

REVIEW

Microbial fuel cells: A potent and sustainable solution for heavy metal removal

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Abstract

The global water pollution problem is becoming increasingly crucial. One of the major contributors to water pollution is the presence of heavy metals. Heavy metals pose significant threat to both humans and all ecosystems. Various factors influence the removal of heavy metals from wastewater, including pH, temperature, natural organic matter (NOM), and ionic strength, which vary based on the chemical properties of the pollutants. More effective and modern approaches receive attention and extensively researched to substitute traditional methods such as adsorption, membrane filtration, and chemical-based separation. Among these methods, Microbial fuel cells (MFCs) are particularly intriguing. This review article focuses on MFCs and their potential applications in various fields, including clean water production. MFCs represent an innovative technology that not only generates electricity, but also demonstrates significant potential for heavy metal removal from wastewater. Cathodic chamber of MFCs effectively reduces heavy metals, while organic substrates act as carbon and electron donors in the anodic chamber. Through various mechanisms, including direct and indirect metal reduction, biofilm formation (metal sequestering), electron shuttling, and synergistic interactions among microbial communities, microorganisms exhibit remarkable efficiency in removing metals. Studies showed that dual- and single-chamber MFCs could efficiently remove a range of heavy metals, including chromium, cobalt, copper, vanadium, mercury, gold, selenium, lead, magnesium, manganese, zinc, and sodium, while simultaneously generating electricity, achieving high removal efficiencies ranging from 25% to 99.95%. This range of efficiency varies depending on the specific contaminant being targeted, the concentration of the contaminant, as well as the operating conditions such as pH and temperature. Moreover, MFCs demonstrated a wide range of power outputs, typically ranging from 0.15 W/m² to 6.58 W/m², depending on the specific configuration and conditions.

These findings underscore the potential of MFCs as a sustainable and efficient approach for both wastewater treatment and energy generation.

Keywords: Microbial fuel cell (MFC), heavy metal removal, wastewater treatment, sustainable energy generation, metal reduction mechanisms.

Introduction

Clean water is indispensable for life. Together with the demand for clean potable water, the pollution of clean water resources is also increasing (Xia et al., 2017). Along with the droughts that occur with climate change in progress, there is a rise in the toxicity of chemical pollutants (Xia et al., 2017; Noyes et al., 2009). Humanity is having to fight major health problems, not only due to scarcity of clean drinking water, but also for agricultural irrigation. Water-related health disorders are more common in developing countries (Lin et al., 2022). For example, about 1.6 million people die each year due to water-pollution-related diseases such as diarrhea and sepsis, and 90% of these deaths are in children under the age of 5. One of the greatest water pollution causes is heavy metal contamination. Heavy metals are substances that are difficult to dissolve in nature. These metals mix into water due to various industrial activities and agricultural runoff, and since they are difficult to dissolve in water resources, they can remain for a long time. This causes great harm to human health and the ecosystem (Pandit and Kumar, 2015).

Table 1. Characteristics of common heavy metals (EPA, 2024; WHO, 2017).

Heavy Metal	Human Health Effects	Common Sources	Maximum Level		Contaminant	
			EPA		WHO	
Arsenic (As)	Circulatory system issues	Electronics production	0.010	mg	0.010	mg
	Skin Damage	Naturally occurring	L ⁻¹		L ⁻¹	
Cadmium (Cd)	Carcinogenic	Chemical industries	0.005	mg	0.003	mg
	Kidney damage	Naturally occurring	L ⁻¹		L ⁻¹	
Chromium (Cr)	Diarrhea, vomiting, nausea	Steel manufacturing	0.1	mg L ⁻¹	0.05	mg L ⁻¹
	Allergic dermatitis	Naturally occurring				
Copper (Cu)	Liver and kidney damage	Household plumbing	1.3	mg L ⁻¹	2.0	mg L ⁻¹
	Gastrointestinal issues	systems				
		Naturally occurring				
Mercury (Hg)	Nervous system damage	Electronics industries	0.002	mg	0.006	mg
	Kidney damage	Fossil fuel combustion	L ⁻¹		L ⁻¹	

Silver (Ag)	Breathing problems	Naturally occurring	0.10 mg L ⁻¹	100 µg L ⁻¹
	Stomach pain	Naturally occurring		
Selenium (Se)	Kidney damage	Naturally occurring	0.05 mg L ⁻¹	0.05 mg L ⁻¹
	Breath problems	Chemical industries		

In the developing world, industrial and urban activities are increasing in parallel with pollution caused by heavy metals. Various factors, such as polluted wastewater discharge from several industries, emissions from vehicles, and other urban activities are examples of such contributing factors (Joseph et al., 2019). According to the United Nations report, about 80% of all industrial and domestic wastewater in developing countries are released into the environment without any pretreatment (Xia et al., 2017). In addition, polluted urban stormwater runoff, rainwater contamination into potential drinking water sources, and agricultural runoff also increase pollution (Lye, 2009). Heavy metals and mixed organic substances mix with water bodies through direct discharge or domestic wastewater discharge. Textile, dye, leather and pharmaceutical industries produce most of such discharges. Heavy metals such as Cr, Cd, Pb, As and Hg are highly toxic and carcinogenic, and may create significant damage to vital organs (Balali-Mood et al., 2021). Organic pollutants pose additional toxicity and carcinogenicity, particularly upon mixing with heavy metals, and producing chemical complexes. Delayed maturation or complete growing inability of plants may be caused by the result of heavy metals-organic pollutants interactions ((Briffa et al., 2020). Likewise, the beneficial microbial ecosystems may be adversely affected (Ajiboye, 2021).

Treatment methods for drinking water, such as heat treatment, solar disinfection, and chlorination are mostly insufficient. Since wastewater removal efficiencies vary depending on energy, time, and environmental conditions, these techniques cannot completely remove chemical contaminants in drinking water and require additional technological equipment (Senanu et al., 2023). Some of the technologies and treatment methods that provide high removal efficiency for heavy metals, which are nowadays under investigation in developed countries, are as follows: microbial bioremediation, employing various modified adsorbents, activated carbon adsorption, membrane filtration, electrocoagulation, and carbon nanotechnology. On the other hand, since these technologies are not cost-effective, local employees should be trained to purify contaminated water in the developing world, and the cost should be low and access to the technologies used should be easy (Joseph et al., 2019). Therefore, this review article focuses on bioremediation by microbial fuel cells and the use of cheap, widely available materials that do not result in additional energy requirements for the removal of heavy metals from water supplies.

Impact on water quality and heavy metal removal

The main parameters influencing removal of heavy metals from water are NOM, pH, temperature, and ionic strength (Joseph et al., 2019).

Chemical properties of heavy metals

All living organisms require trace amounts of heavy metals such as copper, zinc, iron, and chromium for growth and development, but heavy metals taken in large amounts can cause major problems of toxicity (Tchobanoglous et al., 2003). Table 2 shows the chemical characteristics of some heavy metals in the environment.

Table 2. Some chemical characteristics of common heavy metals (Murray et al., 2004).

Heavy metal	MW(g/mol)	Oxidation state(s)	Electronegativity (Pauling Scale)
Arsenic	74.9	-3, +3, +5	2.18
Cadmium	112.4	+2	1.69
Cobalt	58.9	-1, 0, +2, +3	1.88
Mercury	200.6	+1, +2	2.00
Zinc	65.4	+2	1.65

The effect of pH

pH plays a critical role in heavy metal accumulation in water bodies. Heavy metals are usually found in their cationic state and have high solubility at low or neutral pH values. Studies demonstrated that stability and mobility of copper increased when the pH value decreased (Violante et al., 2010). As the pH increases, heavy metals interact with hydroxide ions and cause oxidation, then precipitate in water. Lead is an example of this phenomenon (Olaniran et al., 2013). In case of chromium, increasing pH converts the more stable Cr(3) to more toxic Cr(4) via oxidation. Removal of heavy metal ions by adsorption can be done in lower levels at low pH (Pantsar-Kallio et al., 2001). With the increase in pH value, the concentration of H⁺ ions decrease, thus the adsorption area increases, resulting in higher levels of heavy metal removal. Exceptions to this phenomenon, such as the removal of chromium from anionic species with increasing pH was also observed, where adsorption decreases as pH increases (Li et al., 2018). This exception arises from electrostatic repulsion, since negative surface charges on the adsorbent prevent the adsorption of anionic species. In conclusion, it can be stated that pH significantly affects the removal and behavior of heavy metals. Joseph et al., (2019) also showed that heavy metals decrease at low pH values (<4) in general, and this is more pronounced in between pH 5 and 7 (Joseph et al., 2019).

The effect of NOM

NOM usually comes from humic and fulvic acids, which are formed by the accumulation and decomposition of plant and animal substances. NOM has a wide range of organic acids and is highly reactive in conjunction with heavy metals, resulting in changes in their mobility and toxicity. Detecting the effects of NOM on heavy metals can be difficult due to a wide variety of additional factors, including pH, humification, and oxidation state (Kumpulainen et al., 2008). Heavy metals and NOM can interact via various mechanisms; the acidic nature of NOM is achieved through such mechanisms as surface adsorption, ion exchange and chelation. Metals such as zinc and copper can also form various complexes with NOM. Additionally, it has been shown that treating chromium in heavy metals that interact with NOM can reduce chromium from its toxic form to a more stable and less harmful form. (Yang et al., 2015; Joseph et al., 2019). In conclusion, there appears to be no clear relationship between NOM and heavy metal removal.

The effect of temperature

Another important parameter in removal of heavy metals is temperature. Removal of heavy metals and complexation reactions on the surface are carried out by increasing the temperature and continue to accelerate as the temperature increases. With increasing temperature, the adsorption zone expands and heavy metal removal increases (Chen et al., 2010). Study results showed that as temperature was increased from 5°C to 40°C, a large amount of Cr(4) in the peanut shell was removed.

Increase in adsorption surface was proportional with the increase in diffusion rate, consequently, the adsorption process proceeded faster at higher temperatures (Moussavi and Barikbin, 2010). Contrasting results were also reported. In a study with red algae, total chromium removal decreased from 90% to 78% as the temperature increased. Likewise, a decrease in the removal of heavy metals such as Ni(2) and Pb(2) was observed with increasing temperature. These results appeared to result from decreased surface activity (Sari and Tuzen, 2008; Joseph et al., 2019). Thus, when examining the effects of temperature on heavy metal removal, each adsorbent and its corresponding metal ion should be studied separately.

The effect of ionic strength

Ionic forces in the water source have a great impact on the removal of heavy metals. Chloride ion in water dissolves and forms metal-chloride complexes with uncharged or negatively charged heavy metals, which are difficult to remove. The heavy metal-chloride complex exhibits low-affinity adsorption and heavy metal-chloride accumulation occurs (Ferraz and Lourenco, 2000). For example, a decrease in the removal of Ni(2) and Cu(2) was detected as the ionic strength increased. This decline was caused by the increase in dissolved zinc and copper concentration with increasing salinity (Villaescusa et al., 2004; Wang et al., 2017). As a result, higher ionic strength causes a decrease in the adsorption of heavy metals by influencing the electrostatic interactions. Contradictory results were also reported in a study, in which As(3) and Ni(2) removal increased by about 25%, as the ionic strength of a solution increased from 0.01 to 1.0 M Cl. In a research with crab shell pieces, it was observed that when ions such as K⁺ and Na⁺ were added for the removal of copper and cobalt, the heavy metal removal increased by 2-5% (Yang et al., 2016; Joseph et al., 2019).

Techniques for eliminating heavy metals

Adsorption-based separation

Because of its low cost, high removal capacity, ease of use, and capability to regenerate the adsorbed heavy metal ions, the adsorption method has been described as a straightforward technique (Yang et al., 2019). Carbon-based nanoporous, chitosan, mineral and magnetic adsorbents are prominent in this separation method.

Due to their exceptional surface areas (500-1500 m²/g), carbon-based nanoporous adsorbents such as activated carbons (ACs), carbon nanotubes (CNTs) and graphene (GN) are widely used in heavy metal removal applications (Karnib et al., 2014). Oxidation, sulfuration and nitrogenation are the most widely applied techniques in carbon adsorption. According to Kumar et al. (2015), these techniques are used to improve pore structure, specific surface area, adsorption capacity, thermal stability and mechanical strength. Carbon-based adsorbents have become more expensive due to their various procedures, therefore researchers are working to create more effective and economical surface modification methods. One of the naturally occurring adsorptive polymers used to remove heavy metals is chitosan. However, some properties such as poor chemical and mechanical stability and biodegradability may affect how widely chitosan-based adsorbents can be used. Microorganisms can access oxidizable or hydrolyzable bonds in chitosan, which can lead to its biodegradation (Stafiej, 2007).

Mineral adsorbents such as clay, zeolite and silica are known to be frequently used and considered suitable for the cost-effective removal of heavy metals (Gu et al., 2018). Clay, in particular, is desirable because it significantly reduces water pollution and improves water quality. Studies have shown that scientists often use ion exchange processes to remove heavy metals and physical or chemical adsorption with mineral adsorbents due to their low cost (Qasem et al., 2021). Typically, magnetic adsorbents

are made of magnetic materials with magnetic properties, such as iron oxide nanoparticles. After the adsorption process, they are easily removed from the solution by applying an external magnetic field (Mehtaa, 2015). As a result, the adsorption method provides effective heavy metal removal from wastewater, reducing their concentrations to safe levels (Tamjidi et al., 2019).

Membrane-based filtration and separation

The high efficiency, applicability, and simplicity of membrane separation techniques make them viable strategies for the removal of heavy metals. A permeable membrane is used in ultrafiltration; a membrane filtration technique to separate heavy metals according to gradients in concentration or pressure. In this method, ultrafiltration, nanofiltration, microfiltration, semi-permeable spiral-wound membranes, ion-exchange membranes will be examined.

In ultrafiltration, bigger particles, such as heavy metal ions, are retained while solvent molecules and tiny particles are selectively allowed to pass through a membrane with a particular pore size. The membrane acts as a barrier to movement, preventing particles larger than a given size threshold from passing through (Xiang et al., 2022).

Membranes for nanofiltration (NF) are essential to the treatment of wastewater. Because of their exceptional separation capabilities, they are frequently used in a variety of wastewater treatment-related operations (Abdel-Fatah, 2018). Regarding pore size range and separation capabilities, nanofiltration (NF) is regarded as a technology that falls between reverse osmosis (RO) and ultrafiltration (UF) (Bellona, 2015). Compared to RO membranes, NF membranes have larger pores, but UF membranes have the largest pores (UF: 5–20 nm, NF: >1 nm, RO: 0–1–1 nm) (Xiang et al., 2022). Because NF membranes have a specified molecular weight cutoff (MWCO), solutes can be separated according to their molecular weight and size. The MWCO of NF membranes is higher than that of RO membranes, but lower than that of UF membranes. Water can have ions, dissolved particles, and chemical substances selectively removed using NF membranes (Mondal and Wickramasinghe, 2008).

Microfiltration is an adaptable and popular separation method that provides effective microbial control and particle removal in a range of applications. It offers a practical and affordable way to get rid of bacteria and particles smaller than microns from fluids, which enhances process effectiveness, protects the environment, and produces better-quality products. Membranes with pore sizes between 0.05 and 10 microns are thought to be ideal for microfiltration. Numerous materials, including silica, zirconia, ceramics, polyamides, polypropylene, and composite materials, can be used to create MF membranes (Hakami Het al., 2020).

Semi-permeable spiral wound membranes are used to filter heavy metals and other impurities from water in the reverse osmosis process. Reverse osmosis membranes can effectively limit the passage of suspended solids, ions and other unwanted substances due to their small pore size (typically between 0.1 and 1 nm) (Garud et al., 2011). Clean water molecules can flow through these membranes when water is pushed by high pressure, but contaminants are left behind and washed away as a trash stream (Lee et al., 2011).

Ion exchange membranes are alternately positioned in a direct current field in electrodialysis (ED). Ionic solutes are separated by ED using anion exchange membranes (AEM) and cation exchange membranes (CEM) (Xu and Huang, 2008). These two membrane types are alternately aligned in a membrane stack to form repeating units. These units consist of compartments with cation exchange membranes on the right and anion exchange membranes on the left. The membrane stack is powered by providing a difference in electrical potential using electrodes at either end (Van der Bruggen, 2015; Gurreri et al., 2020).

Chemical-based separation

Chemical precipitation is a commonly employed technique for eliminating dissolved metals from solutions, particularly in the treatment of process wastewaters containing hazardous metals. Particles are formed when soluble metal compounds undergo a chemical interaction with particular precipitating agents that turns them into insoluble forms. Then, using techniques like settling or filtering, these particles can be extracted from the mixture (Dahman, 2017). The kind and concentration of metals in the solution, the precipitating agent selected, the reaction conditions (particularly pH), and the possibility of other substances that could impede the precipitation reaction affect the efficiency of the chemical precipitation process (Ramakrishnaiah and Prathima, 2012). Coagulation and flocculation procedures are widely used in drinking water treatment due to their high effectiveness in reducing turbidity. The main objective of coagulation and flocculation processes is to collect colloids and other small particles present in water and form larger particles called flocs (Muruganandam et al., 2017). In the first stage, called coagulation, a coagulant is added to the water to reduce repulsive interactions between colloids, which eventually causes the particles to become unstable. The destabilized particles come together to form flocs in the subsequent flocculation stage due to attractive factors, such as van der Waals interactions (Ho et al., 2020).

Gas bubbles are used as transporters in the flotation separation process. During this process, suspended particulate matter adheres to the bubbles and rises to the surface of the aqueous solution, regardless of whether it is hydrophobic by nature or may become so through conditioning. It's important to keep in mind that this upward motion defies gravity (Gharai and Venugopal, 2016).

Microbial fuel cell technology

Interest in ecological and sustainable renewable energy sources has increased in recent years. Among these sources, bioenergy is the world's fourth-largest energy source and can be derived from various forms of biomass (Kilinc and Catal, 2023, Arslan et al., 2020; Dahiya, 2020). A promising technology to address environmental pollution and energy needs is the MFCs (Sonmez et al., 2024). They are especially beneficial, because they produce electricity, while yielding byproducts like methane (CH_4), hydrogen (H_2), and hydrogen peroxide (H_2O_2) from the chemical energy found in wastewater. Because of their ability to perform two tasks at once, MFCs can clean wastewater and recover energy, which makes them a viable option for both pollution reduction and energy recovery. MFCs have several advantages over conventional wastewater treatment techniques, such as lower energy consumption and less sludge production than aerobic treatment. Additionally, they exhibit adaptability in difficult circumstances like low substrate concentrations and temperatures (less than 20°C), which can restrict the use of other treatment technologies. On the other hand, some of the drawbacks of MFCs are high cost, low power output, and short operational lifetimes of the technology. These difficulties are exacerbated by problems like membrane fouling, catalyst instability, and the difficulty of maintaining microbe-based systems. Long-term dependability and efficiency of MFCs are impacted by cathode catalyst and membrane deterioration, which frequently limits the device's lifespan. Furthermore, even though MFCs have a lower environmental impact than some other technologies, they still need to be carefully managed to avoid any unfavorable outcomes, such as the formation of byproducts and unstable systems. All things considered, MFCs have a lot of potential for producing energy and treating wastewater sustainably, although more research is required to get past the obstacles and improve their functionality (Naha et al., 2023; Guo et al., 2020).

The MFCs utilize exoelectrogenic microorganisms, including bacteria, algae, and fungi present in the anode compartment made of carbon; a sturdy conductor, to create a biofilm structure on the an-

ode. This process converts chemical energy derived from biomass into electricity or other chemical products in an electrochemical manner (Sukkasem, 2024; Fan et al., 2024; Kilinc and Catal, 2023; Akagündüz et al., 2022; Cebecioğlu et al. 2022). They are composed of two compartments separated by a proton exchange membrane: an anode chamber and a cathode chamber (Figure 1).

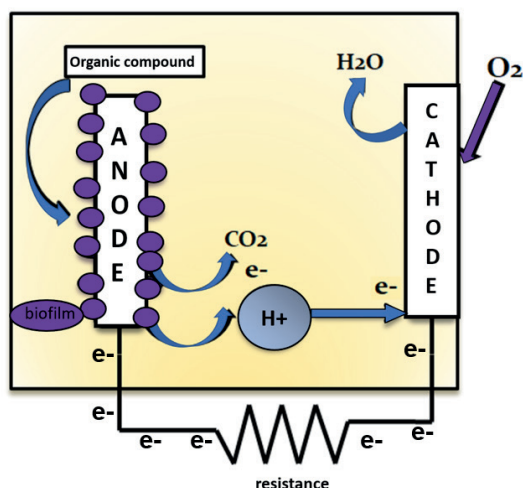
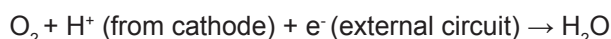
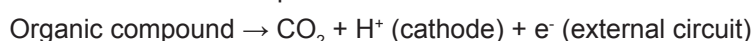


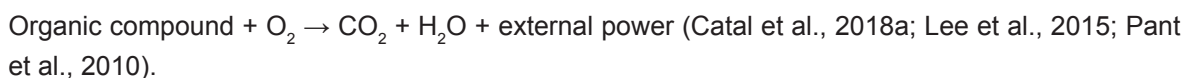
Figure 1. The operating principle of the single chamber microbial fuel cell has been modified from Akagündüz et al., (2022).

In the anode chamber, electroactive microorganisms adhere to a conductive electrode. The microorganisms form a biofilm in the anode chamber, which oxidizes organic compounds, releasing electrons and protons. Protons and electrons released from the anode chamber flow through an external circuit to the cathode chamber where they combine with a terminal electron acceptor (usually oxygen) to form water or other reduced products. This process produces an electric current that can be harvested for power generation.

The anodic and cathodic reactions are presented below:



These two half-reactions lead to an overall reaction:



The scaling-up process is one of the major obstacles in bringing MFCs to commercial applications, even with the technology's successful demonstration in lab settings. It is not always possible to transfer lab-scale reactor performance directly to field applications. For example, expanding the anodic chamber's size can actually result in a decrease in overall performance, rather than a proportionate increase in power output. Moreover, increased internal resistances and cathode kinetics constraints mean that larger electrode surface areas do not always translate into higher power harvesting rates. Modular MFC units with sophisticated power management systems have been created to address these problems, but mass transport constraints and voltage reversal continue to be major roadblocks to the widespread adoption of this technology (Jadhav et al., 2021).

Notwithstanding these difficulties, studies on low voltage generation and the treatment of wastewater contaminated by pharmaceuticals are the two real-world applications where microbial fuel cells have proven effective (Akagündüz et al., 2022; Catal et al., 2018b). In addition, MFC technology has

successful applications in the recovery of ammonium and nitrogen from urine (Sharma and Mutnuri, 2019), drug recovery (Akagunduz et al., 2022; Akul et al., 2022), biosensor studies used in water quality assessment (Adekunle et al., 2021), removal of toxic dyes from the environment (Cebecioğlu et al., 2022) and in removal of various pollutants from environment (Catal et al., 2019; Ozdemir et al., 2019). Microbial fuel cell is a promising technology for simultaneous removal of heavy metals from wastewater and electricity generation. In MFCs, heavy metals such as chromium, cobalt, copper, silver, mercury, vanadium, gold and selenium are effectively reduced in the cathode chamber, while organic substrates serve as carbon and electron donors in the anode chamber. Numerous studies have investigated the presence of electrochemically active bacterial species in MFCs, with over 20 distinct species being identified. Notable examples include *Aeromonas*, *Ochrobactrum*, *Arcobacter*, *Pseudomonas*, *Desulfuromonas*, *Desulfobulbus*, *Thermincola*, *Geothrix*, *Comamonas*, *Geopsychrobacter*, *Propionibacterium*, *Shewanella*, *Klebsiella*, *Enterobacter*, *Acidiphilium*, *Citrobacter*, *Rhodospirillum rubrum*, *Rhodopseudomonas*, *Geobacter* and *Clostridium*. These microorganisms have been widely observed in alum sludge or activated sludge (Catal et al., 2024; Wang et al., 2016). *Aeromonas* species are resistant to acid and are gram-negative bacteria that can be found in a variety of settings, including food, water, and soil. They are used in biotechnology, including in MFCs, despite being pathogenic. For instance, it has been demonstrated that *A. hydrophila* breaks down chitin to produce metabolites that improve MFCs' ability to produce energy (Li et al., 2017). *Ochrobactrum* species are well-known for their capacity to produce electricity in MFCs and eliminate heavy metals like lead. In a two-chamber MFC, *Ochrobactrum* greatly enhanced power generation and eliminated 84.86% of Pb^{2+} (et al., 2023). *Arcobacter* species can reduce Fe and Mn in low oxygen environments and are associated with diseases in humans and animals. In MFCs, *Arcobacter butzleri* demonstrated encouraging outcomes in the oxidation of acetic acid and the production of electricity (Fedorovich et al., 2009). A significant factor in MFCs and industrial applications are the exoelectrogenic qualities of *Pseudomonas* species. Using oily wastewater, *P. citronellolis* showed a significant reduction in COD and production of electricity in MFCs (Varnava et al., 2024). Sulfur and metals like iron and manganese are reduced by species of *Desulfuromonas*. They help MFCs form an anodic biofilm, which increases power density (Xu et al., 2023). According to Sun et al. (2009), *Desulfobulbus* species are essential for sulfate reduction and sulfide oxidation, which sustain continuous current production in MFCs. A thermophilic Gram-positive bacterium called *Thermincola ferriacetica* is well-known for its ability to transfer electrons directly and produce stable electricity at high temperatures in MFCs (Marshall and May, 2009). *Geothrix fermentans* is useful in MFCs for energy production, because it can oxidize organic acids and transfer electrons directly to electrodes (Bond and Lovley, 2005). It has been discovered that *Comamonas* species, which are significant in bioremediation, are essential for the production of electricity in MFCs contaminated with wastewater from fish markets (Padmanabhan et al., 2023). According to Holmes et al. (2004), *Geopsychrobacter* species are psychrotolerant bacteria that can transfer electrons to electrodes and grow in low temperatures, enabling the production of electricity in MFCs. *Propionibacterium* species are classified into two groups: cutaneous and classical. The former is employed in a variety of industries. High power density MFCs have demonstrated successful performance from *P. freudenreichii* ssp. *shermanii* (Reiche et al., 2015). The extracellular electron transfer capabilities of *Shewanella* species are noteworthy, because they improve MFC performance without the need for mediators. It has been demonstrated that *S. oneidensis* MR-1 can generate electricity from a variety of carbon sources (Dai et al., 2020). Significant pathogens, *Klebsiella* species are also investigated for their potential to produce energy in MFCs. *Shewanella oneidensis* and *Klebsiella pneumoniae* worked together to pro-

cess glycerol in MFCs to efficiently produce energy (Li et al., 2017). *Enterobacter* species play a key role in the generation of biohydrogen and bioremediation. In MFCs, *Enterobacter* sp. was employed as a sensor to track the production of hydrogen and the health of the microbiota (Lim et al., 2022). Certain acidophilic bacteria that can reduce iron are called *Acidiphilium* species. Borole et al. (2008) reported that *A. cryptum* was effectively employed as an anodic biocatalyst in MFCs, thereby augmenting power output in low pH conditions. Because of their capacity to decrease iron, *Citrobacter* species have demonstrated potential in MFC applications. *Citrobacter* sp. LAR-1 produced electricity in MFCs with success (Liu et al., 2016). With the capacity to produce a sizable current density in MFCs using sugars as fuel, *Rhodospirillum rubrum* is essential in anaerobic conditions (Liu et al., 2006). In microbial electrochemical cells fed with acetate, *Rhodospseudomonas palustris* strain RP2 is well known for its capacity to break down hydrocarbons and produce energy (Venkidusamy and Megharaj, 2016). In MFCs, *Geobacter* species are renowned for having a high potential for electrical output. When nanofluid proteins were overexpressed, *G. sulfurreducens* generated more electricity, demonstrating their importance in bioremediation and energy production (Wang et al., 2023). *Firmicute* bacteria, such as *Clostridium* species, have thick cell walls that allow them to survive in challenging conditions. In MFCs, *Clostridium butyricum* has been utilized, and after 10 hours of inoculation, it produced a maximum current of 0.22 mA (Cao et al., 2019). These microbes are important for the biological and electrochemical processes that are necessary for the removal of metal from MFCs, in addition to help generate electricity.

Metal removal in MFCs involves a variety of biological and electrochemical processes. Direct metal reduction is where certain microorganisms have the ability to directly convert metal ions from high to low oxidation states through their electron transfer capacity. Bacteria such as *Shewanella* and *Geobacter* are notable for their use of extracellular electron transfer mechanisms to accomplish this reduction. Additionally, metal removal can occur indirectly via metabolic pathways. Microorganisms utilize organic substrates, such as wastewater contaminants or electron donors, as a source of carbon and energy. As they metabolize the organic matter, metabolic byproducts like organic acids or hydrogen sulfide are produced, which can react with metal ions to form less soluble precipitates such as metal sulfides or metal hydroxides. These precipitates are more easily separated from the soluble fraction, resulting in metal removal from the system. Biofilm formation on electrode surfaces within MFCs plays a significant role in metal removal. In MFCs, biofilm growth on the electrode surfaces is crucial to the removal of metal. Complex bacterial colonies that stick to surfaces are called biofilms. Biofilms let cells communicate with each other and regulate the admission of heavy metals and other hazardous materials from the outside. To protect themselves, bacteria in biofilms create metal-binding proteins such as metallothionein (MT) and extracellular polymeric substances (EPS). When heavy metals enter the cell, these proteins respond by sequestering the metals within the cell. As a result, they offer stable complexes and lessen cellular toxicity. Zinc removal has been found to be significantly aided by the MT SmtA protein generated by the cyanobacterium *Synechococcus elongatus* (strain PCC7942). According to a different study, MTs produced by the *Mycobacterium tuberculosis* (strain H37Rv) strain are crucial for the elimination of copper. Certain microorganisms produce redox-active compounds known as electron shuttles or mediators. These compounds indirectly transfer electrons from microorganisms to metal ions, enhancing the reduction process. This mediated electron transfer mechanism allows for the utilization of microorganisms that may not directly interact with the metal ions, but still contribute to metal removal through shuttle-mediated electron transfer. In MFCs, a diverse microbial community with varied metabolic capabilities is often present. Synergistic interactions among microorganisms occur, where one group of microorganisms provides reducing

equivalents or metabolites that are utilized by other microorganisms involved in metal removal processes. These cooperative interactions contribute to the overall efficiency of metal removal in MFCs (Roy et al., 2023; Noori et al., 2022; Abbas et al., 2017; Rabaey et al., 2007; Rabaey et al., 2004).

Methods

This review paper primarily focuses on the application of MFCs for the removal of heavy metals. We searched a number of databases, including PubMed, Web of Science, and Academia, adhering to PRISMA principles. In light of papers published by researchers in the previous 30 years, we searched the aforementioned databases using the following keywords: microbial fuel cell, heavy metal removal, wastewater treatment, sustainable energy generation, and metal reduction processes. Using the PRISMA checklist, reviewers independently chose reviews, extracted data, and evaluated the included reviews' methodological quality. In order to settle differences and come to a consensus, the researchers presented and debated these results.

The literature presents numerous studies on metal removal using microbial fuel cells. Presents studies reveal the potential of MFCs as innovative technologies that provide dual benefits in both energy production and wastewater treatment (Table 3).

Table 3. Summary of various studies conducted on heavy metal removal using microbial fuel cells.

Study	Metal	Microbial Species	MFC Configuration	Electron Donor	Metal Concentration	pH Range	Maximum Removal Efficiency	Maximum Power Output
Zhang et al. (2021)	Chromium Cr(VI)	Anaerobic sludge	Double-chamber MFC	Sodium acetate	6-15-40-100 mg.L ⁻¹	7	66.5%	35.3 mWm ⁻²
Wang et al. (2008)	Chromium Cr(VI)	Domestic wastewater	Double-chamber MFC	Sodium acetate	100 mg.L ⁻¹	2-6	100%	0.150 Wm ⁻²
Huang et al. (2013)	Cobalt (Co(III))	Domestic wastewater	MFC with LiCoO ₂ electrodes	Sodium acetate	50 mg.L ⁻¹	1-3	99.1% (conversion ratio to soluble Co(II))	298 mWm ⁻³
Heijne et al. (2010)	Copper (Cu)	Mixed microbial culture from operating MFCs	Double-chamber MFC	Sodium acetate	1000 mg.L ⁻¹	3	99.88% (anaerobic), 99.95% (aerobic)	0.43 Wm ⁻² (anaerobic), 0.80 Wm ⁻² (aerobic)
Tao et al. (2011)	Copper (Cu(II))	Mixed microbial culture from operating MFCs	Membrane-free bio electrochemical system	Sodium acetate	600-2000 mg	2	91.95% and, 47.54% respectively.	0.585 mW
Zhang et al. (2009)	Vanadium (V(V))	Anaerobic granular sludge	Double-chamber MFC	Glucose	500 mg.L ⁻¹	2	25%	0.572 Wm ⁻²
Wang et al. (2011)	Mercury (Hg(II))	Domestic wastewater	Double-chamber MFC	Sodium acetate	25-100 mg.L ⁻¹	2	98.2% and, 99.5% respectively.	0.433 Wm ⁻²
Choi and Hu (2013)	Gold (Au(III))	Mixture sludge with artificial wastewater	Double-chamber MFC	Tetrachloroaurate	100-2000 mg.L ⁻¹	1-6.5	99.8%	6.58 Wm ⁻²
Catal et al. (2009)	Selenium (Se(IV))	Domestic wastewater	Single-chamber MFC	Acetate or glucose	50-200 mg.L ⁻¹	7	99%	2.90 Wm ⁻²

Yang et al. (2021)	Copper (Cu)	Anaerobic sludge and, <i>Chlorella</i>	Three-chamber MFC	Sodium acetate	30 mg.L ⁻¹	not specified	99%	0.42 Wm ⁻²
Zhang et al. (2020)	Copper (Cu)	Anaerobic sludge	Three-chamber MFC	Glucose	500 mg.kg ⁻¹	2	94.78% (with 1 mol.L ⁻¹ HCL)	363.04 mWh ⁻¹ (with 1 mol.L ⁻¹ HCL)
Zhang et al. (2023)	Lead (Pb2+)	<i>Ochrobactrum</i> -related strain CD-1	Double-chamber MFC	Sodium acetate, sodium citrate and, glucose respectively	2500 mg.L ⁻¹	not specified	52.3%,37.5% and, 19.2% respectively	371.0 mWm ⁻² (with sodium acetate)
Munoz-Cupa and Bassi, (2023)	Cu(II), Mg(II), Mn(II), Zn(II) and, Na (I) respectively	<i>Shewanella oneidensis</i> MR-1	Double-chamber MFC	Sodium lactate	13.5, 7.5, 415, 10.5 and, 2410 mg.L ⁻¹ respectively	7	93%, 85%, 93%, 88% and, 36% respectively (for anode chamber)	517.6 mV

A study by Zhang et al. (2021), focused on the removal of chromium (Cr(VI)) in a dual-chamber MFC system with electrochemically active bacteria and an abiotic cathode and its effect on power generation. The findings revealed that the MFC system with an abiotic cathode exhibited high efficiency in removing heavy metals, particularly Cr(VI), achieving a maximum removal rate of 66.5%. Furthermore, the MFC system simultaneously generated electricity, with the highest power density of 35.3 mW m⁻² observed at an initial concentration of 100 mg L⁻¹ Cr(VI). Similarly, Wang et al. (2008), investigated the removal of Cr(VI) using a dual-chamber MFC with graphite plates for both cathode and anode. The electron donor used was sodium acetate at a concentration of 2.64 g L⁻¹. The study used four different initial concentrations of K₂Cr₂O₇, and the pH range was 2-6. The study found that the system removed Cr(VI) with 100% efficiency at a concentration of 100 mg L⁻¹ in 150 hours. The maximum power output was 0.150 W m⁻² at a concentration of 200 mg L⁻¹ Cr(VI) and pH 2.

In another study, Huang et al. (2013), investigated the removal potential of cobalt (Co(III)) from contaminated water using LiCoO₂ particles as electrode material and sodium acetate as electron donor in dual chamber MFC. The conversion of insoluble Co(III) with a solid/liquid ratio of 50 mg L⁻¹ to soluble Co(II) was investigated using a resistor of 2000 Ω in the pH range of 1-3. The researchers reported that 99.1% of insoluble Co(III) was converted from soluble CO(II) at the end of 48 hours. They also reported that the power generation was 298 mW m⁻³ at a resistor of 2000 Ω.

Heijne et al. (2010), investigated copper removal and maximum power generation in a dual chamber MFC using sodium acetate as electron donor. The researchers used two different systems, anaerobic and aerobic cathode. They reported that 99.88% removal of copper with a concentration of 1000 mg L⁻¹ was achieved in 6 days in the anaerobic cathode. They reported that 99.95% removal of copper with a concentration of 1000 mg L⁻¹ was achieved in 7 days in the aerobic cathode. They also reported that the maximum power generation was 0.43 W m⁻² in the anaerobic cathode and 0.80 W m⁻² in the aerobic cathode.

Tao et al. (2011), conducted a study on copper (Cu(II)) removal and power generation in a 16 mL volume bioelectrochemical system (BES) without a membrane. They used anaerobic microorganisms and CuSO₄ as a catholyte solution in the system. The researchers worked on two concentrations, 600 and 2000 mg, and operated for 480 hours and 672 hours, respectively. As a result, they reported that the removal efficiency of 600 mg Cu(II) was 91.95% and 2000 mg Cu(II) was 47.54%. They reported that the maximum power generation in the system was 0.585 mW at 2000 mg Cu(II) concentration and pH 2.

Zhang et al. (2009), investigated vanadium(V(V)) removal and maximum power generation in a dual chamber MFC system (500 mL volume, pH 2) with the anode chamber (250 mL) containing 100 mg L⁻¹ sulfur and the cathode chamber containing 500 mg L⁻¹ V(V). As a result, the researchers reported that the removal of sulfur and organics was 84.7% and the reduction ratio of V(V) was 25.3% within 72 hours. They also reported that the maximum power generation was 572.4 mW m⁻².

In another study, Wang et al. (2011) investigated the removal of mercury (Hg²⁺) from artificial wastewater using a double chamber MFC system (120 mL anode chamber, 120 mL cathode chamber), and reported that the removal efficiency of Hg²⁺ in the concentration range of 25 -100 mg L⁻¹ was 98.2-99.5% in 10 hours. They also reported that the maximum power output was determined as 0.433 W m⁻² at a concentration of 100 mg L⁻¹ Hg²⁺.

Choi and Hu (2013), investigated the removal of gold (Au(III)) and maximum power output using double chamber MFC. Tetrachloroaurate was used as electron acceptor in the study. They investigated the removal of Au(III) ranging from 100 to 2000 mg L⁻¹ at pH 2. As a result, they determined that the removal efficiency of 99.8% could be achieved at 2000 mg L⁻¹ concentration of Au(III) in five days. They also reported that the maximum power generation at 2000 mg L⁻¹ Au(III) concentration was 6.58 W m⁻².

The study by Catal et al. (2009), investigated the removal of selenium (Se(IV)) from water using a single-chamber MFC with a carbon cloth anode and a coated carbon cloth cathode. Acetate or glucose was used as the electron donor, and SeO₃²⁻ was used as the metal salt at concentrations ranging from 50 to 200 mg L⁻¹ Se(IV) at a pH of 7. The results showed that using an acetate-fed microbial fuel cell, 99% of 75 mg L⁻¹ Se(IV) could be removed within 48 hours. The maximum power output was 2.90 W m⁻² at a Se(IV) concentration of 25 mg L⁻¹.

Yang et al. (2021) established a three-chamber MFC supported by algae (*Chlorella*) to assess the removal efficiency of copper (Cu²⁺) and electricity production. With a starting concentration of 30 mg L⁻¹ Cu²⁺, the first cathodic chamber removed about 86.2% of the Cu²⁺, with the remaining amount being absorbed by algae. This resulted in a 99.9% removal efficiency for the entire system. The researchers reported that the anode and cathode potentials were affected by the Cu²⁺ concentration, with the uptake of Cu²⁺ by algae being a significant factor. The maximum power density was measured to be approximately 0.42 W/m².

A three-chamber microbial fuel cell (TC-MFC) was employed in Zhang et al. (2020) study to examine the removal of copper and the production of electricity. In the investigation, auxiliary reagents such as 1 mol L⁻¹ HCl, citric acid, and acetic acid at varying concentrations (0.05–1.0 mol L⁻¹) were used to test TC-MFC, which included anodic, cathodic, and soil chambers. The initial preparation of the soil sample included 500 mg kg⁻¹ of copper contamination. The application of 1 mol L⁻¹ HCl produced the greatest electricity generation (363.04 mW h) and copper removal efficiency (94.78%) over the course of the 74-day experiment. According to the study, the most effective auxiliary reagent for removing copper from the TC-MFC system was 1 mol L⁻¹ HCl, which also produced excellent efficiency. Zhang et al. (2023) used *Ochrobactrum*-related strain CD-1 to investigate the effects of various carbon sources (sodium acetate, sodium citrate, and glucose) on power density and their efficacy on Pb²⁺ removal in a dual-chamber MFC system. Using sodium acetate allowed for the study's highest power density of 371.0 mW m⁻² to be achieved in less than 6 hours. When glucose and sodium citrate were used, lower potentials and power densities were noted, with the claim that glucose in particular significantly slowed down the production of power. Furthermore, Pb²⁺ removal efficiency with sodium acetate was reported to be 52.3%, with sodium citrate to be 37.5%, and with glucose to be 19.2%.

Munoz-Cupa and Bassi (2023), used a dual-compartment microbial fuel cell inoculated with *Shewanella oneidensis* MR-1 in the anode compartment to investigate heavy metal removal and simultaneous energy production. The study employed synthetic wastewater that included phenol, Cu (II), Mg (II), Mn (II), Zn (II), and Na from refinery processes. In the anode compartment, the maximum open circuit voltage at a concentration of 5 (13.5, 7.5, 415, 10.5 and, 2410 mg L⁻¹ respectively) was 517.6 mV, whereas in the cathode compartment, it was observed to be 27.7 mV. At the anode, the metal removal efficiencies for Cu (II), Mg (II), Mn (II), Zn (II), and Na were 93%, 85%, 93%, and 36%, respectively. 98% of Cu (II), 49% of Mg (II), 57% of Mn (II), 59% of Zn (II), and 36% of Na were removed in the cathode compartment.

Because different techniques and system configurations are employed in different studies on metal removal in MFCs, notable discrepancies are observed. Research focusing specifically on the elimination of copper and chromium metals has demonstrated these variations. The evaluations conducted for chromium include noteworthy examples from Zhang et al. (2021) and Wang et al. (2008). Zhang et al. (2021) removed chromium with 66.5% efficiency in a dual-chamber MFC system. Wang et al. (2008), on the other hand, attained 100% efficiency in a dual-chamber MFC system at a lower metal concentration. This could be attributed to various factors, including the system's pH range and the electrode materials employed (Saravanan et al., 2022).

Heijne et al. (2010), Tao et al. (2011), Yang et al. (2021), Zhang et al. (2020), and Munoz-Cupa and Bassi (2023) are a few examples of studies on copper removal in MFCs. Heijne et al. (2010) used both aerobic and anaerobic cathodes to remove copper, and they were successful in both systems with high efficiencies: anaerobic cathodes produced 99.88% efficiency, while aerobic cathodes produced 99.95% efficiency. By contrast, Tao et al. (2011) found that when using a membraneless system at high copper concentrations (2000 mg L⁻¹), the efficiency was 47.54%. Long-term studies and the absence of a membrane in the system could be the cause of this low efficiency (Du et al., 2007; Saravanan et al., 2022). Using various MFC configurations and carbon sources, Yang et al. (2021) and Zhang et al. (2020) studies also achieved successful results in copper removal. Zhang et al. (2020) used 1 mol L⁻¹ HCl to achieve 94.78% removal, while Yang et al. (2021) used a three-chamber MFC to achieve 99% efficiency. Munoz-Cupa and Bassi (2023) worked on copper with different metals, achieving 93% efficiency. The variations in MFC configurations, carbon sources, and metal concentrations employed could be the cause of these removal efficiencies discrepancies (Du et al., 2007; Jatoi et al., 2020). Additionally, the variety of microorganism sources used may have an impact on the removal efficiency. Other researchers used different microbial mixtures, but Munoz-Cupa and Bassi (2023) used the *Shewanella oneidensis* MR-1 strain for copper removal. Utilizing a mixed microbial consortium has been shown in earlier research to improve metabolic cooperation and aid in the development of a biofilm layer, thereby improving MFC performance (Nevin et al., 2021).

Research on other metal species yields results that are likewise quite variable. For instance, Huang et al. (2013) found that cobalt had a high conversion rate. Working with gold, Choi and Hu (2013) produced a high-power output (6.58 W/m²) and removal efficiency (99.8%). Selenium removal efficiency of 99% was attained by Catal et al. (2009); however, the efficiency of the single-chamber system may have differed based on the carbon source and pH levels (Saravanan et al., 2022; Jatoi et al., 2020). These variations rely on how different metal removal and energy production systems are designed and used. A number of variables affect efficiency and power output, including the types of microorganisms used, pH range, metal concentration, and materials used in MFC systems. Therefore, each study's unique conditions and methodology should be considered when evaluating the results.

Conclusions

In the developing world, the need for water is increasing along with water pollution. One of the main causes of water pollution is heavy metal pollution from various sources. Heavy metals must be eliminated from wastewater because of their toxic and cancer-causing properties, which endanger ecosystems and humans alike. The removal of heavy metals is influenced by numerous variables and techniques. These factors are pH, ionic strength, temperature and organic matter. Enhancing these parameters can lead to better metal removal performance from MFC. The interaction between heavy metal properties and these factors should be considered separately. Evaluating the strengths and weaknesses of each technique highlights the need for innovative and economically viable alternatives such as MFCs. The MFCs are a cutting-edge technology that extracts heavy metals from wastewater in addition to producing electricity. In MFCs, organic substrates act as electron donor in the anodic chamber and reduce heavy metals in the cathodic chamber. Metals are metabolized by microorganisms via a variety of pathways, such as electron shuttling aided by redox-active substances, biofilm formation on electrode surfaces, direct metal reduction, and synergistic interactions among microbial communities. Research revealed that a variety of heavy metals, including chromium, cobalt, copper, vanadium, mercury, gold, selenium, lead, magnesium, manganese, zinc, and sodium could be effectively removed by dual- and single-chamber MFCs, while also producing electricity. These MFCs were able to achieve high removal efficiencies, which ranged from 25% to 99.95%. This efficiency range is dependent on the particular contaminant being targeted, the contaminant's concentration, and the operational parameters (pH, temperature, etc.). Additionally, MFCs showed a broad range of power outputs, typically ranged from 0.15 W/m² to 6.58 W/m², depending on the particular configuration and conditions. Even under difficult circumstances, MFCs have benefits like lower energy consumption and less sludge production. However, obstacles like exorbitant expenses, low power output, problems with catalyst degradation and membrane fouling compromise their long-term viability. The scalability issue with MFCs is an additional drawback. The performance of laboratory-scale reactors cannot always be directly applied to field settings. When scaling, expanding the anode chamber's size could result in leaks in the anode chamber or a drop in overall performance instead of a proportionate increase in power output. To solve these issues, scalability studies require more research. Combining MFCs with other techniques for treating wastewater could be an additional option.

Future perspectives

The field of heavy metal removal in MFCs holds promising future prospects. Advancements in MFC technology, along with ongoing research efforts, are expected to further enhance the efficiency and effectiveness of heavy metal removal from wastewater. Future studies may focus on optimizing MFC configurations by exploring novel electrode materials, improving electron transfer kinetics, and enhancing the catalytic activity of biocatalysts. Additionally, the development of tailored microbial consortia with enhanced metal-reducing capabilities could improve the removal efficiency for specific heavy metals. Further investigation into the impacts of factors such as pH, metal concentrations and, temperature on MFC performance will enable a better understanding of their influence and facilitate the design of optimized MFC systems. Moreover, exploring sustainable and renewable electron donors, such as organic waste streams or renewable energy sources, could enhance the environmental and economic viability of MFC-based heavy metal removal. Overall, with continued research and technological advancements, microbial fuel cells have a promising future for efficient and sustainable heavy metal removal, contributing to the development of environmentally friendly wastewater treatment strategies.

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Conflict of interest

The authors declare no conflict of interest.

Data availability statement

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Ethics committee approval

Ethics committee approval is not required for this study.

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