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Review

Outlook on the Role of Microbial Fuel Cells in Remediation of Environmental Pollutants with Electricity Generation

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Abstract: A wide variety of pollutants are discharged into water bodies like lakes, rivers, canal, etc. due to the growing world population, industrial development, depletion of water resources, improper disposal of agricultural and native wastes. Water pollution is becoming a severe problem for the whole world from small villages to big cities. The toxic metals and organic dyes pollutants are considered as significant contaminants that cause severe hazards to human beings and aquatic life. The microbial fuel cell (MFC) is the most promising, eco-friendly, and emerging technique. In this technique, microorganisms play an important role in bioremediation of water pollutants simultaneously generating an electric current. In this review, a new approach based on microbial fuel cells for bioremediation of organic dyes and toxic metals has been summarized. This technique offers an alternative with great potential in the field of wastewater treatment. Finally, their applications are discussed to explore the research gaps for future research direction. From a literature survey of more than 170 recent papers, it is evident that MFCs have demonstrated outstanding removal capabilities for various pollutants.

Keywords: Microbial fuel cell; pollutants; remediation; wastewater; electricity

1. Introduction

Due to industrial expansion and unplanned urbanization, water pollution is proliferating through the toxic discharge of organic and inorganic materials that cause hazards to human beings and other living organisms. Various types of toxic substance are discharged into water bodies from different sources as a result of growing industrialization, human population, depletion of natural resources, and high agricultural and domestic waste. Wastewater is a serious problem for the whole world from small villages to big cities. In Malaysia, people use almost 99% of surface water for different domestic purposes. In contrast, they use 1% from groundwater, and the total internal water resources in Malaysia are almost 580 km^3 per year [1]. Generally, in Malaysia, surface water is mostly used as drinking water but in a few provinces of Malaysia such as Kedah, Kelantan, Perlis, Sabah, Terengganu, Pahang,

and Sarawak groundwater is used for drinking purpose. Therefore, water is most essential and vital part of all living beings for their survival. Water pollution occurs due to presence of various types of toxic substances like metal ions, organic dyes, inorganic compounds and other types of pollutants. Among these pollutants, the toxic metals (Hg, Pb, Cd, Cu, Ni, Zn, Cr, V, As, Mn, Fe,) and organic pollutant especially dyes (such as azo dyes, congo red, methyl orange, ethyl green, gentian violet, methyl red, rhodamine) are considered as potential contaminants for water resources [2–4]. Two major sources of toxic metals are: (i) natural sources which include soil erosion, urban run offs, aerosols particles and volcanic activities (ii) human sources which include metal finishing, chemical processing industries, electroplating, and dyeing processes, textile industries, mining extraction and nuclear power. Azimi et al. [5] reported that the toxic metals are non-biodegradable, and usually carry high solubility in both surface and groundwater. It can be harmful to a living organism if the concentration of metal is higher than the tolerance limit because some metal is dangerous even in trace amounts such as Hg, As. Toxic metal can enter into the human body through drinking water, food, and air. Excess metals in the human body have adverse effects such as chromium that can cause skin irritation, skin ulceration, kidney failure, nerve tissue, circulatory system, and liver damage problems [6,7]. High exposure of cadmium in the body can lead to renal dysfunction, lung disease (lungs cancer), and bone defects [8]. Similarly, mercury and lead are also harmful to human health. They can cause various diseases like acrodyma, minamata disease and huterrussel syndrome, respiratory system damage, brain, kidneys, heart, and skin diseases [9]. In 2007, a case study was carried out by a scientific community and observed that almost 137 million people are affected by arsenic-contaminated wastewater [10]. Furthermore, the most commonly found toxic metals in Malaysian wastewater are mercury (Hg), copper (Cu), chromium (Cr), cadmium (Cd), thallium (Tl), arsenic (As), lead (Pb), zinc (Zn), iron (Fe), manganese (Mn) and nickel (Ni) [11,12]. Other potential hazards of water are organic dyes, which can contaminate surface and groundwater when entering water bodies. Organic dyes are complex in nature and also considered as potential pollutants for living beings [13–15]. Dyes are a unique form of synthetic organic materials used in several dyeing industries. Nowadays, dyes have become a major cause of water pollution due to improper disposal from various sources such as domestics/commercial wastes, pharmaceutical companies' wastewater, tanneries and leather factories, textile factories, oil refineries, and metal process industries and pesticides [16,17]. To date, more than 40,000 dyes and 7000 pigments have been reported, and the annual dyestuff production is 700,000 tonnes across the world [18]. Several countries produce different types of synthetic dye and pigment, which are photolytically, chemically and physically stable, and extremely persistent in nature. Nidheesh et al. [19] reported that approximately 1.5 million litres of waste are released every day into natural water resources from different mills. Dyes are complex colour structure and highly visible even at lower concentrations and having adverse effects on aquatic life [19]. Thionine-based textile dye, azo dyes, textile dyes, and congo red are well-known dyes that are hazardous and carcinogenic in nature [20,21]. These dyes enter into the body through ingestion and cause bladder cancer and DNA diseases [22]. These dyes not only affect the marine environment but also dangerous for a human being [23]. These pollutants (heavy metals and organic dyes) enter into the water bodies and contaminate aquatic systems, which are becoming a global environmental issue. From the aquatic system, these pollutants enter into the food chain of humans and other organisms through biological and geochemical mechanisms. These pollutants are very toxic and persistent in nature.

Various treatment methods such as adsorption, ozonation, ion-exchange, electrolytic reduction, electrochemical degradation, monitoring natural recovery, coagulation, in situ and ex situ treatment, thermal treatment, chemical precipitation, and in-situ confinement have been reported for the removal of toxic metal and organic dye pollutants from wastewater [24]. These techniques are effective and give better results but have some drawbacks such as the high energy required, high operation cost, high consumption of chemicals, and heavy waste products released. Therefore, the scientific community introduced an innovative technique, called microbial fuel cells (MFCs) for the degradation of toxic metals and organic dye pollutants from wastewater. This idea was first introduced by M.C. Potter

(a professor of botany at the University of Durham) in early the 20th century (1911) using microbes in the pollutant degradation process and obtaining energy from bacteria [25]. Later, in the 1970s, it was found that bacteria have electrochemically active redox proteins that can transfer electrons to the anode [26]. Nowadays, this technique is receiving much more attention than other conventional methods. MFCs are innovative, an eco-friendly device to generate electricity along with pollutant removal from wastewater, where microbes break down the organic dyes and toxic metals. The exoelectrogenic bacteria transfer electrons to the anode and the electron moves to the cathode chamber by using an external circuit. The proton moves from anode to cathode directly in the presence of oxidative environment [27]. However, many factors play a major role in the performance of MFCs such as internal resistance, catalyst, ion concentration, chemical substrate and electrode spacing, MFCs modelling and electrode material properties [28]. The electrode material is a significant factor to make MFCs more efficient and prolific at commercial scale. In MFCs, electrotroph microbes accept electrons from electrodes and convert the toxic compound into a less toxic nature [29]. There are many reported electrodes such as carbon-based electrodes (Carbon black, graphite, carbon cloth, carbon brushes, carbon paper, carbon fiber, carbon meshes), metal/metal oxide (Ag, Au, Cu, Pt, Zn, TiO_2 etc.), conducting polymers such as polyaniline, polythiophene, polypyrrole [30,31]. A good electrode material supposed to have some unique properties such as high conductivity, high chemical stability, excellent mechanical and thermal stability, low resistance, high surface area, and excellent biocompatibility [32]. According to the literature review, graphene oxide is considered as the most effective and dynamic material for the electrode. The graphene oxide is gaining much attention for electrodes preparation due to high surface area, excellent mechanical stability, thermal stability and good conductivity [33]. The conducting polymer and other material composites also exhibit a remarkable result. In this review article, the scope of MFCs in wastewater treatment, especially in the removal of toxic metal and different dye pollutants along with general mechanisms of substrate oxidation at the anode, were discussed. The basic setup of MFCs is also summarized. The MFC approach is an ideal technique for removing pollutants from wastewater with simultaneous generation of energy by using waste material as a catalyst. Different electrode materials have been discussed for the removal of pollutants (organic dyes/toxic metals) with simultaneous electricity generation. From the wide literature review, very few works are reported for degradation of highly toxic pollutant such as Pd, As, Cd, Hg, azo dye, rhodamine B and rhodamine 6G. However, outcomes show that future research should be carried out on the remediation of toxic metal and dyes-based pollutants to make the environment clean.

2. Basic Setup and Type of Microbial Fuel Cells (MFCs) Based on Configurations

MFC approach is the most emerging technology in the modern era in which chemical energy is changed into electrical energy by using microbes as biocatalyst. This idea was first introduced by M.C. Potter in 1911 using microbes in the pollutant degradation process [34]. MFCs are mainly categorized on the basis of their configuration, single chamber, double chamber, and stacked MFCs, as shown in Figure 1. The basic setup of all MFCs is almost similar, such as anode, cathode, substrate, and electrolytes. The ideal MFCs is a double chamber which produces high power generation as compared to a single chamber. The basic machinery setup consists of two chambers, namely anodic and cathode chamber. The anode and cathode electrode are separated using proton exchange membrane (PEM) which allowed the proton to travel from anode to cathode chamber [35]. Different types of electrode materials were used in MFCs such as carbon-based, metal/metal oxide or doped/composites material. However, the anode chamber was filled with wastewater or sludge and provided organic substrate such as glucose for microbial growth on the surface of the anode. The microbes form biofilm around the anode and during their respiration substrate oxidation occurs, leading to the generation of protons and electrons. The outer circuit was used to transfer the electrons from the anode to the cathode, which is commonly copper, aluminium, silver made wire. Similarly, the cathode chamber was filled with electrolytic solution, and oxygen was supplied through air diffuser. The oxygen assists as a perfect electron acceptor due to toxic free effect and favoured as an oxidizing substance, which

helps to make simple operation of MFC [36]. According to the configuration of cathode and anode chambers, a modest MFC prototype can serve as single-chambered or double-chambered. These two are commonly used designs while several variations have been attempted in MFC design and setup. The single, double and stacked MFCs are three basic types of MFCs, are classified based on their configuration. The single-chamber MFC (SMFC) has only anode chamber, and they do not have any defined cathode chamber, and works without any type of PEM. On the other hand, double-chamber MFC (DMFC) has two types of chamber, namely anode and cathode which are connected through PEM or salt bridge. The PEM helps to transfer the protons from anode to cathode, whereas in the SMFC protons move directly without any PEM. Similarly, stacked MFCs can be present in series and also in parallel mode. In some studies, this combination enhanced the voltage output of the system [37]. Several studies were summarized based on these types of configurations, which are included in Tables 1 and 2.

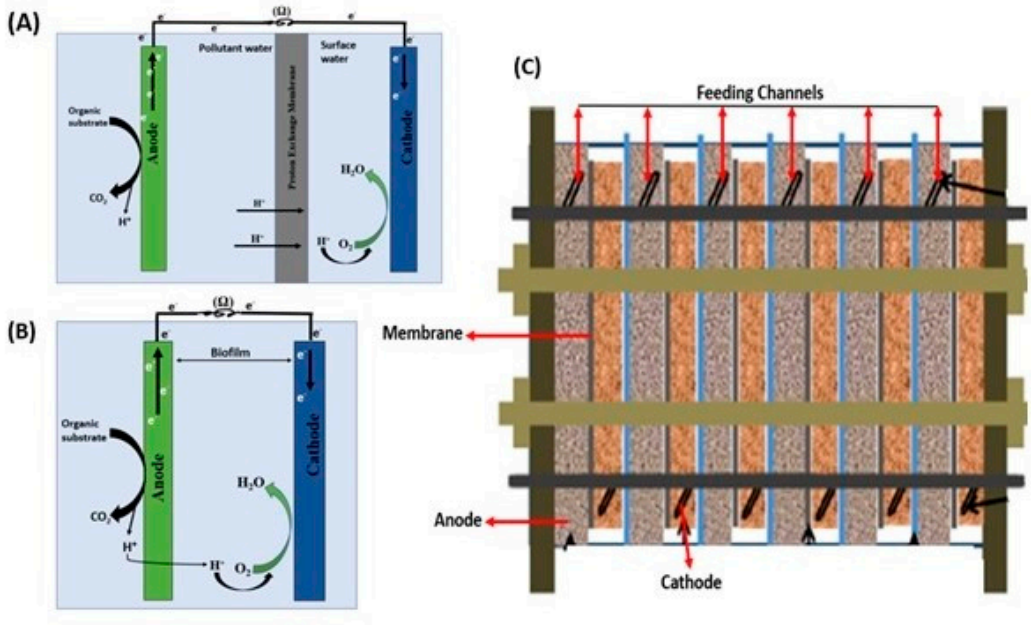

Figure 1. Basic configuration of microbial fuel cells (MFCs). (**A**) Double-chamber MFC (DFMC), (**B**) single-chamber MFC (SFMC), (**C**) stacked MFC.

3. Pollutant Removal through MFCs

The MFC device offers sustainable green energy sources, and the scientific community is interested in this method actively because it uses waste material for the MFCs setup and biodegradable material as fuel to run the system. The MFC device has some essential components, i.e., electrodes, different types of microbes and MFC design. They play a valuable role in the MFC operation to reduce the metals from highly toxic state to less toxic state and remove dyes-based pollutant from water. Several studies have been conducted to show the MFCs device working efficiency in terms of wastewater treatment.

3.1. Degradation of Toxic Metal through MFCs

Toxic metals are originated from industrial, medical, and household wastewater. However, these toxic metals create many problems in an aquatic environment due to non-biodegradability, their toxic nature, and bioaccumulation [38,39]. The conventional methods of wastewater treatment encountered a problem, i.e., if concentrations of metals are high, all conventional methods become useless because it decreases the working efficiency [40]. So, MFCs have become an emerging research direction for environmental researchers to degrade toxic metals from water resources. The reduction of soluble, toxic metals (U(VI), Cr (VI), Cu (II), Cd (II)) from high toxic state to less contaminated and insoluble

form with less potential electrode is carried out by MFCs [41]. Many reported electroactive bacteria have the ability to reduce toxic metals. However, all toxic metals cannot be removed by using reduction path; some require an oxidation route to degrade the toxic metals from wastewater. For example, arsenic cannot be degraded by reduction; it requires oxidization at the anode with the formation of a precipitate [42]. In metal recovery or removal, the Cu^{2+} metal is considered very attractive because it is widely present in domestic, commercial and industrial wastewater. Copper can be easily removed due to its high potential of reduction through MFCs [43]. Ryu et al. [44] studied the removal of chromium and showed that different concentration rates also affected the removal efficiency of metals. The initial concentration of inoculum was 5 mg/L with 93% of removal efficiency, but in 25 mg/L, the removal efficiency was observed to be 61%. The electrode was made up of graphite felt (anode and cathode). Actinobacteria and B-proteobacteria actively showed their degradation performance with (5 mg/L) initial concentration after 144 h, but the result showed less degradation efficiency after 144 h when microbes were treated at 192 h within 25 mg/L inoculum sample. The high potential rate and high current density produced by a reduced concentration of the toxicity that may be directed to high sensitivity of different devices like sensors are studied by Stein et al. [45]. Consequently, the instant response to toxic heavy metals directs that it can be functionalized to a biomonitor. Xafenias et al. [46] showed the performance of Cr (IV) by using *Shewanella oneidensis MR-1* as a biocatalyst and lactate as a substrate to strengthen the *Shewanella oneidensis MR-1* growth. The achieved removal percentage was 67%, along with 32.5 mA/m^2 energy production. The MFC operation time was 192 h at a natural pH range with 200 mg/L initial concentration. Xafenias et al. [46] also used graphitic rod as electrodes to provide enough growth to *Shewanella oneidensis MR-1* for better reduction. Similarly, chromium removal is 98% by using activated charcoal as electrodes from algae biomass studied by Singhvi and Chhabra [47]. The achieved result was high energy output i.e., 207 mA/m^2 with a high removal rate because Xafenias et al. (2013) used a neutral pH range and Singhvi and Chhabra (2013) used an acidic environment, even though both used same initial concentration. pH is a significant parameter regarding the removal or degradation process. The less acidic environment cannot provide power to microbes to degrade the metal more effectively. Varia et al. [48] examined the electrodeposition of precious metal gold on Pt- graphite electrodes using the electroactive *Shewanella genus*. The initial concentration used was 200 ppm and removal efficiency was 6% from 0.6 V to −0.2 V current density. Nancharaiah et al. [49] studied that metal wastes pollution is a serious threat to the environment. The preference to use graphite felt material as anode and cathode for the treatment of copper from wastewater. The studied showed that different parameters were analysed like temperature, reaction duration (time) and initial concentration. The removal efficiency was found to be 99% in acidic conditions with a concentration of 1 mg/L at 144 h time. When initial concentration was increased to 480 h with 200–600 mg/L, the efficiency of removal decreases. The power density was achieved much better at 144 h with low initial concentration. Abbas et al. [50] used sediment microbial fuel, an emerging type of MFC technique; it is an anoxic and membrane-less technique for the removal of toxic metals. The different type of parameters was observed to know the degradation performance of toxic metals. Chromium and copper were treated by using a sediment sample. The whole set of experiments was carried out at different pH range and temperatures. High removal efficiency (96%) was observed at pH 2 and temperature 37°C. The energy output was observed approximately 400–450 mW/m^2. However, the significance of work is the high removal rate at highly acidic condition and power output was quite better, but still, this energy output is not enough to use at larger scale. In 2016, the possibility of in situ electro-kinetic treatment for heavy toxic metals was analysed by Habibul et al. [51]. The result showed less electricity production and poor efficiency after 143 days. The energy output was 7.7 mW/m^2 with 31% removal of cadmium from the contaminated soil sample using graphitic granules as the anode, which failed to provide an active flow of electrons. Carbon felt served as a cathode to oxidize the sample. The work also showed that operation at a low acidic environment could enhance the removal efficiency and electricity production. Qiu et al. [52] defined a capable approach for degradation of vanadium from pollutant water. Herein, MFC with biocathode carbon fiber felt was summarized for

the reduction of vanadium and green electricity generation. Electrochemical and bacterial reductions were carried out and complete remediation was achieved within seven days for V (V) with an initial concentration of 200 mg/L. The achieved power density was 529 ± 12 mW/m^2. Gai et al. [53] reported the inhibition ratio, i.e., 46%, 28%, were observed for 1 mg/L Pb^{2+} and 1 mg/L Cd^{2+} solution, respectively. While on the other side very high inhibition ratio (76%) was found in wastewater with 1 mg/L Pb^{2+} and 1 mg/L Cd^{2+} solution. However, at low concentration of the heavy metal, MFCs exhibited a confident degree of tolerance. Kumar et al. [54] found a significant result for the removal of chromium by using different conditions and materials and reported high energy output, i.e., 970 mW/m^2 by using graphite material as an electrode. The inoculum source was activated using anaerobic sludge. After 2 h, at pH 7, chromium removal rate was observed 76% with high energy output when initial concentration was 20 mg/L. However, when initial concentration was 10 mg/L, the removal efficiency increases from 76% to 94% but the energy decreases from 970 mW/m^2 to 6.4 W/m^3. The usage of substrate for bacterial growth is very significant because the bacterial ability is of key importance in order to degradation of initial concentration of inoculum. The proper pH, substrates, and initial concentration of inoculum are necessary for better removal of toxic metals. Huang et al. [55] investigated the degradation of binary Cd (II) and Cr (VI) through the MFC catholyte. The removal efficiency was observed 73% for chromium and 61% for cadmium in anaerobic culture by using graphite felt as cathode and carbon rod as an anode in the double-chamber MFC. The energy production 14.2 mW/m^2 was achieved in the pH range of 5.8 to 6 at 24 h operation time. The removal efficiency was better, but energy output was observed to be very low. Hence, it is highly recommended to use different materials to enhance energy production along with removal efficiency. Wang et al. [56] studied highly toxic thallium (Tl) removal efficiency by MFC because it was gaining attention in developing significant techniques to remove thallium more efficiently. In MFCs, spontaneous oxidation of Tl(I) was observed. The removal efficiency was 67% during 72 h with 100 µg/L initial concentration. The result exhibited the highest power density, i.e., 457.8 ± 15.2 mW/m^2 and the electrochemical procedure described some bad effects of thallium accumulation in energy output. The product achieved after oxidation was less mobile which might precipitate logically in pH series. MFC is very cost-effective to deal with wastewater pollutants, especially in the case of thallium. This removal efficiency can be increased by fabricating high-conductive, high surface area-based electrodes because carbon felt was used as anode and plain carbon paper as cathode. This direction might be useful for the researcher if they employ high conductive and high surface area-based materials like graphene oxide, reduced graphene oxide or nanocomposites that showed excellent performance for the removal efficiency. Liu et al. [57] used graphite felt as electrodes to treat wastewater containing Ni, Cu, and Hg. The study showed the concentration parameter to explore the concentration and energy output relation. The voltage output was high at low concentration, but as concentration increases, the current density decreases. Energy output and concentration of inoculum are inversely proportional to each other. The experiment altered the time duration of the reaction, as Ni treated for 30 days obtained 150–200 mW/m^2 energy and Cd and Hg treated for 7 and 15 days achieved a removal rate of 60% and 55% along with energy output of 700–750 mW/m^2 and 800 mW/m^2, respectively. In 2019, Zhang et al. [58] analysed the Cr (VI), which is mostly focused upon heavy metal due to its toxicity and high mobility. A new reactor combination of MFC was developed using *Platanus acerifolia* leaves and applied for remediation of chromium ions. The anaerobic sludge was used as inoculum material. When the initial concentration was 50 mg/L, after 16 h reaction, the removal efficiency was observed at 98%. The reaction was carried out at pH 2. There are many reported works on chromium removal because it is widely present in wastewater. Li et al. [59] also studied the removal rate of chromium from wastewater through MFC. The aim was to convert the Cr (VI) to Cr (III), meaning from highly toxic to less toxic. The buffer solutions of catholyte affected the chromium reduction process. At pH 2, the removal rate of Cr (VI) increased and reached 99.9% when potassium dihydrogen phosphate was added. The starting concentration was 100 mg/L, and it produced 52.1 mW/cm^2 current. The Zhang et al. [58] and Li. et al. [59] research groups used carbon felts as anode and cathode electrodes and removal efficiency was almost 99.9%

but there is a major drawback, to overcome the energy crisis, enough energy output needs to be produced. Wu et al. [60] investigated the scope of reduced graphene oxide. Reduced graphene oxide is an upgraded form of graphene oxide. In this study, reduced graphene oxide is employed as a catalyst with a cathode in MFC without any permeable exchange membrane to enhance the copper recovery and energy generation. The outcomes demonstrated that a reduced graphene cathode is providing higher electron transfer ability than conventional graphene oxide. The energy output was reported 67%, which is higher than that of other materials and copper degradation efficiency was improved 43% compared to graphene oxide. It was noticed that initial concentration, pH, temperature, and electrodes are important factors in enhancing energy production. *Pseudomonas* and *Geobacter* species indicate the inter-specific synergism of bacteria for resourceful electricity and copper recovery. It will be very significant for toxic metal and energy output from lower concentrations of wastewater through a microbial fuel cell. Liuet al. [61] studied the conversion and distribution of platinum in MFC and showed an achievable approach to degrade the platinum from pollutant water and produce Pt/C catalysts to work in MFCs. The result demonstrated that 90% removal was achieved by using 16.88 mg/L initial concentration to produce high-power density, i.e., 844.0 mW/m^2. In the early stages, the working efficiencies of MFCs were not good and were found to be very low. However, continuous efforts of researchers and rising development in MFCs device became an emerging and excellent path to treat toxic metals along with current generation. Currently, MFCs architectures state that the removal rate is up to 100% and chemical oxygen demand is 99% in certain cases [62]. These kinds of performance prove that MFCs is sustainable water treatment method. However, recently Heming et al. [63] studied the treatment of hexavalent Cr from wastewater system by using different proton exchange membranes. From the results, the removal rate of Cr was 99.4 ± 0.2% but the energy generation was very low. The drawback of this study was membrane fouling, which occurs due to Cr ions in cathode chamber. The fouling is the main factor in reducing the efficiency of energy generation in the case of Cr metal. Therefore, a membrane-less MFC system must be used and designed to avoid these kinds of issues. Zhang and co-workers [64] also used the environmentally sustainable MFC system to remove copper metal from soil. They reported a 94% removal rate of copper from the soil system with 363.04 mW energy generation. The overall performance was quite good. In this study, authors reported that HCl is the best auxiliary reagent for the elimination of copper metal from soil through three chamber-microbial fuel cells. This condition was found to be best in terms of high removal of copper from soil and current generation performance and reduction of copper in the catholyte. Similarly, Vijay et al. [65] investigated the MFC performance for the removal of uranium from the water system. Before that there was no work reported on uranium removal by MFCs. In modern world, the nuclear waste becomes a serious threat to green environment because nuclear waste contains a high amount of U(VI) which are very dangerous for human health. Proteobacteria has a capacity to convert it into insoluble form which has a less toxic effect. The produced power efficiency was 2.91 W/m^3 but still nuclear waste needs considerable attention to improve the removal rate of U(VI) from the environment. Despite all developments, there are still some problems that create troubles during MFCs operation, such as low removal capability, low power production, and very expensive. Therefore, to improve energy production and metal degradation efficiency, researchers should develop membrane-less MFCs using a highly efficient electrode material [66]. The energy production and metal recovery mainly depend upon the generation of electrons and growth of bacteria. These two factors can be improved by inserting an excellent electrode, which has a larger surface area for better bacterial growth and can improve the generation of electrons. The carbon-based electrodes are an efficient material as electrodes in MFCs. However, in the early period, carbon material showed some drawbacks such as lower electrical conductivity and less surface area for colonization of microbes. Recently, the scientific community introduced a new allotrope of carbon called graphene, which shows a very high surface area for bacterial growth, high conductivity, high mechanical and thermal stability, as compared to other carbon-based materials [67,68]. Therefore, this is considered a very innovative and outstanding material for improving the working efficiency of MFCs for the degradation of metal

along with energy output. However, after a wide literature review, we found that there are very few works reported for the removal of highly toxic metals such as Pb, Hg, Cd, and As. Several factors lower the MFC performance in the case of a highly toxic metal such as electrode material, substrate, solution pH, and temperature. Therefore, an optimized environmental condition must be employed while using high conductive electrode materials such as graphene derivatives and its composites. Furthermore, different researchers proved MFCs efficiency in terms of the degradation of toxic metals, energy efficiency, and different parameters was summarized in Table 1.

Table 1. Degradation of toxic metals with their energy outputs through MFCs.

Target Metal Pollutants	Type of MFCs	Type of Electrodes		Inoculum/ Microbes	Operating Time (hr)	Temp (°C)	pH	Initial Conc.	Removal Efficiency (%)	Power Density	Reference
		Anode	Cathode								
Cr (VI)	DMFC	Graphite plates	Graphite plates	Domestic wastewater	150	25	2	100 mg/L	100	150 mW/m^2	[69]
Cr (VI)	DMFC	Unpolished graphite plate	Natural rutile-coated polished graphite	Anaerobic sludge	26	22	2	26 mg/L	97	-	[70]
Se	SMFC	Non-wet proofed carbon cloth	Wet proofed carbon cloth	Mixed culture (Acetate and glucose use as source)	<48	30	-	75 mg Se/l 200 mg Se/l	99	-	[71]
V (V)	DMFC	Carbon fiber felt	Carbon fiber felt	Anaerobic granular sludge	72	35	1	25 mL	87.9	578.3 mW/m^2	[72]
Cr (VI)	DMFC	Graphite plate	Graphite granular	Indigenous bacteria from Cr (VI)-	173	22–26	2	39.2 mg/L	2.4 ± 0.2 mg g VSS^{-1}/h	6.9 mW/m^3	[73]
Cu (II)	DMFC	Graphite felt	Graphite plate	Anaerobic sludge	144	35	-	500 mg/L	70	314 mW/m^3	[74]
Cu (II)	DMFC	Graphite felt	Graphite plate	Anaerobic sludge with Copper	144	35	-	500 mg/L	70	314 mW/m^3	[74]
Cu (II)	DMFC	Graphite plate	Graphite felt	Anaerobic sludge	20	35	3.5	200 mg/L	>99	314 mW/m^3	[75]
Cu (II)	DMFC	Graphite plate	Graphite plate	Anaerobic sludge	20	35	4.7	6412.5 ± 26.7 mg Cu^{2+}/L	>99	339 mW/m^3	[75]
Hg (II)	DMFC	Graphite felt	Carbon paper	Anaerobic sludge	10	30	2	100 mg/L	98.22–99.54	433.1 mW/m^2	[76]
Cr (VI)	DMFC	Graphite felts	Graphite felts	Anaerobic sludge	144 and 192	35	-	5 mg/L 25 mg/L	5 mg/L With 93, 25 mg/L With 61	-	[44]

Table 1. *Cont.*

Target Metal Pollutants	Type of MFCs	Type of Electrodes		Inoculum/ Microbes	Operating Time (hr)	Temp (°C)	pH	Initial Conc.	Removal Efficiency (%)	Power Density	Reference
		Anode	Cathode								
Cu (II), Pb (II)	DMFC	Carbon felt	Carbon felt	Dilute synthetic sample	14–36 days	25	3	1.1 mg/L Cu^{2+}, 2.5 mg/L Pb^{2+}	Pb 92 Cu 99	17.1 to 25.2 mW/m^2	[77]
Cd (II), Zn (II)	DMFC	Carbon felt	Carbon felt	Dilute synthetic sample	56 days	25 °C	3	7.4 mg/L Cd^{2+} 19.5 mg/L Zn^{2+}	Cd 82 Zn 89	-	[77]
Cr (VI)	DMFC	Carbon fiber felt	Carbon fiber felt	Anaerobic sludge	240	30	6	100 mg/L	75.4 ± 1.9	970.2 ± 60.5 mW/m^2	[78]
Ag	DMFC	Carbon brush	Carbon cloth	Sludge mixture	8	25	7	50–200 ppm	99.91	4.25 W/m^2	[79]
V (V)	DMFC	Carbon fiber felt	Carbon fiber felt	Anaerobic sludge	240	30	6	100 mg/L	67.9 ± 3.1	970.2 ± 60.5 mW/m^2	[78]
Cr (VI)	BMFC	Graphite felt	Graphite rod	*Shewanella oneidensis* MR-1	192	30	7	200 mg/L	67	32.5 mW/m^2	[36]
Pb, Se	DMFC	Carbon cloth	Carbon cloth with Pt coating.	Oil sands tailings affected water	800	21 ± 0.5	1	581 ± 26 Se, 35.8 ± 13 Pb.	97.8 Se, 32.5 Pb	392 ± 15 mW/m^2	[80]
Au (III)	DMFC	Carbon brush	Carbon cloth	Tetrachloroaurate wastewater	12	25	2.8	2000 ppm	99.89 ± 0.00	6.58 W/m^2	[81]
Cr (VI)	DMFC	Activated charcoal	Activated charcoal	Algae biomass	96	-	2	200 mL	98	207 mW/m^2	[47]
Ag^+	DMFC	Carbon cloth	Graphite	NH_3 chelated silver waste water	21	-	6.2	-	99.9	317 mW/m^2	[82]
Co	DMFC	Graphite felt	Graphite felt	Lithium cobalt oxide Solution	-	35	1	200 mg/L	62.5 ± 1.8	298 ± 31 mW/m^3	[83]

Table 1. *Cont.*

Target Metal Pollutants	Type of MFCs	Type of Electrodes		Inoculum/ Microbes	Operating Time (hr)	Temp (°C)	pH	Initial Conc.	Removal Efficiency (%)	Power Density	Reference
		Anode	Cathode								
Cu (II)	DMFC	Carbon cloth	Carbon cloth	*Klebsiella* sp. MC-1	75	25 × 5	5	50 mg/L	99.1	412 W/m^2	[84]
Cd (II), Zn (II)	SMFC	Carbon cloth (no wet proofing)	carbon cloth (30 wet proofing)	Sewage sludge	-	32	6.8	200 mM Cd; 400 mM Zn	Cd 90 Zn 97	3.6 W/m^2	[85]
Au (III)	MFC	Pt-graphite	Pt-graphite	*Shewanella* genus	-	25	2	200 ppm	60	-	[85]
V	Tubular MFC	Carbon fiber felt	Carbon fiber felt	Anaerobic sludge	72	25	7	500 mg/L	25	0.572 W/m^2	[49]
Ag^+	Tubular MFC	Carbon cloth	Graphite felt	Anaerobic sludge	21	26	9.2	1000 mg/L	99	0.3 W/m^2	[49]
Ag^+	Tubular MFC	graphite plate	Graphite felt	Anaerobic sludge	26	-	2	200 mg/L	95	0.109 W/m^2	[49]
Ag^+	Tubular MFC	Carbon brush	Carbon cloth	Anaerobic sludge	8	-	7	200 mg/L	99	4.25 W/m^2	[49]
Se	SMFC	Carbon cloth	Carbon cloth	Anaerobic sludge	48	25	7	75 mg/L	99	2.90 W/m^2	[49]
Au	Tubular MFC	Carbon brush	Carbon cloth	-	-	-	2	200 mg/L	99.8	6.58 W/m^2	[49]
Co	Tubular MFC	Graphite felt	Graphite felt	Anaerobic sludge	48	30	1–3	1000 mg/L	99.15	-	[49]
Cr (VI)	Tubular MFC	Graphite plates	Graphite plates	Anaerobic sludge	150	25	2–6	200 mg/L	100	0.150 W/m^2	[49]
Cr (VI)	Tubular MFC	Graphite plates	Graphite plates	Anaerobic sludge	26	25	2	26 mg/L	97	-	[49]
Cr (VI)	Tubular MFC	Carbon cloth	Carbon cloth	Anaerobic sludge	48	25	2	100 mg/L	99	0.767 W/m^2	[49]
Cu (II)	Tubular MFC	Graphite plate	Graphite foil	-	6 days	-	3	1 mg/L	99.8	0.80 W/m^2	[49]
Cu (II)	Tubular MFC	Graphite felt	Graphite felt	Anaerobic sludge	-	25	2–5	10–200 mg/L	>99	0.319 W/m^2	[49]

Table 1. *Cont.*

Target Metal Pollutants	Type of MFCs	Type of Electrodes		Inoculum/ Microbes	Operating Time (hr)	Temp (°C)	pH	Initial Conc.	Removal Efficiency (%)	Power Density	Reference
		Anode	Cathode								
Cu (II)	Tubular MFC	Graphite felt	Graphite felt	-	480	27	2	600 mg/L	92		[49]
Cu (II)	Tubular MFC	Graphite plate	Graphite plate	Anaerobic sludge	264	25	4.7	200 mg/L	>96	339 mW/m^3	[49]
Cd (II)	DMFC	Graphite granules	Carbon felt	Contaminated soil	143 days	25	6.8	100 mg/L	31	7.5 mW/cm^2	[51]
Pb (II)	DMFC	Graphite granules	Carbon felt	Contaminated soil	108 days	25	6.9	900 mg/L	44.1	3.6 mW/cm^2	[51]
Cr (VI), Cu (II)	Sedimental MFC	Graphite felt	Graphite felt	Sediment sample	90 days	37	2	250 mg/L	96	400–450 mW/m^2	[50]
V (V)	DMFC	Carbon fiber felt	Carbon fiber felt	*Dysgonomonas* and *Klebsiella*	7 days	22 ± 2	-	200 mg/L	60.7	529 ± 12 mW/m^2	[52]
Cr (VI)	DMFC	Graphite brushes	Graphite granules	Anaerobic sludge	-	25	7	10 mg/L	94	6.4 W/m^3	[54]
Cr (VI)	DMFC	Graphite brushes	Graphite granules	Primary clarifier effluent	2	22 ± 3	7	20 mg/L	76	970 mW/m^2	[54]
Cr (VI)	SMFC	Carbon brush	Carbon cloth	-	-	30	7	100 mg/L	99	419 mW/m^2	[54]
Cu (II)	DMFC	Graphite felt	Graphite plate	Activated sludge	28 days	35	-	100 mg/L	96	140 mW/m^2	[54]
V (V)	DMFC	Carbon fiber felt	Carbon fiber felt	-	-	30	-	-	68	970 mW/m^2	[54]
Cu^{2+}	SMFC	Carbon brush	Carbon cloth	Anaerobic sludge bed.	5	35 ± 1	6	12.5 m/Lg	98.3	0.2 W/m^3	[86]
Zn (II)	SMFC	Carbon cloth	Carbon cloth	Activated sludge	-	25	-	-	97	3600 mW/m^2	[54]
Cr (VI), Cd (II)	DMFC	Carbon rod	Graphite felt	Anaerobic pure culture	24	30	5.8–6.0	Cr (VI) 385 µM and Cd (II) 179 µM.	73 for Cr, 61 for Cd.	14.2 mW/m^2	[55]

Table 1. *Cont.*

Target Metal Pollutants	Type of MFCs	Type of Electrodes		Inoculum/ Microbes	Operating Time (hr)	Temp (°C)	pH	Initial Conc.	Removal Efficiency (%)	Power Density	Reference
		Anode	Cathode								
Ni	DMFC	Graphite felt	Graphite plate	Anaerobic sludge	24	30±1	7.1	26.4 mg/L	95	-	[26]
Cd (II)	DMFC	Graphite felt	Graphite felt	Mixed microbial culture	7 days	25	7.1	50 mg/ml	60	700–750 mW/m^2	[53]
Hg (II)	DMFC	Graphite felt	Graphite felt	Mixed microbial culture	15 days	25	6.8	25 mg/ml	55	800 mW/m^2	[53]
Toxic TI	SMFC	Carbon felt	Plain carbon paper	Anaerobic sludge	72	22 ± 2	-	100 µg/L	67	457.8 ± 15.2 mW/m^2	[56]
Cu (II)	DMFC	Carbon brush	Reduced Graphene oxide	*Geobacter* sp. and *Pseudomonas* sp.	-	25	6	12 mg/L	98	0.95 W/m^2	[60]
Cr (VI)	DMFC	Carbon felt	Carbon felt	*Shewanellade*coloration-S12, *K. pneumonia*	3.5	30	2	10 mg/L	99.9	52.1 mW/cm^2	[59]
Cr (VI)	DMFC	Graphite plate	Graphite plate	Anaerobic cultures mixed with Cr (VI)	45 days	22–24	-	80 mg/L	0.46 mg Cr (VI)/g VSS·h	55.5 mW/m^2	[87]
Cu (II)	DMFC	Porous graphite felt	Carbon rod	Microbial culture	72	20± 3	2	50 mg/L,	55	-	[88]
Ni	DMFC	Graphite felt	Graphite felt	Mixed microbial culture	30 days	25 ± 1	7	32.9 g/180 ml	-	150–200 m W/m^2	[61]
Pt	DMFC	Graphite plate	Graphite plate	Anaerobic sludge bed	24	25	7	16.88 mg/L.	90	844.0 mW/m^2	[57]

MFC = Microbial fuel cell; DMF = Double-chamber MFC; SMFC = Single-chamber MFC; *SMFC = Sediment double-chamber MFC; TMFC = Tubular double-chamber MFC.

3.2. Organic Dye-Based Pollutant Removal through MFCs

Dye-based wastewater from different sources such as different manufacturing industries, agricultural activities, pharmaceutical companies is one of the critical problems for the aquatic environment. The different kinds of dyes pollutant badly affect the aquatic environment due to their toxicity and intense colour. Furthermore, organic, natural dyes are an extremely visible material and it is more dangerous even in the negligible amount discharge into the water bodies (surface or groundwater), which may show the intense colour that leads to unstable environmental conditions for human beings and other living organisms [89,90]. Many dyes such as azo dyes are well known for carcinogen. Precisely, the azo dyes hold aromatic amines, which are extremely lethal, cancer-causing [91,92]. Thus, the effective removals of these dyes are the most challenging problems. In this section, different types of dyes such as methyl orange, methyl red, azo dyes, thionine-based textile dye etc. and their removal efficiency, different electrodes are summarized in Table 2. Different dyes have substantial and significant applications in many industries such as paper, rubber, textile, concrete plastic and drugs [93,94]. Therefore, it is quite dangerous as different dyes used at an industrial level are released into the water sources, which is moderately harmful to the natural environment. Dyes are extensively used in fabric manufacturing industries and it is predictable that 10–15 of dyes are mixed with ground water during dyeing [95]. Currently, the release of wastewater containing dye is considered an important ecological problem. Essential properties of dyes are that they are stable during washing and have good resistance to bacterial degradation [96,97]. Consequently, it is not easily degradable by using or following routine normal conditions to remove it from wastewater. Recently, researchers made it possible to remove through MFCs by using microbes as fuel. New studies propose that MFCs will be an effective technique for commercial and practical use in the near future and significantly become an ideal device for generating sustainable energy [98]. MFCs offer a practical application for decolorization of organic dye with simultaneous electricity generation from degradable material [99]. The organic dye pollutants can cause a major negative impact in the natural environment. However, despite all work, still there is a lot of research gap to be investigated regarding the organic dye's pollutants. The scientific community considers it a tough job to work on dye-based pollutants and their removal process. Research showed that the world would suffer from severe water shortage and natural resources by 2020, when water usage is expected more than water sources [100]. Therefore, removing water pollutants is a major problem for healthy human society and maintaining the stability of the ecosystem. Hou et al. [101] studied the congo red dyes decolorization along with production of energy by using an air-cathode single-chamber MFC in the presence of different membranes such as proton exchange, ultrafiltration and microfiltration membranes. According to the results, the MFC with an ultrafiltration membrane generates high power density i.e., 324 mW/m^2 attached with an improved coulombic efficiency compared to the microfiltration membrane. The MFC with an ultrafiltration membrane achieved a better decolorization rate, i.e., 4.77 mg/L, followed by microfiltration membranes which showed 3.61 mg/L, and proton exchange membranes showed 1.72 mg/L. These results proved that the ultrafiltration membrane have good efficiency with low cost and easy operation. The overall removal rate was around 90% which was quite good due to the active performance of membranes. Electrode performance was lower due to usage of simple carbon paper which is not as conductive when compared to other material. In 2011, an MFC was attached with aerobic bio cathode in order to design a novel route for removal of azo dyes and it was demonstrated by Sun et al. [91] and proved first time that MFC attached to aerobic bio cathode can be effectively applied to decolorize azo dye, with cost effectiveness and energy output. The inoculum sources were based on aerobic sludge and treated by using porous-based carbon paper as electrode to generate a flow of electrons through microbes in double chamber MFC and showed the removal efficiency 90% with 213.93 mW/m^2 energy output. Yadav et al. [102] studied the performance of the new designed MFC called a wetland-microbial fuel cell to generate energy and remediation of dyes from wastewater. The general MFC based on anaerobic and aerobic chambers where both reduction and oxidation reactions occur. Similar in wetland MFC two chambers, anaerobic and aerobic, are found where reduction/oxidation processes

occur. Experiments were carried out by using methylene blue concentration in presence of synthetic wastewater. According to experimental results, 76.2%, 80.87%, 69.29% and 93.15% of removal were observed after 96 h operation time with different initial concentration, i.e., 2000, 1500, 1000 and 500 mg/L, respectively. The wetland-MFC holds the ability to remove chemical oxygen demand (COD) by around 75% by using 1500 mg/L dyes concentration from wastewater. The maximum power density was 15.73 mW/m^2 and highest current density was 69.75 mA/m^2, respectively. Later, Fang et al. [103] used a constructed wetland-MFC for decolorization of different dye along energy outputs. The energy was instantaneously generated throughout the co-metabolism process of azo dye and organic substrate i.e., glucose. Fang et al. [103] used an open-circuit and non-planted system as a reference to explore the value of used electrodes (Granular-activated carbon and stainless-steel mesh) and plants in the removal of azo dye along with electricity production. The results showed that plants grown in the cathode increased the cathodic potential and promoted dye decolorization efficiency. The electrodes enhanced the dye decolorization in the anodic chamber. The planted wetland-MFC attained the highly improved rate of decolorization (91.24%) and voltage output was around 610 mV. The external circuit connection supported the electrogenic bacterial growth (*Geobacter sulfurreducens* and Beta Proteobacteria) and discouraged *Archaea's* growth at the anodic chamber. Sun et al. [104] explored the mechanism of degradation for congo red using SMFC in presence of microfiltration membrane. In this experiment, glucose and congo red mixture was used as fuel in SMFC. The congo red bonds were condensed to make aromatic amines. The *Geobacter species* is a well-known bacterial species to produce electricity without assistance of congo red. However, *Methylobacterium*, *Azospirillum*, *Rhodobacter*, *Trichococcus*, *Desulfovibrio* and *Bacteroides* species were only noticed in the presence of congo red. From the results, these species were responsible for removal of congo red. The used electrode was graphite felt and carbon paper as an anode and cathode in presence of anaerobic sludge with 300 mg/L initial concentration of congo red and produced power density was 72.4 mW/m^2. Guo et al. [105] explored the importance of graphene in a MFC in order to improve the energy production and methyl orange degradation respectively. The anode electrode was modified with graphene in this work to examine the graphene credibility in power generation. The anaerobic sludge was served as inoculum with methyl orange concentration to degrade the respective dye. The energy production was achieved at approximately 368 mW/m^2. In the meantime, compared with blank anode, decolorization efficiency and 16% COD reduction rate were enhanced with graphene modification of the anode. Thung et al. [106] developed up-flow membrane-less SMFC to study bioreactor for acid orange 7 decolorization along with energy generation. The performance was assessed in terms of current, power density output, COD and removal efficiency of dye from synthetic wastewater. The outcomes shown current generation, i.e., 174.3 ± 5.8 mV and COD efficiency reduced as the initial concentration of acid orange 7 increased. These findings proved that ability of up-flow membrane-less SMFC in azo dye-based wastewater is quite good, i.e., around 90% removal efficiency and simultaneous better energy output. Chen et al. [107] studied the effect of textile-based dye and its decolorized metabolites MFC remediation. The *Proteus hauseri* bacteria were found in MFC on surface of porous carbon cloth (electrode) to remove thionine-based textile dye from wastewater. The result showed that 83.4 mW/m^2 energy output was observed with 50% removal efficiency. When the monoazo dye and diazo dyes, such as new coccine, were used as electron acceptor, the COD removal rate and azo dye degradations efficiencies increased i.e., 73 ± 3% (anode) and 95.1 ± 1% (cathode), respectively achieved by Oon et al. [108]. This study proved that the monoazo based dyes decolourisation rates were higher than other diazo-based dyes. The highest power density in the case of new coccine decolourisation was 20.64 mW/m^2, and the current density was 120.24 mA/m^2. The studied explained that the dye structure hold strong influenced on decolourisation efficiency and current production performance during MFC operation. Removal of dye mostly resulted at the anodic part of microbial fuel cell. The authors concluded that closed circuit system is more efficient in dye removal and oxidation of organic matter as compared to open circuit system. Logroño et al. [109] designed the air-free SMFC by using microalgal as biocathodes. These designed reactors were used for the removal of real dye textile wastewater along with the generation of energy. The results

revealed a highest coverage area in biocathodes by microalgal cells and showed power density around 123.2 ± 27.5 mW/m^3 with 42% removal efficiency of real dye after 30 days operation in the presence of carbon fibres as anode and cathode electrode. A distinguishing combination of both anaerobic and aerobic in an up-flow membrane-less SMFC was developed to study the mechanism and interrelation between biodegradation of the dye acid orange 7 and energy output. The acid orange 7 decolorization rate was around 89–96% in different configurations during system operation and voltage output was affected when concentration of acid orange 7 was increased. The outcome was 32.84 ± 23.57 mV in term of voltage after 2 months' continuous operation of up-flow membrane-less SMFC. The production of energy depends upon performance of the electrode [110]. The photo-electrocatalytic microbial fuel cell for degradation of methyl orange along with power production by using simple carbon paper as electrode was studied by Han et al. [111].The result was very poor in terms of power density, i.e., 0.119 W/m^2 but the degradation efficiency was much better i.e., around 84.5% from mixed anaerobic sludge of wastewater. The graphene oxide supported the degradation of green dye through MFC was studied by Khalid et al. [112]. It successfully removed the green dye and proved that bioactive properties of graphene oxide on the anode is superior in character to achieve 80 degradation rates. However, power density and current density were poor, i.e., 0.04 mW/cm^2 and 0.0025 mA/cm^2. The power outcome observations proposed the usage of graphene oxide and its composite as electrodes to enhance the power output. Miran et al. [113] studied the degradation process of textile diazo-based dye through DMFC in presence of microbes such as Proteobacteria, Deltaproteobacteria and Desulfovibrio. The microbial community analysis presented that Deltaproteobacteria (52.7), Desulfovibrio (48.2) and Proteobacteria (89.4), were prominent at class, phylum, and genus stages, respectively. The energy outcomes were 258 ± 10 mW/m^2 with 90% degradation rate of textile dyes after 24 h operation time of MFC. Sarma et al. [114] explained the phenomena of composite polymer doped with magnetic nanoparticles on the anode to increase the dye's degradation rate and power output. The experimental data revealed that the removal efficiency was good which are near 90% and electricity generation found 4.9 ± 0.5 W/m^3 in the presence of polymer-coated magnetic composite electrode and *Synechococcus* sp. The *P. aeruginosa* catalysed the H-typed MFC to remove methyl orange from wastewater. The experiment was carried out by using graphite/polyester composite as electrodes in both chambers and produced high energy output, i.e., 1575 ± 223.26 μW/m^2. The flow of electrons is depending upon the bacterial growth on surface of electrode and electrode material conductivity. The degradation removal was also enhanced by using high-tech material in MFC operation and it was 89.55% for methyl orange and these observation were carried out by Narayanasamy and Jayaprakash [115]. Kumar et al. [36] studied the MFC for bioelectrochemically dealing with wastewater streams and degraded the congo red along with power generation, i.e., 103 mW/m^2 and the degradation efficiency was almost 98% in the presence of 300 mg/L initial concentration of inoculum source in SMFC after 36 h continuous operation system. Carbon paper served as electrode on both sides of the anode and cathode to generate the flow of electrons but due to less efficiency of the electrodes it failed to produce high voltage. You et al. [116] first time introduced a well-organized double chamber microbial electrolyte/ultraviolet (UV) in order to degrade the methyl orange. The external voltage was applied i.e., 0.2 V and the cathode aeration also employed i.e., 20 mL/min. The degradation efficiency was 94.7% at initial pH 7 with UV illumination. The carbon brushes and graphite plate served as anode and cathode electrode in DMFC to generate the electricity. Dai et al. [117] studied the degradation of sulfide-mediated azo dye by using SMFC. Many textile industries developments produce different complex compounds such as sulfide and azo dyes which can deteriorate our environment. The SMFC with air cathode were utilized to consider the interaction, relation, mechanisms between congo red and sulfide. The results exhibited that active removal of azo dyes is more than 88% and sulfide removal is almost 98% and it happened in neutral pH medium, accompanied by the highest energy output i.e., 23.50 mW/m^2. This work provides an alternate for various dye and sulphide pollutants removal single-chamber air cathode-microbial fuel cells. Later, Sonu et al. [118] studied the upscaling of MFCs and used stacked MFC to decolorize the real textile-based dyes. They made a series and parallel stack arrangement to

evaluate the performance of MFCs. From the results, power generation efficiency was observed to be 38.6 mW/m^2 in series mode while 0.47 mW/m^2 in a parallel-stack MFC. Similarly, the decolourisation rate of textile dye was 82.14% and 74.5%, respectively in both stack modes. This study documented that framework (biochar and parallel stacking) could achieve better dye removal with simultaneous electricity generation. However, the drawback of this study is the high cost which makes it unsuitable at commercial scale. Yoong et al. [119] studied the constructed wetland–MFC for decolorization of azo dyes with energy generation, considering the molecular structural and kinetics effect along with decolorization mechanisms. The maximum decolorization rate was 96%. However, there are still several hazardous dyes that need significant attention such as rhodamine B, rhodamine 6 g, brilliant green etc. The MFCs are a much better approach in terms of dye treatment as compared to photocatalysis. Therefore, future research must focus on decolorizing hazardous dyes through MFCs by using optimized operational conditions.

Table 2. List of dye removal efficiency, energy output through MFCs.

Target Dye-Based Pollutant	Type of MFCs	Type of Electrodes		Inoculum/ Microbes	Operating Time (Hr)	Temp. (°C)	Initial pH	Initial Conc. (mg/L)	Removal Efficiency (%)	Power Density	Reference
		Anode	Cathode								
Acid orange 7	DMFC	Graphite rod	Graphite rod	Microbial consortium	336	25	7.00	0.06	78	0.31 ± 0.03 W/m^3	[120]
Methyl orange Orange I Orange II	DMFC	Carbon felt	Carbon felt	-	18	30	3–9	-	-	34.77 mW/m^2	[121]
Methyl orange	DMFC	Unpolished graphite	Rutile– coated graphite cathode	Anaerobic sludge	24	25 ± 1	-	10–20	73.4	0.13 ± 0.03 W/m^2	[122]
Model textile dyes	SMFC	Activated carbon	Hydrophobic carbon cloth	*Proteus hauseri* ZMd44	480	30	-	450–560	75	103 mW/m^2	[123]
Amaranth	DMFC	Granular graphite	Spectrographic pure graphite	-	12	-	3.00	75	82.59	137.37 mW/m^2	[89]
Active brilliant red X-3 B	DMFC	Porous carbon paper	Porous carbon paper	Aerobic sludges	12	-	7.00	300	90	213.93 mW/m^2	[91]
Congo red	SMFC	Carbon papers (non-wet proofed porous)	Carbon papers with Pt (wet porous)	Mixture of aerobic and sludge	-	30 ± 1	-	300	90	324 mW/m^2	[101]
Acid orange 7	DMFC	Carbon cloth	Carbon cloth	*Shewanella oneidensis*	30	25	7.0	350	>98	-	[124]
Methylene blue	WMFC	Carbon	Carbon	Marine sludge	96	25	4–6.1	500	93.15	15.73 mW/m^2	[125]
Congo red	SMFC	Plain carbon papers (non-wet proofed)	Carbon paper (wet-proofed)	Culture of aerobic and sludge	26	30 ± 1	-	-	85	107 mW/m^2	[126]
Active brilliant red dye	DMFC	Granular-activated carbon	Stainless steel mesh	Anaerobic sludg	72	25 ± 2	-	-	85.65	610 mW/m^2	[103]
Dye	DMFC	Granular activated carbon	Stainless steel mesh	Anaerobic sludge (*Geobacter Sulfurreducensand)*	72	25 ± 2	-	150	91	610 mW/m^2	[103]
Azo dye	DMFC	Graphite-granules	Graphite-granules	Anaerobic sludge	48	-	3–7	-	85	34.77 mW/m^2	[127]
Congo red	SMFC	Graphite felt	Carbon paper	Anaerobic sludge	2880	30 ± 1	7	300	70	72.4 mW/m^2	[104]
Acid orange 7	SMFC	Carbon Fabric	Carbon fabric	Azo dye acclimated mixed microbial	60	26	8.2	-	>90	-	[128]

Table 2. *Cont.*

Target Dye-Based Pollutant	Type of MFCs	Type of Electrodes		Inoculum/ Microbes	Operating Time (Hr)	Temp. (°C)	Initial pH	Initial Conc. (mg/L)	Removal Efficiency (%)	Power Density	Reference
		Anode	Cathode								
Methyl orange	DMFC	Carbon paper/graphene	Carbon paper	Anaerobic sludge	180	30 ± 1	6.8–7	-	51	368 mW/m^2	[105]
Acid navy blue R	DMFC	Graphite rods	Graphite rods	Anaerobic sludge	-	25	-	3000	-	0.125 mW/m^2	[129]
Thionine-based textile dye	SMFC	Porous carbon cloth	Porous carbon cloth	*Proteus hauseri* ZMd44	12	25	7	40	-	83.39 ± 0.28 mW/m^2	[130]
Navy blue r(ANB) dyes	SMFC	Graphite rod	Graphite rod	Aerobic and anaerobic Sludge	48	27 ± 2	7.5–8.0	200	-	2236 mW/m^2	[131]
Acid orange 7	SMFC	Carbon felt	Carbon felt	Mixed culture anaerobic sludge	2160	-	-	75	90	174.3 ± 5.8 mW/m^2	[106]
Azo dye	DMFC	Activate carbon	Stainless steel mesh	Concentrated anaerobic sludge	72	25 ± 2	-	300	96.5	0.852 W/m^3,	[103]
Azo dye	SMFC	Carbon felt	Carbon plate	Mixed anaerobic sludge	6	25	7.1	50	80.6	167.4 ± 11.6 W/m^2	[107]
Thionine-based textile Dyes	SMFC	Porous carbon cloth	Porous carbon cloth	*Proteus hauseri*	48	30	-	40	50	83.4 mW/m^2	[107]
Congo red	DMFC	-	-	*Shewanella oneidensis* MR-1	24	28–40	6.0–8.5	2 g/L	99.25	-	[132]
Real dye textile wastewater	SMFC	Carbon fibres	Carbon fibres	Algal media	720	25–26	7.5	-	42	123.2 ± 27.5 mW/m^3	[109]
Azo dye	DMFC	Carbon felt	Carbon felt	Anaerobic sludge	72	28 ± 2	-	-	95.1	20.64 mW/m^2	[108]
Dyes	DMFC	Carbon rod	Carbon rod	Mixed culture (*Pseudomonas aurogenosa* and *Pseudomonas fluresence)*	2	-	-	2500	-	469.48 mW/m^2	[133]
Methyl orange	DMFC	Carbon paper	Carbon paper	Mixed anaerobic sludge	36	-	-	-	84.5	0.119 W/m^2	[111]
Congo red	DMFC	Graphite rod	Graphite rod	Mixed anaerobic sludge	72	20 ± 3	7.00	-	90	808.3 mW/m^3	[134]
Azo dye	DMFC	Graphite brush	Activated carbon	Mixed-waste sludge	720	-	6–8.5	260	85	-	[135]
Methyl orange	DMFC	Graphite/polyester composite electrode	Graphite/polyester composite electrodes	*P. aeruginosa*.	12	32	7.00	-	89.55	1575 ± 223.26 mW/m^2	[115]

Table 2. *Cont.*

Target Dye-Based Pollutant	Type of MFCs	Type of Electrodes		Inoculum/ Microbes	Operating Time (Hr)	Temp. (°C)	Initial pH	Initial Conc. (mg/L)	Removal Efficiency (%)	Power Density	Reference
		Anode	Cathode								
Acid orange 7	DMFC	Carbon felt	Carbon plate	Azo dye orange II	1460	-	7.00	150	96	32.84 ± 23.57 W/m^2	[110]
Green dye	DMFC	Stainless steel meshes	Chromium plate	*Geobacter sulfurreducens*	168	35	6.8	-	80	0.04 mW/m^2	[112]
Textile diazo dye	DMFC	Graphite felt	Graphite cloth	Proteobacteria, Deltaproteobacteria and Desulfovibrio	24	30	7.0	100	90	258 ± 10 mW/m^2	[113]
Azo dye	WMFC	Carbon felt	Carbon felt	Mixed-culture sludge	463 days	28 ± 2	7.00	500	94–95	8.67 mW/m^2	[136]
Methyl orange	DMFC	Carbon brush	Graphite plate	Anaerobic sludge	2	27	7	25	94.7	-	[116]
Thionine-based textile dye	SMFC	Porous carbon cloth without catalyst	Porous carbon cloth with polytetrafluoroethylene as catalyst	*Proteus hauseri* ZMd44	120	25	7	40	-	83.39 ± 0.28 mW/m^2	[137]
Congo red	DMFC	Plain carbon felts	Carbon felt	Anaerobic sludge	720	35	-	100	86.4	400 mW/m^2	[137]
Congo red	SMFC	Carbon paper	Carbon paper	Mixture of aerobic and anaerobic sludge	36	30	-	300	98	103 mW/m^2	[36]
Congo red	SMFC	Graphite fibre brush	Graphite fibre with platinum	Anaerobic sludge	24	25	7.00	200	≥88	23.50 mW/m^2	[117]

MFC = Microbial fuel cell; DMF = Double-chamber MFC; SMFC = Single-chamber MFC; *SMFC = Sediment double-chamber MFC; TMFC = Tubular double-chamber MFC; WMFC = Wetland Microbial fuel cell.

4. Mechanism of Electricity Generation and Pollutant Removal in MFCs

To describe the mechanism, we need to study the mechanism of pollutant removal through MFCs with electricity generation. An extensive variety of microbes are available to generate electricity by transferring the electrons to the anode. The most common electron-producing microbes' groups are Actinobacteria, Firmicutes, Proteobacteria phyla, fungi, algae and yeast which can generate electricity. Furthermore, *Geobacter* spp., *Rhodoferax ferrireducens*, *Aeromonas hydrophila*, *Clostridium butyricum*, *Shewanella* spp., *E. coli* etc. are commonly reported microbes in MFCs [138]. The microbes form a biofilm around the anode, and transfer the electrons by using different mechanism such as long-range via conductive pili, short-range mechanisms through redox-active molecules and electron transfer through shuttling molecules, as shown in Figure 2. Generally, anode is not considered as part of aquatic atmosphere in chamber, microbes growth forms the biofilm on the surface of the anode and used power for respiration purposes. During the respiration process, microbes release electrons and protons that transfer to the anode and cathode [139]. The protons are transfer directly from anode to cathode by using proton exchange membrane and electrons using external circuit with specific external resistance. For the first time, Bond et al. [140] studied the transfer of electrons towards electrodes via self-produced electron shuttles in case of *Geobacter fermentans.* Both Gram-positive and -negative microbes can transfer the electrons by using self-produced shuttles and commonly *Desulfuromonas* species *and Geobacter* families involved in this mechanism. Through the transfer of electrons through redox-active protein molecules, *Geobacter sulfurreducens* can transfer the electrons from microbes to anode in the presence of oxygen-free enzymatic metabolism. Several redox-active proteins molecules are available in exoelectrogens such as OmcZ, OmcS, OmcE, OmcT, and OmcB. Similarly, the transfer of electrons through conductive pili also plays a significant role in electricity generation mechanism. The *Pelotomaculum thermopropionicum*, *Shewanella oneidensis*, *Methanothermo bacterthermautotrophicus* and *G. sulfurreducens* used the pili to transfer the electrons successfully [141]. The microbe's pili correspond to electron transfer from exoelectrogens biofilm, while the direct electron transfers mechanism is mostly demonstrated in *Pelotomaculum thermopropionicum* and *aerobic Synechocystis* [142]. This mechanism helps to enhance the mutual growth by transferring the electrons individually [143]. However, the pollutant treatment also depends on the ability and growth of microbes as discussed in electricity generation mechanism. Both processes are directly proportional because generation of electrons depends on the respiration process of microbes which ultimately depend on organic substrate. However, microbes serve as electron acceptors, usually known as electrotrophs which open a new research door for remediation of pollutants, especially toxic metal dyes through reduction [144]. The Figure 2 represents the reduction mechanism of toxic pollutants by exoelectrogens. Several studies demonstrated that the electrotrophs gene expression is not similar to exoelectrogens such as omcZ genes and pilA. However, in case of *G. sulfurreducens* which reduced the Cr^{+4} to Cr^{+3}, mean toxic state to insoluble state through accepting the electrons [145]. The basic operational concept is based on the biological conversions at the surface of the anode which are used to transfer the electrons and drive reductive precipitation of metal ions. The bioelectrochemical system provides an opportunity to remediate the wastewater through reduction and oxidation reactions to generate the electricity. The anode biofilms oxidize the organic substrate giving the driving power for an electrochemical reduction of metals and recovery procedure at the cathode site. The reduced metals are either precipitated in solution or deposited on the surface of the cathode, or remain soluble, depending on the solution chemistry and properties of reduced metals. The metal ions reduction turns into spontaneous phase at the surface of the cathode which offers the redox potential of a cathode half-cell reaction. It is higher or almost comparable to anode potential which is generated in bioelectrochemical cells [98]. Thus, the metal reduces precipitation along with optimistic redox potentials, such as V (V), Hg (II), Au (III), C r(VI), Se (IV) and Ag (I). In bioelectrochemical cells, external energy is also required to achieve the reduction of metal ions at the cathode if reduction potential of the cathode is less than anodic potential. This condition is thermodynamically not favourable for electron flow [134]. Therefore, there are very rare chances of adsorption to any carbon-based electrodes. After a literature review, we found that

energy-dispersive X-ray spectroscopy (EDX) is a technique to differentiate the MFCs and adsorption process by studying the morphology of electrodes before and after MFCs operation [99]. Similarly, the degradation of organic dyes such as azo dyes, methylene blue, methylene red etc. are studied in MFCs to degrade the dyes from toxic state to insoluble state by promoting the reduction and oxidation process [146]. The energy is provided via electrodes to generate the electrons which creates a promising and stable environment for the reduction and oxidation of pollutants. However, in case of fixed CO_2, the process is known as electrosynthesis which is similar to mechanism of photosynthesis [146]. Primarily, the cathode was working as donor for electrons in pure cultures. Recently, some groups have been recognized which serve as electrotrophs in case of pure culture such as *Moorella thermoacetica*, *Clostridium ljungdahlii*, *Sporomusa ovata*, *G. metallireducens*, *G. sulfurreducens*, and *Clostridium aceticum*. The aforementioned microbial species generally exist in mono layer on the surface of the cathode. [140]. Usually, a dense biofilm is noticed on surface of anode and very thin biofilms is observed on surface of cathode in case of pure culture. However, the biofilm stability entirely depends on current generation to cathode which is important to understand the species interactions to promote electron transformation. Furthermore, both toxic metal and dye degradation are briefly summarized in Figures 2 and 3.

MFCs are essentially used for current generation and the biocatalyst (microbes) oxidize the organic substrate in the anode compartment to produce electrons and protons [34]. MFC chambers are electrically connected by a multimeter and resistor box which help to measure the current. The primary step of current generation by MFCs is adaptation of exoelectrogens at the anode and the produced biofilm on surface of anode electrode [147]. Therefore, exoelectrogens make a conductive biofilm with few micrometres thickness. The development of biofilm by exoelectrogens is exclusive, distinctive and varies between microorganisms [148–150]. The scientific community is highly engaged regarding development of MFCs [151]. Research scholars are putting countless efforts into finding more efficient material to use in MFCs to enhance the energy output. Most of the researchers used different conditions to develop different design and different materials for MFCs to enhance energy production. Xiao et al. [152] described the electrode material and found that electrodes are responsible for energy production and graphene and obtained a promising position in terms of electrode material to use in MFC, but there is little research on graphene. According to result the power density with graphene at cathode i.e., 3.3 W/m^3 and 2.5 W/m^3. Gnana et al. [153] studied the effect of reduced graphene oxide as the anode material in the presence of *E. coli* microbes and produced 1068 mW/m^2 energy output in DMFC. Khan et al. [154] studied the bio-electrochemical degradation in both SMFC and DMFC by using organic compounds with instantaneous energy production. The highest cell potential was noted to be 787 mv in SMFC and 1021 mV DMFC, respectively. The results showed power densities in case of SMFC and DMFC i.e., 872.7 mW/m^2 and 1468.85 mW/m^2. Recently, Hung et al. [155] studied coffee waste-derived carbon anode and obtained the 3927 mW/m^2 power density. This study demonstrated that the high quality of an electrode can increase the energy generation to meet the energy requirement via MFC approach. Therefore, there is still a major lack of research on graphene and its doped material to use as an electrode like graphene/ZnO, graphene/TiO_2 etc. Ali and co-workers [156] carried out the MFCs operation by employing the FeS/rGO nanocomposites as catalyst to enhance the energy generation in the presence of Cr-based sludge. They reported 100% removal efficiency of Cr with 15 mg/L initial concentration and a high reduction rate of 1.43 mg/L/h which is 4.5 time higher than casual MFC system. The highest power density observed was 154 mW/m^2. This study has proved the maximum rate of reduction and higher energy generation as compared with earlier studies. There were a lot of efforts reported to improve current production through MFCs as shown in Table 3. The most important key is to improve energy output in the MFCs operation. The important parameters are pH, exoelectrogens, substrate, temperature, electrode material and MFCs designing. Improving the electrodes efficiency by using different composites materials and controlling the solution pH at required temperature is supposed to give better results in MFCs.

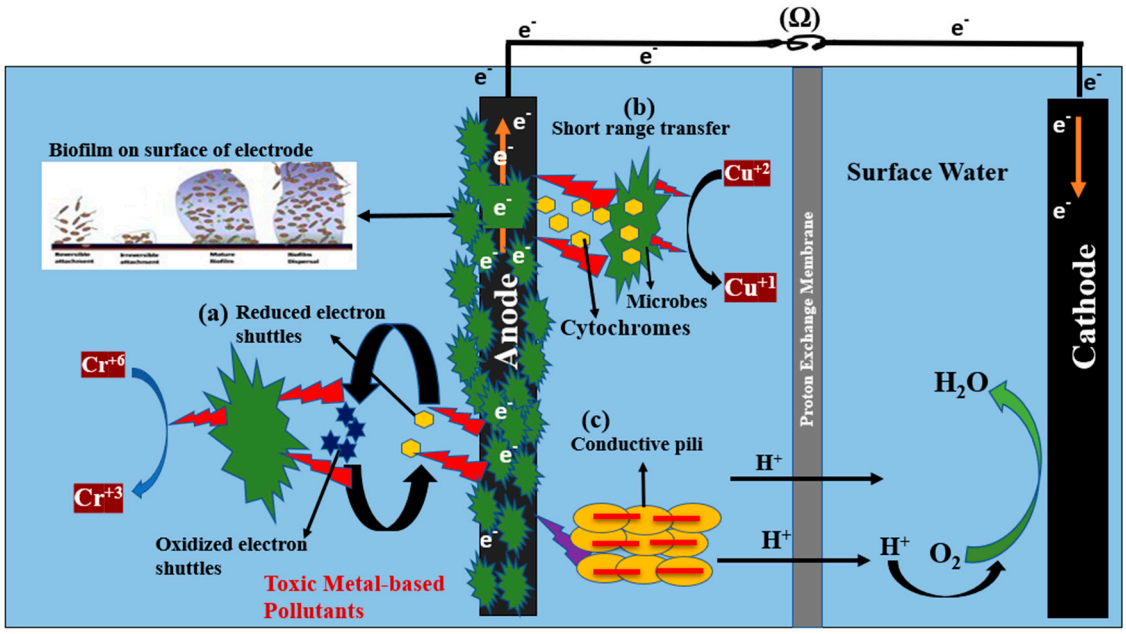

Figure 2. Reduction mechanisms of toxic metals through MFCs (**a**–**c**). Different mechanisms of electron transfer from microbes to electrodes.

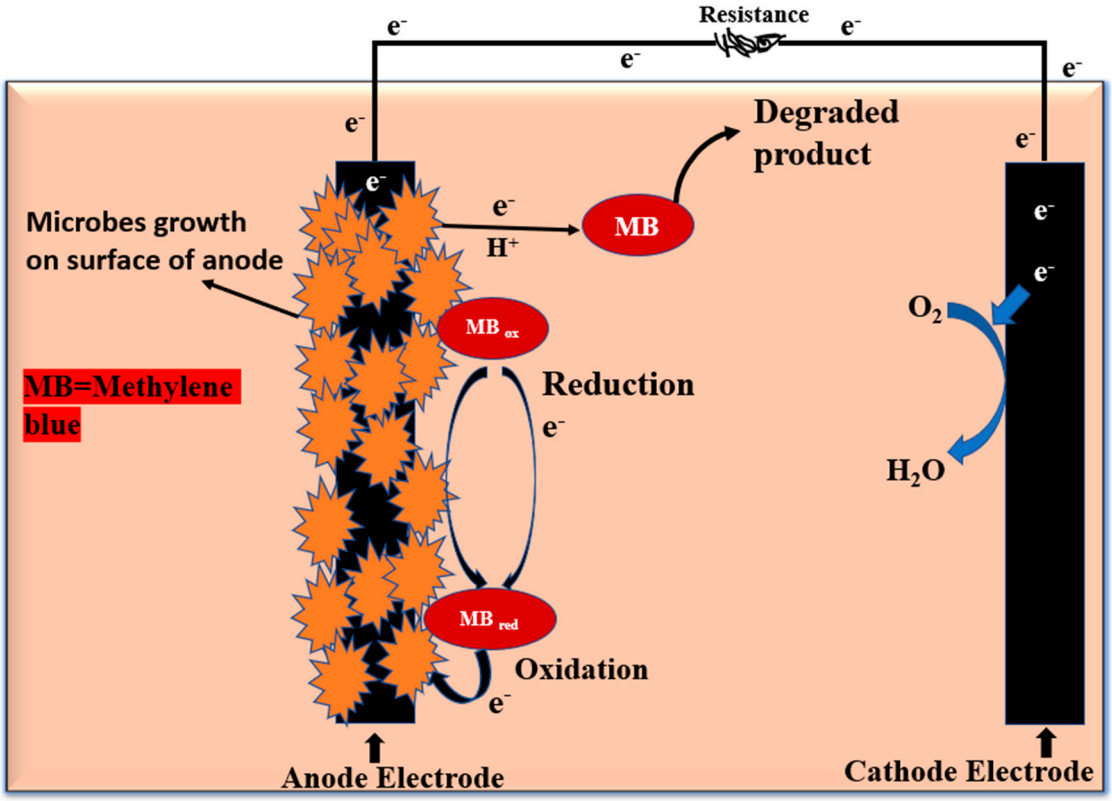

Figure 3. Degradation mechanism of organic dyes through MFCs.

Table 3. List of electrodes and microbes with energy output through MFCs.

Type of Electrodes		Microbes	Power Density	Reference
Anode	**Cathode**			
Plain carbon paper	Plain carbon paper	*C. acetobutylicum* and *C. Thermohydrosulfuricum*	7.18 mW/m^2	[156]
Activated Carbon	Hydrophobic carbon cloth	*Proteus hauseri* ZMd44	103 mW/m^2	[123]
Graphite felts	Graphite felts	Actinobacteria, B-Proteobacteria,	-	[44]
Graphite plates	Platinum meshes	*Shewanella oneidensis*	1410 mW/m^2	[157]
Activated carbon cloth	Graphite foil	*D. desulfurisers* strain	0.51 mW/cm^2	[157]
Carbon cloth/graphene	Carbon cloth	*P. aeruginosa*	52.5 mW/m^2	[158]
Activated carbon	Carbon cloth	-	1.7 mW/m^3	[151]
Graphite felt	Graphite rod	*Shewanella oneidensis* MR-1	32.5 mW/m^2	[46]
Granular activated carbon	Stainless steel mesh	*Geobacter Sulfurreducens* and Beta Proteobacteria	610 mW/m^2	[46]
Carbon paper/graphene sheet	Carbon cloth	*S. oneidensis* MR-1	610 mW/m^2	[159]
Polyaniline (PANI) networks onto graphene nanoribbons (GNRs)-coated on carbon paper	Carbon paper	*S. oneidensis* MR-1	856 mW/m^2	[160]
Carbon felt	-	*E. coli*	0.98 W/m^2	[161]
Carbon cloth	Carbon cloth with Pt as catalyst	*Shewanella oneidensis* MR-1	158.1 mW/m^2	[162]
rGO/SnO_2/Carbon cloth composite	Pt rode	*E. coli*	1624 mW/m^2	[163]
Polymer coated magnetic compositeelectrode	Toray carbon paper	*Synechococcus* sp.	4.9 ± 0.5 W/m^3	[128]
Carbon cloth/Reduced graphene/polypyrrole	Carbon paper	*E. coli*	1068 mW/m^2	[152]
Carbon cloth	Carbon cloth	*Klebsiella* sp. MC-1	412 mW/m^2	[84]
Pt-graphite	Pt-graphite	*Shewanella genus*	-	[48]
Carbon cloth/N-doped graphene nanosheets	Carbon cloth	*E. coli*	1008 mW/m^2	[164]
Carbon cloth/graphene	Carbon cloth	*S. putrefaciens* CN32	679.7 mW/m^2	[165]
Porous carbon cloth	Porous carbon cloth	*Proteus hauseri* ZMd44	83.39 ± 0.28 mW/m^2	[130]
Graphite plate	Graphite plate	*Acidithiobacillus* spp. and *Ferroplasma* sp.	17.6 mW/m^2	[166]
Porous carbon cloth	Porous carbon cloth	*Proteus hauseri*	83.4 mW/m^2	[107]
3D-Graphene	Carbon cloth/Pt	*E. coli*	1516 ± 87 mW/m^2	[167]
Carbon fiber felt	Carbon fiber felt	*Dysgonomonas* and *Klebsiella*	529 ± 12 mW/m^2	[52]
Carbon rod	Carbon rod	*Pseudomonas Aurogenosa* and *Pseudomonas fluresence*	469.48 mW/m^2	[133]
Stainless steel meshes	Chromium plate	*Geobacter sulfurreducens*	0.04 mW/cm^2	[112]

Table 3. *Cont.*

Type of Electrodes		Microbes	Power Density	Reference
Anode	**Cathode**			
Graphite felt	Graphite cloth	*Deltaproteobacteria* and *Desulfovibrio*	258 ± 10 mW/m^2	[113]
Graphite/polyester composite electrodes	Graphite/polyester composite electrodes	*P. aeruginosa*.	1575 ± 223.26 mW/m^2	[115]
Carbon brushes	Activated carbon paper	*Geobacter* species	28.4 ± 1.2 W/m^3.	[168]
Carbon felt	Carbon felt	*Shewanella decoloration* S12, *K. pneumonia*	52.1 mW/cm^2	[59]
Carbon brush	Reduced graphene oxide	*Geobacter* and *Pseudomonas*	0.95 W/m^2	[60]
Porous carbon cloth without catalyst	Porous carbon cloth with polytetrafluoroethylene as catalyst	*Proteus hauseri ZMd44*	83.39 ± 0.28 mW/m^2	[137]

5. Future Perspectives and Conclusive Remarks

This review article has attempted to elaborate the importance of MFCs regarding the removal of organic dyes and toxic metals from wastewater by using non-conventional and inexpensive material so that it might be useful for scholars to gain an idea about different types of cost-effective materials to improve the working efficiency of MFCs. This is the newest and most novel approach to generating electricity from waste material by using microorganism as substrate. The main objective of this article is to develop a potential understanding for the reader regarding MFCs to improve their research on this emerging topic. This review was based on the last 10–12 years' reported data, to which improvements have already been made. Despite all the improvements, there are a lot of research gaps. For instance, to improve the production efficiency of energy, bioelectronics devices need more attention, and MFC-based biosensors are also not fully explored yet. The MFCs approach is still an unsuitable technique to use at commercial level despite more than 10 years of comprehensive study and research on this technique [169]. The removal efficiency of organic dye-based pollutants and toxic metals was better in some cases. It was noticed that some parameters affect the biodegradation and energy production process i.e., pH, temperature, initial concentration, choice of substrate, microbes, and the most important is electrode material. It was observed from literature that the degradation efficiency of toxic metal was higher at acidic condition, with a high conductive electrode giving high removal efficiency along with much better power output [170]. Electrode parameter is still in very early stage i.e., preparation of electrodes from waste materials. There are many waste materials to use to convert into graphene oxide and change into electrodes. Therefore, the selection of these parameters is very important for better outcomes [171]. Literature also shows that the modification of electrodes can enhance the removal efficiency through MFCs such as graphene oxide modification with conductive polymers and different metals. Conductive polymer is also very prominent material for making composite to obtain remarkable efficiency from MFCs and making it more prolific. However, little effort was reported in this research direction. Furthermore, MFC-based devices are also capable of applying as biosensors to detect toxic pollutants (metals, organic, inorganic etc.) from wastewater but MFCs-based biosensors are facing certain challenges like poor reliability, lower sensitivity and poor accuracy. Another problem was encountered in biosensors i.e., response time is longer than conventional sensors and generated energy is not enough to operate a sensor consistently in an effective way. However, the scientific community should focus on exploring their values as biosensors because sensors can detect different pollutants easily. It is an easy and accessible technique.

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