Microbial Fuel Cells for Heavy Metal Wastewater Treatment: Mechanisms, Applications, and Challenges

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Abstract. Microbial fuel cells (MFC), as a sustainable and eco-friendly technology, exhibit a dual advantage of "waste-to-resource conversion" in the remediation of heavy metal-laden wastewater. This approach leverages electroactive microorganisms to metabolize organic substrates for bioelectricity generation while concurrently driving the reduction and immobilization of toxic heavy metals. This review systematically elucidates the mechanisms, reactor configurations, and microbial synergies involved in MFC-mediated heavy metal removal. Research findings demonstrate that MFC cathodes enable the bioelectrochemical reduction of highly toxic metal ions (e.g., Cr^{6+}, Cu^{2+}) into less toxic forms (e.g., Cr^{3+}, Cu^{0}) or elemental states, coupled with immobilization via hydroxide or sulfide precipitation. Dual-chamber MFCs achieve up to 92% reduction efficiency for high-concentration wastewater, while single-chamber and biocathode configurations facilitate cost-effective or sulfide-mediated multi-metal removal (e.g., PbS, CuS). Microbial consortia play a critical role: direct electron-transferring microorganisms (e.g., *Shewanella*, *Geobacter*) utilize cytochromes for metal reduction; sulfate-reducing bacteria generate S^{2-} to promote sulfide precipitation; and adsorbent microbes (e.g., *Pseudomonas*) immobilize metals via extracellular polymeric substances. However, practical applications remain constrained by challenges such as inefficient electron transfer, multi-metal competition, and long-term operational instability. Future research should prioritize innovations in electrode materials (e.g., MXene/biochar composites), strategies for electron allocation in multi-metal systems, and modular system integration to enhance treatment efficiency and resource recovery. This review offers theoretical and technical guidance for optimizing MFC in heavy metal wastewater treatment.

Keywords: Microbial Fuel Cell; Heavy Metal; Wastewater.

1. Introduction

Microbial fuel cells (MFC) represent a novel technology that converts chemical energy from organic substrates into electricity via the metabolic activity of electroactive microorganisms, while simultaneously driving redox reactions for heavy metal detoxification [1]. In the anode chamber, exoelectrogenic bacteria (e.g., *Geobacter*, *Shewanella*) oxidize organic matter (e.g., glucose, acetate) to release electrons and protons. These electrons are transferred through an external circuit to the cathode, where they participate in the reduction of heavy metal ions (e.g., Cr^{6+}, Cu^{2+}) or oxygen [2]. Traditional heavy metal removal methods, such as chemical precipitation, ion exchange, and adsorption, face limitations including high energy consumption, secondary pollution (e.g., metal-laden sludge), and poor selectivity in multi-metal systems. For instance, chemical precipitation requires excessive alkaline reagents, complicating sludge disposal, while adsorption struggles with low-concentration metal removal. Stringent environmental regulations necessitate the development of efficient, cost-effective, and environmentally benign alternatives [3].

MFC uniquely integrate wastewater treatment with energy recovery. The cathodic bioelectrochemical reduction process converts toxic metals (e.g., Cr(VI), Cu(II)) into less harmful forms (e.g., Cr(III), Cu^{0}) while generating electricity. Experimental studies report 92% Cr(VI) reduction efficiency in biocathode MFCs with stable voltage outputs (0.38 V) [3]. Capacitive bioanodes further enhance transient current via intermittent operation ("open/closed-circuit" cycles),

accelerating the reduction of Hg^{2+} and Ag^{+} [1]. These advancements highlight MFCs' potential for in situ metal detoxification and energy-efficient remediation.

Despite these advantages, practical challenges persist. For example, limited electron transfer efficiency due to poor proton diffusion and electrode conductivity; competitive electron uptake among coexisting metals (e.g., Cr-Cu-Cd systems); and operational instability under complex wastewater matrices (e.g., high salinity, organic interference). Recent advances in electrode materials (e.g., graphene/biochar composites) and synthetic microbial consortia partially address these issues, but pilot-scale validation remains limited [4].

Although MFCs offer a sustainable solution for heavy metal wastewater treatment by combining bioelectricity generation with metal detoxification, currently there is a lack of comprehensive review about MFCs for heavy metal wastewater treatment. This review aims to advance MFC applications by: 1) analyzing innovative cathode designs for multi-metal removal;2) identifying critical factors influencing biocathode performance;3) elucidating microbial community dynamics in electricity generation and metal removal.

2. Mechanisms of Heavy Metal Removal in MFC

2.1. Operational Principles

MFCs integrate bioelectrochemical reduction and resource recovery. Key processes include: Anode: Exoelectrogens oxidize organics (e.g., glucose, acetate), releasing electrons (e^{-}) and protons (H^{+}). Cathode: Electron acceptors (e.g., metal ions, O_2) undergo reduction. Toxic metals (e.g., Cr^{6+}, Au^{3+}) are reduced to low-toxicity forms (e.g., Cr^{3+}, Au^{0}) for immobilization or recovery. Table 1 describes the reduction reactions, precipitation reactions, key microorganisms, and conditions of different heavy metals, For instance, hexavalent chromium (Cr^{6+}) is reduced to trivalent chromium (Cr^{3+}) via the reaction: $Cr^{6+} + 3e^{-} \rightarrow Cr^{3+}$, followed by precipitation as $Cr(OH)_3$ under near-neutral pH conditions, enabling safe removal and potential reuse in industrial pigments.

Table 1. Metal Reduction Pathways and Microbial Contributions.

Metal	Reduction Reaction	Precipitation Reaction	Key Microorganisms	Critical Conditions	References
Cd	$Cd^{2+} + 2e^{-} \rightarrow Cd(0)$	$Cd^{2+} + 2OH^{-} \rightarrow Cd(OH)_2\downarrow$	*Shewanella, Geobacter*	Cathode pH (>7)	[2]
Au	$Au^{3+} + 3e^{-} \rightarrow Au(0)$	Au nanoparticles on biofilm	*Shewanella, Sulfate reducers*	Reductive metabolites (e.g., cytochromes)	[3]
Ag	$Ag^{+} + e^{-} \rightarrow Ag(0)$	$2Ag^{+} + S^{2-} \rightarrow Ag_2S\downarrow$	*Desulfovibrio*	Sulfate availability	[1]
Cu	$Cu^{2+} + 2e^{-} \rightarrow Cu(0)$	$Cu^{2+} + 2OH^{-} \rightarrow Cu(OH)_2\downarrow$ or $Cu^{2+} + S^{2-} \rightarrow CuS\downarrow$	*Geobacter*	High pH or sulfide-rich environment	[12]
Fe	Anode: $Fe^{2+} \rightarrow Fe^{3+} + e^{-}$, cathode: $Fe^{3+} + e^{-} \rightarrow Fe^{2+}$	$Fe^{3+} + 3OH^{-} \rightarrow Fe(OH)_3\downarrow$	*Bacillus marisflavi*	The anode is acidic, and the cathode is high pH	[13]
Pb	$Pb^{2+} + 2e^{-} \rightarrow Pb(0)$	$Pb^{2+} + S^{2-} \rightarrow PbS\downarrow$ or $Pb^{2+} + CO_3^{2-} \rightarrow PbCO_3\downarrow$	*Anaerobic bacteria*	Enrichment of S^{2-} or CO_3^{2-} is required	[1]
Cr	$Cr^{6+} + 3e^{-} \rightarrow Cr^{3+}$	$Cr^{3+} + 3OH^{-} \rightarrow Cr(OH)_3\downarrow$ or $2Cr^{3+} + 3S^{2-} \rightarrow Cr_2S_3\downarrow$	*Shewanella, Geobacter, Sulfate-reducing bacteria*	Neutral to slightly acidic (reduced), high pH (precipitated)	[4]

2.2. Types and characteristics

The application of microbial fuel cells in the treatment of heavy metal wastewater can be divided into many types according to their structure and function. The double-chamber MFC separates the anode and cathode chambers through a proton exchange membrane, and uses electrogenesis (such as *Geobacter*) to release electrons from anodic oxidation organic matter to drive the reduction and precipitation of heavy metals (such as Cr^{6+} and Cu^{2+}) in the cathode region, which is suitable for high-concentration wastewater treatment [5]. The single-chamber MFC has a simplified structure and relies on the air cathode to generate OH^- to promote hydroxide precipitation (e.g., $Cd(OH)_2$), but the efficiency is limited by oxygen diffusion [5]. The biocathode MFC [6] introduces microorganisms such as sulfate-reducing bacteria to catalyze sulfide generation (such as PbS and CuS) to remove sulfate and heavy metals simultaneously, while the stacked MFC [7] is suitable for the recovery of mixed heavy metals or precious metals (such as Au^{3+}) by increasing the voltage in series by multiple units. In addition, the plant-based MFC combines plant absorption and microbial reduction, which is suitable for ecological restoration scenarios (such as farmland Cd pollution), while the photocatalytic coupling type uses light energy to drive redox reactions, expanding the treatment capacity of polymetals such as arsenic and mercury.

According to the characteristics of different wastewater, the MFC type needs to be differentiated: the double-chamber and stacked systems are suitable for high-concentration industrial wastewater, the biocathode type and plant-based type are biased towards environmental remediation, and the single-chamber type and photocatalytic coupling type are good at low cost and energy efficiency optimization. The optimization strategies include cathode material modification (e.g., biochar enhanced conductivity), functional flora acclimation (e.g., Cr^{6+} reducing bacteria enrichment), and operation parameter control (e.g., pH>7 enhanced precipitation), and in the future, multi-technology coupling (e.g., MFC-adsorption coupling) can be used to further improve the removal efficiency and resource utilization potential of heavy metals. Table 2 describes the core mechanisms, advantages, limitations, and applicability of different types of microbial fuel cells to heavy metals. For example stacked MFCs with vertically connected multiple units enhance treatment capacity and voltage output by cascading electron transfer, effectively treating high-load Cr^{6+} wastewater through modular expansion and shared electrolyte circulation.

Table 2. Performance Characteristics of MFC Configurations.

Type	Core mechanism	Advantage	Limitations	Suitable for heavy metals	References
Double-chamber MFC	PEM-controlled reduction	High efficiency for concentrated metals	Membrane fouling, high cost	Cr^{6+},Cu^{2+},Ag^{+}	[5]
Single-chamber	Air cathode OH^- generation	Low cost, simplicity	Low efficiency, oxygen interference	Pb^{2+}, Cd^{2+}	[5]
Biocathode type	Microbial catalytic sulfide generation or direct reduction	Synchronous desulfurization, environmentally friendly	Slow start-up, need to acclimatize the flora	Cu^{2+},Pb^{2+},Cr^{6+}	[6]
Stacked MFC	Multiple units work together to boost voltage/current	High load capacity, large-scale processing	The system is complex and the internal resistance is uneven	Mixed heavy metals, Au^{3+}	[7]
Plant-based MFC	Plant uptake + microbial reduction	Ecological restoration, sustainable	The cycle is long and dependent on plant growth	Cd^{2+}, Pb^{2+}, Cr^{6+}	[14]
Photocatalytic coupling	Light energy drives reduction/oxidation	Handles polymorphic metals with low energy consumption	Dependent on light, catalyst cost	Cr^{6+},As^{3+},Hg^{2+}	[15]

3. Microbial Consortia and Their Roles

3.1. Direct Bio-Reducing Microorganisms

Certain microorganisms mediate the direct reduction of toxic high-valent metals through specialized electron transfer mechanisms, such as cytochrome systems or enzymatic pathways. For instance, *Shewanella oneidensis* utilizes the cytochrome c-dependent Mtr respiratory pathway to reduce hexavalent chromium (Cr^{6+}) to less toxic trivalent chromium (Cr^{3+}) [8], while also facilitating the reduction of silver ions (Ag^{+}) and gold ions (Au^{3+}) to their elemental metallic states (Ag^{0}, Au^{0}). Similarly, Geobacter *sulfurreducens* employs outer membrane c-type cytochromes to catalyze the reduction of soluble hexavalent uranium (U^{6+}) to insoluble tetravalent uranium (U^{4+}, precipitated as UO_2) and divalent copper (Cu^{2+}) to elemental copper (Cu^{0}). In contrast, *Desulfovibrio desulfuricans* achieves mercury detoxification by reducing ionic mercury (Hg^{2+}) to volatile elemental mercury (Hg^{0}) through hydrogenase and sulfite reductase-driven pathways [9].

3.2. Indirect Reduction and Precipitation

Certain microorganisms indirectly facilitate the precipitation or reduction of heavy metals via metabolic byproducts such as sulfides and ferrous ions (Fe^{2+}). For example, sulfate-reducing bacteria (SRB) including *Desulfovibrio* and *Desulfobulbus* species reduce sulfate (SO_4^{2-}) to sulfide (S^{2-}) [10], which immobilizes soluble metal ions like Pb^{2+} and Cu^{2+} through the formation of insoluble metal sulfides (e.g., PbS and CuS). Meanwhile, *Acidithiobacillus ferrooxidans* in the anode zone oxidizes Fe^{2+} to Fe^{3+}, generating ferric ions that chemically reduce highly toxic hexavalent chromium (Cr^{6+}) to trivalent chromium (Cr^{3+}) [11]. In the cathode zone, Geobacter *metallireducens* further reduces Fe^{3+} back to Fe^{2+}, simultaneously driving the reduction of arsenate (As^{5+}) to arsenite (As^{3+}), which is subsequently stabilized via sulfide precipitation. Additionally, acid-producing bacteria such as *Clostridium* secrete organic acids (e.g., citric acid) that chelate cadmium (Cd^{2+}) and nickel (Ni^{2+}) ions, effectively reducing their bioavailability and ecotoxicity [9].

3.3. Adsorption and Bioaccumulation

Some microorganisms immobilize heavy metals through extracellular polymeric substance (EPS) adsorption or intracellular accumulation mechanisms. For instance, *Pseudomonas aeruginosa* secretes EPS enriched with carboxyl and phosphate functional groups, which adsorb lead (Pb^{2+}) and cadmium (Cd^{2+}) ions by forming stable metal complexes encapsulated within biofilms. Meanwhile, *Bacillus subtilis* specifically binds ionic mercury (Hg^{2+}) via surface-exposed thiol groups (-SH) [14], while intracellular metal transporters facilitate the accumulation of zinc (Zn^{2+}) and copper (Cu^{2+}) within cellular compartments. Additionally, microalgae such as *Chlorella* species leverage photosynthesis-derived hydroxyl ions (OH^{-}) to induce hydroxide precipitation of copper (Cu^{2+}) and chromium (Cr^{3+}), coupled with ion exchange-mediated adsorption of heavy metals. These diverse fixation strategies highlight the functional specialization of microbial species, and the synergistic interactions within microbial communities can further enhance remediation efficiency. Table 3 illustrates the specific functions and mechanisms of different microbial communities in heavy metal immobilization. For instance, *Shewanella oneidensis* employs its outer membrane c-type cytochromes (e.g., MtrC and OmcA in the Mtr pathway) to directly transfer electrons to hexavalent chromium (Cr^{6+}), reducing it to trivalent chromium (Cr^{3+}) with a reported reduction efficiency exceeding 90% under optimal pH (6–8) and low oxygen conditions. This process not only detoxifies Cr^{6+} but also enables potential recovery of Cr^{3+} as stable hydroxide precipitates (e.g., $Cr(OH)_3$), which can be repurposed in industrial applications such as pigment production.

Table 3. Microbial Consortia and Their Roles.

Processing Mechanism	*Representative microorganisms*	Target heavy metals	Key role	References
Direct bioreduction	*Shewanella oneidensis*	Cr^{6+}, Au^{3+}, Ag^{+}	Cytochromes mediate electron transport, reduced to valence or elemental	[8]
	Geobacter sulfurreducens	U^{6+}, Cu^{2+}	Outer membrane cytochrome-catalyzed reduction reactions	[9]
Indirect reduction and precipitation	*Desulfovibrio desulfuricans*	Pb^{2+}, Cu^{2+}, Hg^{2+}	S^{2-} produces sulfide precipitates, reducing Hg^{2+} to Hg^{0}	[10]
	Acidithiobacillus ferrooxidans	Cr^{6+}, As^{5+}	Fe^{3+}/Fe^{2+} cycle-mediated chemical reduction	[11]
Adsorption and bioaccumulation	*Pseudomonas aeruginosa*	Pb^{2+}, Cd^{2+}	EPS adsorption to form metal-biopolymer complexes	[16]
	Bacillus subtilis	Hg^{2+}, Zn^{2+}	Surface group binding and intracellular accumulation	[10]

4. Key challenges

Although MFCs have shown unique advantages in the treatment of heavy metal wastewater, their large-scale application is still limited by the following core problems: 1) Bottleneck of electron transport efficiency: The electron utilization rate of MFC cathode is closely related to the reduction rate of heavy metals, but it is limited by the conductivity of electrode materials, proton diffusion rate and biofilm thickness. For example, during Cr (VI) reduction, the overgrowth of the cathode biofilm may hinder the directional transfer of electrons to the target heavy metal, resulting in a decrease in reduction efficiency. In addition, organic contaminants (e.g., phenolic substances) in complex wastewater may occupy the active site of the electrode by adsorption, further inhibiting electron transfer kinetics. 2) Competition mechanism of multi-metal coexistence: In actual industrial wastewater, a variety of heavy metals (such as Cr, Cu, and Cd) are often contained, and the difference in redox potential leads to electron acceptor competition. Studies have shown that Cr (VI) with high oxidation potential preferentially consumes electrons, while low-potential metals (such as Cd^{2+}) are difficult to reduce effectively due to insufficient electron allocation. This competitive relationship is particularly significant in mixed metal systems, and it is urgent to develop selective control strategies. 3) Insufficient long-term operation stability: The continuous operation of MFC faces problems such as biofilm degradation, electrode passivation, and pH imbalance. For example, precipitation from heavy metal reduction, such as Cr $(OH)_3$), may accumulate on the cathode surface, blocking the proton transport pathway and reducing reactivity. In addition, heavy metal toxicity may inhibit the metabolic activity of anode electrogenesis, resulting in the degradation of electrogenesis performance over time.

5. Conclusion

MFCs offer a promising solution for heavy metal wastewater treatment by synergizing bioelectrochemical reduction, energy recovery, and microbial interactions. Optimizing reactor designs, electrode materials, and microbial consortia is essential to bridge the gap between laboratory success and industrial-scale implementation.

To advance MFCs from laboratory prototypes to industrial-scale heavy metal wastewater treatment systems, future research should prioritize innovations in electrode materials, polymetallic processing strategies, and intelligent system integration. Developing hierarchical porous electrodes with high specific surface areas, such as MXene/biochar composites, could simultaneously enhance electron transfer rates and heavy metal adsorption capacities, while biomimetic interface modifications like conductive polymer coatings (e.g., polyaniline) may regulate biofilm thickness and

reduce mass transfer resistance by 40–60%. For polymetallic wastewater, dynamic electron allocation via "electron storage-release" systems—such as capacitive anodes or Fe^{3+}/Fe^{2+} redox mediators—could prioritize high-priority contaminants like Cr(VI) while diverting residual electrons to deposit Cu^{2+} Integrating metagenomics and metabolomics would further unravel microbial consortia's synergistic responses to multi-metal stress, enabling targeted community engineering. Modular MFC stacks with hybrid series-parallel circuits could adapt to fluctuating wastewater compositions, coupled with machine learning algorithms to optimize pH (6–8) and hydraulic retention time in real time. Additionally, hybridizing MFCs with electrodialysis membranes may enable continuous heavy metal separation and concentration, bridging bioelectrochemical remediation with industrial resource circularity.

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