of simultaneously achieving efficient removal of recalcitrant pollutants and energy recovery for various wastewater substrates and biochar media.

As a critical component of MFCs, biochar exhibits strong competitiveness in terms of cost and raw material availability. Commercial carbon cloth anodes are relatively expensive, whereas certain biochar variants with similar configurations can be obtained at minimal cost. The preparation cost of biochar electrodes ranges from 0.0089 to 0.04 US\$ g^(−1), significantly lower than platinum electrodes; Fe-Mn-modified biochar cathodes cost only US\$5.4 m^{-2}, representing a 97% reduction [5]. Agricultural and forestry wastes like eggplant charcoal, walnut shell charcoal, algal charcoal, and straw charcoal can all be converted into electrode materials in a single step. The wide variety of biochar types allows for simultaneous advantages of waste resource utilization and readily available materials. However, the shortcomings of raw biochar cannot be overlooked. Its surface is generally negatively charged, exhibiting selective adsorption characteristics, and the saturated adsorption capacity of unmodified biochar is very low. For instance, unmodified wheat straw charcoal exhibits a Cd^{2+} saturation adsorption capacity of only ~289 mg g^{-1}, which increases to 350 mg g^{-1} after nitric acid oxidation.

Structural issues also exist in some biochar; low-temperature modification at 300 °C for high-ash sludge charcoal can balance adsorption capacity with carbon framework integrity [9]. Corn stalk charcoal can overcome its insufficient conductivity through multi-step functionalization modifications using pyrolytic-pyridine (ppy)-tin, MWNTs, or Fe-Mn [15]. Modified raw lignocellulosic biochar can achieve a doubling of power output. Therefore, biochar electrodes, due to their low cost and high plasticity, can lay the foundation for subsequent large-scale applications.

2. Biochar and MFCs

2.1 Literature Review Methodology

This review was completed through systematic retrieval of relevant literature from electronic databases, including Web of Science, Scopus, and China National Knowledge Infrastructure (CNKI). The search employed keywords such as 'microbial fuel cells', "biochar", 'wastewater treatment', 'electrode modification', 'power density', and 'pollutant removal', along with their combinations, encompassing both Chinese and English terms. This review prioritizes the latest peer-reviewed journal articles published between 2021 and 2025 to ensure alignment with current research developments. Selection criteria primarily focused on indicators related to the synergistic mechanisms enabling simultaneous power generation and pollutant degradation within microbial fuel cells using modified biochar. A critical evaluation and comprehensive analysis of performance metrics and modification methods was conducted, with particular emphasis on power density, removal efficiency, and modification techniques, aiming to provide a summary.

2.2 Limitations of Raw Biochar

Although biochar possesses inherent advantages in terms of cost and availability, its structural and functional limitations in an "unmodified" state significantly constrain its practical performance in MFCs. First, the conductivity of the raw carbon skeleton is generally insufficient. Biochar exhibits limited sp^2 hybridized domains and low graphitization, resulting in high bulk resistivity and large interfacial charge transfer impedance (Rct), which limits its power density. Secondly, high ash content further impairs electron conductivity. Sludge carbon exhibits ash content as high as 75.7–89.9%, predominantly consisting of insulating SiO_2. After pyrolysis at 300 °C, its specific surface area (SSA) reaches only 11.1 $m^2\ g^{-1}$.while pyrolysis at 700°C increases SSA to 18.9 $m^2\ g^{-1}$ but simultaneously reduces O/C to 0.08 and causes substantial loss of oxygen-containing functional groups, making it difficult to balance adsorption and conductivity [9]. Finally, the surface chemistry is unfavorable for selective reactions, making it challenging to address through simple pore size regulation.

The pore structure of raw carbon also exhibits structural imbalance. Although some biomass precursors can yield SSA values exceeding hundreds of $m^2\ g^{-1}$ (e.g., passion fruit inner membrane at 422.7 $m^2\ g^{-1}$ [4]; NaOH-treated algal charcoal: 664 $m^2\ g^{-1}$ [11]), the pores are predominantly micropores (2 nm) with insufficient mesopores, limiting substrate/proton diffusion. Modeling indicates that when the mesopore fraction falls below 60%, the substrate diffusion coefficient decreases by a factor of 1.7 [5]. Furthermore, surface functional groups are unevenly distributed: oxygen-containing groups like –OH and C=O facilitate metal ion complexation, but active sites such as pyridine-N and pyrrole-N are extremely scarce, failing to meet the demands of efficient oxygen reduction reaction (ORR) or microbial extracellular electron transfer. In summary, pristine biochar exhibits significant shortcomings in electron conduction, selective adsorption, interfacial reactions, and mass transfer efficiency. Overcoming these performance bottlenecks requires multi-level synergistic physicochemical-biological modification.

2.3 Current Status of Biochar-MFC Systems

Although laboratory-scale biochar-MFC systems have demonstrated excellent pollutant removal and electrical energy recovery capabilities, transitioning to long-term, stable, and large-scale operation still faces challenges including insufficient operational stability, lack of process standardization, and poor adaptability to complex wastewater.

2.3.1 Long-term operational stability

Continuous operation experiments indicate that the physicochemical stability of the electrode-membrane assembly is the primary factor determining MFC lifespan. The sludge-based biochar cathode exhibited only 0.02 V voltage decay during 120 days of continuous operation, demonstrating excellent structural stability [4]. However, metal-loaded biochar may experience reduced adsorption capacity due to metal leaching. After five adsorption-regeneration cycles, the Pb^{2+} adsorption capacity of MgO-K-BC decreased by 18%. The Fe-Mn bimetallic cathode exhibited a 5% activity decline over 30 days, accompanied by an increase in internal resistance of 2.4 Ω due to thickening of the anode biofilm. The ppy-tin modified anode showed an 8% voltage decay over 20 days [5]. In contrast, thermal weight loss of sludge char at 380–900 °C was slow, demonstrating superior long-term stability. Regarding membrane fouling, Nafion 117 requires periodic acid washing maintenance, while biochar ceramic membranes cost only 1/32 of Nafion and exhibit superior anti-fouling potential [16].

2.3.2 Lack of standardized process

Current literature exhibits significant variations in key parameters such as electrode dimensions, hydraulic retention time (HRT), carbon loading, and membrane materials, lacking unified benchmarks. Microwave pyrolysis requires power control between 500 – 1,000 W and feedstock particle size <1 mm to achieve uniform heating [12]. For Fe-Mn systems, recommended parameters include a carbon loading of 2.0 ± 0.2 mg cm^{-2} and HRT of 8–12 h. Laboratory standard benchmarks suggest anode dimensions of 5 cm × 5 cm × 0.3 cm and an external resistance of 200 Ω [17-18].

2.3.3 Adaptability to complex wastewaters

In real-world wastewater, co-pollutants such as high salinity, elevated COD, antibiotics, and heavy metals significantly suppress microbial activity and reduce power output, with different wastewater types exhibiting distinct characteristics [19]. For instance, power and removal rates typically decrease by 10–40% in swine wastewater, high-salinity (1% NaCl) conditions, or scenarios containing antibiotics. Authentic pharmaceutical wastewater (COD 2,800 mg L^{-1}, salinity 1.8%, pH 9.2) still maintained 820 mW m^{-2} [20]. Insufficient denitrification carbon sources due to high C/N ratios in brewery wastewater can be addressed through Fe-C micro electrolysis coupling.

2.4 Key Factors Influencing Biochar Materials

Literature review indicates that conductivity, active sites, interfacial properties, and structural stability are the four primary factors for biochar materials.

2.4.1 Conductivity

The resistivity of raw biochar generally exceeds 10 Ω cm. Insufficient graphitization impedes electron transport within the bulk phase and at the electrode-microorganism interface. Experimental data indicate that bulk conductivity can surpass 1000 S m^{-1} when the H/C atomic ratio drops below 0.4 or the Raman I_D/I_G ratio falls below 0.83 [21]. Therefore, high-temperature graphitization above 1000 °C or the introduction of heterogeneous sp^2 networks like tin or MWNTs is necessary to establish continuous conductive pathways, controlling charge transfer resistance R_(ct) to <10 Ω[15].

2.4.2 Active sites

Power density exhibits linear positive correlation with BET surface area (+8.4 mW m^{-2} per 100 m^2 g^{-1}). Mesoporous fraction >60% enhances substrate diffusion coefficient by 1.7-fold.Target SSA: 800–2000 m^2 g^{-1}. Hierarchical microporous-macroporous structure. Pyridine N + graphitic N content ≥72% to maximize ORR activity.

2.4.3 Interfacial properties

The negative charge on pristine biochar surfaces electrostatic repels phosphate and nitrate ions, inhibiting microbial adhesion. Oxygen-containing (–COOH, –OH) and nitrogen-containing (amino, pyridine-N) functional groups must be introduced to regulate the surface ζ-potential from –30 mV to approximately –10 mV, reducing repulsion without excessively compromising conductivity. Additionally, polar functional groups form hydrogen bonds/coordination bonds with outer membrane c-Cyts, lowering the activation energy for interfacial electron transfer.

2.4.4 Structural stability

Excessive pyrolysis temperatures (>700 °C) cause pore structure collapse, resulting in mass losses up to 40% [12]. Combining biochar with metals balances conductivity and structural stability. Electrodes exhibiting minimal activity decline during 30-day continuous operation and relatively low metal leaching can meet long-term stable operational requirements.

2.5 Influencing Factors of MFC Systems

The interface relationship within MFC systems is critical for ensuring efficient and stable operation. Three primary factors are involved: electron transfer, biocompatibility, and interference resistance. The efficiency of interfacial electron transfer between the biochar electrode and the extracellular electricity-generating microbial community directly determines the system's power density. The properties of raw biochar may lack corresponding functional groups, reducing its electricity-generating capacity. The surface chemistry of biochar readily influences the succession of microbial communities, affecting the growth and reproduction of electricity-generating bacteria. Excess acidic oxygen-containing functional groups inhibit electroactive bacteria growth, necessitating pH buffering or trace metal doping to stabilize biofilm thickness. In complex wastewater environments, specific matrix components can disrupt microbial metabolism and cause biofouling. Constructing multi-level barriers protects microbial communities. Concurrently, strategies like resistance adjustment and intermittent operation can reduce fouling rates.

2.6 Challenges in MFC Engineering

As MFCs transition from laboratory to engineering applications, scaling effects, economic viability, and field adaptability present primary challenges. First, increasing MFC volume-from hundreds of milliliters to practical cubic meters-can cause increased electrode spacing to trigger nonlinear amplification of ohmic polarization, resulting in diminished power density with larger volumes. Therefore, a balance must be achieved between modular parallel configurations and three-dimensional folded structures to ensure sufficient surface-to-volume ratio while controlling overall resistance. Second, economic evaluation should extend beyond material costs. A comprehensive life-cycle model encompassing energy consumption for fabrication, chemical usage, maintenance frequency, and carbon credit revenues is recommended to objectively compare the potential and resource consumption of different technological approaches.

Third, wastewater typically exhibits far greater fluctuations in temperature, salinity, pH, and toxic components than experimental conditions. Excessively restrictive process parameters may push power output and removal rates beyond acceptable thresholds. Integrating online monitoring and adaptive regulation can control treatment capacity and resource consumption. Additionally, standardizing modules-including MFC equipment and interfaces-facilitates future scalability, maintenance, and compatibility. Finally, the investment payback period is susceptible to uncertainties from policy and market mechanisms, such as carbon price fluctuations, emission threshold restrictions, and subsidy changes. Attention must be paid to investment stability.

3. Biochar Modification Methods and Results

3.1 Material Modification Methods

3.1.1 Physical modification

Physical modification refers to regulating the pore structure, degree of petrification, and surface morphology of biochar without chemical reagents. This is achieved solely by altering temperature, applying mechanical stress, or exposing the material to radiation. Such methods enhance biochar's surface area, electrical network integrity, and mechanical strength.

Physical modification methods include high-temperature carbonization, microwave pyrolysis, CO_2/steam physical activation, and mechanical ball milling-ultrasonic synergy.

3.1.1.1 High-temperature carbonization

When the final pyrolysis temperature is elevated from the conventional 500–600 °C to 900–1,200 °C, the amorphous carbon in biomass undergoes deep dehydrogenation-deoxygenation condensation. This process expands sp^2 hybridized domains, reduces interlayer stacking defects, and significantly enhances electron mobility. Simultaneously, the intense release of volatiles creates micro-mesoporous interconnected multi-level channels, increasing the specific surface area (SSA).

The surface area of corn stalk charcoal anodes after high-temperature carbonization increased from 85 $m^2\ g^{-1}$ to 820 $m^2\ g^{-1}$, electrical conductivity rose from 0.8 $S\ cm^{-1}$ to 15 $S\ cm^{-1}$, and maximum MFC power density reached 532 $mW\ m^{-2}$, representing a 2.6-fold improvement over the original charcoal [2].

3.1.1.2 Microwave pyrolysis

Microwave electromagnetic fields induce dipole rotation and ion conduction within the carbon skeleton, generating instantaneous "inside-out" bulk heating that rapidly escapes volatile components and forms abundant slit-type mesopores. High-energy electrons in the microwave plasma promote aromatic ring condensation, enhancing graphitization without significantly increasing energy consumption.

Microwave-pyrolyzed walnut shell carbon cathodes exhibit slit-like mesopores (2–4 nm), surface area of 650 $m^2\ g^{-1}$, cathode polarization impedance reduced from 45 Ω to 12 Ω, output power of 8.9 $W\ m^{-3}$, and energy consumption at only 55% of conventional tube furnace methods [9].

3.1.1.3 Mechanical ball milling-ultrasonic synergy

High-energy ball milling generates shear and compressive stresses, inducing slip of graphite microcrystalline layers and size refinement (La reduced from >10 nm to 4–6 nm). Ultrasonic cavitation further exfoliates layers and creates edge defects, shortening ion/electron transport paths. Concurrent introduction of lattice distortion energy facilitates subsequent chemical or biological loading.

After CO_2 activation and ball milling, banana peel carbon developed a hierarchical pore structure (microporous + mesoporous) with a surface area of 1,050 $m^2\ g^{-1}$. When used as an anode, its internal resistance dropped to 1.9 Ω, with power decay <5% after 120 h of continuous operation [7].

3.1.2 Chemical modification

Chemical modification involves reacting biochar with chemical reagents such as acids, bases, oxidants, or metal salts to introduce functional groups, heteroatoms, or metal active sites onto its surface. This alters the biochar's charge properties, electronic structure, and catalytic activity to meet the conductivity, catalytic activity, and stability requirements for MFC anodes/cathodes.

The first method is acid-base activation, defined as the etching of micropores or mesopores onto the biochar framework using strong acid solutions like HCl or KOH, generating functional groups such as carboxyl groups to enhance the biochar's specific surface area and graphitization degree. Co-impregnation of banana peel biochar with $Fe(NO_3)_3$ and $Mn(NO_3)_2$, followed by pyrolysis at 800 °C in N_2, formed Fe_3O_4/MnO_x heterostructures, improving MFC power density and phenol removal efficiency [15]. The second approach involves heteroatom doping, commonly N-doping or P/S doping. Post-doped biochar undergoes pyrolysis to alter its structure, reducing charge transfer resistance. N-doped biochar obtained through doping and co-pyrolysis exhibits increased pyrrole-N content and lower charge transfer resistance, thereby enhancing MFC power density [22]. Finally, metal/metal oxide loading involves treating raw biochar with metal salt solutions followed by pyrolysis or reduction to generate highly dispersed nanoparticles like zero-valent iron. This imparts high conductivity to the biochar while ensuring some self-recycling capability, though metal leaching must be avoided [23-24] .

3.1.3 Biological and composite modification

Biological modification is defined as the enhancement of biochar through living microorganisms or their metabolites, fostering the growth of electroactive biofilms on the carbon surface or inducing extracellular polymer deposition to improve biocompatibility and electron transfer efficiency. Composite modification involves introducing required materials or frameworks into biochar through combined physical, chemical, and biological modifications, while preserving the chemical integrity of the biochar matrix. This creates multiphase synergistic interfaces enabling simultaneous electricity generation and wastewater treatment. Primary biomodification approaches include microbial pre-seeding and enzymatic surface functionalization. Microbial pre-seeding requires preparing anaerobic media enriched with electroactive bacteria. Placing the MFC within this medium allows bacteria to interact with the MFC interface, achieving biomodification and enhancing the MFC's conductivity. Redox enzymes catalyze the polymerization of phenolic precursors (e.g., dopamine) under mild conditions, forming hydrophilic polydopamine on the carbon surface. This provides binding sites for subsequent metal nanoparticle immobilization or enzyme immobilization. Composite modification is currently mostly applied in laboratory settings and involves unstable factors. Theoretically, it can integrate the advantages of physical, chemical, and biological modifications.

3.2 Literature Review of Modification Techniques

Overall, high-temperature carbonization/microwave activation primarily enhances graphitization and pore connectivity. Subsequent loading of heteroatoms or metals introduces ORR/Fenton active sites. Finally, CNT, MOF, or biofilms construct continuous conductive networks and improve biocompatibility. The combined effects of these three processes simultaneously boost power and removal efficiency. A summary of recent studies on modified biochar applications in MFCs, along with their key performance metrics, is provided in Table 1. This comparative analysis highlights the effectiveness of various modification strategies in enhancing power output and pollutant removal.

Table 1. Summary of Modification Techniques and Performance Outcomes for Biochar-Based MFCs

MFC	Modification effect	Source of documentation
Waste banana peel/MOF cathode for phenol treatment	After modification, the power is 142.2 mW m^{-2}.	[4]
Peanut shells/conductive carbon black cathode for isopropanol enhancement	Power increase of 2.47 times.	[4]
Fe-Mn bimetallic doped biochar cathode	After modification, the power is 14.6 W m^{-3}.	[4]
Corn stover-CNT modified anode	After modification, Rct = 1.79 Ω.	[4]
Artificial wetland-MFC	Tetracycline 100% removed, modified power 7.90 mW m^{-2}	[4]
Eggplant-based nitrogen-doped anode	P_max 348.5 mW m^{-2}, COD removal 87.8%	[22]
Walnut shell-$ZnCl_2$/polyaniline/hot melt adhesive anode	P_max 51 mW m^{-3}, COD removal 85%, NH_4^+-N removal 88%	[22]
Algae charcoal-NaOH modified anode	P_max 0.60 W m^{-2}, nitrobenzene removal 99.9%	[11]
Mg-modified palm charcoal	NH_4^+ recovery rate 54.8%	[3]

Anammox-biocarbon particles	NH_4^+/NO_2^- each 40 mg L^{-1}, TN removal >98%	[3]
Microwave orange peel charcoal 700 W-700 °C	SSA 1,015 m^2/g, tetracycline removal 100%	[9]
300 °C sludge charcoal	Cu^{2+} Langmuir Q_m = 2.389 mg g^{-1}, carbon fixation rate 24%	[9]
Branch charcoal 616 °C	Iodine adsorption 447.96 mg g^{-1}, maximized micropores, internal resistance reduced by 30%	[25]
Ppy-tin/CS anode	P_max 2.44 W m^{-2}, COD removal 91%, Rct 1.79 Ω	[5]
Fe-Mn bimetallic cathode	P_max 14.6 W m^{-3}, phenol removal 96.8%, stable for 30 days	[5]
CS/$MWNT_4$ anode	P_max 2.15 W m^{-3}, internal resistance 1.79 Ω, stable for 6 months	[15]
Cyanobacteria carbon/KOH-N anode	P_max 1.610 W m^{-2}, tetracycline removal 95.12%	[17]
Peanut shell-Cu/Co anode	Co-modified 205.49 mW m^{-2}, Cu-modified 171.18 mW m^{-2}	[26]
Chlorella biochar	P_max 2,068 ± 30 mW m^{-2}	[27]
Alfalfa leaf N-doped	P_max 1,328.9 mW m^{-2}, superior to Pt/C	[27]
Sugarcane bagasse charcoal cathode	Power 2,316 mW m^{-2}, isopropanol removal 98.1%	[14]
MIL-53(Fe)/banana peel charcoal	Power 142.2 mW m^{-2}, SA removal 93.8%, cost 0.374 USD vs Pt/C 24.39 USD	[13]
CW-MFC iron-carbon filler	Ciprofloxacin removal 91.2%, power 3.552 mW m^{-2}	[7]
Fe-C/coconut shell charcoal	Denitrification + CO_2 electrolysis, voltage peak 397.8 mV	[28]

As shown in the table above, after systematic modification, the conductive network, active sites, and structural stability of biochar have been enhanced. High-temperature charcoal or microwave activation first endows biochar with a high specific surface area and graphitized framework, providing a solid physical foundation for subsequent modifications. Chemical modifications such as the loading of heteroatoms and metals create highly efficient catalytic/adsorption sites on the framework, reducing charge transfer resistance and accelerating pollutant removal rates. Biological modification enhances power density while ensuring mechanical and electrochemical stability for long-term operation, balancing low-energy consumption with resource recovery. Overall, composite modification demonstrates the potential for biochar electrodes to achieve scalability in terms of power output, removal efficiency, and practicality.

4. Summary

The global volume of wastewater treatment is enormous, and traditional wastewater treatment faces issues such as high energy consumption and complex substrates, gradually shifting toward the direction of simultaneously achieving wastewater treatment, energy recovery, and carbon emission reduction. The MFC-biochar coupling system, with its advantages of "treating waste with waste" and "simultaneous electricity generation," has gained increasing attention in recent decades and has become an important focus in wastewater treatment and waste utilization. Due to industrialization, there are numerous types of wastewater, and most treatment methods are not universally applicable. Some wastewater treatment methods struggle to adapt to their complexity, and there is an urgent need to find a method that can accommodate various types of wastewater treatment.

Biochar is abundant, inexpensive to produce, easily accessible, and diverse in type. However, due to the limitations of its chemical composition, it often suffers from insufficient graphitization, high ash content, and single-pore size, leading to high resistance, scarce active sites, and weak mechanical strength in MFCs. When the reactor volume is scaled up, increased electrode spacing, uneven flow fields, and membrane fouling further exacerbate these defects, becoming one of the key factors contributing to reactor instability.

To address these issues, physical modification, chemical modification, and biological modification have been employed to varying degrees to alter the inherent limitations of biochar. Physical modification achieves graphitization of the skeletal structure and the formation of hierarchical pore channels through high-temperature carbonization or microwave activation. Chemical modification introduces high-activity sites through heteroatom doping, metal loading, or surface functionalization, altering the surface structure to establish pathways for electricity generation. Biological modification enhances interfacial biocompatibility through methods such as pre-coating with electroactive bacteria, simultaneously achieving wastewater treatment and electricity generation.

Current laboratory data indicate that through composite modification strategies, the specific surface area can be increased to 800 – 1,500 m^2 g^{-1}, the charge transfer resistance reduced to below 2 Ω, the power density increased by 1–2 orders of magnitude, and the removal rates of recalcitrant organic matter, nitrogen, phosphorus, and antibiotics all exceed 90%. Additionally, some long-term operational performance degradation is low, and the material cost of modified biochar is relatively low, offering good economic advantages. Currently, there are no publicly available data on large-scale continuous operation. The proposed parallel-series modular approach could provide a potential scaling-up pathway for future large-scale experiments.

Due to significant differences in MFC configurations and wastewater matrices, future implementation of modularization will require addressing numerous issues, including modular configuration design, real-time monitoring, adaptive adjustments, and full-lifecycle economic model assessments. Through standardized modules, intelligent operations and maintenance, and carbon trading policies, small-scale pilot projects can be initially implemented, providing new insights for low-carbon treatment of certain existing high-organic composite wastewater streams. If the results are relatively good, it may be considered to establish fixed-capacity, scalable modular operations to establish preliminary standards for low-carbon wastewater treatment. Policy aspects, which depend on external variables such as carbon trading and subsidies, are beyond the scope of this discussion.

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