


Review

Metal Recovery and Electricity Generation from Wastewater Treatment: The State of the Art

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Abstract: The recovery of metal resources from wastewater is very important for both resource recovery and wastewater treatment. Compared with traditional metal-polluted wastewater treatment technologies, advanced wastewater treatment technologies with the functions of both recovering metals and generating electricity have been developed rapidly in recent years. These advanced technologies include microbial fuel cells, photo fuel cells, coupled redox fuel cells, etc. In this paper, these advanced technologies are elaborated from their principles to their applications in wastewater treatment for metals recovery and electricity generation. The recent progress of these technologies was also reviewed. The effects of different metal ions, cell configurations, and various operating parameters on their performance were also discussed. Although these technologies are promising, the challenges and the efforts needed to overcome them are also highlighted.

Keywords: heavy metal; microbial fuel cell; photo fuel cell; coupled redox fuel cell; wastewater treatment; resources recovery



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1. Introduction

Mining, metal processing, electroplating, batteries, and other industries often discharge a large amount of wastewater containing metals, such as lead, cadmium, mercury, chromium, copper, zinc, nickel, vanadium, etc. [1]. Because metals, especially heavy metals, cannot be degraded, after their discharge into the water environment, they may cause serious environmental problems. They may also enter the human body through the food chain, and a certain number of metals will affect the organs and nervous system and cause harm to human health [2]. Therefore, it is very important to remove metals from wastewater.

Traditionally, various chemical technologies have been applied in metal-polluted wastewater treatment, such as chemical precipitation, electrolysis and reduction, etc. In chemical precipitation methods, metal ions are removed in the form of insoluble hydroxide, sulfide, or carbonate precipitation. However, the precipitation method is limited due to its consumption of large amounts of chemicals and the discharge of toxic sludges, which may cause other safety concerns [3]. The electrolysis method can recover metals via electrodeposition on a cathode, but this method usually has the disadvantage of high energy consumption [4]. The reduction method usually consumes a large amount of chemicals and may produce toxic sludge [5]. In addition, there are also many physical chemical methods for metal-polluted wastewater treatment such as ion exchange, adsorption, solvent extracting, membrane filtration, etc. [6]. Ion exchange, adsorption and solvent extraction methods usually use resins, adsorbents and solvent to purify water, but concentrated wastewater may be produced. In membrane separation, membrane fouling is usually serious and frequent maintenance of the membrane filtration system is required. The metal-polluted wastewater is concentrated without metal recovery in the membrane separation method. In general, research shows that traditional metal-polluted wastewater treatment techniques usually have drawbacks such as the production of toxic sludge, high energy consumption, low

recovery efficiency, and the potential to cause secondary pollution [7,8]. In addition, metals with large exploitation face resource shortage problems. Thus, the effective recovery of metals through wastewater treatment has great economic value but faces great challenges. Therefore, it has become a major research topic to develop novel metal recovery technologies for wastewater treatment with the characteristics of no secondary pollution, low energy consumption, high treatment efficiency, and low operation costs.

Electrochemical technologies, such as microbial fuel cells (MFCs), photoelectrochemical fuel cells (PFCs), and coupled redox fuel cells (CRFCs), have undergone tremendous scientific and technical growth over the past decade, because they can directly convert the chemical energy in waste into electricity and recover metal resources. These technologies have shown promising application in energy, resource recovery, and wastewater treatment [9]. In particular, in recent years, these electrochemical technologies have been widely applied in metal-polluted wastewater treatment for metal resource and electricity recovery. Many reputed researchers have been involved and a number of papers have been published in this area. In order to promote research work on these electrochemical technologies, it is necessary to provide a review in this area. This review is intended to introduce the basic knowledge, the most relevant features, and the recent research progress in terms of the corresponding electrochemical technologies.

2. Microbial Fuel Cells

In a typical MFC, bacteria on the anode can oxidize organic matter into carbon dioxide and release protons and electrons, while oxygen can combine with protons and electrons to produce water on the cathode. This technology can realize wastewater treatment and power recovery simultaneously and provides a promising solution to solve the energy and environmental challenges. It has thus become one of the major topics in environmental engineering.

For the metal removal in an MFC, metal ions in aqueous solution usually function as electron acceptors, and their reduction and recovery mostly occur on the cathode [10–12]. The mechanism for the cathodic removal of metals is relatively simple, as illustrated in Figure 1. The metal ions function as electron acceptors on the cathode to replace oxygen, while the same organic oxidation reactions occur on the bioanode as in traditional MFCs. In this case, metal ions were mainly reduced to lower valences or metals to be recovered [13,14]. In order to avoid their effects on the bioanode, the MFCs were usually separated by an ion exchange membrane. In addition, metal ions can be reduced by reductants produced on the cathode in MFCs. Liu et al. reported that H_2O_2 can be directly generated on the MFC cathode and metal ions can be further reduced by H_2O_2 [15,16].

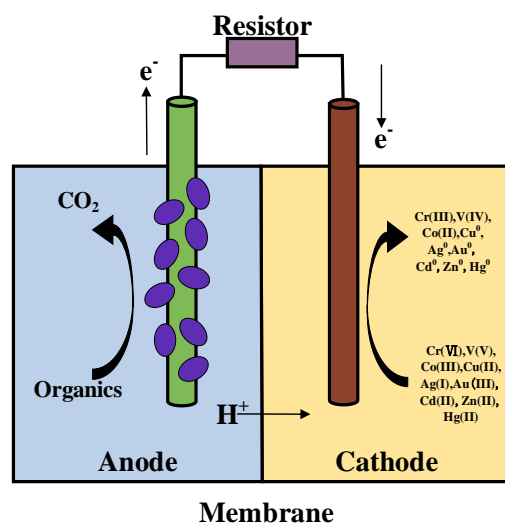


Figure 1. Metals removal on the cathode of MFCs.

However, in some cases, some metal ions may be directly adsorbed by the bacteria on the anode and metals can be transformed. The principles of metal ion removal on a bioanode are illustrated in Figure 2. As in the illustration, the bacteria on the anode can adsorb the metal ions and transfer the metal ions to cellular substances or precipitates. Miran et al. [17] enriched sulfate reducing bacteria (SRB) and exoelectrogens on the anode and used the bioanode in an MFC for copper removal. It was found that in 48 h, over 63% of copper could be removed by SRB through the direct adsorption and ca. 7% of copper was removed by the copper sulfide precipitation. The sulfide was produced by SRB via sulfate reduction. In this case, biosorption and sulfides precipitation are the major mechanisms for metal ion removal in the MFCs. Liu et al. [18] also proposed similar mechanisms for Zn and Cd removal. Under a low initial concentration of less than 0.5 mM, the Zn and Cd removal efficiency can reach 97% and 90%, respectively, with decreased power generation performance.

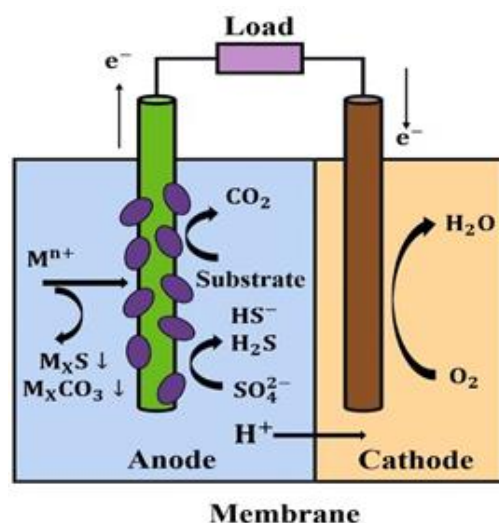


Figure 2. Metal removal on a bioanode.

To date, many reports have shown that the metal ion removal efficiency and electricity production performance in MFCs are mainly affected by the metal ion type and concentration, electrode materials, anode substrates, and microbe community [19,20]. It is very meaningful to better understand these factors and their effects on the system in order to develop efficient and applicable technologies for metal-polluted wastewater treatment. As different metal ions usually have different oxidation potentials (shown in Table 1), their reduction performance is thermodynamically different. In the following section, this topic will be reviewed from the perspective of different metal ions.

Table 1. Oxidation potentials for typical metal ions.

Typical Ions	Reactions	Standard Oxidation Potential/V
Cr(VI)	$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	1.232
V(V)	$\text{VO}_2^+ + 2\text{H}^+ + \text{e}^- \rightarrow \text{VO}^{2+} + \text{H}_2\text{O}$	0.991
Co(III)	$\text{CoO}_2^- + 4\text{H}^+ + \text{e}^- \rightarrow \text{Co}^{2+} + 2\text{H}_2\text{O}$	1.61
Cu(II)	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	0.341
Ag(I)	$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	0.80
Au(III)	$\text{AuCl}_4^- + 3\text{e}^- \rightarrow \text{Au(s)} + 4\text{Cl}^-$	1.002
Hg(II)	$\text{Hg}^{2+} + 2\text{e}^- \rightarrow \text{Hg}$	0.851
Cd(II)	$\text{Cd}^{2+} + 2\text{e}^- \rightarrow \text{Cd}$	−0.403
Ni(II)	$\text{Ni}^{2+} + \text{e}^- \rightarrow \text{Ni}$	−0.257
Zn(II)	$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$	−0.762
Pb(II)	$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$	−0.126

2.1. Chromium

Chromium is widely found in the textile, electroplating, metallurgy, and pharmaceutical industrial sectors. Chromium is usually present as Cr(VI) and Cr(III). Cr(VI) is more water-soluble at a broad pH range, and it is a more dangerous and carcinogenic form than Cr(III). Cr(III) can form hydroxide precipitation at the appropriate pH range and be removed from water. Therefore, reducing Cr(VI) in wastewater to Cr(III) is a common detoxification mechanism [21].

Tandukar et al. [22] treated chromium-containing wastewater in an MFC with a biocathode, and they found that when the Cr(VI) concentration was below 80 mg/L, the Cr(VI) reduction rate was fast because a high Cr(VI) concentration may harm the bacteria on the cathode. The maximum Cr(VI) reduction rate was 0.46 mg Cr(VI)/g·h on the biocathode and the maximum power density was 55.5 mW/m². Huang [23,24] studied Cr(VI) reduction on different carbon-based cathodes in a tubular MFC and found that when using a biological cathode with a low set potential, Cr(VI) could be quickly removed from the polluted environment by electrical and biological adsorption. The synergetic effect can improve the performance for Cr(VI) reduction compared with the traditional electrochemical reduction method. The above research indicated that a biocathode was effective in Cr(VI) reduction under low concentrations. Thus, the bacteria on the cathode are very important to improve performance. Romo et al. studied the microbe diversity on the biocathode and found an efficient microbe for Cr(VI) reduction, and the Cr(VI) removal rate could reach 97.8% [25]. These microbes can also be used in the bioremediation of Cr(VI)-contaminated soil and water. Zhao et al. constructed a biocathode inoculated with corynebacterium LZU47-1 in an MFC for Cr(VI) removal [26]. The Cr(VI) removal rate could reach 98.6% due to the large surface area, high electric conductivity, and high electron transfer rate of the biocathode. Besides an effective biocathode, other cathode materials and anode materials were also investigated to improve the Cr(VI)-MFC performance. Gupta et al. [27] prepared a cathode by using composites of Al₂O₃/Ni nanoparticles and carbon nanofiber, with good conductivity and adsorption capability. Thus, Cr(VI) can be almost completely removed in MFCs with a composite cathode.

The substrates for bioanodes are also an important factor in the MFCs for Cr(VI) removal. Substrates for bioanodes with a lower oxidation potential will generate a higher cell voltage in MFCs. However, the MFCs' performance is affected by the substrates' metabolism on the bioanode. To date, substrates widely used in MFCs include glucose, acetate, and organic wastewater. Zhao et al. [28] constructed a dual-chamber microbial fuel cell with glucose solution in the anode chamber and chromium-containing wastewater in the cathode chamber. In this glucose substrate MFC, the maximum power output was 108 mW/m² and the Cr(VI) removal rate was 92.8% after 10 h. The experimental results showed that a low catholyte pH and high initial Cr(VI) concentration can improve the electrical production performance of MFCs. Carboxymethyl cellulose was also used as the substrate for a bioanode in an MFC, and Cr(VI) could be reduced to less toxic Cr(III) with 95.2 ± 2.7% of Cr(VI) removal rate [29].

In addition, MFCs were used to simultaneously remove Cr(VI) and Cr(III) [30]. The principle is to use the energy generated from Cr(VI) reduction in the Cr(VI)-MFC to drive Cr(III) reduction in another Cr(III)-MFC, because Cr(III) reduction generally needs an external energy input. It was found that Cr(VI) removal could reach 99.9%, while Cr(III) removal could reach 82%, when a Cr(VI)/Cr(III) ratio of 2 was used.

2.2. Vanadium

Vanadium is a trace element in organisms and has wide application in various industrial sectors, such as vanadium alloys, chemical synthesis, ceramic coloring, etc. Vanadium-contaminated water is usually discharged from industrial application sectors, mining, and V₂O₅ production. Pentavalent vanadium (V(V)) is the most toxic form of vanadium; when its concentration exceeds 1–10 µg/L, it will be harmful to animals and plants. Meanwhile, tetravalent vanadium (V(IV)) is less toxic and is insoluble in neutral and alkaline

water [31]. For V(V)-contaminated water treatment, researchers usually reduce V(V) to a V(IV) precipitate to reduce vanadium's pollution and toxicity.

With the development of MFCs, many papers have been published on the use of V(V) as an electron acceptor in MFCs, as a new vanadium wastewater treatment technology to recover electricity. In some of these studies, dual-chamber MFCs were employed and over 70% V(V) could be reduced in the cathode chamber, with an electricity of over 600 mW/m² produced [32,33]. In this type of MFC, because the cathode and anode were separated by a membrane, a high concentration of V(V) caused little harm to the bacteria on the anode, and the electricity production was higher under a higher V(V) concentration due to the thermal dynamics. However, some researchers also used single-chamber MFCs to treat vanadium-polluted wastewater. In single-chamber MFCs, V(V) may cause harm to the bacteria on the anode and a high V concentration cannot be applied. In addition, the V(V) may directly accept electrons from the anode, and this may cause a decrease in electricity generation. Hao et al. used a single-chamber MFC to treat vanadium-polluted wastewater, and found that the V(V) removal rate reached of 77.6% with acetate as the anode substrate [34]. Even in dual-chamber MFCs with biocathodes, harm to cathodic bacteria was also noted when the vanadium concentration was high [35,36]. However, a biocathode may enhance the charge transfer, which may facilitate vanadium removal under low concentrations. As V and Cr usually coexist in wastewater, Zhang et al. [37] investigated the simultaneous reduction of Cr(VI) and V(V) and found that Cr(VI) could enhance the V reduction, with higher treatment efficiency.

2.3. Cobalt

Cobalt is a rare metal with a content of 0.001% in the earth's crust, which mainly arises from the by-products of copper and nickel refinement. Cobalt can regulate or stimulate certain enzymes, and it is an essential element in processing vitamin B12. The content of cobalt in a lithium battery can reach 5–10% (*w/w*). However, Co(III) has a strong toxic effect on animals, plants, and human beings. Thus, wastewater containing cobalt has to be treated properly before its discharge.

MFCs have been employed in cobalt wastewater treatment recently, because Co(III) has a very high redox potential of +1.61 V, and it can function as a good electron acceptor to be reduced to Co(II). Dual-chamber MFCs were employed to leach Co from LiCoO₂ and it was found that Cu(II) addition could improve the Co leaching rate by over 3 times [38]. Huang et al. utilized a cathode with LiCoO₂ in MFCs and found that the Co leaching rate increased by 3.4 times compared to the chemical leaching method [39]. Moreover, cobalt existed as Co(II) rather than Co(III) in the leachate, indicating that Co(III) functioned as a good electron acceptor on the cathode. Huang et al. [40] further used both cobalt and oxygen as the electron acceptors in MFCs and found that oxygen can be reduced to OH[−] and OH[−] can further react with the produced Co(II) to form a Co(OH)₂ precipitate. They also optimized the operation parameters and found that when the dissolved oxygen concentration was 0.031 mg/L and the pH was 5.6, the cobalt removal and recovery efficiency were the highest, with a simultaneous electricity production of 1.5 W/m³.

2.4. Copper

In recent years, with the rapid development of industry, wastewater containing copper has been discharged in metallurgy, electroplating, circuit board printing, and other industries. At present, precipitation, chemical reduction, adsorption, flocculation, and other methods are usually used to treat industrial wastewater containing copper. However, these traditional methods are unable to recover copper directly and may also cause secondary pollution. MFCs can be used to treat this type of wastewater and recover copper resources and electricity. Heijne et al. directly used Cu(II) ions as the electron acceptors in a dual-chamber MFC, and copper could be directly recovered on the cathode under a pH of 3 [41]. Due to the separation between the cathode and anode chamber, the microbes' activity on the bioanode was not affected. Wang et al. [42] found that the addition of NO₃[−] and pH in the catholyte could

also affect the Cu(II) recovery performance due to their effects on copper crystal growth. The copper-reducing product was also affected by the anode substrate, because different substrates may possess different potential for copper reduction.

Generally, anode substrates with lower oxidation potential may favor the production of metal copper, while a higher oxidation potential may favor the production of Cu₂O. It was found that when excess sludge was used as the anode substrate, Cu(II) could be mainly reduced to metal copper, while, when the sludge loading was low, Cu(II) could be mainly reduced to Cu₂O [43]. When glucose was used as the anode substrate, Cu(II) could be reduced to metal copper completely, with a higher electrical power production [44]. For copper wastewater treatment using MFCs, besides the substrate, the electrode material and cell configuration also showed significant effects on the performance. For example, electrode modification may enhance the charge transfer efficiency [45]; a suitable volume ratio between the cathode and anode chamber may result in high COD removal efficiency and high Cu(II) reduction efficiency simultaneously, together with high coulombic efficiency [46,47].

The above-mentioned copper-polluted wastewater treatment in MFCs usually used a dual-chamber configuration. This configuration can prevent the possible toxicity of copper towards the microbes on the anode and gives a higher power output. Single-chamber MFCs also have been developed to treat wastewater containing copper and the copper concentration is usually as low as tens mg/L to avoid toxicity towards microbes [48]. In the single-chamber MFC, the microbe community can vary according to the Cu(II) concentration, and it was generally found that *proteus* and *bacteroides* were important for electricity generation, while *actinomyces* and *acidobacterium* were important for copper removal. Electrode modification by rGO can also enhance the electrode structure and electron transfer performance [49]. In addition, when using a carbonized clay cup as a cathode, the copper recovery and electricity generation could be greatly enhanced in a single-chamber MFC [50].

2.5. Silver and Gold

Silver is a precious metal that is widely used in industrial sectors and in jewelry making, and its recycling has been of concern. Wastewater containing silver usually comes from the electronics, jewelry, and photography industries. Silver ions in wastewater can be toxic towards animals and plants. MFCs have attracted much attention in recent years to treat wastewater containing silver.

Choi et al. recovered metal silver on a cathode from wastewater containing free silver ions, while organic wastewater was simultaneously treated on a bioanode in an MFC [51]. In this MFC, over 99% of silver ions were removed and recovered with a power output over 5 W/m². In addition, other types of silver ions, such as ammonia-chelated silver ions, thiosulfate-chelated silver ions, and cyanide-chelated silver ions [52], could also be recovered in such MFCs. However, chelated silver ions usually have a lower oxidation potential; thus, chelated silver ions, as electron acceptors, generate a lower power output in MFCs. When researchers characterized the recovered silver on the cathode, nanostructured silver particles were usually observed [53]. Nanostructured silver particles have shown more promising applications in catalysis, electronics, and sensors, etc. This may offer new opportunities to recover high-value nanoparticles through MFCs.

As one of the precious metals, the recovery of gold is of high economic value, and it has aroused widespread concern. Due to the high redox potential (1.002 V), Au (III) can be directly reduced to metal gold on the MFC's cathode. Choi et al. reported the reduction of Au(III) to metal gold on an MFC's cathode by using chloroauric acid as a gold source and electron acceptor [54]. They found that almost all the gold ions could be reduced to metal gold, with electricity produced. In some cases, nanostructured gold can also be produced, and the generated gold nanoparticles can function as catalysts for other reactions [55].

3. MFC–MEC Coupling System

In the treatment of metal-polluted wastewater, some metal ions, as shown in Table 1, have high redox potentials, and can be used as electron acceptors of an MFC cathode to drive the reaction to occur spontaneously and generate electric energy. However, for metal ions with low redox potential (such as Pb(II), Ni(II), Zn(II) etc.), their redox potentials are low, and the reaction cannot occur spontaneously. A bias voltage is usually required to reduce and remove them on the cathode of the microbial electrochemical systems, named the microbial electrolysis cell (MEC). Till now, MECs can be used to reduce metal ions including Zn(II), Pb(II), and Ni(II) [56,57] by applying external voltage. Since MEC operation requires a bias voltage, the electricity generated by a MFC can be used to drive an MEC. Thus, an MFC–MEC coupling system, which uses the voltage generated from an MFC to drive the reactions in an MEC, can be built to remove metal ions with high redox potential from MFC and to remove metal ions with low redox potential from MEC, respectively. Thus, the coupling system has the advantages of in situ utilization of the electricity from the MFC and accelerating the metal ions' reduction without an external electricity input [58]. In the MFC–MEC coupling system, the MFC's bioanode is usually connected with the MEC's cathode, while the MFC's cathode is usually connected with the MEC's anode, as shown in Figure 3.

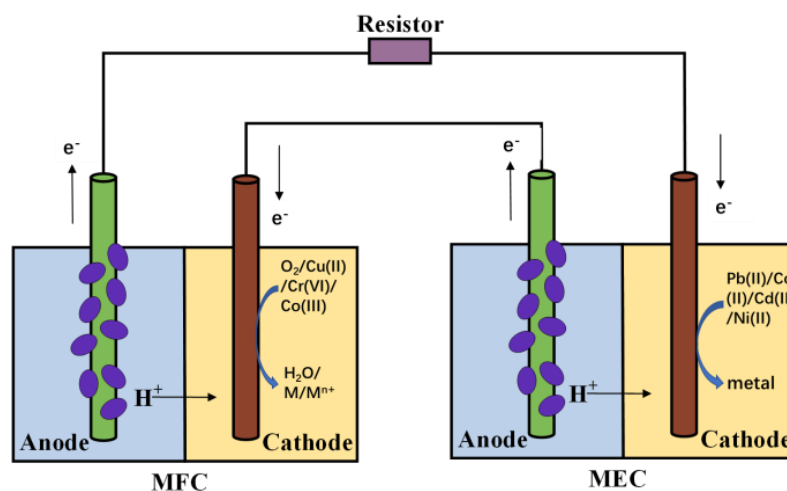


Figure 3. The illustration of the MFC–MEC coupling system.

In this MFC–MEC coupling system, the species including metal ions and oxygen with higher oxidation potential are usually processed in the MFC, while the metal ions with a lower oxidation potential are usually treated in the MEC. Both the MFC and MEC can employ metal ions as the electron acceptors. Luo et al. constructed an MFC–MEC coupling system, in which the MFC was used to reduce Cu(II) and generate a bias voltage, and the bias voltage was applied directly to the MEC to reduce Ni(II) [59]. In Luo's system, wastewater containing copper and wastewater containing nickel could be simultaneously treated, with efficient copper and nickel recovery, respectively. Huang et al. constructed an MFC–MEC coupling system to recover cobalt [60]. The MFC was used to reduce Co(III) to Co(II) with bias voltage generation, while the MEC was used to further reduce Co(II) to metal cobalt. Thus, in this MFC–MEC coupling system, Co(III) in LiCoO₂ can be recovered as metal cobalt, and this system is promising for lithium battery recycling. Similar configurations were also constructed to treat wastewater containing Cu(II)/Co(II) [61], Cr(VI)/Cu(II)/Cd(II) [62], Cu(II)/Co(II)/Li(I) [63], Cu(II)/Cd(II) [64], and Cr(VI)/Pb(II) [65,66]. In these studies, the reaction conditions and cathode materials could be optimized to improve the coupling systems' performance. In addition, there are also a few MFC–MEC coupling systems in which the MFC employs oxygen as an electron acceptor while the MEC employs heavy metal ions as the electron acceptor [67].

4. Photo Fuel Cells

In the above microbial electrochemical technologies, due to the microbes' metabolism, the system can only be operated under normal temperature and pH conditions. An overly low or high temperature or extreme pH may retard the microbes' activity and even damage the system. In addition, the microbes generally cannot tolerate the toxicity of high concentrations of metal ions and a membrane needs to be used to separate the metal-polluted wastewater from the microbes, which would inevitably cause high costs for the technology.

In PFCs, a photoelectrode is usually employed to utilize photo energy to drive the chemical reaction. The photo energy can help to overcome the thermal dynamic barrier of the chemical reaction. As shown in Figure 4, the anode loaded with semiconductor photocatalyst is inspired and generates electron-hole pairs under light illumination. The positive holes with strong oxidation power can decompose most of organic wastes on the anode, and photogenerated electrons are transferred to the cathode via an external circuit and thereby current is formed. By varying the electron acceptors, this PFC can be used to degrade organics, produce hydrogen, or recover metals from wastewater. Kaneko et al. [68] first proposed a PFC using TiO_2 as a photoanode, Pt as a cathode, and NH_3 as an electron donor. Under ultraviolet irradiation, the photodecomposition of NH_3 was achieved on the photoanode, and H_2 was generated on the cathode. This design is likely to provide alternative solutions to the global energy and environmental crisis. Liu et al. [69] proposed a multifunctional PFC to reduce Cr(VI) and oxidize methylene blue with electricity generation. In Liu's design, the photogenerated electrons were transferred to the cathode to reduce Cr(VI) ; thus, the electron hole separation on the photoanode could be accelerated, and the oxidation of organics by the holes could be enhanced. In 6 h, over 96.8% Cr(VI) and almost all methylene blue was removed with a 1 W/m^2 power output. The methylene blue removal efficiency is obviously higher than in the traditional photocatalysis process.

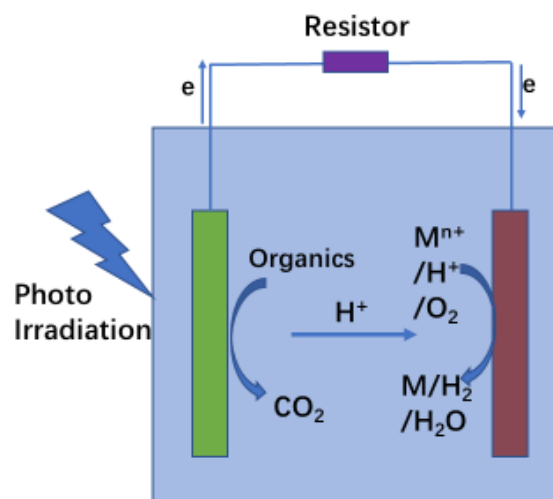


Figure 4. Principle for a photo fuel cell.

In order to further improve the PFCs' efficiency for metal-polluted wastewater treatment, researchers coupled the bioanode with the photo-cathode. Li et al. [70] introduced a photo-cathode into the microbial electrochemical reactor to build a photocatalytic microbial fuel cell. The anode was inoculated with anaerobic-activated sludge to cultivate exoelectrogens, and the cathode was composed of a TiO_2 photocatalyst. Potassium dichromate solution was used in the cathode chamber. After 26 h, over 97% Cr(VI) was reduced to Cr(III) , and the maximum current output was 235 mA/m^3 . The maximum output voltage under light was 0.80 V, which was higher than that under dark conditions (0.55 V). Moreover, the reduction rate of Cr(VI) under light was 1.6 times faster than that in the dark. In addition, they also compared the bioanode with an abiotic anode. They found that under

the same conditions, the bioanode could increase the Cr(VI) reduction rate by 5 times. The above comparisons indicated the synergetic effect of bioanode and photo-cathode coupling, and the coupling system can improve both wastewater treatment and electricity generation performance. A similar bioanode and photo-cathode coupling system was also employed to treat Cr(VI) and organics in wastewater [71]. In this configuration, with the exception of the Cr(VI) and oxygen reduction via the electrochemical process, the refractory organics can be degraded simultaneously on the photo-cathode by the photocatalytic process, as shown in Figure 5.

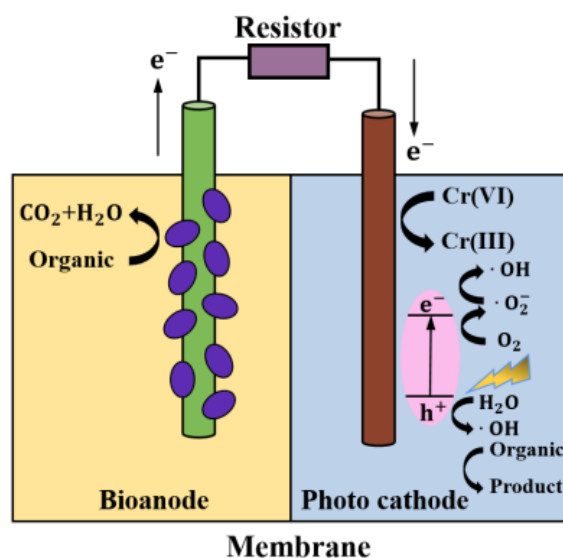


Figure 5. Bioanode coupling photo-cathode for organics oxidation and Cr(VI) reduction.

In short, the above bioanode and photo-cathode coupling system can utilize solar energy as an additional energy source to overcome the reaction's thermal dynamic barrier and achieve efficient power production spontaneously. However, one of the limitations of this coupling system is that the photo-cathode may be contaminated by the metal ion-reducing product. In addition, this coupling system is limited to biodegradable organic wastewater in the anode chamber due to the bioanode.

5. Coupled Redox Fuel Cells

In CRFCs, as shown in Figure 6, the substances with low oxidation potential will be oxidized on the anode to release electrons and protons, and the substances with high oxidation potential will be reduced on the cathode, thus converting the chemical energy in the fuel and oxidant into electrical energy. Usually, many organic pollutants in wastewater, such as urea, phenol, ethanol, and formaldehyde, have a low oxidation potential and can be used as fuels for CRFCs. O_2 , H_2O_2 , or metal ions in wastewater have a high oxidation potential and can be used as oxidants. Chemical energy contained in fuels and metal ions was directly converted to electricity via electrocatalyst instead of bacteria, thus avoiding the pH limitation. The power density achieved in coupled redox fuel cells usually surpassed that of MFCs. Xu et al. designed a urea-Cr(VI) CRFC to oxidize urea on a Ni/C anode [72]. Urea could be oxidized completely with a maximum power output of 3.4 W/m^2 , while Cr(VI) could be removed with a coulombic efficiency of over 98%. However, different fuels would need different anode catalysts. Zhang et al. [73] designed phenol-Cr(VI) and urea-Cr(VI) CRFCs, employing Pt/C as anode catalyst, and found that over 99% Cr(VI) could be removed together with phenol and urea degradation.

Methanol is widely used in traditional fuel cell technologies due to its high energy density, ease of handling, and safety. Furthermore, electrocatalysts for methanol oxidation are commercially available. Thus, the combination of methanol and metal ions has also been employed to construct coupled redox fuel cells. Zhang et al. [74] designed an alkaline

methanol fuel cell with Cr(VI) as the oxidant and over 96% Cr(VI) could be removed. When the current density was 2.3 A/m^2 , the power density reached 1.9 W/m^2 . Chen et al. [75] designed a methanol–Cr(VI) CRFC for Cr(VI) removal. Methanol could be oxidized on the anode and Cr(VI) could be reduced on the cathode efficiently. It was also found that the Cr(VI) removal efficiency and the power density output increased with the temperature. At 45°C , the maximum power output could reach as high as 903 W/m^2 , and the Cr(VI) removal rate could reach 91%. This research indicated the coupled redox fuel cells' applicability at higher temperatures.

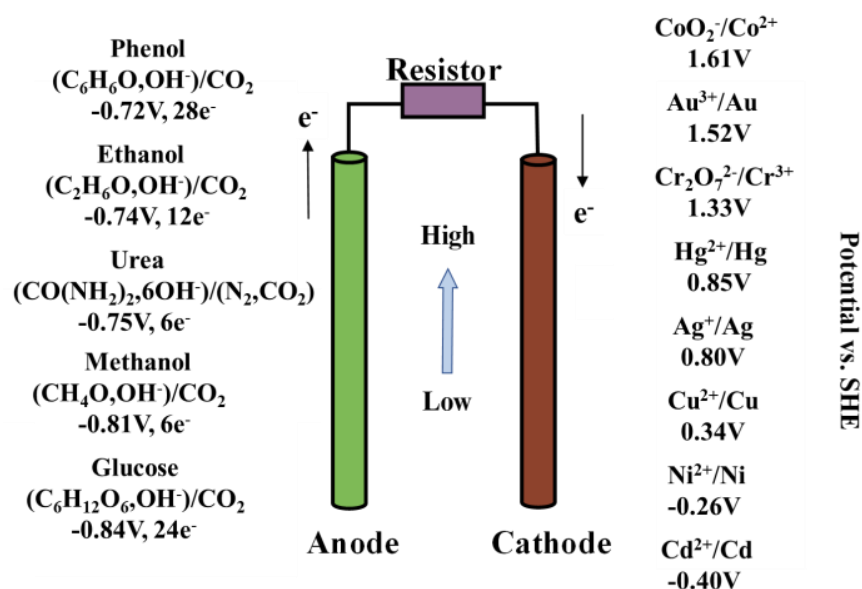


Figure 6. Typical pollutants' redox potentials and their possible combination in coupled redox fuel cells.

In CRFCs, due to its high oxidation potential and toxic properties in the environment, Cr(VI) was mostly studied. In addition, other metals with higher oxidation potential such as Au(III), Ag(I), Cu(II) and their chelated ions also showed promising recovery and electricity generation performance. Though the publications in this field are relatively in shortage, in order to compare the performance of different CRFCs, Table 2 was designed and the corresponding data were shown. From Table 2, it can be roughly seen that the metal removal efficiency and cathodic efficiency are usually high for different metals, though these data may vary by using different reaction times. In addition, the open-circuit voltage and the power output can be greatly varied by changing the reaction temperature, pH and metal ions because these reactions are thermodynamically affected by these parameters.

Table 2. Performance comparison of different CRFCs.

System	Power/W/m ²	Metal Removal/%	OCV/V	Cathodic Efficiency/%	Refs. No.
Phenol-Cr	0.18	99	1.06	>98	[76]
BPA-Cr	0.78	95	1.08	91	[77]
Urea-Cr	0.3	98.6	1.59	74.6	[78]
EtOH-Cr	1.9	96	1.46	63	[74]
MeOH-Ag	17.4	90	1.28	89	[79]
MeOH-Cr	903	91	1.70	/	[75]
Urine-Cr	3.4	90	1.30	98	[72]
EtOH-Au	1.6	96.2	1.4	/	[80]
EtOH-Cu	0.8	96.1	0.96	/	[80]
EtOH-[Ag(NH ₃) ₂] ⁺	0.6	45.7	0.95	/	[80]
EtOH-[Cu(NH ₃) ₄] ²⁺	0.5	55.8	0.92	/	[80]
NaBH ₄ -Cu	7.2	99.9	1.65	100	[81,82]

However, in the above CRFCs, an ion exchange membrane is usually needed to separate the anode and cathode chambers. After long-term operation, the fouling of the membrane and the penetration of metal ions into the anode chamber may arise. Thus, a high-quality ion exchange membrane is expected to be required for this technology's application. In addition, different fuels may need different anode catalysts; the development of efficient anode catalysts for specific organics such as phenol and BPA is another challenge.

6. Conclusions

It is promising to recover metal resources and electricity from metal-polluted wastewater treatment, especially under the present fossil fuel energy crisis and environmental pressure. In this review, the principles involved in recovering metals and electricity from metal-polluted wastewater treatment via microbial fuel cells, photo fuel cells, coupled redox fuel cells, and their couplings were elaborated.

These technologies have led to significant research progress at the laboratory scale in recent years. However, these studies have also faced different challenges. For microbial electrochemical technologies, bacteria with a high activity and durability to temperature and pH variations create challenges. For CRFCs, the acquisition of an active and stable catalyst for various organic pollutants causes great challenges. For PFCs, the low light transmission efficiency of wastewater may be a challenge. In general, these technologies usually employ artificial wastewater; their applicability and long-term durability for real wastewater need to be confirmed with further research efforts. These technologies' costs are relatively higher because expensive membranes and catalysts are usually needed, and this high cost would inevitably slow down their development. These technologies' characteristics determined their limitations and applicability for different wastewater conditions.

With the development of molecular biology and materials science, research in catalysts, ion exchange membranes, microbes screening, and structural design are expected to advance rapidly and further promote these promising technologies' development. Their applications under proper conditions for metals recovery and wastewater treatment are believed to be very promising.

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