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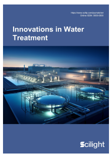

Review

Wastewater Treatment at the Cathode of Microbial Electrochemical Systems: Focusing on Carbon-Based Materials

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Abstract: The cathode of the microbial electrochemical systems (MESs) can continuously provide electrons to drive microbial or electrode-based reduction reactions for pollutant degradation. Cathode material is a key factor influencing the efficiency of MESs in wastewater treatment. Carbon-based materials have attracted widespread attention due to their property tunability and low toxicity. This review focuses on enhancing the performance of MESs for wastewater treatment through the modification of carbon-based cathodes. It summarizes common modification strategies for carbon-based cathode materials and evaluates their application performance in both abiotic and biotic cathode systems. The results indicate that the modification of carbon-based cathodes significantly improves the wastewater treatment efficiency of MESs. Moreover, this review discusses the current limitations, noting that most studies remain at the laboratory stage, and proposes future research directions for practical implementation. Overall, carbon-based cathode modification is a promising strategy to advance MESs toward practical wastewater treatment and resource recovery.

Keywords: microbial electrochemical systems; carbon-based materials; wastewater treatment; cathode; electrode modification

1. Introduction

Currently, the discharge of various types of wastewater, including domestic sewage and industrial effluent, has led to increasingly prominent water pollution problems. Domestic wastewater is complex in composition but relatively low in toxicity, while industrial wastewater originates from diverse sources, resulting in a wide variety of pollutants that significantly increase treatment difficulties. Based on pollutant characteristics, industrial wastewater can be categorized into types such as industrial organic wastewater, heavy metal-containing wastewater, and wastewater with refractory pollutants. Industrial organic wastewater is rich in pollutants such as benzene compounds and phenols, with chemical oxygen demand (COD) concentrations reaching up to tens of thousands of mg/L. Wastewater containing heavy metals carries toxic substances like chromium, cadmium, lead, and mercury, which can accumulate in the environment and have their toxicity progressively amplified through the food chain [1]. Meanwhile, wastewater with recalcitrant pollutants contains substances such as antibiotics, PFAS, and halogenated hydrocarbons, which are highly stable and biologically toxic. If these wastewater discharges are not properly treated, they can pollute water bodies, disrupt ecological balance, and even lead to bioaccumulation, increasing the risk of cancer in humans [2]. According to 2022 data from the United Nations Water Mechanism, 73 countries (covering 41.6% of the global population) reported total wastewater generation and treatment data, with a total volume of 136 billion cubic meters. Among them, only 42 countries (representing 12% of the global population) reported that 60% of their wastewater (accounting for 45.4% of total wastewater, or 61.8 billion cubic meters) was safely treated by at least secondary treatment. However, due to difficulties in monitoring wastewater generation and discharge, the actual treatment situation may be even worse [3].

Microbial electrochemical systems (MESs) is a technology that integrates microbial metabolism with electrochemical reactions, primarily encompassing microbial fuel cells (MFCs), microbial electrolysis cells (MECs), microbial electrosynthesis, and other related technological systems [4]. As a type of green and environmentally friendly technology, it not only enables pollutant degradation but also allows for resource recovery and utilization during the degradation process, thus holding broad application prospects in the field of wastewater treatment. In the MES, electrons generated by anodic electroactive microorganisms through the metabolism of organic matter are transferred via an extracellular electron transfer chain to the anode. These electrons travel through an external circuit to the cathode, while protons migrate through the electrolyte or membrane to the cathode within the system. Under electrochemical drive, electron acceptors at the cathode receive electrons and undergo reduction reactions, ultimately enabling the degradation of pollutants in the system. As summarized in Figure 1, the development of microbial electrochemistry dates back to 1911, when Potter first discovered and confirmed that microorganisms were capable of generating voltage and current. Subsequently, researchers conducted systematic investigations into the phenomenon of microbial electricity generation. In 1962, Davis first proposed the concept of microbial fuel cells, and in the 1980s, Derek Lovley and Kenneth Nealson successively isolated two key electrogenic strains, namely *Shewanella oneidensis* MR-1 and *Geobacter metallireducens* GS-15, thereby clarifying the core characteristics of electroactive microorganisms. Subsequently, in 2004, Bruce Logan applied MES to wastewater treatment, with the core of the system focused on achieving efficient wastewater treatment at the anode. In 2007, Peter Clauwaert [5] utilized denitrification reactions centered on a bioanode to achieve denitrification in wastewater. That same year, Logan's team investigated enhancing wastewater treatment performance through anode modification. In 2010, Feng et al. [6] employed a modified cathode to reduce wastewater at the cathode, using carbon nanotubes/γ-FeOOH to degrade azo-dye-containing wastewater. Since then, the field of wastewater treatment centered on modified cathodes has continued to evolve and improve, and microbial electrochemical systems are gradually being scaled up to meet the demands of practical wastewater treatment. The operational performance of MES is influenced by multiple key factors, including electrode materials, the types and activity of electroactive microorganisms, substrate composition and concentration, electrolyte pH, temperature, external resistance, and applied voltage. These factors directly affect microbial metabolism and interfacial electron transfer processes, thereby influencing the system's pollutant removal efficiency [7].

As summarized in Table 1, several reviews have focused on the removal of pollutants in MESs. In MESs, the anode is dominated by oxidation reactions, and anodic oxidation is directly associated with the efficiency of microbial extracellular electron transfer and the degradation rate of organic substrates, serving as the core limiting step for the system's power generation capacity and the removal of primary pollutants. Hence, some reviews have explored the promotion of the anodic oxidation process to achieve the degradation and removal of primary pollutants [8,9]. However, due to the high reaction energy barriers and slow degradation kinetics of certain pollutants, they are difficult to be oxidatively degraded at the anode and are more readily reduced at the cathode, such as heavy metals, azo dyes, and other pollutants. Accordingly, some reviews, while focusing on the removal of specific classes of pollutants in MESs, have indicated that such refractory pollutants can be efficiently degraded at the cathode, highlighting the indispensable role of the cathodic removal of system pollutants [10,11]. Furthermore, other reviews have primarily focused on the influence of different cathode materials on pollutant removal efficiency in MESs. This is because the cathode material decisively affects the overall electron transfer rate, microbial attachment on the biocathode, material stability, and operational stability in cathodic-centric wastewater treatment within MESs [3,12]. Additionally, given that carbon-based materials align with green development principles, this review focuses on modified carbon-based cathode materials and explores their mechanisms to optimize the operation of MES, thereby enhancing wastewater treatment efficiency.

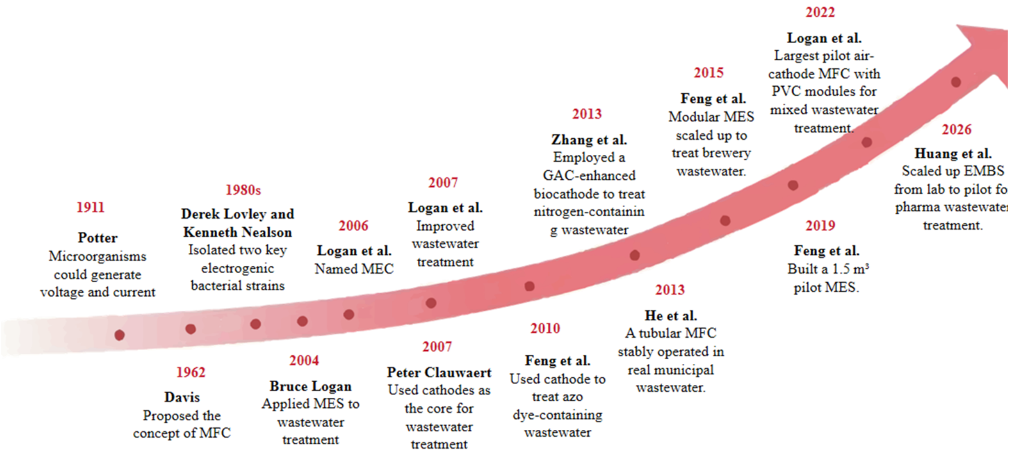


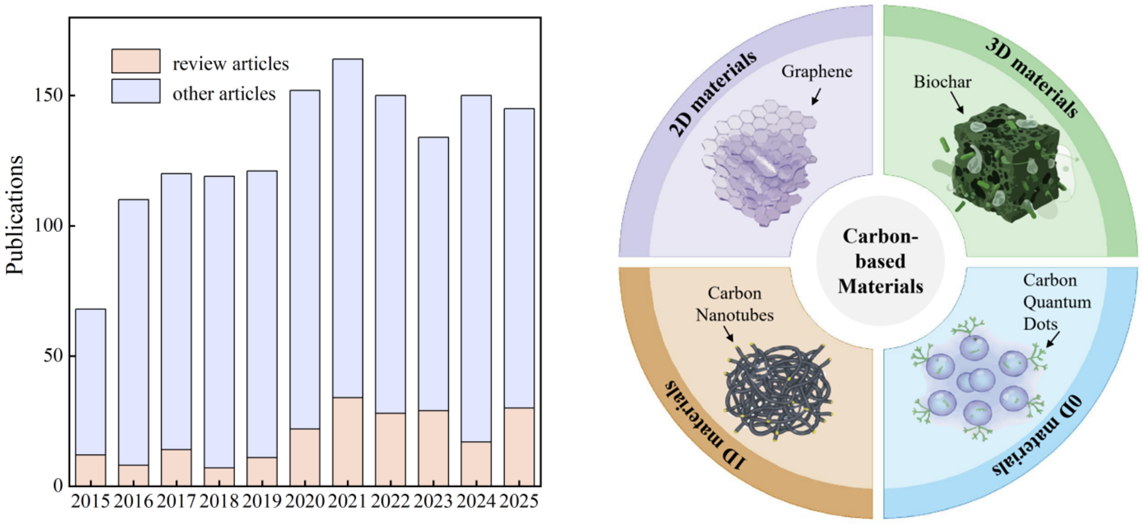
Figure 1. Development and scale-up application of MES.

Table 1. Relevant reviews of MES in the field of wastewater treatment.

Number	Year	Journal	Review Title	Highlights of the Review	Reference
①	2025	Water Research	Recent advancements in antibiotics removal by bio-electrochemical systems (BESs): From mechanisms to application of emerging combined systems	analyzed the detoxification mechanism of antibiotic treatment by BESs, and summarized BES hybrid systems for practical use.	[10]
②	2025	Reviews in Environmental Science and Bio-technology	Microbial fuel cell mediated azo dye degradation: a comprehensive review on anode, cathode, membrane interfaces and scale-up potential	The anodic dye degradation, electrode materials, microbial catalyst, co-substrate, degradation at a biotic/abiotic cathode, and various membranes used in MFCs.	[11]
③	2025	Journal of Environmental Chemical Engineering	Electrode materials for copper removal from wastewater by bioelectrochemical systems: A review	focusing on BES reactor concepts, working principles, and development history; practical cases of treating copper-containing wastewater; and the impact of electrode materials and operating parameters on BES performance.	[4]
④	2025	Journal of Environmental Chemical Engineering	Recent advancements in heterogeneous cathode catalysts for in-situ hydrogen peroxide synthesis in bio-electro-Fenton process and its application in wastewater treatment: A review	emphasis was laid on the noble metal, metallic, bimetallic, carbonaceous, and waste-derived composite catalysts regarding H_2O_2 yield in the BEF system.	[12]
⑤	2025	International Journal of Hydrogen Energy	Two-dimensional materials-based cathodes for high-performance microbial fuel cells	This review discusses the potential benefits of 2D materials as cathodes to promote reduction reactions in microbial fuel cells (MFCs).	[13]
⑥	2021	Carbon Energy	Carbon material-based anodes in the microbial fuel cells	Systematic summary of main carbon materials for MFC anode modification.	[8]
⑦	2023	Journal of Power Sources	Progress on anodic modification materials and future development directions in microbial fuel cells	summarizes and reviews the current application of various anodic modification materials in MFCs.	[9]

2. Carbon-Based Cathode Materials

There are many commonly used cathode materials, among which noble metal-based cathodes have attracted significant attention due to their high catalytic activity, stability, and selectivity, such as platinum-based materials. However, these materials suffer from limitations, including high cost and poor durability. Thus, numerous efficient alternatives to noble metal-based cathodes have been widely reported in recent years, including various high-performance carbon-based cathode materials. Carbon-based materials possess well-developed porous structures and excellent chemical stability. Additionally, they are environmentally friendly, low-cost, non-toxic, and feature large specific surface areas that enable effective adsorption of organic pollutants in wastewater. They also exhibit good electrical conductivity, resist performance degradation caused by electrode polarization, and can tolerate complex water conditions. Therefore, many researchers have focused on developing efficient and low-cost carbon-based materials to further enhance their multifaceted properties, as shown in Figure 2a. This paper specifically focuses on the application of carbon-based materials as cathodes in MESs for wastewater treatment.



(**a**) (**b**)

Figure 2. (**a**) The number of MES-related literature publications from 2015 to 2025. The data were obtained on March 11, 2026, from the Web of Science Core Collection using a search query with the specific keywords as follows: (“wastewater” OR “waste water” OR “sewage” OR “effluent”) AND (“biochar” OR “carbon nanotube” OR “graphene” OR “graphite” OR “carbonaceous” OR “carbon material” OR “carbon-based”) AND (“microbial electrolysis cell” OR “microbial fuel cell” OR “microbial electrochemical” OR “bioelectrochemical”); (**b**) Common carbon materials.

2.1. Common Cathode Carbon-Based Materials

Due to differences in morphology and structure among various carbon-based materials, their performance in MES applications also varies. Carbon-based materials can be primarily classified into zero-dimensional, one-dimensional, two-dimensional, and three-dimensional structures based on their structural dimensions [14]. Figure 2b illustrates the distinctive structural and performance characteristics of certain carbon materials. Zero-dimensional carbon-based materials refer to those with nanoscale dimensions in all three spatial directions, typically appearing as spherical or dot-like structures. As shown in the figure, carbon quantum dots (CDs) are carbon nanomaterials smaller than 10 nm in size, featuring a conjugated sp^2/sp^3 core structure and surface-rich functional groups such as carboxyl, hydroxyl, and aldehyde groups. They are usually synthesized via hydrothermal methods using precursors like glucose, exhibiting unique fluorescent properties and high biocompatibility. CDs can be immobilized on the surface of substrate electrodes and introduced into MES as efficient oxygen reduction reaction (ORR) catalysts, thereby increasing the specific surface area and enhancing interactions between microorganisms and the electrode. However, their long-term stability still needs improvement [15,16].

One-dimensional carbon-based materials refer to nanostructures that are significantly longer in one dimension compared to the other two, typically exhibiting tubular or fibrous morphologies with high aspect ratios and excellent electronic transport properties. For example, carbon nanotubes (CNTs), due to their high specific surface area, strong energy conservation, and chemical stability, are commonly used as catalysts. The properties of CNTs depend on their structure, such as chiral angle, length and diameter, which can endow them with unique characteristics, while the synthesis method can have a certain influence on the formation of the structure. To date, researchers have developed various methods for synthesizing carbon nanotubes, including chemical vapor deposition (CVD), laser ablation, and arc discharge. Among these, the earliest method is arc discharge technology, and CNTs produced by this technique may exhibit some structural defects [17]. CVD technology has been established as one of the best methods for producing CNTs, in which CNTs can be formed by the decomposition of carbon precursors on a catalytic substrate surface. Among these, thermal wire or plasma CVD is considered the standard method for CNT synthesis, offering relatively low cost and the ability to produce various forms of CNTs, such as straight or helical structures [17,18]. Moreover, carbon nanotubes have small dimensions, and the bonding state on their surface differs from that in the interior of the particles, with incomplete surface coordination, which helps increase active sites. However, its biocompatibility is insufficient, and modification can promote bacterial biofilm formation and adhesion [19].

Two-dimensional carbon-based materials refer to materials that are atomically thin in one dimension and extend over two other dimensions. Graphene is a typical two-dimensional carbon nanomaterial, composed of sp^2-hybridized carbon atoms arranged in a tightly packed honeycomb structure. Its synthesis methods can be categorized into top-down and bottom-up approaches, making it a highly promising cathode electrode material [17]. Top-down methods include mechanical exfoliation, solution exfoliation, electrochemical exfoliation, and chemical exfoliation-reduction. In these approaches, graphite serves as the starting material. Compared to mechanical and solvent exfoliation, electrochemical exfoliation is more environmentally friendly and faster for graphene synthesis. In the chemical exfoliation-reduction method, graphene is produced by first oxidizing graphite to obtain graphene oxide (GO), followed by reducing GO [18]. In contrast, bottom-up approaches primarily involve the synthesis of graphene from small molecules through catalytic processes, mainly including CVD and epitaxial growth methods. Among these, CVD is considered the most versatile technique for producing continuous graphene films, involving the decomposition of a carbon source at high temperatures on a transition metal catalyst substrate. The decomposed carbon atoms deposit onto the surface and subsequently assemble into graphene films under elevated temperatures. Several advanced techniques have been developed, such as plasma-enhanced chemical vapor deposition (PECVD) and microwave-assisted CVD. Similar to CVD, epitaxial growth is also a substrate-based method, in which monolayer graphene is grown via vacuum graphitization on single-crystal carbides (SiC). The large specific surface area of graphene combined with its directional transport channels creates numerous active sites, effectively enhancing oxygen reduction reactions. However, due to strong π-π stacking and van der Waals interactions within graphene, monolayer graphene tends to undergo irreversible aggregation, thereby losing its unique advantages [13].

Three-dimensional carbon-based materials refer to structures that have macroscopic dimensions in all three spatial directions, or are assembled from low-dimensional carbon materials into three-dimensional configurations, typically appearing as bulk or felt-like forms. For example, carbon felt and graphite felt are often used as substrate materials in MES due to their three-dimensional morphology. Both are produced from carbon fibers at different temperatures. Carbon felt is formed by a large number of carbon fibers randomly interwoven and overlapped, creating an interconnected pore network inside. It has a low degree of graphitization and poor electrical conductivity, but exhibits good chemical stability [20]. In contrast, graphite felt has a high degree of graphitization, closely resembling the crystal structure of graphite, and features a three-dimensional interconnected porous network. Its individual fibers are thicker and denser, forming a regular and robust three-dimensional structure with excellent electrical conductivity, although its specific surface area is relatively small. Biochar is a solid carbon material derived from biomass (such as straw, wood, and nutshells) through pyrolysis or gasification. Its macroscopic shape is irregular, mostly appearing as blocks, granules, or similar forms. Biochar typically possesses well-developed internal pores, so it can be classified as a three-dimensional morphology. It has been shown that biochar can be produced by a one-step pyrolysis method, which is simple and convenient [21]. It can be used as a non-biological cathode catalyst to enhance ORR efficiency. Due to its large specific surface area, incorporating biochar into biological cathodes provides abundant sites for bacterial attachment, while its excellent biocompatibility minimizes toxicity to microorganisms. However, the application potential of pristine biochar is limited by the relatively low diversity of its surface functional groups, which are mainly oxygen-containing groups such as hydroxyl and carboxyl. This results in poor adsorption selectivity for specific pollutants. Furthermore, it lacks sufficient catalytic active sites, making it difficult to meet the demands of efficient catalytic degradation [22].

In summary, directly using such carbon-based materials as cathode materials in MES still has certain limitations, such as insufficient active sites and high electron transfer resistance, while stability and conductivity also need improvement. Moreover, different carbon-based materials exhibit varying performance in MES. Some carbon-based materials, when used as substrate materials, can improve wastewater treatment efficiency through modification. Therefore, before employing these carbon-based materials as cathodes for wastewater treatment, they should be modified to compensate for their shortcomings.

2.2. Common Modification Methods for Cathode Carbon-Based Materials

When researchers modify carbon-based cathode materials to address issues such as insufficient catalytic activity and limited electron transfer rates of pristine carbon materials, they often employ methods such as coating and impregnation, electrochemical deposition, calcination and pyrolysis, and hydrothermal methods. These methods differ to some extent in their modification mechanisms and applicable scenarios

2.2.1. Coating and Impregnation Methods

Coating and impregnation methods are widely used by researchers for the modification of carbon-based cathodes. Among them, the coating method is favored for its relative simplicity and directness. It typically involves coating the surface of a carbon-based electrode with a mixture of a catalyst to be introduced and a binder, such as Nafion or PTFE. For example, Wang et al. [23] applied a nano-jarosite/biochar composite onto a graphite plate for Cr(VI) removal in an MFC cathode. Nevertheless, the coating method may lead to an uneven distribution of the catalyst on the electrode and cause loss of catalyst active sites [18]. For three-dimensional carbon-based electrodes, such as carbon brushes, the impregnation method can be used. This method involves immersing the carbon-based electrode material into a uniformly mixed slurry of catalyst and binder. After immersion, the electrode is taken out and dried. For such three-dimensional carbon materials, the impregnation method results in a more uniform distribution of the catalyst. However, some catalyst loss still occurs when using the impregnation method for modification [24]. Regardless of whether the coating method or the impregnation method is used, the amounts of catalyst and binder depend on the properties of the catalyst and the carbon-based material, and need to be determined according to specific practices. For example, Liu et al. [25] found that when 83% of the cathode material consisted of biochar, the composite cathode exhibited both low electrical resistance and high copper adsorption capacity.

2.2.2. Electrochemical Deposition Method

Electrochemical deposition is a liquid-phase modification technique that deposits metal ions or functional precursors from an electrolyte onto a carbon-based cathode surface via reduction reactions driven by an applied electric field. This method can be operated in various modes, such as potentiostatic, galvanostatic, or cyclic voltammetry, but generally only achieves the deposition process [7]. Nonetheless, it can also directly induce polymerization of monomers in solution on the working electrode surface by applying a voltage or current, thereby generating a conductive polymer. Meanwhile, other components present in the system can be co-deposited into the polymer network. For example, Pang et al. [26] used electropolymerization of pyrrole to prepare PPy/graphene, which was then applied in an MFC cathode for Cr(VI) removal. Furthermore, when a specific chemical state is required, such as reducing an oxidized precursor to a target product, post-treatment is often necessary. However, some studies have achieved the desired chemical state directly through one-step electrodeposition and simultaneously deposited it onto carbon-based materials. For example, cyclic voltammetry scanning in a citrate buffer solution directly produced reduced graphene oxide (rGO) modified carbon brushes. In this process, GO is electrochemically reduced to rGO on the electrode and simultaneously deposited onto the carbon fiber surface [27]. Similarly, Yang et al. [28] also prepared graphene/polypyrrole (rGO/PPy) modified electrodes by a one-step electrodeposition method. They used them as biocathode electrodes in an MES system to enhance the removal efficiency of nitrate from wastewater. After deposition, the morphology changes are often observed by SEM/TEM. Compositional analyses such as XPS and Raman spectroscopy are also performed. These techniques are used to detect the introduction of new elements or the appearance of characteristic structures, thereby verifying the degree of modification.

2.2.3. Calcination and Pyrolysis Methods

Modifying carbon-based electrode materials by calcination typically involves first loading functional precursors onto the carbon substrate via impregnation or other methods. Then, calcination is performed at a specific temperature and under a specific gas atmosphere to convert the precursors into the target active phase. Calcination is usually carried out in an air or an inert gas atmosphere. In air, it removes volatile substances, while an inert atmosphere is mainly used to prevent excessive oxidation of materials at high temperatures. Calcination of carbon-based electrode materials can increase their graphitization degree and thus enhance electrical conductivity.

Moreover, during pyrolysis, organic matter generates carbon dioxide and water vapor that escape, creating hierarchical pores, which increase the specific surface area and pore volume of the carbon material. Additionally, calcination can be used to dope carbon-based electrode materials with elements to improve performance. For example, John et al. [29] immersed carbon cloth in solutions of iron(III) nitrate nonahydrate at different concentrations, followed by ultrasonication and drying. They then calcined the material in a muffle furnace for one hour to introduce Fe, thereby enhancing the degradation efficiency of dyes. Unlike calcination, pyrolysis emphasizes the decomposition of organic matter and the formation of carbon frameworks under oxygen-free or anoxic conditions. The pyrolysis method involves treating precursor materials under inert gases (such as N_2 or Ar) or specific atmospheres to induce thermal decomposition and carbonization reactions, directly producing carbon-based electrode materials or carbon composites. Since pyrolysis temperature not only affects the final product's structure but also indirectly determines its electrocatalytic performance, precise control over parameters such as pyrolysis temperature, heating rate, and holding time enables accurate regulation of the graphitization degree, pore structure, and the heteroatom content of the resulting carbon materials. Typically, low-temperature pyrolysis (<400 °C) primarily involves the volatilization of small molecules and removal of functional groups, while medium-temperature pyrolysis (400–800 °C) favors carbon skeleton rearrangement and aromatization. High-temperature pyrolysis (> 800 °C) significantly enhances graphitization and promotes the formation of defective structures, but may lead to the loss of some active sites [30]. Among them, the pyrolysis of biomass precursors has received particular attention. Lignin, cellulose, and other components naturally contain various elements such as C, N, O, and S. Through pyrolysis, heteroatom self-doped carbon materials can be directly obtained. Moreover, after pyrolysis, further performance enhancement can be achieved by combining with methods such as KOH activation.

2.2.4. Hydrothermal Method

Under hydrothermal conditions, the physicochemical properties of water change significantly, with a decrease in the dielectric constant and an increase in the ionic product, which can promote various chemical reactions. Using the hydrothermal method to modify carbon-based materials involves placing them in a sealed high-pressure autoclave, where water serves as the solvent and reaction medium. Under high-temperature and high-pressure conditions, the modification of carbon-based materials or the in-situ synthesis of functional components is achieved [31]. In the modification of carbon-based cathode electrodes, the hydrothermal method is often used to grow nanostructures such as metal oxides, metal sulfides, or metal phosphides in situ on the carbon material surface. It can also be employed for the pre-carbonization of carbon-based precursors and the regulation of surface functional groups. For example, Zhang et al. [32] prepared a 3D binder-free BGA cathode electrode via a hydrothermal method to enhance the performance of the cathode for methyl orange (MO) removal. The hydrothermal method drives the nucleation and growth of crystalline materials by creating a supersaturated state of solutes. By adjusting conditions such as pH, temperature, reaction time, and surfactants, the anisotropic growth of nanocrystals can be precisely controlled. This enables the tailored synthesis of different morphologies, such as nanorods and nanosheets [33]. Since it is typically carried out at lower temperatures, the product can retain more oxygen-containing functional groups and surface chemical activity, but has a lower degree of graphitization and relatively poor electrical conductivity.

In practical research, the above methods can be used to enhance performance by introducing nanostructures or performing element doping on carbon-based cathode materials. These methods may face issues such as high energy consumption and high cost. In addition, a combination of multiple modification methods can also be employed. This approach utilizes the synergistic effects among different methods to tune the structure and properties of materials, thus meeting more complex application requirements.

3. Abiotic Cathode MESs and Their Cathode Modification Strategies

Cathodes in MESs can be divided into abiotic and biotic cathodes depending on whether the reaction is catalyzed by microorganisms. In the abiotic cathode system of MESs, the cathode material or its surface-modified catalysts reduce the overpotential of the electron acceptor reduction reaction, accelerate reaction kinetics, and enhance interfacial electron transfer. This promotes the reduction and transformation of electron acceptors such as organic pollutants by accepting electrons at the cathode [34,35].

In the cathodic reactions of MFCs, the oxygen reduction reaction (ORR) is considered the most promising electron-accepting reaction due to its high redox potential and sustainability [36]. However, the slow ORR reaction kinetics and high overpotential severely limit the performance improvement and practical application of MFCs. For instance, Yuan et al. [37] compared banana-derived unactivated biochar cathodes; chemically activated and modified biochar cathodes exhibited increased specific surface area and nitrogen content, thereby enhancing ORR catalytic activity [38]. Moreover, for MECs, since the voltage generated by electricity-producing microorganisms on the anode electrode is insufficient to enable efficient pollutant degradation or hydrogen evolution reaction (HER) in the cathode chamber, an external power source is required to overcome the chemical potential barrier [39]. Additionally, modifying the cathode electrode can enhance pollutant degradation efficiency by reducing the overpotential of the electron acceptor reduction reaction [40]. Therefore, modifying the cathode material is crucial. It is also an effective approach to enhance the degradation efficiency of pollutants in wastewater. Studies have shown that various modification strategies, such as introducing defects or active sites and enhancing electrical conductivity, can effectively improve the performance of cathode materials in MFCs. Consequently, the removal efficiency of pollutants is increased, as shown in Table 2.

Table 2. Modification of carbon-based cathodes in abiotic cathode systems.

Cathode	Pollutant	Modification Method	Benefits of Modification	Treatment Efficiency	System	References
FeNC-N-H	phenol	A one-pot polycondensation-pyrolysis strategy	the lowest charge transfer resistance (Rct) of 20.3 Ω	the removal rate can reach 94.1%	MFC	[41]
nano-jarosite/biochar@GP	Cr(VI)	Coating-pyrolysis method	the cathode decreased from 2580 Ω to 111 Ω	the degradation efficiency increased 5.2-fold.	MFC	[23]
GO/MgO@CC	COD	Coating method	the Rct of GO/MgO is only 3.2 Ω	the removal rate can reach9.5%	MFC	[42]
biochar/CCB	Cu^{2+}	Coating-pyrolysis method	using only 17% of the high-cost CCB	the removal rate can reach 95% within 5 days	MFC	[25]
rGO/CB	AO7	Electrodeposition method	the resistance decreased by about 6 times	the decolorization efficiency reached 91.1 ± 0.1% at 4 h.	BES	[27]
Fe_3O_4/AC @CF	2,4-DCP	Driven by magnetic	the H_2O_2 production is as high as 1.9 times that of the Fe_3O_4@CF cathode	the removal rate at 6 h is 78.8%	BEF	[43]
Fe@CC	Chrysoidine Y dye	Impregnation-calcination method	the H_2O_2 production is 81.63 μmol/L	the maximum removal rate is 73.14%	BEF	[29]
nZVI-biochar/CCB	Isopropanol	Coating method	the catalyst can generate 13.54 mg/L of hydrogen peroxide under non-aerated conditions	100% removal can be achieved within 24 h	BEF	[44]
Fe@Co/GF	VA, SA and HBA	one-pot self-assembly strategy	it can generate 152.40 μmol/L of hydrogen peroxide	the degradation rates reached 100%, 94.32%, and 100% respectively	BEF	[45]
Fe@Co/GF	Levofloxacin	Co-precipitation method	the maximum power density of the bio-electro-Fenton system is 12.64 W/m^3	degradation rate was able to reach 80.78% within the 1 h	a dual-chamber motion BEF	[46]
Fe–Mn–Mg/CF	Syringic acid (SA)	Impregnation-calcination method	hydrogen peroxide reached 15.8 mg/L within 5 h	the maximum removal rate reached 95.6%	BEF	[47]
N-rGO/Fe_3O_4	Methyl Orange (MO)	In-situ reduction method	at the 45th hour, the maximum H_2O_2 production reached 1.53 mg/L	the removal rate reached 68.91%	BEF driven by SMFC	[48]
second-cPANI/CB	MO and CIP	Electrodeposition method	when an efficient ·OH scavenger was added, the degradation rate of CIP dropped sharply from over 90% to 20.61%	the removal rates were 100% and 99.64%, respectively	BEF	[49]

Table 2. *Cont.*

Cathode	Pollutant	Modification Method	Benefits of Modification	Treatment Efficiency	System	References
PDA/BiOBr@CC	SA	Coating method	the cathode achieved an average current of 0.18 ± 0.02 mA and a current density of 119.2 ± 10.4 mA/m^2	the removal rate reached 96.5 ± 1.1%	PBES	[50]
PANI-CdS QDs/CC	Cr (VI)	Chemical oxidation and precipitation method	the PANI-CdS electrode achieved a stable photocurrent density of 0.48 A/m^2	the reduction rate reached 97.4%	PMFC	[51]
FM/CN@CF	Tetracycline	In situ solvothermal method	exhibits the narrowest band gap (2.08 eV) and the strongest visible light absorption	the removal rate remained in the range of 63.0% to 75.9%	PBEF	[52]
$BiVO_4$/RGO	2,4-DCP	Hydrothermal method	the maximum current density from the illuminated BPES reached ~60.31 A/m^3	the degradation activity was enhanced by 1.5 times	BPES	[53]
AgBr-CuO on graphite plate	reactive black 5	Electrophoretic deposition (EPD) method	under illumination, the maximum power density was 28.33 mW/m^2	the degradation rate increased to 55.56% within 72 h	PMFC	[54]
MoS_2/TiO_2 @graphite plates	Cr (VI)	Coating method	the photocurrent of 1 wt% MoS_2/TiO_2 is more than twice that of pure TiO_2	the removal rate reached 99.57% within 8 h	PMFC	[55]
BGA	Methyl orange	Hydrothermal method	the average PL lifetime for BGA was 5.83 ns	the removal rate reached 97.28 ± 0.64%	PMFC	[32]
$NiCo_2O_4$/MoS_2/GF	Cr(VI), phenol	A two-step hydrothermal and calcination method	the photocurrent density of the $NiCo_2O_4$/MoS_2/GF electrode is as high as 4458.05 mA/m^2	the degradation rates are 83.58% and 71.58% respectively	PMFC	[56]

Carbon materials often suffer from limited catalytic performance due to insufficient active sites and defects. Modification can address these limitations. For instance, Xu et al. [41] developed a hierarchical Fe-N-C catalyst with a high density of exposed FeN_x sites by co-doping straw-derived biomass carbon with iron and nitrogen via a one-pot polycondensation-pyrolysis strategy within a conventional MFC system. This catalyst significantly enhanced the oxygen reduction reaction, promoting the generation of hydrogen peroxide and hydroxyl radicals, achieving removal efficiencies of 94.1% for phenol and 98.3% for methylene blue in wastewater treatment. The improved performance is attributed to the abundant Fe-N_x active sites and porous carbon framework resulting from modification, which facilitates oxygen diffusion, accelerates the oxygen reduction reaction, and thereby enhances the cathodic reaction rate. Appropriate modification of carbon-based materials can compensate for the insufficient conductivity of carbon-based cathode materials, reduce resistance, and promote charge transfer, thereby enhancing pollutant removal efficiency. In cathodic MFCs, this is often achieved by introducing other high-performance materials to leverage their synergistic effects. For example, Cui et al. [27] modified carbon brushes (CB) by depositing rGO onto them via a one-step electro-deposition method. The incorporation of rGO significantly reduced the cathodic charge transfer resistance, enabling a decolorization rate of 91.1 ± 0.1% for azo compounds (acid orange 7, AO7) within just 4 h. Similarly, Wang et al. [23] introduced a nano-jarosite/biochar composite with a carbon-skeleton dispersion into a graphite plate via coating and pyrolysis. In the MFC, this composite simultaneously increased power output and enabled efficient removal of hexavalent chromium. The conductive carbon skeleton derived from biochar ensured efficient electron transfer. MeanwMeanwhile, the introduction of nano-jarosite provided active sites for Cr(VI) reduction. Then, these features promoted the removal of hexavalent chromium. Moreover, appropriate modification can not only enhance pollutant removal efficiency but also reduce costs. For instance, Liu et al. [25] prepared biochar from peanut shells via pyrolysis and modified its surface by coating with polyvinyl alcohol (PVA) and highly conductive carbon black (CCB). The modified cathode in a microbial fuel cell (MFC) removed 95% of Cu^{2+} from wastewater within five days, achieving an efficiency 1.52 times higher than that of a pure CCB cathode. Additionally, the use of only 17% of the high-cost CCB significantly lowered the cathode preparation cost. However, due to the low proportion of added CCB, the resistance of the composite cathode was considerably higher than that of the highly conductive pure CCB cathode. Furthermore, carbon-based cathode modification can enhance ORR catalytic efficiency through structural regulation. For example, Li et al. [42] coated carbon cloth with a GO/MgO composite. After loading, the GO/MgO formed a nanoflower-like porous structure, providing abundant active sites for the ORR and significantly reducing the ORR overpotential. The modification provided a stronger driving force for electron transfer for the anodic degradation of pollutants, indirectly enabling an average COD removal efficiency of 79.5% in the system. This value was much higher than that of the pristine GO cathode and only slightly lower than that of the Pt/C cathode. Moreover, its stability was much longer than that of the Pt/C cathode, and the cost was low.

In abiotic cathode MFCs within MES, modification can address issues such as limited active sites, insufficient conductivity, and high cost of cathode materials, while also enhancing ORR catalytic efficiency, thereby improving their application performance in wastewater treatment. In addition to MFCs, abiotic cathode MES systems also include bio-electro-Fenton and photoelectrocatalytic systems. Many studies have focused on modifying carbon-based cathodes in these systems to enhance their catalytic performance and pollutant removal efficiency.

3.1. Bio-Electro-Fenton System

Bioelectro-Fenton (BEF) technology utilizes anodic bioelectricity generation to drive the Fenton reaction at the cathode for treating water pollutants, significantly reducing external power consumption compared to conventional electro-Fenton processes [48]. As summarized in Figure 3a, in the BEF system, electricity-producing microorganisms attached to the anode metabolize organic matter as a carbon source under anaerobic conditions, converting it into simple molecules such as carbon dioxide and water while releasing protons (H^+) and electrons (e^-). Taking glucose as an example, the reaction is described by Equation (1). Protons are actively transported out of the cell via the electron transport chain or ATP synthase, then pass through the exchange membrane into the cathode chamber. Electrons migrate along a series of electron carriers across the cell membrane, periplasmic space, and outer membrane, eventually reaching the extracellular environment via extracellular electron transfer and transferring to the anode surface, ultimately flowing through the external circuit to the cathode [57]. In the cathode chamber, electrons move from the lower-potential biological anode to the higher-potential cathode. Dissolved oxygen adsorbed on the cathode surface accepts electrons and undergoes a two-electron reduction reaction, combining with H^+ to form H_2O_2. The generated H_2O_2 reacts with Fe^{2+} in the Fenton reaction to produce highly reactive hydroxyl radicals (Equations (2)–(4)). These hydroxyl radicals, due to their strong oxidizing power and non-selective nature, can break chemical bonds in pollutants, enabling efficient degradation of contaminants.

$$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^- \quad [58] \tag{1}$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{2}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \tag{3}$$

$$\cdot OH + \text{Organics} \rightarrow CO_2 + H_2O \tag{4}$$

The cathodic ORR is significantly influenced by the catalytic performance of the cathode materials used. Carbon-based materials such as carbon cloth, carbon felt, biochar, reduced graphene oxide, and carbon nanotubes have been employed as cathodes or catalysts in BEF systems due to their high specific surface area, excellent conductivity, superior stability, and high hydrogen evolution potential (which favors improved ORR efficiency). These carbon-based materials typically support the two-electron pathway for H_2O_2 synthesis and demonstrate unique capabilities in selectively catalyzing the two-electron ORR [12]. In contrast, conventional carbon electrodes often suffer from limitations such as insufficient active sites, slow O_2 reduction kinetics, and low H_2O_2 yields. Therefore, further optimization of carbon-based cathode materials to enhance selectivity toward the two-electron ORR and related properties is crucial for improving the reaction efficiency of BEF systems. As shown in Table 2, studies have found that modifying carbon-based cathodes can significantly enhance pollutant removal rates in BEF systems by increasing hydrogen peroxide production.

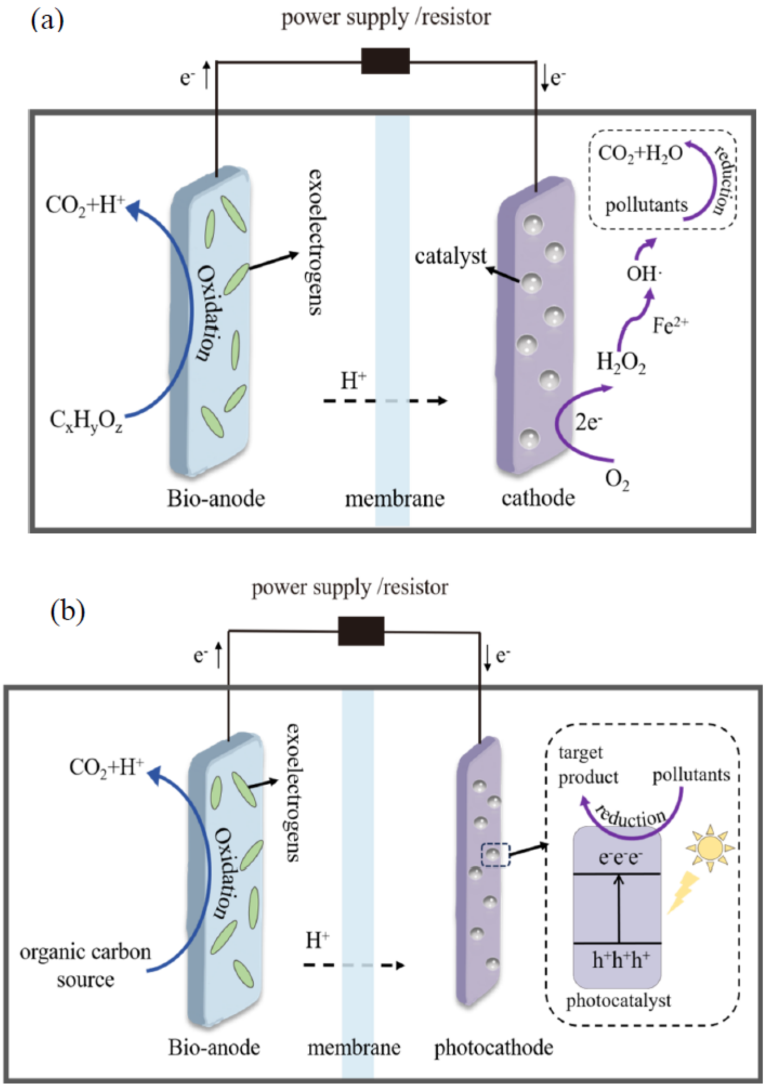


Figure 3. (**a**) Mechanism diagram of bio-electro-fenton; (**b**) Mechanism diagram of bio-anode coupled photocathode system.

While the cathode undergoes the two-electron ORR to produce H_2O_2, there is also a competing four-electron ORR that generates H_2O. Therefore, the selectivity of the two-electron ORR must be enhanced to increase the yield of H_2O_2 [59]. When modifying carbon-based cathode materials in this system, increasing the electron transfer rate is often used to enhance the amount and rate of H_2O_2 production, thereby accelerating pollutant removal. For example, Wu et al. [43] introduced Fe_3O_4 and activated carbon (AC) onto the surface of carbon felt (CF) in situ using a magnetic field, avoiding the issue of binder blocking catalytic sites. Electrochemical tests, including electrochemical impedance spectroscopy and cyclic voltammetry, showed that the electron transfer rate of the modified cathode material was significantly improved, and the H_2O_2 yield was 1.9 times higher than that of the Fe_3O_4@CF cathode. A comparison of pollutant removal performance with an unmodified carbon-based cathode showed that after 6 h, the Fe_3O_4/AC@CF cathode achieved a maximum removal efficiency of 78.8% for 2,4-DCP, which was significantly superior to those of Fe_3O_4@CF (21.2%) and CF (9.1%). In BEF systems, modifying carbon-based cathode materials can also enhance hydrogen peroxide production by increasing active sites or reducing system resistance, thereby improving pollutant removal efficiency. For instance, Liu et al. [44] mixed conductive carbon black (CCB) with nano-zero-valent iron-biochar (nZVI-biochar) to form a continuous conductive network, significantly reducing electron transfer resistance. The results showed that the charge transfer resistance (RCT) of the BEF system decreased from 479.5 Ω to 158.5 Ω (a reduction of 3.03 times). Consequently, at the optimal ratio, the system achieved 100% removal of 400 mg/L isopropanol within 24 h, and the treated wastewater exhibited almost no biological toxicity. Sun et al. [48] introduced abundant Fe-N_x active sites through modification, and graphitic N doping enhanced the two-electron ORR pathway, thereby increasing the H_2O_2 yield. After modification, the removal efficiency of MO at an initial concentration of 10 mg/L reached 68.91% within 25 h. In addition, defect structure regulation via modification can also improve pollutant removal in BEF systems.

Numerous studies have demonstrated that pores and edge defects in the carbon skeleton can enhance the selectivity of the two-electron ORR [43,60,61]. For example, Li et al. [45] prepared Fe@Co/GF materials via a one-pot self-assembly strategy. The synergistic effect between Fe and Co increased defect structures and significantly promoted the in-situ generation of hydrogen peroxide and hydroxyl radicals, resulting in excellent electrochemical performance and catalytic reactivity. Under the modified system, the degradation efficiencies of vanillic acid (VA), syringic acid (SA), and 4-hydroxybenzoic acid (HBA) reached 100%, 94.32%, and 100%, respectively, within 22 h. Applying the Fe@Co/GF modified material to an optimized BEF system can also effectively enhance the degradation rate of pollutants. Li et al. [46] constructed a dual-chamber dynamic BEF system using Fe@Co/GF as the cathode, enabling simultaneous degradation of levofloxacin and tetracycline in the cathode and anode chambers, respectively. After modification, the system exhibited enhanced radical generation and reduced reaction resistance. Consequently, under optimal conditions, the Fe@Co/GF-cathode BEF system achieved a total levofloxacin removal efficiency of 91.09% within 24 h.

In conventional electro-Fenton systems, Fe^{2+} relies on external addition, whereas BEF can achieve in-situ iron supply through electrode material modification, eliminating the need for additional iron-based reagents. In BEF systems, iron is typically introduced to enhance reaction performance, enabling in-situ iron supply and strengthening the redox cycle of Fe^{3+}/Fe^{2+}, thereby improving pollutant removal efficiency. For instance, John et al. [29] employed impregnation and calcination methods to introduce iron into the system. The Fe^{3+} in modified Fe@CC could gain electrons at the cathode and be reduced to Fe^{2+}, which rapidly activates H_2O_2 to generate •OH while being oxidized back to Fe^{3+}, forming an efficient Fe^{3+}/Fe^{2+} cycle that continuously provides catalytic active sites for the Fenton reaction. Under optimal operating conditions, the maximum degradation efficiency of alkaline orange Y dye reached 73.14% at 20 ppm, with H_2O_2 production reaching 81.63 μmol/L. Additionally, modifications can create multivalent characteristics that enable synergistic cycles, thus sustaining highly efficient cathodic Fenton reactions. Wang et al. [47], for example, prepared a Fe–Mn–Mg/CF cathode catalyst via impregnation and calcination. The introduction of Mg^0 and MgO reduced the catalyst's ohmic resistance and enhanced electronic conductivity, while also synergizing with the multi-valent properties of Fe and Mn to promote continuous and efficient Fenton reactions. As a result, the degradation rate of the refractory pollutant syringic acid (SA) reached up to 95.6% within 25 h, representing an improvement of over 40% compared to Fe–Mn/CF. Notably, some studies have optimized carbon-based cathodes by introducing non-metal elements without adding iron. These modified carbon materials directly activate H_2O_2 to produce •OH for pollutant degradation. Chen et al. [49], for example, fabricated polyaniline-derived nitrogen-doped carbon nanofibers as cathode materials using techniques such as cyclic voltammetry and electrodeposition. This system achieved pollutant degradation without any iron source, eliminating the need for iron salts or iron-based catalysts. Instead, it relied entirely on the metal-free catalytic activity of the nitrogen-doped carbon material, generating •OH in situ through activation of H_2O_2 at active sites (pyridinic nitrogen and graphitic nitrogen). Under optimal conditions, MO removal reached 100%, and 99.64% of 10 mg/L ciprofloxacin (CIP) was removed within 48 h.

3.2. Photoelectrocatalytic System

Conventional photocatalysis for pollutant degradation relies solely on photogenerated electrons to provide electrons for reduction reactions, resulting in weak reduction ability and easy recombination of charge carriers, thus leading to limited efficiency. In contrast, in the abiotic cathode photoelectrocatalytic system, photocatalysis can be coupled with microbial electricity generation from the anode to achieve synergistic enhancement. The related mechanism is shown in Figure 3b.

$$\text{Organic matter} + H_2O \rightarrow CO_2 + H^+ + e^- \tag{5}$$

In this system, microorganisms in the bioanode decompose carbon sources as shown in Equation (5). During this process, due to the significantly lower electrochemical potential of the anodic microbes compared to that of the cathode, biological electrons can transfer via the electrode and external circuit to the photoanode under the influence of the potential difference. Within the cathode chamber, upon illumination, the photoanode generates photogenerated electrons and holes. The photogenerated holes can combine with biological electrons, thereby extending the lifetime of photogenerated electrons [62]. Additionally, the direct combination of biological electrons and photogenerated holes promotes rapid electron production by anodic microbes, continuously increasing the output current. Photogenerated electrons migrating to the surface of the photoanode merge with biological electrons flowing from the bioanode through the external circuit, providing ample electrons for reduction reactions and directly participating in cathodic reduction processes. Consequently, this system enables pollutant removal in the cathode chamber through the cooperative action of anodic microbes and the photoanode. The degradation mechanism primarily targets reducible functional groups such as nitro groups. Furthermore, some pollutants are degraded via oxidation by photogenerated holes (h^+), which oxidize water molecules to produce highly reactive hydroxyl radicals (·OH) [52]. Meanwhile, electrons (e^-) mainly assist and synergistically promote hydrogen peroxide generation, enabling ·OH to carry out non-selective oxidative attacks on organic pollutants, ultimately mineralizing them into harmless CO_2 and H_2O.

The substrate material of photoelectrodes is the core of PEC technology, significantly influencing electron transfer efficiency, the recombination rate of photogenerated carriers, and the stability of photoelectrodes. As a catalyst support, carbon-based materials not only help address issues related to the separation and recovery of photocatalysts but also serve as conductive electrode substrates that promote cathodic reduction reactions, although they themselves lack photocatalytic activity. Using only photocatalyst materials as cathode materials may result in low visible light utilization and rapid carrier recombination. Therefore, as shown in Table 2, modifying carbon-based electrode materials with photocatalysts or similar materials can compensate for their respective shortcomings and thereby enhance the reaction efficiency of photoelectrochemical systems.

In abiological cathodic photoelectrocatalytic systems, pollutant removal efficiency is primarily improved by suppressing the recombination of electron-hole pairs. A common strategy involves constructing heterojunctions to effectively separate photogenerated electrons and holes. For example, Ahmadpour et al. [54] first synthesized a p-n heterojunction photocatalyst AgBr/CuO via a precipitation method, then immobilized it onto a graphite cathode surface using electrophoretic deposition (EPD) to modify the cathode. Under visible light irradiation, AgBr and CuO each generate photogenerated electron-hole pairs; the built-in electric field drives the holes from AgBr and electrons from CuO to combine at the heterojunction interface, while the electrons from AgBr remain in the conduction band (CB) and the holes from CuO stay in the valence band (VB), achieving spatial separation of electron-hole pairs and greatly reducing recombination. As a result, the degradation rate of Reactive Black 5 (RB5) reached 55.56% within 72 h, compared to only 11.74% for bare graphite electrodes under the same conditions. Shi et al. [56] constructed a Z-scheme heterojunction $NiCo_2O_4/MoS_2$ incorporated into graphene foam (GF). After modification, electrons from the CB of MoS_2 recombined with holes from the VB of $NiCo_2O_4$, preserving the strong reducing electrons in the CB of $NiCo_2O_4$ and the strong oxidizing holes in the VB of MoS_2. Meanwhile, GF served as a highly conductive substrate, rapidly extracting photogenerated electrons and preventing recombination between e^- and h^+. The modified system achieved a photocurrent density of 4458.05 mA/m^2, enabling Cr(VI) removal of 83.58% and phenol removal of 71.58% in a mixed-pollutant system, with a synergistic effect observed between the two pollutants. Specifically, Cr(VI) removal mainly relied on direct electron reduction, whereas phenol degradation was primarily driven by hole (h^+) oxidation and the generated hydroxyl radicals (·OH). Shan et al. [55] also employed this mechanism to improve Cr(VI) removal efficiency. They fabricated a Type-II MoS_2/TiO_2 heterojunction and fixed it onto a graphite plate cathode surface via coating. Photogenerated electrons migrated from the CB of TiO_2 to the CB of MoS_2, while holes moved in the opposite direction, achieving effective spatial charge separation. Consequently, Cr(VI) removal reached 99.57% within 8 h.

Alternatively, cathodes coupling photocatalysts with conductive polymers can be constructed. Upon light excitation, the photocatalyst generates photogenerated electrons, and the conductive polymer acts as an electron mediator to transfer these electrons, thereby promoting the separation of photogenerated electrons and holes. Ren et al. [50] constructed a PDA/BiOBr@CC photocathode and applied it in a self-powered photobioelectrochemical system (PBES). Under visible light irradiation, BiOBr absorbs photons to generate electron-hole pairs. The deposited polydopamine layer, through its conjugated structure, serves as an effective electron mediator, facilitating charge separation and migration, thereby promoting the generation of •OH and $•O_2^-$ radicals. This leads to efficient degradation of sulfonamide into small-molecular organic acids and ultimately complete mineralization. The system achieved a sulfonamide removal efficiency of 96.5 ± 1.1%. Similarly, Talooki et al. [51] fabricated a PANI-CdS quantum dot (QD) photocathode. Carbon cloth (CC), acting as a support with a large surface area, provides abundant interfacial channels for charge exchange between PANI nanofibers and CdS nanoparticles. Under conditions of pH = 2, initial concentration 10 mg/L, and 8 h of illumination, the Cr(VI) reduction rate reached as high as 97.4%.

Furthermore, modification of carbon-based photocathode materials can also enhance photocatalytic H_2O_2 production in the system, thereby improving pollutant removal efficiency. Qi et al. [52] prepared an FeMn-LDH/g-C_3N_4@CC (FM/CN@CC) photocathode using an in-situ solvothermal method in a photo-BEF (PBEF) system. Pyridinic N enhanced O_2 adsorption and promoted H_2O_2 generation, while the Fe^{2+}/Fe^{3+} and Mn^{2+}/Mn^{3+} redox couples efficiently activated H_2O_2 to produce •OH, thus accelerating pollutant removal. Under low-power LED irradiation (80 W) and over a wide pH range (3–11), the removal efficiency of tetracycline remained between 63.0% and 75.9%. In abiotic cathode photoelectrocatalytic systems, modification can also compensate for the high interfacial charge transfer resistance of the photocathode, thereby promoting electron transfer and pollutant removal. For example, Zhang et al. [32] prepared a BiOCl/reduced graphene oxide aerogel

(BGA) using a hydrothermal method. The 3D porous structure of BGA reduced charge transfer resistance and accelerated electron migration at the catalyst-electrode-electrolyte interface. As a result, the removal efficiency of MO (initial concentration 40 mg/L) reached 97.28 ± 0.64% within 48 h at the cathode. Similarly, Tu et al. [53] combined $BiVO_4$ with RGO to form a Bi–C chemical bonding interface. The modification led to better light absorption, faster electron transfer, and more efficient photogenerated electron-hole separation, while also constructing a continuous electron transport channel. Consequently, the degradation activity of B/G (5 wt%, 9 h, 150 °C) toward 2,4-DCP was enhanced by a factor of 1.5.

4. Removal of Pollutants by Modified Biocathode MES

Unlike abiotic cathode MES, biocathode microbial electrochemical systems rely on the metabolic synergy of electroactive microbial communities to achieve efficient removal of various pollutants. Among them, antibiotics, inorganic nitrogen pollutants, sulfate, and heavy metals are four highly representative wastewater components and targets for removal. These pollutants are widely present in industrial wastewater, agricultural wastewater, and municipal sewage. Traditional treatment processes often face bottlenecks such as low efficiency, high cost, or secondary pollution. For example, chemical precipitation for heavy metal removal requires large amounts of chemicals, increasing treatment costs; physicochemical nitrogen removal may produce byproducts that cause secondary pollution. As shown in Figure 4, the core mechanism of pollutant removal in the modified biocathode MES lies in the ability of microorganisms to exchange electrons with the electrode via extracellular electron transfer, accept electrons from the cathode, and use pollutants such as nitrate and sulfate as electron acceptors for reduction reactions, thereby achieving pollutant removal. In addition, during pollutant degradation, the electrons and protons generated from degradation can drive reduction reactions at the biocathode to produce hydrogen. In biocathode MES systems, modification can compensate for deficiencies in the conductivity and biocompatibility of biocathode materials by improving electron transfer efficiency, microbial attachment capacity, and substrate diffusion rate, thereby enabling efficient pollutant removal.

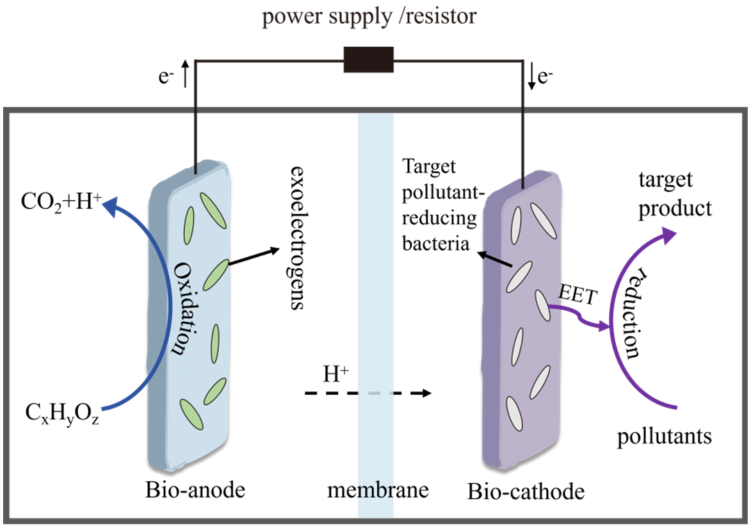


Figure 4. Mechanism diagram of MESs with a biocathode.

4.1. Removal of Antibiotics by Modified Biocathode MES

Studies have shown that antibiotics can have significant impacts on environmental health. For example, oxytetracycline (OTC) exhibits obvious toxicity to Pseudokirchneriella subcapitata, with a median effective concentration (EC_{50}) value of only 1.04 mg/L. Moreover, the long-term effects of antibiotics can lead to bioaccumulation in the food chain and promote the growth of antibiotic-resistant bacteria, thereby posing a serious threat to human health [63,64]. In a biocathode, cathodic electroactive bacteria accept electrons from the electrode. Antibiotics in the cathode chamber accept electrons from the cathode and are removed through direct electrochemical or microbial reduction. Due to the electron-accepting nature of biocathodes, they are generally applicable for degrading electron-accepting antibiotics. Moreover, the microelectrochemical system containing a biocathode relies on extracellular electron transfer and enzymatic catalysis of electroactive microorganisms. This makes the degradation pathway milder and more efficient and stable for the degradation of low-concentration, recalcitrant antibiotics.

Studies have shown that appropriate modification of the biocathode in a microbial electrochemical system can improve its biocompatibility. This facilitates the formation of a well-adapted functional electrode, reduces competition from undesirable microbial communities, and alleviates toxicity to microorganisms, thereby enhancing antibiotic removal efficiency. Xu et al. [65] used carbon cloth as a substrate and modified it by in-situ fabrication and immobilization of biogenic palladium nanoparticles (Pd-NPs) on the biocathode. The Pd-NPs directly bound to microbial cells, achieving biocompatible integration through a biosynthetic process, which made it easier for microorganisms to form mature biofilms on the electrode surface. Consequently, the improved biocompatibility significantly increased the abundance of *Geobacter* and also enriched antibiotic-degrading bacteria such as *Alicycliphilus*. Ultimately, under conditions without additional carbon sources, the modified biocathode achieved a 1.7-fold higher removal efficiency than the unmodified one, especially within 4 h. Furthermore, in microbial electrochemical systems, modifying the biocathode material can enhance electron transfer efficiency at the cathode interface. This overcomes the limitation of relying solely on the microorganisms' own extracellular electron transfer (EET), thereby achieving efficient antibiotic degradation. For example, Sun et al. [66] used a carbon-based material as the substrate and introduced cobalt and polypyrrole for functional optimization, obtaining a GO/Co/PPy modified photobiocathode. Notably, in this study, the cathode integrated Chlorella vulgaris, which produced oxygen via photosynthesis to serve as an electron acceptor, reducing energy consumption. Cyclic voltammetry (CV) tests showed that the modified electrode exhibited a much higher oxygen reduction reaction (ORR) peak current than the control, indirectly reflecting its improved conductivity. In this system, the modified material directly reduced electron transfer resistance through its high conductivity, compensating for the inefficiency of the microorganisms' own EET. As a result, the system achieved efficient degradation of oxytetracycline, and the maximum power density of the modified system was nearly four times that of the bare biocathode.

4.2. Nitrogen Removal by Modified Biocathodes

Conventional denitrification relies on organic carbon sources as electron donors. In contrast, in a microbial electrochemical system with a biocathode, the cathode itself can serve as an electron donor for microorganisms. Denitrifying bacteria directly obtain electrons from the cathode surface via extracellular electron transfer (EET), achieving autotrophic denitrification. The denitrification mechanism can be summarized as efficient electron transfer from the cathode, through a two-electron pathway, to functional microorganisms at the cathode, which then reduce nitrogen pollutants (nitrate, ammonia, etc.) to nitrogen gas, thereby completing the denitrification process.

The two-pathway electron transfer for denitrification includes direct electron transfer (DET) via cytochromes c and indirect electron transfer (IET) involving flavins and ubiquinones. In microbial electrochemical systems with a biocathode, modification of the biocathode can accelerate these two pathways, thereby increasing the reaction rate and improving nitrogen removal efficiency. Wang et al. [67] prepared a PPy/rGO/CF electrode by modification, which exhibited a unique three-dimensional scaly morphology. The modification promoted the electron transfer rate. The conductive network of PPy/rGO facilitated direct contact between cytochromes c and the electrode, shortening the electron transfer distance. Moreover, the modified electrode stimulated microorganisms to secrete more redox mediators such as flavins and ubiquinones, thereby promoting efficient electron transfer between microorganisms and the electrode. As a result, under closed-circuit operation with a carbon-to-nitrogen ratio (C/N) of 4, the nitrate removal efficiency reached 96.5 ± 0.3%, which was 13.8 ± 0.4% higher than that of the unmodified carbon felt (CF) biocathode. Alternatively, modification can also improve the biocompatibility of the biocathode. Enhanced biocompatibility reduces the toxicity of the cathode electrode surface to microorganisms, providing a stable growth microenvironment for denitrifying functional bacteria and promoting their rapid enrichment, thereby improving the nitrogen removal efficiency of the system. For example, Sun et al. [68] prepared a TiO_2/Co-WO_3/SiC catalyst and incorporated it into a carbon fiber cloth substrate to form a modified photobiocathode. High-throughput sequencing data showed that the microbial species richness on the modified electrode was significantly higher than that on the anode, in natural seawater, and in the pre-acclimated microorganisms. Moreover, the cathode enriched a large number of denitrifying functional bacteria, which were able to stably colonize the modified electrode surface and exert denitrification. Notably, this system had a bacteria-algae symbiotic cathode. Algae naturally growing in the cathode chamber absorbed NH_4^+-N for growth, and their photosynthesis released O_2 to enhance nitrification. At the same time, denitrifying bacteria attached to the cathode (e.g., *Marinobacter*, *Lactobacillus*) participated in the biological reduction of NO_3^--N, showing a synergistic effect. After modification, the system achieved excellent nitrogen removal performance, with NH_4^+-N removal efficiency of 94.05% and total inorganic nitrogen removal efficiency of 77.35%.

4.3. Sulfate Reduction by Modified Biocathodes

In a microbial electrochemical system with a biocathode, the core mechanism of sulfate reduction is that sulfate-reducing bacteria (SRB) use the cathode as an electron donor. They obtain electrons in two ways: one is by directly receiving electrons from the electrode via outer-membrane c-type cytochromes. The other is through hydrogenase-catalyzed hydrogen production (Equation (6)), with H_2 serving as an indirect electron carrier [69]. Electrons are then used by SRB to activate intracellular dissimilatory sulfite reductase (encoded by the *dsrA* gene), driving the sulfate reduction reaction (Equation (7)) and thus achieving sulfate degradation [70].

$$2H^{+} + 2e^{-} \rightarrow H_2\uparrow \tag{6}$$

$$SO_4^{2-} + 8e^{-} + 10H^{+} \rightarrow H_2S\uparrow + 4H_2O \tag{7}$$

In a biocathode, microorganisms replace the catalysts used in conventional abiotic cathodes. They can catalyze sulfate reduction using their own intracellular enzyme systems. Different cathode electrode materials have different internal resistances, which affect the overall system performance. Appropriate modification of carbon-based biocathodes can enhance the sulfate reduction rate by lowering the internal resistance of the electrode material and reducing its toxicity to microorganisms. For example, Hu et al. [70] used an in-situ microbial reduction approach with a graphite plate as the cathode substrate and graphene oxide (GO) as the modifier. They took advantage of the metabolic activity of SRB enriched on the cathode surface to reduce non-conductive GO into highly conductive graphene in-situ.

After modification, the oxygen-containing functional groups on the microbially reduced graphene surface were significantly reduced; FTIR confirmed the disappearance of O–H and C=O groups. This reduced the toxicity of the material to microorganisms and also increased the specific surface area of graphene, providing more attachment sites for SRB, thereby increasing the SRB population. Moreover, the high conductivity of graphene, together with the highly conductive pili produced by SRB, formed a synergistic conductive network, which reduced the charge transfer resistance. As a result, with the addition of 30 mg/L GO, the sulfate reduction rate in the MEC reached 230 g/(m^3·d), compared to only 135 g/(m^3·d) without GO addition. Therefore, in microbial electrochemical systems with a biocathode, rational modification of the biocathode is key to enhancing the sulfate reduction rate and removal efficiency.

4.4. Removal of Heavy Metals by Modified Biocathodes

In MESs with a biocathode, functional microorganisms in the biocathode can drive the reduction or precipitation of heavy metal ions in wastewater by directly or indirectly obtaining electrons. However, the inhibitory effect of heavy metals on microorganisms reduces removal efficiency. Therefore, modifying the biocathode, for example, by reducing the internal resistance of the system, can enhance heavy metal removal [71,72].

In biocathodes microbial electrochemical systems, modification can shorten the mass transfer distance and reduce internal resistance, thereby increasing system power output and improving heavy metal removal. For example, Song et al. [73] used graphite felt as the base material and added graphene oxide (GO), which was microbially reduced to graphene, to form a graphene biocathode for Cr(VI) reduction in a microbial fuel cell. After modification, the extremely high specific surface area of graphene provided more Cr(VI) adsorption sites than pure graphite felt or graphite-felt biocathodes, allowing rapid Cr(VI) enrichment on the cathode surface and shortening the mass transfer distance. Moreover, the modification reduced internal resistance and decreased energy loss during electron transfer. As a result, with an initial Cr(VI) concentration of 40 mg/L, complete Cr(VI) removal was achieved within 48 h, whereas the control electrode achieved only 58.3% removal [74]. Additionally, modified biocathodes can promote the formation of cathode biofilms, which enhance microbial tolerance to heavy metals and thus improve heavy metal removal efficiency. For instance, Dai et al. [75] used carbon cloth as the cathode substrate and uniformly coated 50 mg of ZIF-67 onto its surface using a Nafion solution, finally obtaining a ZIF-67 modified SRB biocathode. After modification, ZIF-67 promoted SRB attachment through electrostatic interactions, forming a thicker and more intact biofilm, which enabled synergistic reduction of sulfate and antimony. This process relies on the precipitation reaction between sulfide produced by SRB and metal ions. The high conductivity of the modified ZIF-67 reduced the system's charge transfer resistance, provided more electrons for sulfate reduction, and increased the biomass involved in sulfate reduction, ensuring a continuous and efficient sulfate reduction reaction. Consequently, the system generated more sulfide ions to enhance antimony removal, achieving synergistic removal of both pollutants. Similarly, Zhong et al. [76] introduced CF-PQ7 onto the surface of carbon cloth for modification. Polyquaternium-7 (PQ7) has excellent adhesivity and biocompatibility. Its quaternary ammonium groups can bind to SRB cell membranes through electrostatic interactions, while also improving the hydrophilicity of the carbon cloth, promoting rapid microbial attachment. The cotton-derived CF contains pyridinic N and graphitic N, which provide active sites for electron transfer. Together, these features increased the U(VI) removal efficiency to 93.8%.

Furthermore, during heavy metal degradation, the electrons and protons generated from heavy metal reduction can simultaneously drive reduction reactions at the biocathode to produce hydrogen, truly achieving a synergistic coupling of pollution treatment and resource recovery. For example, in the study by Dai et al. [75], the hydrogen production capacity of the modified biocathode increased by about 22.2% in the absence of Sb, reaching a maximum hydrogen production of 0.923 ± 0.04 m^3 H_2/m^3. Even in an Sb-contaminated environment, the system maintained high hydrogen production stability. Gas chromatography (GC) detection showed that the hydrogen purity in the modified group reached 73.27%, with no by-products such as methane, indicating an efficient and specific hydrogen production process. This can be attributed to the modification that optimized the biofilm structure and enhanced the metabolic activity of SRB, thereby improving sulfate reduction efficiency. The electrons and protons generated during sulfate reduction simultaneously provided substrates for the hydrogen evolution reaction, indirectly supporting hydrogen production and significantly enhancing both environmental and economic value.

5. Application of Modified Cathode-Based MES in Actual Wastewater Treatment

In MESs, modification of carbon-based cathodes can effectively enhance pollutant removal rates. Applying this technology to real wastewater treatment scenarios can avoid the differences between simulated wastewater and actual water bodies, making the research results more valuable for engineering applications. Moreover, actual wastewater has a complex composition, which more realistically tests the anti-interference ability and long-term stability of modified carbon-based cathodes.

Actual wastewater may cause an electron imbalance and low conductivity due to complex, low-biodegradable pollutants. Its complexity often affects MES pollutant removal efficiency, with impacts varying by wastewater type. For example, high-salinity wastewater can increase mass transfer resistance and inhibit microbial activity via osmotic pressure, reducing biocathode performance. Many studies have shown that modified carbon-based cathodes can withstand the challenge of high-salinity wastewater in MESs with abiotic cathodes. For example, Chen et al. [77] optimized the photoelectrocatalytic performance of g-C_3N_4 by doping with Ce and applied it to real industrial high-salt amine-containing wastewater. Doping with Ce increases active sites and effectively enhances the stability of the material system, which helps the system resist high salinity in actual wastewater and improves the interaction between the material and relevant pollutants in the wastewater. After dilution pretreatment, the actual wastewater characteristics were preserved. After modification, the charge transfer resistance (R_{ct}) was 42.5 Ω, significantly lower than the 175.0 Ω of pure g-C_3N_4. The photocurrent density increased, carrier recombination was effectively suppressed, and the ability to activate peroxymonosulfate (PMS) to produce $\bullet SO_4^-$, •OH, and other reactive radicals was enhanced. These two radicals synergistically oxidized and degraded COD and NH_4^+-N. Finally, with the addition of 0.5 mmol/L PMS, the modified photocathode enabled the system to achieve a COD removal efficiency of 94% and an NH_4^+-N removal efficiency of 86%. Thus, in terms of structural stability and catalytic adaptability, the modified cathode demonstrated tolerance to actual wastewater and achieved efficient treatment. In addition, many studies have also shown that modified carbon-based cathodes can withstand the challenge of high-salinity wastewater in microbial electrochemical systems with biocathodes. Zhang et al. [78] introduced heterotrophic nitrification-aerobic denitrification sludge (HNADI) onto the surface of carbon cloth for biofunctionalization modification. They applied it to treat actual pickling high-salinity wastewater. Before use, the wastewater pH was only adjusted to 7.0 with 1 mol/L HCl, without any other composition adjustments, thereby preserving the actual wastewater characteristics. The modification makes the biofilm in the biocathode thicker and denser, which can buffer the impact of high-salinity wastewater. After modification, in actual wastewater, the total nitrogen (TN) removal efficiency reached 92.5%, the ammonia nitrogen (NH4+-N) removal efficiency reached 92.9%, and COD removal efficiency reached 91.1%. Thus, the system achieved synergistic degradation of nitrogen and organic matter. In addition, actual etching terminal wastewater (ETW) can affect heavy metal recovery and long-term system stability due to its low pH, or impair pollutant removal efficiency due to heavy metal ions causing active site poisoning or contamination. Huang et al. [79] combined the semiconductor composite catalyst WO_3/MoO_3/g-C_3N_4 with a graphite felt substrate to form a modified photocathode. They applied it in a light-assisted self-driven bioelectrochemical coupling system to treat actual etching terminal wastewater (ETW). The modified photocathode has increased active sites and strong stability, and also exhibits good adaptability to wastewater pH, ultimately achieving efficient and selective recovery of heavy metal ions. In contrast, Zhang et al. [80] loaded a CDs/g-C_3N_4 semiconductor composite catalyst onto graphite felt to form a modified photocathode. They applied it in a light-assisted microbial electrolysis cell system that required an applied voltage of 0.8 V for treating actual ETW. Their cathode material had a lower cost and strong chemical stability, and ultimately enabled stepwise in-situ deposition of heavy metals on the photocathode. Therefore, modifications need to be carried out according to the characteristics of different actual wastewaters to optimize the operation of MESs.

However, it is important to note that, compared to studies on enhancing the removal efficiency of real wastewater pollutants through carbon-based cathode modification in MESs, existing research has predominantly focused on performance optimization under simulated wastewater conditions or on the physicochemical modification mechanisms of carbon-based materials themselves. Practical application examples for complex real wastewater are relatively scarce. Due to the complex composition and large fluctuations in water quality of actual wastewater, modification strategies for carbon-based cathodes need to meet the requirements of salt tolerance, anti-interference ability, and long-term stability in real water bodies. Therefore, applied research in this direction still has broad exploration space and presents significant challenges.

6. Conclusions and Perspective

Numerous studies have confirmed that optimizing the performance of modified carbon-based cathode materials is a key approach to enhancing the operational efficiency of microbial electrochemical systems and improving wastewater treatment. Research has shown that precise control of modification strategies can achieve increased active sites, construction of defect structures, and reduced electron transfer resistance in carbon-based cathode materials. In both abiotic and biotic carbon-based cathode systems, efficient removal of pollutants from wastewater can be realized. In abiotic cathode systems of MESs, electrode modification can improve pollutant removal efficiency by addressing issues such as limited active sites and insufficient conductivity of the cathode materials. In biotic cathode systems of MESs, electrode modification can focus on compensating for the inadequate biocompatibility of cathode materials and enhancing the microbial extracellular electron transfer (EET) capability, thereby achieving efficient pollutant degradation. Current research on the modification of carbon-based cathodes in MES is mostly focused on simulated wastewater systems, while applications for real complex wastewater remain scarce. This leaves broad exploration space for subsequent development in this field. In future research and development of carbon-based cathode modification technologies for MES, researchers could focus on the following aspects:

- Break the limitations of single-domain material applications by actively drawing on high-performance modified materials already validated in other fields, such as electrocatalysis and photocatalysis, and attempting to apply them to carbon-based cathode modification in MES, thus providing new ideas and support for the promotion of MES technology.
- Deeply investigate the compatibility and mechanisms of cathode modification, and actively test the modified materials in actual wastewater to assess the salt tolerance, anti-interference ability, and long-term stability of the modified cathode in real water bodies.
- When testing cathode material performance in MES, it is often difficult to determine the optimal application conditions. Therefore, machine learning can be used to simulate optimal application environmental conditions or optimal material doping ratios to save time and cost. Additionally, theoretical calculation methods such as density functional theory (DFT) can be employed to predict and optimize the electronic structure and catalytic performance of materials at the atomic level, thereby assisting modification design.
- Attempt large-scale trials of modified cathode materials to facilitate their transition from laboratory research to practical engineering applications.

Author Contributions

S.Z.: Conceptualization, Investigation, Visualization, Formal analysis, Writing—original draft. S.L.: Conceptualization, Visualization, Writing—review & editing. K.S.: Formal analysis, Writing—review & editing. Q.J.: Writing—review & editing. F.W.: Writing—review & editing. B.W.: Writing—review & editing. Z.M.: Writing—review & editing. J.X.: Conceptualization, Funding acquisition, Supervision, Resources, Project administration, Writing—review & editing. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement

Data will be made available on request.

Conflicts of Interest

The authors declare no conflict of interest.

Use of AI and AI-Assisted Technologies

During the preparation of this work, the manuscript language has been polished by the authors with the assistance of AI. After using this service, the authors reviewed and edited the content as needed and takes full responsibility for the content of the published article.

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