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REVIEW ARTICLE

Monitoring Heavy Metals by Microbial Fuel Cell: A Review

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ABSTRACT: Heavy metals, often introduced into surface waters through anthropogenic activities, pose significant environmental and human health risks. The urgent need for their rapid, simple, and portable detection has intensified due to the increased leaching of these metals into aquatic systems. Microbial fuel cells (MFCs) have emerged as a promising and cost-effective bioelectrochemical technology for sustained, long-term operation *in situ* application. This paper reviews the progress in MFC-based biosensors for detecting heavy metals, which can be categorized into two types: biofilm-based MFC biosensors and those utilizing redox reaction at the cathode. In biofilm-based MFC biosensors, the presence of heavy metals inhibits the metabolism of exoelectrogenic bacteria, leading to a proportional reduction in electrical signals (voltage or current), which can be exploited for metal detection. Conversely, the redox reaction of heavy metals at the cathode proportionally increases electrical signals, providing another detection method. Future research should focus on the enrichment of functional bacteria, including novel exoelectrogenic strains and microbial consortia that work synergistically, as well as the development of innovative materials that offer cost-effective alternatives to expensive noble metal catalysts.

KEYWORDS: Environmental Monitoring, Pollution Control, Biosensors, Heavy Metals, Electrode.

Introduction

Heavy metal pollution in surface water is a significant global environmental issue, stemming from both natural sources, such as rock weathering, and anthropogenic activities, including industrial production and sewage discharge. Zhou and colleagues analyzed historical data on total concentrations of 12 heavy metals in global surface water from 1972 to 2017, revealing a shift in the primary sources of metal pollution from mining and manufacturing to rock weathering and waste discharge.[1] Industries such as mining, electroplating, and smelting release large volumes of heavy metal-laden wastewater, raising widespread concerns about water contamination.[2] For instance, Li and colleagues reported that in 2012, approximately 221.6 × 10^8 tons of industrial wastewater were discharged, containing around 388.4 tons of heavy metals, including Pb, Hg, Cd, Cr, and T-Cr.[3] In typical electroplating wastewater, Cu concentration can reach up to 1500 mg/L.[4] When such wastewater is discharged without adequate treatment, it contaminates surface water, posing significant threats to human health. In response, many countries have enacted stringent regulations to limit the discharge of heavy metals in wastewater systems. The detection and monitoring of these heavy metals has become a critical area of focus due to their excessive leaching into the environment.

Conventional testing methods and modern innovative sensors can be used to detect heavy metals. Traditional testing techniques for heavy metals, such as flame or furnace spectroscopy and atomic absorption spectroscopy, are highly selective and sensitive, making them the gold standard for quantifying and monitoring heavy metal ions. However, these methods are costly, lacking field portability, requiring skilled operators, and thus not suited for rapid detection.[5, 6] With the rise in heavy metal pollution due to industrial development, there is increasing interest in developing fast, portable, and automated detection systems.[7] This leads to advancement in sensors, including Enzyme-immobilized biosensors, Aptamers-based biosensors, Ion imprinted sensors, and electrical sensors.

Microbial fuel cells (MFCs) have emerged as a cost-effective and promising bio-based electrochemical technology for long-term running and *in situ* monitoring. Researchers have explored MFC-based technologies for detecting environmental contaminants and degrading contaminants while simultaneously generating power.[8–12] MFCs function by harnessing microbial metabolism to convert chemical energy directly into electrical energy via microbial metabolic processes. In most MFC biosensors, exoelectrogenic bacteria are inoculated in the anode chamber to sense contaminants. When the metabolic activity of these bacteria is inhibited by a contaminant, the value of voltage or current is weakened, forming the basic principle of biofilm-based MFC biosensors.[13] Recently, novel MFC-based sensors have been developed that utilize the cathode through redox reaction, instead of exoelectrogenic bacteria, to sense heavy metals.[14, 15] These sensors can monitor repeated pollution events, as the sediment adsorbs heavy metals, thereby protecting exoelectrogenic bacteria from being harmful by heavy metals.

Several recent review articles have explored MFC-based biosensors for detecting heavy metals.[16, 17] Kumar and colleagues provided an overview of the mechanisms behind MFC-based biosensors for on-site toxicity compounds' detection, such as BOD, COD, heavy metals, organic toxicants, antibiotics, and acidic toxicity.[17] They emphasized the critical roles of biofilm and external resistance in these processes. On the other hand, Noori and colleagues focused on microbe-electrode interacti-

DOI: 10.36838/v7i7.15

ons within MFC for heavy metal detection, highlighting how the electrode's microenvironment influences these interactions, which in turn leads to a decrease in current due to the intrinsic toxicity of heavy metals.[16]

This review addresses recent advancements in MFC-based heavy metals detection, categorizing the technologies into biofilm-based MFC biosensors and cathode-based MFC biosensors driven by redox reactions. It further discusses the monitoring mechanisms and limitations of each approach while providing a forward-looking perspective on the development of advanced MFC biosensors to overcome existing challenges.

Discussion

MFCs Technologies and Their Functions:

A classical MFC is a bio-electrochemical system that transforms chemical energy into bioelectric energy using microbes as biocatalysts. It consists of an anaerobic chamber and an aerobic chamber, separated by a proton exchange membrane, with an anode and a cathode electrode placed in their respective chambers.[18] These electrodes link through an external circuit, allowing energy to be harvested through an electric load.

The source of organic matter in the MFC system varies widely, ranging from pure compounds to complex mixtures, including organic acids (e.g., acetate, glucose, and sodium formate), sugars (e.g., glucose and mannitol), alcohol, phenolic compounds, polysaccharides, disaccharides, biomass, and synthetic wastewater,[18] with acetate and glucose being the most commonly utilized substrates for electricity generation.[19] Recent advancements have led to the development of novel MFC technologies, such as plant-MFC (P-MFC), sediment-MFC (S-MFC), algae-MFC (A-MFC), and constructed wetland integrated MFC (CW-MFC).[18, 20] These advanced MFCs utilize different fuel substrates; for instance, P-MFCs harness plant roots, S-MFCs rely on organic-rich sediment, and A-MFCs use algae biomass as fuel.

The primary function of MFC is electricity generation through the oxidation of organic matter, a key feature of this technology.[21] Beyond generating bioelectricity, MFCs offer significant benefits in wastewater treatment by utilizing the organic matter in wastewater as a fuel source. This dual capability positions MFCs as a highly balanced and environmentally harmonious form of energy production, directly converting waste into electric power. Recently, MFCs have gained attention for their innovative application as biosensors for quick and online monitoring of wastewater, including chemical oxygen demand (COD), toxic compounds, volatile fatty acids, and microbial activity.[22] MFCs can also detect heavy metals using biofilm-based MFC biosensors, where the inhibition of exoelectrogenic bacteria's metabolic activity results in weakened electrical signals (voltage or current),[16] including anodic biofilm-based (Figure 1) and cathodic biofilm-based (Figure 2) biosensors. Alternatively, heavy metals can be detected at the cathode-based biosensors through redox reactions, as shown in Figure 3. Table 1 provides a summary of MFC-based sensors for monitoring heavy metals in aqueous solution, which will be discussed in the following sections.

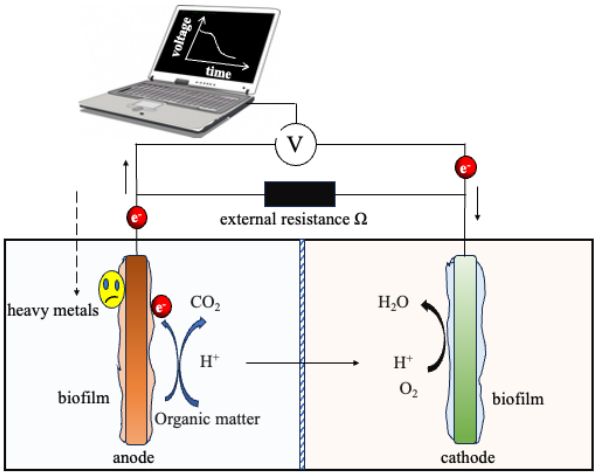

Figure 1: Schematic illustration of the anodic biofilm-based MFC biosensors setup for heavy metal detection. Exoelectrogenic bacteria within the anode chamber generate electrical signals, which serve as indicators of metabolic activity. This kind of biosensor operates by measuring the inhibition ratio of electrical signals, as increasing heavy metal concentrations suppress exoelectrogenic bacterial metabolism on the anode. The inhibition ratio is defined as the relative decrease in output current (or voltage) caused by the toxicant, compared to the baseline current (or voltage) before exposure.

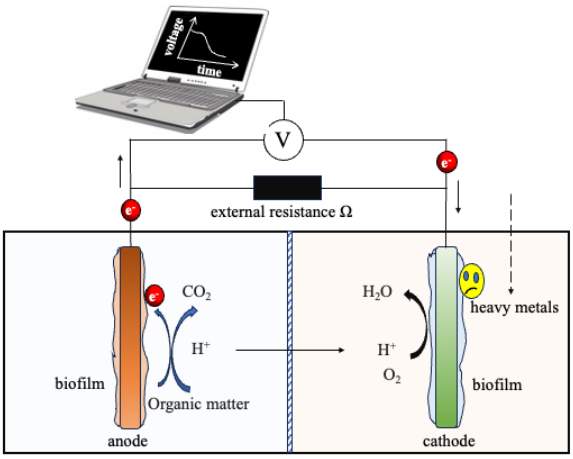

Figure 2: Schematic illustration of cathodic biofilm-based MFC biosensors setup. The formation of electroactive biofilm on the cathode enables certain microbes to utilize electrons for respiration through reversible metabolic pathways. The kind of biosensor operates by measuring the inhibition ratio of electrical signals, as elevated heavy metal concentrations suppress electroactive bacterial metabolism on the cathode. An electroactive biofilm is a layer of microorganisms that grow and attach to the electrode surface of an MFC.

DOI: 10.36838/v7i7.15

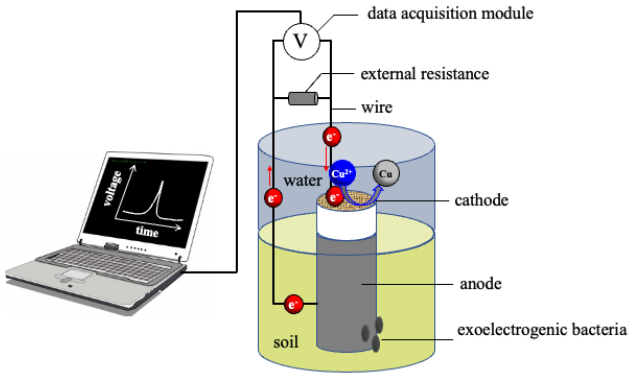

Figure 3: Schematic illustration of a cathode-based MFC biosensor utilizing redox reaction. The cathode-based MFC sensor detects heavy metals through cathodic reactions, generating a voltage signal that peaks as heavy metal concentrations increase on the cathode. The kind of biosensor operates by measuring the increase ratio of electrical signals, as elevated heavy metals produce more electrons on the cathode.

Table 1: Types of MFC-based biosensors for heavy metal detections using various cathodes, anodes, and microorganisms. This table summarizes the types of heavy metals detected, the corresponding MFC biosensor types, the anode and cathode materials used, and the main microorganisms involved in MFC systems.

Heavy metals	Biosensor types	Anode	Cathode	Microorganisms	Detection range and response time	Reference
Cu^{2+}	anodic biofilm	Carbon Cloth	Carbon cloth/Pt	Mixed microbial consortium	–	23
Cu^{2+}	anodic biofilm	Stainless steel	Platinum	Mixed microbial consortium abundance with Geobacter and Clostridium	5.0-320 mg/L, 30 s	14
Cu^{2+}	anodic biofilm	Stainless steel	Platinum	Paddy sediments	12.5-400 mg/L, 20 s	15
Cu^{2+}	Cathodic biofilm	MWCNT/ activated carbon sheet	MWCNT /activated carbon sheet	Soil	100-500 mg/L, 24 min	24
Cu^{2+}	anodic biofilm	Carbon felt	Carbon felt	Activated sludge	1.0-50 mg/L, 1.0 mg/L (45 min), 50 mg/L (10 min)	25
Pb^{2+}	anodic biofilm	Graphite felt	Graphite felt	Mixed microbial consortium	1.0-5.0 mg/L, 10 min	26
Pb^{2+}	anodic biofilm	Graphite plate	PVDF/activated carbon	Mixed microbial consortium	0.1-5.0 mg/L	27
Pb^{2+}	anodic biofilm	Graphite plate	PVDF/activated carbon	Sewage sludge	1.0-2.0 mg/L, 3 min	28
Pb^{2+}	anodic biofilm	Graphite plate	PVDF/activated carbon	Sewage effluent	1.0-3.0 mg/L, 60 min	9
Cd^{2+}	anodic biofilm	Carbon Cloth	Carbon Cloth	Enriched electroactive bacteria	1.0-50 µg/L, 4 min	29
Cd^{2+}	anodic biofilm	Carbon paper	Carbon paper/Pt	Mixed microbial consortium	1.5 mg/L	30
Ni^{2+}	anodic biofilm	Graphite plate	Graphite plate	Mixed microbial consortium	20-180 mg/L	31
Cr^{6+}	anodic biofilm	Carbon Cloth	Carbon cloth/Pt	Mixed microbial consortium	1.0-8.0 mg/L	32
Cr^{6+}	anodic biofilm	Carbon Cloth	Carbon cloth/Pt	Anaerobic sludge	1.0-100 mg/L	33
Cr^{6+}	Cathode-based with redox reaction	Stainless-steel tube	Platinum mesh	Soil	10-120 mg/L	34
Hg^{2+}	anodic biofilm	Graphite felt	Graphite felt	Mixed microbial consortium	1.0-5.0 mg/L	26
Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}	anodic biofilm	Activated carbon/carbon felt/stainless	Activated carbon/carbon felt/stainless	Aerobic sludge and anaerobic sludge	0.0.4-82.71 mg/L	35
Cu^{2+}, As^{5+}	anodic biofilm	Carbon felt	Carbon fiber brush	Anaerobic sludge	1.0-10 mg/L for Cu^{2+}, 0.5-5.0 mg/L for As^{5+}	36
Cu^{2+}, Cr^{6+}, Zn^{2+}, Ni^{2+},	anodic biofilm	Graphite sheet	Graphite sheet	Anaerobic sludge	5-20 mg/L	37
Hg^{2+}, Cr^{6+}, Pb^{2+}	Cathodic biofilm	Titanium-coated TiO_2/IrO_2 mesh	Graphite rods	Soil	Hg^{2+}: 0.5-2.5 mg/L; Cr^{6+}: 1-19 mg/L; Pb^{2+}: 10-48 mg/L; 1 min	38

Biofilm-Based MFC Biosensors for Monitoring Heavy Metals:

In most MFC biosensors, exoelectrogenic bacteria are employed to detect heavy metals. The monitoring mechanisms of these biosensors rely on measuring the inhibition ratio of the generated electrical signals. As heavy metal concentrations increase, they inhibit the metabolic activity of the bacteria, resulting in decreased electrical signals. Commonly used exoelectrogenic bacteria are acclimated within the anode chamber of the MFC. For example, a dual-chamber MFC-based biosensor has been developed and optimized for monitoring Cu in wastewater. Under conditions of 1000 Ω external resistance and 50 mM $K_3Fe(CN)_6$ as catholyte, a linear relationship was observed between maximum voltage output and the concentration of heavy metals.[36] The proportional inhibition ratio for both metals suggests that the electrical changes were primarily due to electrogenic bacteria's activity on the surface of the anode. Researchers have also isolated electroactive microbial consortia from industrial wastewater to assess their bio-sensing capabilities against four heavy metal contaminants: Cr^{6+}, Cu^{2+}, Ni^{2+}, and Zn^{2+}.[37] The inhibition ratios for these metals increased with their concentrations, and Sodium acetate was used as a major organic substance to enhance biosensors' reusability. These electrochemically active biofilms, typically formed under anaerobic conditions, require a lengthy formation period.

Compared with the extensive research on exoelectrogenic bacteria in the anode chamber, there is a limited investigation into the role of these bacteria in cathodic biofilm-based MFC biosensors.[16] Developing electroactive biofilm on the cathode

leverages the reversible metabolic pathway of certain microbes, allowing them to uptake electrons for respiration. This setup enables biological reactions at the cathode, with reaction kinetics potentially influenced by the adverse effects of incoming pollutants. Cathode-based biosensors have been proposed to enhance the detection range of MFCs in autotrophic microbial systems. For instance, Prévoteau and colleagues constructed an electroautotrophic biofilm on a carbon electrode at +0.2 V vs. Ag/AgCl, successfully detecting heavy metals such as Hg^{2+}, Cr^{6+}, and Pb^{2+}.[38] The observed current decline and subsequent recovery demonstrate the self-regenerative capabilities of cathode-based microbial sensors. To further advance sustainable, low-cost, and responsive technology, photo-microbial fuel cell sensors for detecting heavy metals in wastewater have been explored. These sensors offer a broader detection range compared to traditional MFC biosensors.[39]

Key factors influencing the performance of MFC biosensors include the types of microorganisms used, concentration and type of heavy metal, environmental conditions, electrode materials, design, substrate availability, and the presence of interfering substances. For instance, Nong and colleagues investigated two types of MFC biosensors for Pb^{2+} detection, operating at temperatures of 10 ˚C and 25 ˚C. Their study revealed that the inhibition rate of voltage was 22.81% at 10 ˚C, compared to only 5.9% at 25 ˚C.[9] Electrochemically active biofilms, typically formed under anaerobic conditions, often require prolonged periods to develop. However, Wang and colleagues demonstrated that using aerobic sludge as an inoculation source enabled the rapid formation of stable electrochemical biofilms within 35 hours.[25] To enhance MFC performance, various anode materials have been explored. For example, Xu and colleagues modified a 3D porous nitrogen nanotube sponge anode with chitosan and Polyaniline, improving microbial enrichment, adhesion, and power density.[40] Additionally, the combination of a photocathode with a microbial anode enhanced sensitivity for Cu^{2+}due to the P-N heterojunctions in CuO/ZnO that improved electron transport.[39] Furthermore, incorporating biochar as a filler in CW-MFC biosensors increased output voltage and detection range due to oxidative phosphorylation promoted by biochar.[35] Biofilm-based MFC biosensors face limitations in differentiating individual metals in mixed contamination, as their signals reflect cumulative metabolic inhibition. Future designs could integrate synthetic microbial consortia with metal-specific genetic reporters to enhance selectivity.

Cathode-based MFC biosensors utilizing redox reaction:

Biofilm-based MFC sensors that rely on exoelectrogenic bacteria for heavy metals detection typically struggle with repeated contaminations, as the bacteria must be recovered or reinoculated after each event. To address this limitation, Wu and colleagues introduced a sediment MFC (SMFC) sensor that uses the cathode to detect heavy metals, thereby protecting the exoelectrogenic bacteria from inhibition and eliminating the need for reinoculation.[14] When Cu^{2+} solutions were added to the overlaying water, the sensor produced a voltage signal that peaked, with the increase from baseline to peak voltage linearly correlated with Cu^{2+} concentrations up to 160 mg/L. Liu and colleagues further explored this method to monitor Cu^{2+},[15] demonstrating that a cathode-based SMFC sensor could detect Cu^{2+} with minimal stress on exoelectrogenic bacteria, as Cu^{2+} was inactivated by the flooded soil. Additionally, a carbon-felt-based cathodic SMFC biosensor was developed for long-term monitoring of heavy metal ions in soil, generating a stable output voltage of about 400 mV within 2-5 minutes of metal ions injection and effectively detecting Cd^{2+}, Zn^{2+}, Pb^{2+}, and Hg^{2+} over four months without significant performance degradation.[41] These SMFC biosensors, utilizing a floating cathode for detection of heavy metal shocks, showed the ability to keep long-term stability in the field, producing voltage peaks in response to repeated heavy metal pollutant events. The voltage peaks refer to the maximum voltage output observed during a certain period of operation. The oxygen reduction reaction (ORR), which typically occurs on the cathode in the MFC system, plays a crucial role in power generation. When heavy metals are introduced, they are reduced to the lower valence state on the cathode by consuming electrons generated by bacteria, as confirmed by the detection of $Cr3^{+}$ on the cathodic surface after the introduction of $Cr6^{+}$.[34] Similarly, the reduction of Cu^{2+} to Cu^{+} on the SMFC sensor's cathode triggered a voltage peak, further confirming this reduction process.[14] This reduction reaction accelerates electron consumption on the cathode, instantly increasing the current and generating a voltage peak.[34] The key redox reactions involved are as follows:

$$Cu^{2+} + e^{-} \rightarrow Cu^{+} \quad (1)$$

$$Cr_2O_7^{2-} + 14H^{+} + 6e^{-} \rightarrow 2Cr^{3+} + 7H_2O \quad (2)$$

While redox-based cathode biosensors excel in detecting specific metals (Cu^{2+}, Cr^{6+}), their performance in multi-pollutant systems requires further validation.

Biofilm-based and redox-based MFC biosensors each offer distinct advantages and limitations for heavy metal detection. Biofilm-based sensors rely on the metabolic activity of exoelectrogenic bacteria, where the presence of heavy metals inhibits electron transfer, leading to a measurable decline in electrical output. This approach is often limited by slow response times and reduced reusability due to biofilm damage from repeated metal exposure. In contrast, redox-based biosensors detect heavy metals through direct electrochemical reactions at the cathode, producing rapid voltage peaks at metals are reduced. These biosensors exhibited faster response times, greater reusability, and enhanced stability. However, redox-based systems are particularly effective for detecting redox-active metals.

Challenge and Future Perspective:

Despite significant progress in the MFC biosensors for heavy metals detection, several challenges and opportunities for future research remain:

Enriching functional bacteria:

Exoelectrogenic bacteria, the biocatalytic core of MFCs, are vital for converting chemical energy into electrical energy through extracellular electron transfer. However, microbial activity can decline over time due to factors like nutrient depletion, toxicity of metals, or microbial aging. Long-term stability is essential for practical monitoring, but microbial performance can degrade, affecting the lifespan and reliability

DOI: 10.36838/v7i7.15

of the biosensor. What's more, only a limited number of exoelectrogenic species that significantly enhance power output have been identified to date.[42] Discovering new exoelectrogens and gaining a deeper understanding of their electron transfer mechanisms are essential for further advancement. While research has predominantly focused on exoelectrogens at the anode, there is a pressing need to explore those at the cathode more extensively. Additionally, microbial consortia that cooperate synergistically could further enhance power generation.[43] Understanding individual microbial behaviors and community interactions in natural habitats is crucial for developing effective synthetic consortia. Future research should focus on exploring cooperative microbial communities and applying metabolic engineering techniques to optimize electricity generation. Genetic modifications to enhance specific metal ion interactions or boost electron transfer capabilities are promising.

Materials innovations:

Advancements in materials science are poised to significantly enhance the efficiency of MFC. The development of advanced materials with improved catalytic activities can facilitate more effective interactions between microbes and electrodes, promoting biofilm growth and enabling more efficient electron transfer. This, in turn, can increase the sensitivity and selectivity of MFCs.[44] Conductive materials that bridge biological connections for electron transport and those that enhance electron transfer rates are particularly crucial for the advancement of MFC technology. Cost-efficient materials, such as metal oxides and conductive polymers, are especially promising as they can replace expensive metals while improving overall MFC efficiency. The properties of anodic materials, including biocompatibility, microbial adhesion, electrochemical efficiency, and effective electron transfer mechanisms, are vital for biocurrent generation and the practical application of MFCs.[45, 46] Additionally, the development of efficient and low-cost catalysts, such as $CoMn_2O_4^-$ doped graphene oxide, can accelerate electron transfer and enhance electrochemical activity at the cathode, offering a viable alternative to expensive noble metal catalysts.[47] Further research into such efficient and cost-effective catalysts is needed.

Moreover, introducing sunlight into MFC to construct advanced photo-MFC technology offers numerous benefits and can be pursued.[48] Theoretical guidance for selecting electron shuttles to optimize sustainable energy production is also crucial. The performance of MFC heavily depends on the properties of the cathode, with redox potential being a crucial factor. Cathode materials should possess high redox potential to efficiently capture protons, thereby enhancing MFCs' performance.[49] In an MFC sensor utilizing redox reactions at the cathode, heavy metals can act as electron acceptors. To maintain high reaction rates, platinum (Pt)-based catalysts are often employed due to their effectiveness in reducing the activation energy of cathode reactions. Thus, exploring alternative cathode materials, like single-atom-doped carbons and transition metal complexes, could provide a cost-effective substitute for expensive noble metal catalysts.

Wireless and remote sensing for MFC biosensors:

Wireless and remote sensing capabilities are key to the advancement and practical deployment of MFC biosensors. These capabilities enable real-time, continuous, and long-distance monitoring of water quality without the need for on-site intervention, making it particularly suitable for large-scale or remote areas that are otherwise difficult to monitor. However, wireless MFC biosensors typically require power for data transmission and processing, which can be a challenge when deployed in remote or off-grid locations. While MFCs themselves can generate electricity, the additional power requirements for wireless communication and data storage might exceed what the MFC can produce, particularly in continuous operation scenarios. To address the energy demand, there is a need to optimize MFCs for better energy harvesting, potentially incorporating energy storage systems such as capacitors or rechargeable batteries. Alternatively, integrating energy harvesting technologies (e.g., solar panels) alongside the MFC system could help ensure a long-term, uninterrupted power supply. However, balancing the energy needs for MFC functionality and wireless data transmission while maintaining system longevity is still a challenge.

Conclusion

This paper reviewed recent advancements in MFC biosensors for the detection of heavy metals, focusing on biofilm-based MFC biosensors and those employing redox reactions at the cathode. It was observed that MFC-based biosensors can detect a variety of heavy metals across a wide range of concentrations through appropriate techniques. However, further research is needed to explore MFC biosensors that utilize redox reactions at the cathode, particularly regarding detection mechanisms, influencing factors, and reaction pathways. Enhancing the effectiveness of MFC biosensors for heavy metals monitoring will likely depend on advancements in chemical processes, molecular biology, and innovative materials. Additionally, integrating wireless and remote sensing capabilities will be crucial for the broader deployment and practical application of MFC biosensors.

Acknowledgments

I would like to express my thanks to my tutor, Huan Deng, from Nanjing Normal University, for guiding me in this research project.

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DOI: 10.36838/v7i7.15