Review

Synchronous Cr(VI) Remediation and Energy Production Using Microbial Fuel Cell from a Subsurface Environment: A Review

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Abstract: Applying microbial fuel cell (MFC) technology for eco-remediation of Cr(VI) pollution from a subsurface environment has great scientific value and practical significance due to its promising advantages of pollutant remediation and renewable energy generation. The aim of the current review is to summarize the migration characteristics of Cr(VI) in a subsurface soil/water environment and investigate the factors affecting the MFC performance for synchronous Cr(VI) remediation and power generation, and sequentially highlight diverse challenges of MFC technology for in situ remediation of subsurface groundwater and soils. The critical review put forward that Cr(VI) removal efficiency and energy production of MFC can be improved by enhancing the adjustability of cathode pH, setting potential, modifying electrode, and incorporating other technologies into MFC. It was recommended that designing typical large-scale, long-term continuous flow MFC systems, adding electron shuttle media or constructing artificial electron according to actual groundwater/soil and Cr(VI) pollution characteristics, site geology, and the hydrogeology condition (hydrochemical conditions, colloid type, and medium) are essential to overcome the limitations of the small size of the laboratory experiments and improve the application of technology to in situ Cr(VI) remediation. This review provided reference and ideas for future research of MFC-mediated onsite Cr(VI) remediation.

Keywords: microbial fuel cell; hexavalent chromium; subsurface environment; remediation; energy production

1. Introduction

The existence of hexavalent chromium Cr(VI) in waste water and soil has caused serious environmental and health issues. Occurrences of Cr(VI) in the environment can be distinguished in two major sources, i.e., natural sources and man-made sources. Natural sources are mainly the weathering of bedrocks due to water-rock interactions [1], while man-made sources are the legacy of human activities. As one of the most widely used metals in the industry, Cr has been released from leather tanning, electroplating, paint manufacturing, and some other industries [2]. Due to its non-biodegradability, Cr(VI) can remain persistent in the environment for a long time and accumulate in the food chain through contaminated subsurface environments, which eventually threaten human health as well as the environment and ecology [3]. Therefore, the United States Environmental Protection Agency (US EPA) stipulated that the maximum limit of Cr (VI) concentration in drinking water and discharged wastewater cannot exceed 0.05 mg/L and 0.5 mg/L, respectively [4]. Thus, the effective removal of Cr(VI) from the subsurface environment has attracted extensive attention from both eco-environmental regulators and academia worldwide. Compared with other valence states of Cr, Cr(VI) and Cr(III) are relatively stable, and Cr(III) generally exists as precipitates in the environment [5] with lower toxicity.
and mobility than Cr(VI). It remains an indispensable trace element for some functional cells Cr(III) participates in the glucose/oil metabolism in the organism [6]. Hence, converting Cr(VI) to Cr(III) is a reliable way to remediate Cr(VI) pollution in the environment. Considering the nature of subsurface and linkages between Cr(VI) and drinking water sources, the in situ biological/ecological remediation of Cr(VI) remains crucial.

At present, Cr(VI) remediation strategies including solidification [7], stabilization [8], phytoremediation [9], bioremediation [10], elution [11, 12], and electric remediation [13] are widely studied. These traditional remediation methods have some disadvantages relating to higher energy consumption and costs, as well as incomplete removal of pollutants. The introduction of chemical reagents can also cause secondary pollution and excessive sludge formation. Thus, the application of these previous technologies has been severely limited. Compared with the above conventional remediation methods, the unique advantage of simultaneously generating electricity and Cr(VI) removal in microbial fuel cell (MFC) technology has attracted the attention of many researchers [14]. Research on MFC to generate electricity can be traced back to the beginning of the 20th century, however Logan [15] firstly used MFC in water pollution treatment and successfully achieved the removal of organic pollutants and energy production. The system had a removal efficiency of 60% for COD and a power density of 26 mW/m² [15]. Similarly, a large number of studies have shown that MFC can also effectively remove heavy metal pollution in the subsurface environment. Among them, the remediation of Cr(VI) has received widespread attention. Tandukar et al. [16] first applied the dual-chamber MFC for the remediation of Cr(VI) polluted wastewater. The complete removal of Cr(VI) was achieved after operating 300 h and the maximum power reached 55.5 mW/m², where Cr(VI) existed in the form of Cr(OH)₃ precipitates. Microbes decomposed the inorganic and organic components in the anode and generated electrons transferred to the cathode through the external circuit, which reduced the Cr(VI) into Cr(III) and generated electricity. These findings proved that MFC can effectively remove Cr(VI) and produce energy through bioelectrochemical reduction [16]. Thus it is essential to develop MFC as a method of ecological remediation of Cr(VI) in subsurface environments.

Bioelectrochemical active bacteria, such as Aeromonas, Pseudomonas, and Thiomonas, metabolize substrate in the anode to generate electrons that are transferred to the cathode through the external circuit, thus promoting the cathodic reduction of the target electron receptor [17]. Sindhuja et al. [18] found that when cow dung was used as the main component of the anode in MFC, Geobacter Metallofordii became the dominant population and Cr(VI) was completely reduced after 10 days. Moreover, researchers have found that abiotic electrodes can effectively reduce the operating cost of Cr(VI) pollution remediation technology. Gupta et al. used transition metal aluminum (Al)/Nickel (Ni) and carbon nanofibers to prepare electrodes with high conductivity and the enhanced catalytic reduction of Cr(VI) [19]. Some studies have shown that when the α-Fe₂O₃ modified polyaniline nanocomposite electrode was utilized as a cathode, the power density of the MFC system increased by 1.75 times [20]. At the same time, electrode potential also had a significant impact on the Cr(VI) reduction process. Huang et al. [21] found that the reduction performance of Cr(VI)and electricity generation efficiency can be effectively improved when the potential of the biological cathode is set at −300 mV. Therefore, an optimized design of MFC electrodes for Cr(VI) contaminated sites is the core issue in both the scientific and engineering field.

Cr(VI) pollution is a typical and intractable pollution problem for the subsurface environment. Subsurface environmental conditions also affect Cr(VI) reduction and power generation in the MFC system. Results show that acidic conditions are more conducive to the reduction of Cr(VI) in MFC. Li et al. [22] found that the removal efficiency of Cr(VI) reach up to 99.5% under the pH condition of 2, and the power generation was 1600 mW/m². Huang et al. [23] found that when pH conditions changed from alkaline (pH = 8.0) to weak acidic (pH = 5.0), the reduction efficiency of Cr(VI) increased from 21.2% to 27.3%, and the electricity generation efficiency was also increased from 6.0% to 89.8%.
Similarly, the temperature can directly influence the performance of MFC by encouraging the growth of the anodic community at optimized conditions. It was suggested that the temperature range of 25–30 °C in the system was the most suitable for the growth and metabolism of most microorganisms, and a high Cr(VI) removal efficiency was achieved at the same time [24]. Oxygen (O₂) is an essential element for the growth and metabolism of aerobic microorganisms, however it has a negative impact on anaerobic microorganisms in MFC. In the cathode region, O₂ and Cr(VI) form a competitive relationship to inhibit the reduction of Cr(VI) [25]. However, some heterotrophic microorganisms can decompose part of organic matter in the presence of O₂ and improve the reduction efficiency of Cr(VI) in the cathode chamber [9]. Therefore, oxygen content can affect the growth activity of microorganisms and thus, have a non-directional effect on the remediation efficiency of Cr(VI) pollution. Therefore, it is necessary to carry out targeted research in different characteristic environmental conditions of the sites, to ensure the effective application of MFC at Cr(VI) contaminated soil and groundwater.

In summary, remediation of Cr(VI) using MFC has been tackled in a few studies that produced some preliminary achievement. However, there is still a lack of systematic, in-depth analysis and comprehensive effort based upon current experience on Cr(VI) remediation for subsurface environments using MFC. The effective mechanism of different influencing factors on remediation efficiency, and the practical application of MFC in different contaminated sites are still timely needed. Considering the demand for efficient and cost-effective eco-remediation technology for Cr(VI) polluted water and soil under the worldwide commitment to the overall aims of peak carbon dioxide emissions and carbon neutrality, this paper systematically reviewed the state-of-art experience of using MFC for eco-remediation of Cr(VI) pollution and the dominant factors influencing the MFC performance on Cr(VI) removal, based upon a review summary of the migration and transformation of Cr(VI) in a subsurface environment. From the understanding of the above critical reviews, a few points of scientific research gaps and potential focuses for engineering problems in the field of eco-remediation of Cr(VI) contaminated subsurface environment by MFC were proposed and possible future research direction toward innovative technology were prospected. It is anticipated that the current review will effectively promote the research and development of efficient and cost-effective technologies for increased practical applications of MFC-mediated remediation for synchronous Cr(VI) cleanup and new energy production for contaminated lands.

2. Characteristics of Cr(VI) and the Law of Migration and Transformation

In the 21st century, Cr is the most abundant element in the earth’s crust, with an average content of about 100 mg/kg in rocks [26]. Cr usually exists in the form of trivalent or hexavalent. Cr(OH)₃ and minerals containing Cr(III) widely exist in soil and show a strong complexion ability and low solubility [27] while, Cr(VI) has the feature of high solubility, high mobility, high toxicity, significant genotoxicity, and carcinogenesis [28]. Many studies have revealed that inducing free radical generation and leading to DNA damage might be the carcinogenic mechanism of Cr(VI) [29]. The morphology of Cr(VI) is also related to the pH of the solution. When the pH is between 2 and 6, Cr(VI) mainly exists as HCrO₄⁻ and Cr₂O₇²⁻ ions, while that exists in the form of CrO₄²⁻ when pH is higher than 6 [30]. The toxicity of Cr(VI) is about 100 times higher than that of Cr(III), so the reduction of Cr(VI) to Cr(III) and immobilization of Cr(VI) are common methods for the remediation of Cr(VI) contamination.

The biogeochemical cycle of Cr(VI) is determined by its chemical redox transformation, adsorption and desorption, dissolution, and precipitation [31]. When Cr(VI) enters into the soil and water, the adsorption effect of soil particles in the infiltration process can inhibit the migration of Cr(VI), and the metal oxides such as Fe(III) in soil and media show a good adsorption capacity for Cr(VI) [32]. After entering the groundwater environment, Cr(VI) can be naturally reduced by Fe(II), minerals containing Fe(II), sulfur, organic compounds, and anaerobic and aerobic microorganisms, and then achieve the immobilization
of Cr(VI) [33–35]. The detoxification mechanism of Cr(VI) by microorganisms mainly includes the following four aspects [36]: (1) Cr(VI) directly gains electrons by consuming biodegradable organic matter; (2) adsorption of Cr(VI) by microbial extracellular polymeric substances (EPS); (3) in microbial cells, Cr(VI) penetrates the cell membrane and enters into the cytoplasm, where Cr(VI) is reduced by chromate reductase, or binds to metallothionein and accumulates in the cell; and (4) Cr(VI) is reduced through the redox medium of microbial exogenous nutrients. Some reasons, including the fluidity of water, the presence of colloid in groundwater, the negatively charged characteristics of soil particles, and the existence of other competitive anions, result in the reducing adsorption rate of Cr(VI) and the higher mobility of Cr(VI) [37–39]. Based on a large amount of data, the migration and transformation rules and transfer paths of Cr(VI) in a subsurface environment are summarized as follows, as shown in the conceptual model in Figure 1.

Figure 1. Conceptual model of Cr(VI) migration and transformation: (a) 3D diagram and ecological effects, and (b) pathways of transformation in a subsurface environment.
3. Mechanism of Cr(VI) Reduction and Synchronous Energy Productivity in MFC

3.1. Bioelectrochemical Reduction of Cr(VI)

Bioelectrochemical reduction of Cr(VI) using MFC has been proven to be a feasible approach. For the first time, Wang et al. [40] used synthetic wastewater containing Cr(VI) as a catholyte electron acceptor and anaerobic microorganisms as an anode biocatalyst. In 150 h, Cr(VI) with an initial concentration of 200 mg/L was completely removed, and the maximum power density produced was 150 mW/m². Aiyer et al. [41] found that Cr(VI) was reduced at the cathode by obtaining electrons using a two-compartment MFC, with the highest reduction rate compared with Cu(II) and V(IV) under the same concentration. Some studies have shown that more than 60% of Cr(VI) can be directly reduced by obtaining electrons at the cathode [42], which proves that bioelectrochemical reduction is the key process of Cr(VI) removal by MFC. The study found that some microorganisms evolved over billions of years to complete the electron transfer by exchanging electrons with insoluble minerals or related natural extracellular electron receptors [43]. This outstanding feature promotes the development of MFCs. The extracellular transport of electrons to electrodes takes place in three different ways, including a direct way (within nanowire and redox active proteins) and indirect way (by electron mediator), which is illustrated in Figure 2 [44]. In the bioelectrochemical reduction of Cr(VI), the interaction between the abiotic cathode and biological cathode determines the mode and routes of electron transfer, which has been widely studied [45]. The most important characteristic of abiotic cathodes is the conduction of electrons that are produced from the oxidization of organic matter by anodic microorganisms through the electrode surface [46], which achieved the conversion from chemical energy to electric energy as well as the simultaneous removal of Cr(VI). By summarizing previous results, we draw the abiotic cathode mechanism in Figure 3a [16,42,47]. However, the traditional MFC with abiotic cathode has some problems such as difficult chemical regeneration, demand for platinum and other precious metals catalysts, as well as a high cost. The results show that a biological cathode can overcome these defects due to microorganisms participating in the cathode reactive process [48]. Moreover, the accumulated bacteria can promote electron transfer and decrease the charge transfer resistance [49], along with increasing reduction efficiency. Biological cathode uses microorganisms as the catalyst to transfer electrons towards the electron acceptor through an external circuit [21] and By summarizing previous results, its mechanism is shown in Figure 3b [16,42,47]. Tandukar et al. [16] used a biological cathode MFC for the first time for Cr(VI) remediation. They found that the removal rate of Cr(VI) was significantly increased in the presence of microorganisms in the cathode, hence proving that the catalytic action of cathodic microorganisms for effective Cr(VI) reduction in MFC. Studies have also shown that bacillusin cathode can significantly improve the reduction performance of Cr(VI) in both autotrophic and heterotrophic environments [47].

![Figure 2](image_url)

Figure 2. Three ways of electron reaching the electrode: (a) indirect electron transport by electron mediator; (b) direct electron transport within redox active proteins; and (c) direct electron transport within nanowire.
3.2. Other Reduction Mechanisms of Cr in MFC

Due to the presence of other substances and organisms in the MFC system, the bioelectrochemical reduction of Cr(VI) is not the only mechanism involved. Adsorption by electrodes and bacteria could also be the alternate pathways for Cr removal in the cathode chamber [42]. Wu et al. [47] used a graphite carbon stick as an abiotic MFC cathode to reduce Cr(VI), and found that Cr(VI) was reduced to Cr(III). Finally, part of Cr(III) was adsorbed on a graphite carbon stick cathode after reaction. Habiul et al. [42,50] found that the absorption by plants Pennisetum and reed could remove approximately 13% to 23% of Cr(VI) in the system by comparing MFC without a plant. In addition, the removal rate of Cr(VI) in a plant-microbial fuel cell (PMFC) system with Pennsylvania was higher than that in a phragmites communis PMFC system because transport factors in plants absorbed Cr(VI) and then transferred it to stems, leaves, and the entire plant [51].

3.3. Energy Conversion

MFC can be regarded as a primary battery. The Gibbs free energy is negative in the MFC redox reaction, so the reaction can be carried out spontaneously and the electromotive force can be converted into battery voltage ($\Delta E^0$). $\Delta E^0$ is shown in Equation (1). The potential difference between the anode and cathode ($\Delta E_{cell}^0$) determines whether the system can generate electricity (Equation (2)). Negative free energy and positive electromotive force determine that MFCs can undergo redox reactions and generate electrical energy [52].

$$\Delta E^0 = - \left[ \sum v_i \Delta G_p^0 - \sum v_i \Delta G_r^0 \right] / nF = - \frac{\Delta G}{nF}$$ (1)

$$\Delta E_{cell}^0 = \Delta E_\text{cathode}^0 - \Delta E_\text{anode}^0$$ (2)

where the $\Delta G$ value represents the free energies (J/mol) ($\Delta G_p^0$ represents the free energies of products and $\Delta G_r^0$ represents the free energy of reactants), $F$ is Faraday’s constant (96,485.3 C/mol), and $v$ represents stoichiometry factors of the redox reaction.

For instance, MFCs can treat acidic wastewater and generate spontaneous electricity due to two major mechanisms: (1) The Gibbs free energy of the reaction being negative and (2) the electromotive force being positive [53,54]:

$$C_2H_4O_2 + 2O_2 \rightarrow 2CO_2 + 2H_2O \Delta G^0 = -893.6 \text{ KJ/mol}$$ (3)

$$C_2H_4O_2 + 2H_2O - 8e^- \rightarrow 2CO_2 + 8H^+ \Delta E_{anode}^0 = -0.29 \text{ V}$$ (4)

$$O_2 + 4H^+ + 2e^- \rightarrow 2H_2O \Delta E_{cathode}^0 = 1.23 \text{ V}$$ (5)
\[ \Delta G^0 = -893.6 \text{ KJ/mol} < 0 \Delta E^0_{\text{anode}} - \Delta E^0_{\text{cathode}} = 1.52 \text{ V} > 0. \] (6)

The reaction of Cr(VI) is described as follows: [55].

\[ \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \Delta E^0_{\text{cathode}} = 1.33 \text{ V} \] (7)

\[ \text{Cr}^{6+} + 3e^- \rightarrow \text{Cr}^{3+} \Delta E^0_{\text{cathode}} = 1.09 \text{ V}. \] (8)

During the process of Cr(VI) removal, microorganisms also play an important role in the bioelectricity generation of the MFC system, which directly affects the electron transfer rate and power generation [56]. Microorganisms can obtain all the sources of energy and carbon from the oxidation of complex organic matter and use it for cell growth, for which the chemically inactive substrate is converted into a form that can be used for electrochemical oxidation, thus converting the chemical energy into electrical energy. During the oxidation of respiratory substrates, the released electrons are transmitted through the respiratory chain and transferred to externally available terminal electron receptors. The higher the redox potential of terminal electron receptors, the more energy that can be obtained by microorganisms [57]. Theoretically, MFC has the potential to produce unlimited electricity as long as the production conditions for anode-associated microorganisms remain favorable [43]. Cr(VI) has a higher oxidation potential (1.33 V) than other heavy metals and is a better oxidant than oxygen (1.23 V) [58], which can generate more power in the MFC system [41]. Therefore, when Cr(VI) is used as the target pollutant, it has certain advantages in pollution remediation and synchronous electricity generation for MFC. Preliminary studies show that the maximum power generation of Cr(VI) removal using MFC is 1600 mW/m². Owing to the optimization of process parameters and influencing factors, the power generation of the system is expected to be further improved in the future [59]. It is also predicted that Cr(VI)-contaminated wastewater can replace the commercially available catholyte, thus making MFC technology more sustainable and cost effective for practical applications.

4. Factors Influencing the Cr(VI) Remediation in MFC

4.1. Electrode Position and Potential

The electrode position in bioelectrochemical systems has a significant effect on the remediation potential of MFC. Zhou et al. [60] constructed MFC with different electrode positions to evaluate the performance of MFC on remediation and electricity generation. When the electrode distance was 2 cm, the internal resistance was low and conductivity was high. The maximum power density and Cr(VI) removal rate were 535.4 mW/m² and 0.91 g/m³ h, respectively. Mu and his coworkers investigated the effect of the electrode gap on the Cr (VI) removal performance of wetland MFC. It was observed that as the electrode spacing increased from 5 cm to 15 cm, the output voltage decreased and resistance was increased, and the results showed that the maximum power was obtained when the electrode distance is 10 cm. Although the electrode spacing of 5 cm had the minimum resistance to make the MFC system obtain higher power in theory, it would cause oxygen diffusion into the anode region, thus disturbing the anaerobic conditions where some electrons will be directly utilized by anodic microorganisms without passing through the external circuit [61]. The role of the electrode potential is also crucial for lowering the startup time and improving the performance of MFC. When the electrode potential was set around −300 mV in Cr(VI) remediation, the startup time was reduced by 19 days. Meanwhile, the reduction rate of Cr(VI) was increased up to 19.7 mg/L d and the maximum power density reached up to 6.4 W/m³ [21]. It could be inferred that setting the electrode potential can provide an appropriate condition for microbial adaptation, which may enhance the electrochemical interaction between microorganisms and electrodes, and sequentially improve current generation [62]. According to the existing literature, the limitation of the electrode location may affect the onsite remediation of Cr(VI) contaminated water. Therefore, this huge technological gap needs to be explored further for the development of basic research and technological breakthroughs.
4.2. Electrode Materials

Electrode material types and exposed surface area determine the microbial abundance and carrier of electron transfer thereby, playing a pivotal role in MFC operation. At present, the most commonly used electrode materials are traditional carbon materials, such as carbon cloth, graphite, etc. To further improve the performance, modification and optimization of electrode materials have received continuous attention. Li and his coworkers [63] prepared polypyrrole/sludge carbon electrodes by an electropolymerization loading method and used it as the MFC cathode. The maximum output power and Cr(VI) reduction rate of MFC was 760.7 mW/m$^2$ and 2.16 g/m$^3$ h, respectively, which were 2.79 and 1.51 times that of carbon cloth electrodes (272.5 mW/m$^2$ and 1.43 g/m$^3$ h). The electrochemical analysis found that polypyrrole/sludge carbon electrodes had a low charge transfer resistance. As an electron shuttle, pyrrole can reduce the internal resistance of electron transfer in the system and then significantly improve the power generation and Cr(VI) removal rate of MFC. Studies found that the maximum power density of graphene electrode MFC was 5.7 times that of graphite felt electrode. At the same time, the graphene electrode also effectively improved the reduction efficiency of Cr(VI), and the removal rate of Cr(VI) reached 100% within 48 h with the initial concentration of Cr at 40 mg/L. In contrast, the removal efficiency of Cr(VI) using graphite felt electrode was only 58.3%. Compared with graphite felt, graphene electrode has higher conductivity and microbial attachment sites to enhance the electron transfer rate, thus the MFC with graphene electrode has a higher Cr(VI) reduction rate and high power density [64]. Ali and his coworkers [65] found that the MFC with FeS@rGO nanocomposites (MFC-FeS@rGO) exhibited a 100% Cr(VI) removal efficiency for the concentration of 15 mg/L and also acquired a high reduction rate of 1.43 mg/L which was due to the high conductivity and low internal resistance of MFC-FeS@rGO [66]. Meanwhile, the FeS@rGO nanocomposite provided a larger electroactive surface area to improve the electron transfer [21].

The combination of light and MFC to improve the reduction rate of Cr(VI) and the electrode material has also been proved to be one of the important factors that affect photoelectric combination technology. When using natural molybdenite as raw material, TiO$_2$ nanocomposites modified with MoS$_2$ nanosheets could be prepared by a liquid phase stripping method combined with in situ hydrolysis. These materials were also first used as photocathodes for the reduction of Cr(VI) in MFC. Under visible light irradiation, the removal efficiency of Cr(VI) with the initial concentration of 20 mg/L reached 99.57% within 8 h. This could be due to the introduction of MoS$_2$ nanosheets as a cocatalyst that can expand the absorption of visible light, which can contribute to electron migration and increase the active site, thus promoting more electrons to participate in the Cr (VI) reduction process [67]. Ren et al. [68] designed silicon solar cells and constructed a dual-anode MFC system using a one-dimensional TiO$_2$/Fe$_2$O$_3$ photoanode and conventional biological anode. The maximum power density was 638.3 mW/m$^2$, almost 7.6 times that of ordinary MFC (84.2 mW/m$^2$). The removal efficiency of Cr(VI) at the concentration of 50 ppm was 90.9% within 13.5 h. The dual-anode MFC achieved efficient microbial oxidation and photocatalysis and enhanced the transfer of electrons to the external circuit. The electrons were driven by the built-in electric field in the silicon solar cell, during which the potential barrier of the system is simultaneously decomposed. The output power and Cr(VI) reduction efficiency was significantly improved. In conclusion, electrode modification and optimization can enhance the electron transfer rate and improve the Cr(VI) reduction efficiency. To compare the performance of different electrodes, the remediation and energy production effects of different electrode materials were shown in Table 1.
Table 1. Effect of different electrode materials on Cr(VI) remediation and energy generation.

| Electrode Materials | Cr(VI) Removal Rate (%) | Energy (mW/m²) | Operation Time (h) | Initial Concentration | Features | References |
|---------------------|-------------------------|----------------|-------------------|----------------------|----------|------------|
| Polypyrrole/sludge carbon electrodes | 0.50 g/m³ h | 760.7 | 1200 | 25 mg/L | A low charge transfer resistance | [63] |
| Graphene electrode | 100% | 163.8 | 48 | 40 mg/L | Higher conductivity and microbial attachment sites | [64] |
| FeS@rGO nanocomposites TiO₂ | 100% | 154 | 25 | 15 mg/L | More electroactive surface area | [66] |
| nanocomposites modified with MoS₂ nanosheets 1-D TiO₂/Fe₂O₃ photoanode | 99.57 | 140 | 8 | 20 mg/L | More absorption of visible light | [67] |
| TiO₂ nanocomposites modified with MoS₂ nanosheets | 90.9 | 6383 | 13.5 | 50 ppm | More electrons to the external circuit. | [68] |

4.3. Environmental Conditions of the Anode Chamber

Temperature is an important operating parameter for MFC. Yu et al. [69] found that Escherichia coli in the anodic area had the highest electrical activity at 37 °C compared with the other two MFCs working at 20 °C and 45 °C. Studies on MFC have shown that microorganisms play the best role at temperatures between 25–30 °C, while no obvious current was generated at temperatures below 15 °C, even if the start time is as long as a week [70]. Another limiting condition for the remediation of Cr(VI) is the oxygen content in the MFC system. Generally, anodes must maintain the anaerobic conditions. Otherwise, microorganisms oxidize organic matter by electron transfer via oxygen reduction rather than Cr reduction in the presence of oxygen. As the facultative anaerobes, Ochrobactrum sp. YC211 had a better capacity to remove Cr(VI) under anaerobic conditions than in aerobic conditions with more biological power generation using the MFC system. The maximum power density and Cr(VI) removal efficiency was 445 mW/m² and 97.2%, respectively. Removing Cr(VI) by Ochrobactrum sp. YC211 mainly occurred in the soluble part of cells during the anaerobic process, which could be considered as an enzymatic reaction [71]. However, studies have shown that strain KN400 can oxidize substrates and transfer electrons in the presence of oxygen at the anode, and the bioelectricity generation is comparable to that of anaerobic fuel cells [72]. In the PMFC system, photosynthesis of the plant generates oxygen through the roots and releases oxygen into the solution. However, in the presence of oxygen, some electrons released by bacteria are directly used for oxygen reduction, resulting in the decreased reduction rate of Cr(VI) [73]. Therefore, MFC possesses a better potential for Cr(VI) remediation in an anaerobic groundwater environment in a certain depth, which provides positive and optimistic support for in situ remediation of Cr(VI) using MFC-related technologies. In order to more intuitively compare the effects of different bacteria in MFC systems under different conditions, we summarized the remediation effect and energy production of Cr(VI) under different microbial species and environmental conditions in Table 2.

During the operation of the MFC system, substrates provide energy for microorganisms, and the remediation efficiency and productivity of MFC are also largely related to the composition of substrates and the extent of substrates utilization by microorganisms. Substrates that are easier to decompose by microorganisms can improve the activity of microorganisms and the rate of electrons production [74]. At present, many studies have investigated the effects of different substrates on the contaminants removal rate and electricity production. Tandukar et al. [16] took acetate as the substrate and found the complete removal of Cr(VI) with an initial concentration of 80 mg/L in 300 h, with the maximum power density reaching 55.5 mW/m². Some researchers also used glucose as an MFC substrate to remove Cr(VI), and the maximum power density was 6.67 W/m³ [75]. In addition, substrate formulations that can be better utilized by microorganisms also attract more attention. Wu et al. [76] used 0.31 g/L NH₄Cl, 2.452 g/L NaH₂PO₄·H₂O, 4.576 g/L Na₂HPO₄, 0.13 g/L KCl, and 1 g/L C₆H₁₂O₆·H₂O as substrates, and the removal rate of
Cr(VI) at the initial concentration of 20 mg/L reached 79.3%, 24 h later. Another study reported that the maximum power density of MFC with a specific substrate formulation in the anode chamber (KH₂PO₄ 4.4 g/L, K₂HPO₄ 3.4 g/L, NH₄Cl 1.5 g/L, NaCl 0.5 g/L, acetic acid 1.0 g/L, CaCl₂ 0.0146 g/L, NaHCO₃ 1.0 g/L, yeast extract 0.375 g/L, peptone 0.375 g/L) could reach 89.3 mW/m², and the removal rate of 4 mg/L Cr(VI) was 95% after 456 h for a reaction in MFC [77].

On the other hand, the hydrogeochemical background value of the contaminated site can affect the pollution remediation process. Most studies currently regard COD as the organic background field of Cr(VI) polluted water. Mu et al.'s study showed that the efficiency of Cr (VI) removal increased from 74.2% to 90.7% when the COD concentration in the anode area increased from 100 mg/L to 500 mg/L, and then gradually decreased with the further increase of the COD concentration. When the COD concentration reached 700 mg/L, the Cr(VI) removal rate decreased to 84.0% [61]. Microorganisms oxidize organic matter as their nutrient source and sequentially generate electrons. A higher substrate content contributes to the generation of higher electrical energy [78]. However, when the concentration of organic matter is too high, too much organic matter may lead to the accumulation of organic acids in bacterial cells, thus inhibiting the activity of microorganisms. Accumulating too much organic matter in the system is not conducive to the transfer of electrons and reduces the power generation as well [79].

Table 2. Removal rate and energy production of Cr(VI) under different bacteria type and environmental.

| Bacteria Type          | Cr initial Concentration | pH | Anode Inoculum                          | Temperature | Operation Time | Cr Removal Rate | Energy | Reference |
|------------------------|--------------------------|----|-----------------------------------------|-------------|----------------|----------------|--------|-----------|
| Anaerobic sludge       | 50 mg/L                  | 2  | -                                       | -           | 16 h           | 40%            | 141 µv | [80]      |
| Proteobacteria         | 19 mg/L                  | 7  | sodium acetate                          | 16 h light; 8 h dark | 100 d         | 99%            | -      | -         |
| Proteobacteria         | 200 mg/kg                | 6.86| 3.32 g/L NaH₂PO₄·2H₂O; 10.32 g/L Na₂HPO₄·12H₂O; 2.0 g/L CH₃COONa; 0.31 g/L NH₄Cl; 0.13 g/L KCl; 0.2 g/L MgSO₄·7H₂O; 15 mg/L CaCl₂; 20 mg/L MnSO₄·H₂O and 12.5 mL of trace elements solution. 1 g/L CH₃COONa; 0.31 g/L NH₄Cl. | -           | 16 d           | 62.70%          | 200 mA/m²² | [82] |
| Anaerobic sludge       | 1000 mg/kg               | 7  | -                                       | -           | 16 d           | 80%            | 140 mW/m²² | [41]      |
| Anaerobic sludge       | 1 g/L                    | 7  | 5.38 g/L NaH₂PO₄·H₂O; 8.66 g/L Na₂HPO₄·10H₂O; 0.13/L KCl; vitamin solution (12.5 mL) and trace mineral solution | -           | 8 d            | 80%            | 140 mW/m²² | [41]      |
| Anaerobic sludge       | 100 mg/L                 | 2  | CH₃COONa                                | -           | 10 h           | 99%            | 1.4 W/m²³ | [83]      |
| Anaerobic sludge       | 20 mg/L                  | 2  | -                                       | 33 °C       | 18 h           | 99.57%          | 140 mW/m²² | [84]      |
| Trichococcus pasteurii | 80 mg/L                  | 7  | 0.78 g/L NaCl; 0.58 g/L NaCl; 0.69 g/L CH₃COONa; 0.8 g/L K₂HPO₄; 0.1 g/L MgSO₄·7H₂O; 0.28 g/L NH₄Cl; 0.1 g/L CaCl₂·2H₂O | 22–24 °C    | 25 d           | -              | 5.5 mW/m²³ | [16]      |
| Anaerobic sludge       | 40 mg/L                  | 5  | -                                       | 22–50 °C    | 5 h            | 100%           | 7.2 W/m³ | [23]      |
| γ-Proteobacteria       | 20 mg/L                  | 7  | 0.3 g/L NaCl; 2.452 g/L NaH₂PO₄·H₂O; 4.576 g/L Na₂HPO₄·10H₂O; 0.13 g/L KCl; 1 g/L CaCl₂·2H₂O | 25 °C       | 30 d           | 79.30%          | 9.5 mW/m²³ | [76]     |
| Anaerobic sludge       | 60 mg/L                  | 6.5| -                                       | -           | 3 d            | 93.4%           | 414.4 mW/m³² | [61]      |

4.4. Role of Cathode Conditions in Cr(VI) Remediation

The concentration of Cr(VI) and the MFC performance is heavily interrelated, as a high concentration of contaminants up to a certain range will lead to high electricity generation [42]. However, many high concentrations are far from the concentrations of real wastewater or contaminated soils. Therefore, MFC studies could be exploratory for the in situ remediation of Cr(VI) in soils and waters. It has been reported that Cr(VI) can
be completely removed when the concentration of Cr(VI) was 20 mg/L in constructed wetland-microbial fuel cell (CW-MFC). When the Cr(VI) concentration in the influent increased to 60 mg/L, the removal efficiency of Cr(VI) was still above 90%, and then gradually decreased to 74.3% when the Cr(VI) concentration was further increased to 100 mg/L [61]. It can be seen that when the concentration of Cr(VI) is too high, Cr(VI) is toxic to cathodic microorganisms, which will inhibit the activity of microorganisms and hinder electricity generation. As mentioned above, chromium has different forms in different pH environments, and relevant studies have shown that the pH condition of the cathode is an important environmental factor affecting MFC performance. A higher concentration of Cr(VI) can be reduced when the pH value of the cathode is 2, indicating that the acidic environment favors Cr(VI) reduction [22]. Huang et al. also confirmed the pH dependence of the Cr(VI) reduction process. Compared with pH = 7, the reduction rate and power generation of Cr(VI) increased by 27.3% and 61.8%, respectively, in acidic conditions with the pH value of 5, and the reduction rate and power generation of Cr(VI) decreased by 21.2% and 6.0%, respectively, at alkaline pH = 8. The reason is that the microorganism’s catalysis increases the potential as pH decreases. On the other hand, in terms of chemical reactions on the basis of Equations (7) and (8), the reduction reaction of Cr(VI) is more easily carried out under acidic conditions [23].

4.5. Soil Properties and Media Types

Compared with the surface water environment, the vadose zone and soil involved in groundwater are more complex with multi-phase environmental media, and the environmental conditions of Cr(VI) contaminated soil would significantly affect the removal outcome of MFC. Although acidic conditions promote Cr(VI) reduction, it has been found that the ubiquitous red soil has a lower rate of Cr(VI) removal under the acidic condition due to the existence of more electron receptors (such as Fe(III)) in red soil. These electron receptors compete with Cr(VI) to inhibit the remediation of Cr(VI) [82]. Meanwhile, there is more clay in red soil, which is the inherent adsorbent [85], and its presence prevents Cr(VI) migration to the cathode surface. Another reason is that the clay soil with a smaller particle size has a lower removal rate of Cr(VI). The particle size of the soil medium would affect its pore size distribution. Wang et al. found that the larger the particle size of soil medium, the higher the relative abundance of electrochemically active bacteria, and the better the electricity generation and pollutant removal ability [86]. Mu et al. [61] successfully used the CW-MFC system to remove Cr(VI) from polluted water. The system was composed of a gravel layer (3 cm thick), bottom layer (14 cm thick), anode layer (8 cm thick), intermediate layer, cathode layer (8 cm thick), and top layer from bottom to top. The gravel layer (gravel with a diameter of 4.6 mm) was used to improve the distribution of wastewater in the system. The bottom, middle, and top layers were filled with volcanic slag with a diameter of 35 mm. The anode and cathode were made of granular activated carbon and 12-mesh stainless steel mesh (thickness: 4 cm, diameter: 16.9 cm). The stainless-steel net acted as an electron collector. The removal rate of Cr(VI) with the initial concentration of 60 mg/L reached 93% in the CW-MFC system, and the maximum power density was 458.2 mW/m². Due to the different electronic supply capacities of different soils and media, the remediation performance and electricity generation capacity will be significantly different. Yan et al. [84] showed that when quartz sand and pyrite were used as CW-MFC fillers, the pyrite filler with microbial activity showed a higher capacity for supplying electrons, while quartz sand anode filler could hardly give electrons. The results showed that the pyrite filler group had a better remediation ability. Therefore, the ability of soil and medium for giving and transporting electrons is critical to the efficiency of Cr(VI) reduction and productivity in MFC. However, the remediation of groundwater using MFC is rarely studied. It is urgent to study the types of aquifer media and the influence of groundwater flow fields on the MFC system, which is also a key research point to determine whether MFC technologies can be suitable for the environmentally friendly remediation of groundwater and soil environment.
5. Effect of MFC Design on Cr(VI) Soil and Water Pollution Remediation

Subsurface environments have their unique attributes and vary from site to site. Meanwhile, sediment and wetland environments are also complex. Therefore, people have researched different directions on MFC remediation technologies in different sites. Figure 4 is drawn by summarizing previous research results [42,68,80,87]. This figureshow some experimental device conceptual models for the study of remediating Cr(VI) pollution in a subsurface environment by MFC. Table 3 lists the effects of Cr(VI) remediation and energy recovery in the subsurface environment. This table comprehensively summarizes the application of MFC in a subsurface environment, which can provide a reference for future researchers.

![Figure 4](image-url)

**Figure 4.** Models of an MFC device for treating Cr(VI) in a subsurface environment: (a) removal of Cr(VI) from wastewater by conventional MFC (adapted from Li (2018)); (b) the MFC for Cr(VI) treatment in groundwater and soil (adapted from Zhang (2019)); (c) plant-enhanced MFC for Cr(VI) removal from soil and water (adapted from Habibul (2016)); (d) photoanode MFC for Cr(VI) removal from wastewater (adapted from Ren (2018)).

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**Table 3.** Removal rate of Cr(VI) and energy production in different MFC designing types.

| MFC Type       | Cr initial Concentration | Operation Time | Cr removal Rate | Energy | Reference |
|----------------|--------------------------|----------------|-----------------|--------|-----------|
| Absorption MFC | 50 mg/L                  | 16 h           | 40%             | 141 µv | [80]      |
| Plant MFC      | 19 mg/L                  | light, 8 h dark| 99%             | -      | [42]      |
| Plant MFC      | 200 mg/kg                | 100 d          | 90%             | 23.83 mW/m 2 | [81]      |
| Plant MFC      | 1000 mg/kg               | 16 d           | 62.70%          | 200 mA/m 2 | [82]      |
| Dual MFC       | 1 g/L                    | 8 d            | 80%             | 140 mW/m 2 | [41]      |
| Dual MFC       | 100 mg/L                 | 10 h           | 99%             | 1.4 W/m 2 | [83]      |
| Photoelectric anode MFC | 20 mg/L | 18 h            | 99.57%          | 140 mW/m 2 | [67]      |
| Photoelectric anode MFC | 50 ppm      | 13.5 h         | 90.90%          | 1302 mw/m 2 | [68]      |
| Dual MFC       | 10 mg/L                  | 11 h           | 100%            | 535.4 mW/m 2 | [60]      |
| Cu(III) dual MFC | 11.36 g/L | 8 h             | 51.64%          | 1235.53 mW/m2 | [88]      |
| Biological cathode MFC | 80 mg/L   | 25 d           | -               | 5.5 mW/m 2 | [16]      |
| Biological cathode MFC | 40 mg/L    | 5 h            | 100%            | 7.2 W/m 3 | [23]      |
| Biological cathode MFC | 20 mg/L    | 30 d           | 79.30%          | 9.5 mW/m 2 | [76]      |
| Biological cathode MFC | 0.4 mmol/L | 48 h          | 99.97%          | 6.8 W/m 3 | [48]      |
| Wetland MFC    | 60 mg/L                  | 3 d            | 93.4%           | 414.4 mW/m 3 | [61]      |
| Wetland MFC    | 300 µg/g                 | 70 d           | 68%             | 1.06 W/m 3 | [89]      |
| Photoelectrode MFC | 9 mg/L     | 2.5 d          | 90%             | -       | [90]      |

Note: "-" means no available data.
Table 3. Removal rate of Cr(VI) and energy production in different MFC designing types.

| MFC Type                | Cr Initial Concentration | Operation Time | Cr Removal Rate | Energy         | Reference |
|-------------------------|-------------------------|----------------|-----------------|----------------|-----------|
| Absorption MFC          | 50 mg/L                 | 16 h           | 40%             | 141 µW         | [80]      |
| Plant MFC               | 19 mg/L                 | 16 h light, 8 h dark | 99%             | -              | [42]      |
| Plant MFC               | 200 mg/kg               | 100 d          | 90%             | 23.83 mW/m²    | [81]      |
| Plant MFC               | 1000 mg/kg              | 16 d           | 62.70%          | 200 mA/m²      | [62]      |
| Dual MFC                | 1 g/L                   | 8 d            | 80%             | 140 mW/m²      | [41]      |
| Dual MFC                | 100 mg/L                | 10 h           | 99%             | 1.4 W/m²       | [83]      |
| Photoelectric anode MFC | 20 mg/L                 | 18 h           | 99.57%          | 140 mW/m²      | [67]      |
| Photoelectric anode MFC | 50 ppm                  | 13.5 h         | 90.90%          | 1302 mw/m²     | [68]      |
| Dual MFC                | 10 mg/L                 | 11 h           | 100%            | 535.4 mW/m²    | [60]      |
| Cu(III) dual MFC        | 11.36 g/L               | 8 h            | 51.64%          | 1235.53 mW/m²  | [88]      |
| Biological cathode MFC  | 80 mg/L                 | 25 d           | -               | 5.5 mW/m²      | [16]      |
| Biological cathode MFC  | 40 mg/L                 | 5 h            | 100%            | 7.2 W/m³       | [23]      |
| Biological cathode MFC  | 20 mg/L                 | 30 d           | 79.30%          | 9.5 mW/m²      | [76]      |
| Biological cathode MFC  | 0.4 mmol/L              | 48 h           | 99.97%          | 6.8 W/m³       | [48]      |
| Wetland MFC             | 60 mg/L                 | 3 d            | 93.4%           | 414.4 mW/m³    | [61]      |
| Wetland MFC             | 300 µg/g                | 70 d           | 68%             | 1.06 W/m³      | [89]      |
| Photoelectrode MFC      | 9 mg/L                  | 2.5 d          | 90%             | -              | [90]      |

Note: "-" means no available data.

5.1. Soil and Groundwater Pollution

Plant microbial fuel cells (PMFC) have been widely used for the remediation of Cr(VI) pollution in soil. The advantage of PMFC is that it is a coupling system that can produce organic matter and energy by itself. The characteristics of soil are also favorable to MFC operation. Soil with more nutrients has higher microbial biodiversity and more species that are conducive to organic matter degradation and electron transfer [91,92]. Habibul and his coworkers [42] constructed a PMFC for the remediation of Cr contamination in soil. The device consists of a plexiglass cylinder anode chamber (diameter of 110 mm, height of 170 mm, and working volume of 1 L) filled with 300 g of graphite particles as an anode, and the distance between cathode with the anode was 10 cm. Ryegrass was chosen as MFC plants with fast growth, large biomass, and dense rhizosphere. Ryegrass released secretions into the rhizosphere through photosynthesis, increasing microbial activity, thus improving the electron transfer efficiency and enhancing the bioelectrochemical reduction process. In addition, plant absorption, electrode adsorption, and direct reduction of Cr(VI) by cathodic bacteria play a synergistic role with bioelectrochemical reduction to increase the removal efficiency to 90%. Wang and his coworkers [81] constructed a single PMFC with a soil moisture content of 60% and cythra planted in the system. Finally, 90% of Cr(VI) was removed and the maximum power was 23.83 mW/m². The study found that both soil type and applied resistance would affect the Cr(VI) removal process. Wang et al. [82] found that the Cr(VI) removal efficiency of fluvo-aquic soil were 99.1% and 64.3% with the resistance of 100 Ω and 1000 Ω, respectively, while the Cr(VI) removal efficiency were 62.7% and 50.4% for red clay with a resistance of 100 Ω and 1000 Ω, and finally the maximum power density of this system was 200 mA/m². This result implies that low external resistance can improve remediation efficiency, and the soil medium type also has an important influence on the remediation. In addition, the researchers further improved Cr removal efficiency by adding different adsorption materials into the system. Zhang et al. [80] selected leaves, shell powder, and pine sawdust as the adsorption materials to investigate their adsorption ability for Cr. Finally, leaves with a better adsorption ability were selected as the adsorption material setting above the anode to isolate the contaminated soil from the anode. After running 16 h, the removal efficiency of Cr(VI) in the subsurface reached 96%. Chen et al. [93] built a sandbox to construct a two-compartment MFC and to study its performance in simulating a groundwater environment and found that MFC could be used for the remediation of actual groundwater environmental pollution. Lin et al. [94]
assembled a tubular MFC and inserted it into groundwater remediation well to achieve toluene removal and power generation under extreme matrix conditions, which became one of the effective reference methods for remediation of Cr(VI) pollution in groundwater. MFC systems have diverse applications for in situ remediation of groundwater contaminants, therefore future research directions must target pollutants of soil and water which are difficult to treat in conventional treatment methods.

5.2. Sediment and Wetland Pollution

Metals can be preserved in sediment easily [95], so remediation of sediment is particularly important. Wetlands have special rhizosphere bacteria and rhizosphere enzymes, and thus have a higher microbial activity for catalytic oxidation and reduction [96]. Sediment MFC can be applied to the field of organic high flux, such as deep river downstream. These areas can provide anaerobic conditions for the MFC system and wastewater has great potential in the field of environmental remediation. Razavi et al. [89] used CW-MFC to remove Cr from contaminated sediments, in which the maximum power density and Cr removal rate were 1.06 W/m³ and 68%, respectively. The results revealed that MFC technology has a high possibility to remediate Cr-contaminated sediments. He et al. [90] modified and used ZnIn₂S₄-AgAgCl/GO and ZnIn₂S₄-RGO/MnO₂ photoelectrode (PFC) to effectively remove Cr(VI) in sand and gravel sediments. Under the light, the photocatalyst was deposited on the photoelectrode to generate electrons, which can be used for the current generation and pollutant remediation. Protons entered the cathode chamber through the proton exchange membrane (PEM) to react with electrons and Cr(VI) ions in the cathode chamber. Cr(VI) acted as an electron acceptor and then was reduced to Cr(III) or further removal by the precipitation reaction. Mu et al. [61], used CW-MFC to treat Cr(VI) polluted water and generate power synchronously. Studies show that plants play an important role in the CW-MFC system. The carbon source of this system comes from a plant root exudate. More importantly, plant fibrous roots with a large specific surface area provides a large number of attachment sites for microorganisms. When electrode spacing was 10 cm, the concentration of Cr (VI) and COD in the influent were 60 mg/L and 500 mg/L, the highest power density was 458 mW/m³, and the removal rates of Cr (VI) and COD reached the highest. The results show that the higher surface area and higher biomass are beneficial to power generation [98]. Detailed studies on the removal of Cr(III) formed by Cr(VI) reduction have also been carried out. Hua et al. [99] found that adding citric acid to the cathode could be complex with Cr(III) in the cathode sediments, significantly improving the removal efficiency of Cr(VI) and Cr(III) in the sediments.

6. Challenges of MFC Remediation of Cr(VI) Contaminated Sites

6.1. Applicability of MFC System

At present, the majority of the research on MFC treatment of Cr(VI) pollution mainly focuses on laboratory-scale/pilot-scale experiments, which have mostly used a synthetic solution as the matrix, and the reactor volume is generally less than 1 L. Thus, a small electrode size and decent experimental conditions would easily achieve a higher performance level [100]. Therefore, there is still a long way to go for the practical application of MFC. Compared with the direct reduction of Cr(VI) by microorganisms, MFC has a higher power density and higher tolerance to the Cr(VI) concentration [22]. Proton exchange membranes play an important role in maintaining the anaerobic conditions and migrating protons into the cathode chamber [101]. In addition, the presence of the proton exchange membrane (PEM) avoided the attachment between microorganisms and Cr(VI) under certain conditions, so the MFC system can adapt to the environmental conditions with a higher Cr(VI) concentration. However, PEM should be cleaned every 6 to 7 months to avoid biological fouling, which makes the MFC system more laborious [102,103]. Therefore, PEM fouling is the main limiting factor for the development of MFC for the site and long-term application [104]. In addition, biofouling of cathode clogging, catalyst inactivation, and bacterial biofilm overgrowth would reduce the electrode conductive area [105], thus affecting the
removal of Cr(VI) and electricity generation. It has been reported that Cr(III) products, such as Cr(OH)\(_3\) and Cr\(_2\)O\(_3\), formed by Cr(VI) reduction will be adsorbed on the electrode surface to form a non-conductive covering layer [16]. The presence of coating would lead to the invalidation of MFC electrodes, and the cleaning and replacement of electrodes would be very costly. In addition, subsurface environments have characteristics of a porous structure, due to the electron transfer rate of the porous system being lower than that of the water-soluble system, the internal resistance of the system is greatly increased, so the electron transfer rate in the MFC system would be reduced [106]. Therefore, it is of great significance to improve the applicability of the MFC system to remove Cr(VI).

6.2. Characteristic of Site Specific Cr(VI) Pollution Remediation

Owing to various features, such as high solubility, high fluidity, and easy migration of Cr(VI) in the subsurface environment remediation present some challenges [107]. A study of the surface subsurface contaminated sites with Cr(VI) showed that Cr(VI) was not easily adsorbed when penetrating aquifers consisting of silt, clay, and silty clay layers from top to bottom, however it migrated with groundwater. Compared with the Cr(VI) pollution level (766–10711.4 mg/kg), the maximum adsorption capacity of Cr(VI) in the clay layer was only 1.2 mg/kg, indicating that the Cr(VI) adsorption capacity was very low. Moreover, in the case of rainwater leaching, Cr(VI) adsorbed on the aquifer was desorbed and released into the groundwater [108], thus making in situ remediation a difficult task. After converting Cr(VI) into Cr(III), the pollution risk still exists in the environment. Fortunately, previous studies have shown that if two-dual compartment MFC were connected, the negative influence of Cr(VI) and Cr(III) on the system performance could be simultaneously removed. Cr(VI)-MFC could reduce Cr(VI) and generate electrical energy that could be supplied to Cr(III)-MFC. It was found that Cr(III) could be effectively reduced by keeping the concentration ratio of Cr(VI) to Cr(III) at 2:1. After 10 h of reaction, the removal efficiency of Cr(III) by Cr(III)-MFC increased from 58% to 82%, and Cr(III) was reduced to metal ion Cr [83]. For the contaminated site scale, after the reduction of Cr(VI) to Cr(III), there would be problems such as an unstable state, being easy to react with oxygen, manganese dioxide, and other oxidants existing and resulting in the yellowing phenomenon [109]. Studies have shown that the process of soil microorganisms reducing oxidized manganese could promote the yellowing of Cr [110] and cause secondary pollution. The repulsion between the negatively-charged cathode and the negatively-charged Cr\(_2\)O\(_7\)\(^{2−}\) results in a slow reduction rate of Cr(VI) during the treatment process [29]. It has been pointed out that the material with reversible redox reaction can effectively eliminate the electric repulsion between the negatively-charged cathode and Cr\(_2\)O\(_7\)\(^{2−}\) or CrO\(_4\)\(^{2−}\) anions [29]. Li et al. used Cu(II) as the electronic shuttling medium of MFC to effectively improve the performance of bioelectricity generation and accelerate Cr(VI) reduction. Meanwhile, they found that in the presence of Cu(II), the power density and Cr(VI) reduction rate were 1235.5 mW/m\(^2\) and 1.19 g/m\(^3\) h, which is 1.44 times and 1.17 times of the MFC system without Cu(II) [88]. Therefore, under the background of site pollution, it is of great significance to study the Cr(VI) pollution process, and conversion mechanisms of various valence forms and for the successful application of MFC site remediation.

6.3. Complex Site Environmental Conditions

Groundwater temperature in Northern China is usually kept at 6.5–9.5 °C, while that in Northwest China is kept at 9–12 °C. The groundwater pH in Southern China is generally lower than that in Northern China. The harsh groundwater environment will limit the growth of microorganisms [93]. It was also suggested that the removal process of Cr(VI) is pH dependent. The neutral environment at the anode is encouraging to the generation of the electron from microbial oxidation of substrates and the acidic environment at the cathode is conducive to the reduction of Cr(VI), while the precipitation of Cr(III) is more likely to occur in a neutral environment [111]. Generally speaking, the pH of untreated Cr slag heap is 8.5–13.0 [112], while the pH of industrial chromium-containing wastewater is
between 0.42 and 0.79 [113]. The excessive acid or alkali environment is not conducive to the growth of anode microorganisms. Studies have shown that during sediment purification, the pH of the anodic chamber solution decreases gradually with each batch cycle. This phenomenon is related to the properties of soil and sediment, which inhibit the migration of H+ in pore water. The accumulation of H+ in the anode chamber would form an acidic environment [114]. Then the acidic environment would inhibit the activity of electroactive bacteria and affects the electron transfer, resulting in the decreasing power production during the last days of each batch cycle [115]. In addition, the biological reduction effect is negatively correlated with the Cr(VI) concentration, and excessive Cr(VI) inhibits the reduction process due to its high toxicity [116]. Literature has shown that when the Cr(VI) concentration exceeds 200 mg/L, the metabolic activities of microorganisms in the soil can be severely inhibited, resulting in the failure of a complete reduction of Cr(VI) and also affecting the generation of bioelectric energy [117]. As a strong oxidant, Cr(VI) causes oxidative stress to plant tissues in PMFC. Under continuous exposure to Cr(VI), the level of antioxidant enzymes in plants decreases, which seriously damages the activity of root tip cells, also resulting in the decrease in cell viability and affecting the secretion of organic matter in plant root [118], finally affecting the operation of PMFC. When different nutrients such as nitrate enter into the subsurface environment, organics will directly participate in the denitrification process rather than power generation [119], thus affecting the reduction of Cr(VI). Natural colloid exists widely in a subsurface environment and they would adsorb, carry, and migrate pollutants in a subsurface [39]. In addition, studies have shown that humic acid colloid in acidic soil could directly reduce Cr(VI) due to functional groups of humic acid, such as phenolic hydroxyl groups, which can provide additional electrons to reduce Cr(VI) through a hydrogen transfer mechanism, affecting the migration of Cr(VI) in the subsurface [120]. Conclusively, migration of Cr(VI) in groundwater and soil as well as the influence of organic substances poses diverse challenges for Cr(VI) removal by MFC in a complex site environment. These problems must be resolved to implement MFC technology with sustainable treatments.

7. Summary and Conclusive Remarks

With the continuous consumption of fossil fuels and increasingly prominent environmental problems, governments all over the world are actively advocating and realizing the carbon dioxide issue and related fossil energy management strategy. Energy transition with carbon peak as the environmental goal and carbon neutrality has been established within timeframes. The MFC technology has shown its unique advantages over other technologies under its dual functions of eco-remediation and bioenergy generation. Cr(VI)-contaminated sites with distinct groundwater and soil environment problems have become major ecological and environmental issues for many countries. The diverse potential of MFC and revised ones for the ecological remediation of a Cr(VI)-contaminated subsurface environment has been substantiated. Thus, the importance of developing and optimizing this innovative technology is self-evident. Through the characterization of Cr(VI) and its migration and transformation, this manuscript concluded that when Cr(VI) enters soil and groundwater, the changing morphology and properties of Cr(VI) after complex chemical and physical reactions provide interesting inspiration for the application of MFC in site remediation. By summarizing the mechanism of Cr(VI) remediation, energy conversion as well as influencing and restricting factors for the removal process in MFC, the key methods to improve the operation efficiency were put forward. Much effort was made on the remediation of Cr(VI) pollution in soil and groundwater by MFC, and some good progress was achieved. However, the applicability of the MFC system, the characterization of the Cr(VI) pollution site, and complex environmental conditions could limit the operating of Cr(VI) remediation with MFC if the professional investigation are not good enough. Based on the above comprehensive review of scientific and technological progress, it can be suggested that further enhancement in sustainability and technological applications for the eco-remediation of Cr (VI)-contaminated sites is a prerequisite for field applications. A
better understanding and in-depth improvement of these targets in the MFC research can be achieved in the following aspects:

1. It is suggested to improve the pH adjustability of the cathode to realize simultaneous immobilization of Cr(III) during Cr(VI) remediation so that long-term operation can be sustained in various harsh environmental conditions.

2. The MFC electrode may be modified wisely to avoid secondary pollution along with enhanced electron transfer capabilities for high power generation catering for subsurface environments.

3. MFC possesses the unique advantages of clean/green eco-remediation, however it may pose the problem of low energy productivity for an actual subsurface environment. We should not be limited to the sole use of MFC, but rather integrate other electrochemical technologies, e.g., a bioelectrochemical reactor (BER), with MFC, thus the application range and advantages of MFC can be expanded.

4. Designing large-scale and continuous flow MFC reactors according to the actual characteristics of a subsurface pollution, distribution, and migration of Cr(VI) in groundwater and the type of soil and medium, as well as the geological and hydrogeological conditions of the sites will optimize the Cr(VI) removal potential for the actual applications and help to overcome the limitations of small-scale laboratory experiments.

5. Oxidized Cr-contaminated water, biofouling of cathode clogging, catalyst inactivation, bacterial biofilm overgrowth, non-conductive covering layer forming, and PEM fouling can affect the long-term stability of the MFC operation, which need further study.

6. For soil with high clay content, low permeability, low electrical conductivity, and water-saturated porous media, in situ reaction zones with microbial activity can be constructed or electron transport channels can be constructed artificially to improve the capacity for better electron migration in the system.

7. Natural colloidal components in the subsurface environment can adsorb and carry pollutants, as well as dramatically influence the electron movement as their electrical properties, which make them interact with the electric field formed by MFC. It is essential to explore the influence of colloid on remediation and productivity efficiencies of MFC and directly improve the applicability and operation efficiency of MFC under different site conditions.

8. With the continuous improvement and optimization of MFC technology, MFC systems have diverse applications for in situ remediation of groundwater contaminants, therefore future research directions must target pollutants in soil and water that are difficult to treat in conventional treatment methods.

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