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Review Article

Microbial fuel cells in electricity generation with waste treatment: Alternative electron acceptors

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ABSTRACT

Microbial fuel cell (MFC) have attracted great interest in recent years as a technology that uses microorganisms to oxidize organic and inorganic materials at the anode for the purpose of bioelectricity generation and bioremediation. In MFC systems, energy can be obtained by using all kinds of organic matter as substrate, from simple molecules (acetate, carbohydrates, glucose etc.) to complex compounds (molasses, cellulose, wastewater, waste sludge, domestic agricultural and animal wastes etc.). In addition to wastewater treatment, MFC technology has additional benefits such as sulfate removal, heavy metal removal, denitrification and nitrification. However, the low power efficiencies and potential losses of these systems limit their applicability on a real scale. Although the anode chamber of MFC systems has been studied in detail over many different parameters, the cathodic electron acceptors have been studied relatively less. In MFC systems, electron acceptors are one of the main parameters influencing power generation as they contribute to overcoming potential losses at the cathode. Oxygen has a relatively high redox potential and is the traditional electron acceptor used in MFC systems as it is reduced to form a clean product like water. However, the need for alternative electron acceptors has increased due to the fact that feeding oxygen to the cathode chamber requires additional energy and the need for catalysts due to the slow O_2 reduction rate. Electricity generation by reducing certain electron acceptors at the cathode chamber has promising potential for bioenergy production, and the use of pollutants such as nitrogen species, heavy metals and perchlorate as electron acceptors reduces the cost for their specific treatment. This review aims to summarize the various electron acceptors used in MFC systems, compare their effects on MFC performance, and discuss possible future areas.

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INTRODUCTION

With the rapid growth in urbanization and industrialization, the decrease in crude oil reserves has increased the need for renewable and sustainable energy sources [1]. It is necessary to deal effectively with climate change and waste management for sustainable development. Therefore, providing energy-neutral treatment of domestic and industrial

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wastewater is of interest [2]. Bio-energy techniques such as pyrolysis, gasification, anaerobic digestion and fermentation convert the energy in biomass into heat, electricity and fuel and can significantly reduce greenhouse gas emissions. Microbial Fuel Cell (MFC) technology is a suitable alternative method in which wastewater treatment and bioelectricity production are carried out simultaneously. With MFC technology, it is theoretically possible to recover the rich energy in waste and meet the energy consumed for the operation of treatment plants [3]. "Green electricity" can be achieved by using waste resources in MFC [4]. Conventional sludge stabilization and wastewater treatment plants involve high-energy processes such as aeration, heat treatment and dewatering. On the other hand, wastewater contains more energy than the energy required for its treatment. Microbial fuel cell technology is an interesting approach for simultaneous wastewater treatment and electricity generation. Currently, it is a widely researched area and a lot of research has been done in this area. In the last few years, various parameters such as temperature, substrate and operating conditions have been optimized to increase the efficiency of MFC systems. Compared to other conventional treatment techniques, MFC technology has advantages such as less sludge formation that needs to be disposed of, no need for aeration, and the clean energy generated can be used without the need for a secondary purification process, as in the methane and hydrogen energies formed in anaerobic treatment [5].

Although MFC is a promising alternative, field-scale applications are still limited and anaerobic digesters appear to dominate the market for power generation [6]. MFC technology is seen as an environmentally friendly alternative to the activated sludge treatment process and anaerobic digestion processes for energy recovery [2]. An MFC system simply consists of anode and cathode chambers. With exolectrogenic microorganisms colonizing on the anode surface, organic substrates are oxidized and electrons are released, which are then transferred to the cathode via an external circuit and the reduction reactions are completed. In the cathode, electrons combine with an electron acceptor and electricity is produced. The electron acceptor is reduced by gaining electrons and combines with the protons passing through the proton-permeable membrane to form water [7]. Although there are many different designs of the MFC system, the basic designs can be classified as dual chamber, single chamber, upflow, and miniature MFCs [8]. The typical dual-chamber MFC configuration, physically separated by a proton exchange membrane, is shown in Figure 1.

Microorganisms in the anode chamber oxidize the substrate and the electrons released along with the degradation are transferred via an external circuit (Equation 1). At the same time, the protons in the anode pass over the proton-permeable membrane to the cathode, where they are reduced by the electron acceptor (O_2 in the equation) and form water (Equation 2) [4]. As the substrate breaks down into carbon dioxide and water, electricity is produced as a by-product [10].

$$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^- \quad (1)$$

$$24H^+ + 24e^- + 6O_2 \rightarrow 12H_2O \quad (2)$$

A typical single-chamber MFC does not have a cathodic chamber and the cathode electrode is directly exposed to air. In a single-chamber MFC system, oxygen is directly reduced in the cell on the cathode. This technology also eliminates the need for a conventional polymer membrane, which is very expensive and causes the majority of cell losses [11]. Dual-chamber MFCs can be operated in batch or continuous mode, but are difficult to scale up due to their complex design. Single chamber MFCs, on the other hand, are simpler designs and provide cost savings [10]. Single-chamber MFCs are more suitable for practical applications,

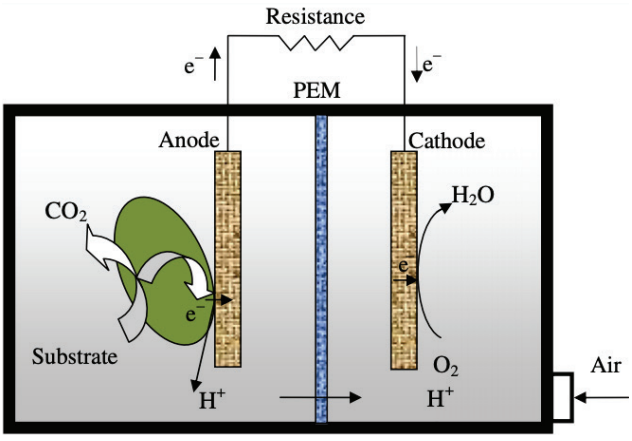

Figure 1. Dual-chamber microbial fuel cell [9].

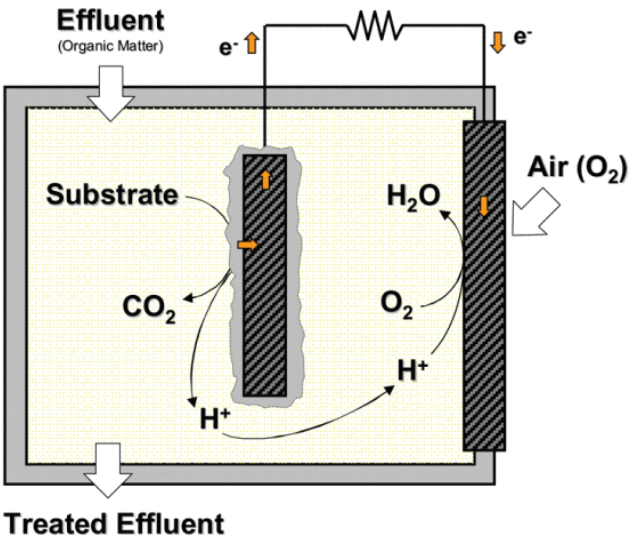

Figure 2. S-chamber microbial fuel cell [11].

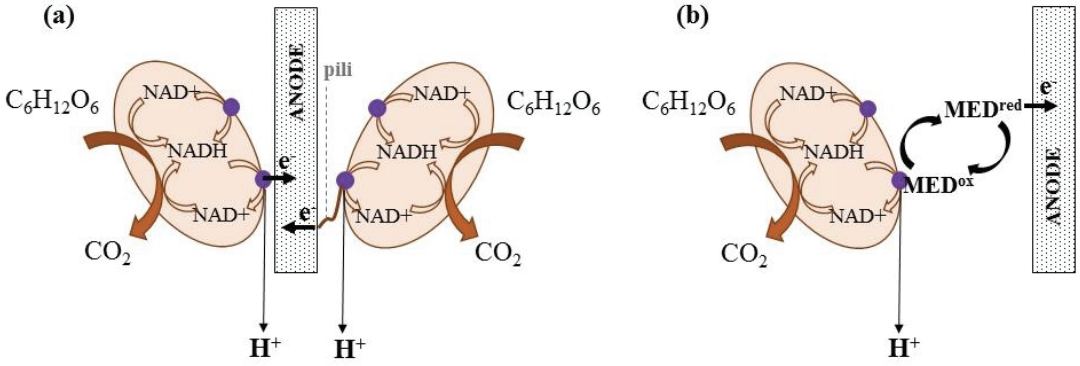

Figure 3. Anode electron transfer mechanisms in MFC systems (a) DET and (b) MET [39].

dual-chamber MFCs have higher internal resistance due to the wide electrode spacing, and are used for basic research such as testing new materials [12].

Various developments have been made on MFC technology in the areas of system designs and configurations [13–15], types of microorganism [16–18], electrode types and electrode modifications [19–22], performance and improvement of operating conditions for biofilm formation [23,24], different and modified membranes [12,25], electron acceptors and basic electron transfer mechanisms [26,27]. Each of these key parameters significantly affects the efficiency and power density of the treatment. Ongoing research on microbial fuel cells in recent years has begun to place emphasis on continuous-flow scalable MFC setups rather than lab-scale batch trials. Scaling up can be done with more than one cell, with more than one electrode in the same cell, or by increasing the size of the cell [28]. MFC technology can treat organic, organometallic and even inorganic contaminants with high removal rates; It produces relatively less sludge at the end of the treatment process. It can also be applied to treat contaminated soil [29] and gaseous pollutants [30].

Expensive materials, low power generation, and difficulties in scaling up have significantly slowed the progress of MFC systems. However, with a better understanding of the electron transfer mechanisms, it has been observed that advanced electrode materials can significantly increase the power generation [28].

The power losses that prevent the achievement of theoretical energy efficiency in the MFC system can be listed as concentration losses, activation losses and bacterial metabolic. To reduce these losses, modifications such as reducing the space between the electrodes, increasing the solution conductivity, increasing the electrode surface area, using catalysts and increasing the biofilm formation are studied in the MFC system. Electron acceptors affect the electricity generation efficiency in MFC systems due to their different physical and chemical properties. In MFCs, the reduction kinetics at the cathode significantly affect the power generation performance. Although there are many studies in MFC systems from different aspects in the anode chamber (electrode type/modification, substrate type/pretreatment, modified microorganisms, etc.), research on the cathode is relatively low. Therefore, it is necessary to search for alternative electron acceptors for both resource recovery and reduction reactions to improve MFC performance [31]. Therefore, in recent years, efforts have been made to investigate, understand and optimize the reduction kinetics of different electron acceptors in MFC systems [32,33].

This study reviews the factors affecting MFC systems, the effects and mechanisms of cathodic electron acceptors, and recent studies on electron acceptors in MFC systems.

MFC – ELECTRON TRANSPORT AND MECHANIMS

The transportation of electrons to the anode electrode is one of the most critical performance factors of the MFC system. Microorganisms arrange their electron transfer pathways in a way that electrons are transferred from an electron donor to a suitable electron acceptor, choosing the electron acceptor with the highest potential available to maximize their energy gain [34]. The main limiting factor governing the performance of the MFC is extracellular electron transfer (EET). Although electron shuttle-mediated EET is the general electron transfer mechanism followed in many bacteria, the bacterial outer membrane is generally a less permeable barrier to electron shuttle transport. This limits the efficiency of the EET and lowers the power generation of the MFC. This membrane permeability is slightly easier in gram-negative bacteria than in gram-positive bacteria due to the presence of a thin membrane [1]. Electron transfer in MFC systems can be achieved by direct electron transfer (DET), which is the direct contact of the cell membrane of the microorganism with the electrode, or by mediated electron transfer (MET), where redox mediators are used [9]. A breakthrough occurred in MFC systems to discover that some microorganisms transfer their electrons directly to the anode electrode. These microorganisms are generally stable and provide a high

columbic productivity. Since some microorganisms (such as *Geobacteraceae sulferreducens, Rhodoferax ferrireducens, Shewanella putrefaciens, Geobacter metallireducens*) are bio-electrochemically active, they can form a biofilm on the electrode surface [35,36]. Such microorganisms have this ability because they generate energy (ATP) by reducing metal oxides under anaerobic conditions and transfer electrons to the anode electrode as the final electron acceptor in the anode chamber [37]. When these microorganisms are present, the anode electrode functions as the final electron acceptor in the dissimilation respiratory chain. DET occurs when the cell wall of the microorganism or pilus (conducting nanowire) comes into direct contact with the electrode surface. This can occur only when the electron-transfer microorganisms are anodophilic [10]. These microorganisms, which break down organic matter, produce electrons and transfer them out of the cell, are also called exoelectrogenic microorganisms. When exoelectrogenic microorganisms contact with the anode electrode surface, their surface cytochromes or pili can transfer electrons. However, the outer layer of most existing non-exoelectrogenic microbial species (such as *Escherichia coli, Bacillus, Proteus,* and *Pseudomonas sp.*) consists of non-conductive lipopolysaccharides and peptidoglycans that limit electron transfer. In this case, DET cannot occur and a mediator is needed to transfer electrons [35]. Usually, redox mediators take electrons from the microbial cell transferred in a reduced state and are transferred to the anode material, which is oxidized in the MFC. A mediator should have properties such as the ability to develop a physical bond with the electrode surface, be electrochemically active, have a low oxidation potential, and not be absorbed by bacteria or the electrode surface. The oxidation potential of the mediator should be closer to the redox potential of the primary substrate [38]. DET and MET electron transfer mechanisms are shown in Figure 3(a) and Figure 3(b), respectively.

FACTORS AFFECTING THE EFFICIENCY OF MFC

Electrode Material

The use of better performing anode and cathode electrode materials can significantly increase electricity generation in an MFC as they affect activation polarization losses [10]. Activation losses refer to the amount of energy lost during the transfer of electrons from the microorganism cell protein to the surface of anode electrode. These losses can be minimized by accelerating electron transfer to the anode electrode or by increasing the catalyst concentration on the cathode electrode [39]. An ideal anode electrode should be highly conductive, physically and chemically stable, non-corrosive, inexpensive, and plug-resistant [40]. Increasing the electrode surface area for a large reaction area, reducing the porosity for increasing electrical conductivity, choosing materials resistant to acids and bases to reduce pollution and extend the electrode life are important in increasing MFC efficiency. In addition to all these, the electrode material must be low cost in order to be commercially usable [5].

Carbonaceous materials are highly preferred for biofilm formation due to their good biocompatibility, conductivity and relatively low cost. Carbon materials can be found in different forms such as plain (paper, mesh, felt, sheet), brush or foam [40]. Although anode electrodes in the form of carbon paper have a high surface area, they are often very fragile, which affects microbial bonding. Carbon cloth is much more durable but expensive. Graphite electrodes have also been used in various studies. Graphite materials are highly conductive and have a high surface area, but their low porosity provides less power compared to carbon felt materials. Over the past few years, non-traditional metal electrodes (such as titanium and stainless steel) have also been studied. Although metals have a much higher conductivity, they are toxic to microorganisms, since their surface properties do not allow the formation of biofilms [5,40]. Various modifications have been developed to increase the anode electrode surface to increase bacterial attachment, enhance electron transfer between the microorganism and the anode electrode surface, and thus improve power generation. These modifications may include physical or chemical treatments of the electrode surface or the use of composite electrodes [41]. Electrodes used in MFC systems can be modified using synthetic components to improve electron transfer and increase biofilm formation. The inclusion of nano-sized materials (such as carbon nanotubes, graphene and metal oxides) that show beneficial properties such as superior conductivity, high surface area, high strength and thermal stability into conventional carbon-based electrodes has greatly increased the MFC performance [42,43]. The cathode electrode, on the other hand, has a different feature as a three-phase chemical reaction takes place between electrons, protons and oxygen on its surface in the presence of a catalyst. The cathode electrode must have a high redox potential and capture protons passing through the membrane with high efficiency. Solid graphite rod, graphite granules, graphite felt, glassy carbon or carbon paper can be used as cathodes. The cost of the various catalysts used at the cathode is a major limitation in terms of economic viability. For this reason, studies on the concept of biocathode, in which biocatalysts are used at the cathode, have attracted attention [5,44].

Mediator

Depending on the transfer of electron produced by microorganisms to the anode electrode, MFCs can be classified as with mediator and mediator-less. Non-anodophilic microorganisms cannot transmit electrons directly to an external acceptor (in this case, the anode electrode). Most microorganisms have a non-conductive lipid outer layer. The peptidoglycans and lipopolysaccharides in this outer layer prevent direct transfer of electrons to the anode. Mediators are synthetic or naturally produced compounds

that accelerate electron transfer [35]. The mediators are reduced by capturing electrons from the cell membrane then releases electrons to the anode, where they are re-oxidized. This cyclical process increases electron transfer and therefore power output. Mediators acts as a shuttle between the electron donor (bacteria) and the electron acceptor (anode), where it supplies electrons to the external circuit. The performance of mediators depends on their molecular structure, polarity, mechanism and dissociation ability [45].

A good mediator should have properties such as high electrode reaction rate, ability to easily cross the cell membrane, ability to capture electrons, good solubility, non-biodegradability and non-toxicity to microorganisms [46]. Commonly used mediators include metalorganics and dyes such as neutral red, methylene blue, meldola blue, Ferric EDTA and thionine. The instability and toxic properties of many synthetic mediators have limited their MFC applications. In addition, some microorganisms can use the compounds they form naturally as mediators. Compounds such as antraquinone-2- disulfonate, oxyanions of sulfur and humic acids can transport electrons from the microorganisms cell membrane to the anode electrode [35].

Membrane

The selectively permeable membrane that separates the chambers in the MFC has a very important role in overall performance. Generally, proton exchange membranes (PEM) or cation exchange membranes (CEM) are used [47]. A good membrane should meet criteria such as high ionic conductivity, selectivity, low internal resistance, low biofouling, chemical, mechanical and thermal stability as well as cost-effectiveness. Single-chamber membraneless MFCs are widely studied, but the absence of membranes results in high oxygen and substrate permeability, thus reducing the coulombic efficiency [48]. PEMs are known to outperform CEMs in conventional hydrogen fuel cells. When PEM surface comes into contact with wastewater / sludge, it becomes contaminated with cation types other than H^+ (Na^+, K^+, NH_4^+, Ca^{2+} ve Mg^{2+}), which reduces performance [49]. The most widely preferred PEM membrane is Nafion 117 due to its highly selective permeability. However, its high cost creates a disadvantage. Instead of Nafion 117, the CEM membrane CMI-7000, whose performance is close to Nafion 117, costs much less. For this reason, it is discussed to use cheaper materials such as glass fiber or not to use membranes at all in order to reduce the waste water / membrane cost [10]. In addition to proton permeable membranes, anion permeable and bipolar (both anion and proton permeable) membranes are also used in MFC. In anion-permeable membranes, protons can be transferred using chemicals such as phosphate anions as a pH buffer [48]. By monitoring the phosphate concentration in the anode and cathode compartments, it has been shown that phosphate anions are transferred across the membrane, thus better maintaining the pH in the anode compartment. However, in this case, the pH in the cathode chamber generally increases more than with Nafion [25].

Environmental Conditions

Acclimation of microorganisms is necessary at the beginning of most MFC studies. The purpose of acclimation is to stimulate the growth of the electroactive groups in the inoculum. The most classical method for acclimation is the addition of certain nutrients and vitamins. In addition to these, electroactive groups can be selected by methods such as providing anaerobic conditions, elimination of other microbial groups (ultrasonification, temperature, etc.), chemical modification of the inoculum (conductivity, pH change) [50,51].

The pH difference between the anode and cathode chambers affects the proton transfer rate. Theoretically, after a certain decrease during the fermentation of the substrate, the pH should begin to increase as more acetate is removed and electrons and protons are transferred. However, during the operation of an MFC, the pH gradually drops over time as the transfer of protons across the membrane is slower than production. Acidification of the anode in MFC systems inhibits microbial activity, reducing electricity production [52]. Although the pH difference seems to be the driving force in proton transfer, contamination of the membrane increases the internal resistance by limiting the transfer. In addition, sudden changes in pH affect microbial activity. Most MFC systems are operated under neutral pH conditions so that they do not affect microbial growth [39].

One of the variables that affect the power density of the MFC is the external resistance. According to Jacobi's Law, the maximum strength will be achieved when the external resistance is equal to the internal resistance [51]. The internal resistance will be lower due to the increase in proton concentration in acidic or alkaline environment. Therefore, it may be necessary to increase the conductivity of the solution or decrease the distance between the electrodes to decrease the internal resistance without changing the pH [10].

Temperature is an important parameter for MFC systems as it is in every system containing microorganisms. High temperatures are generally not preferred in the MFC process, as methanogens can grow and inhibit electron transfer. Since electrochemically active bacteria are the dominant species at ambient temperature (25-30 °C), MFC systems have the advantage of operating at ambient temperature unlike anaerobic digestion systems [3,23]. In MFC systems, conductivity is an important parameter in reducing internal resistance and accelerating mass transfer. It has been demonstrated that the conductivity of MFCs can be increased up to 20 mS/cm high conductivities. Increasing the ionic charge beyond this value will not always improve its performance as it can drastically change the salt tolerance that bacteria can meet. Li et al. [53] examined the effect of 0-150 mM NaCl addition on food waste leachate in

a MFC. They reported the highest power density (1 W/m^3) and the lowest internal resistance value with the addition of 100 mM NaCl.

Type of Substrate

The biofilm attached to the anode surface of the MFC hydrolyzes the complex organic matter into simple molecules that are further oxidized by exoelectrogenic microorganisms. The electrons accepted by the anode flow to the cathode through an external circuit resulting in the production of bioelectricity [3]. The main substrate used for electron generation in most MFC studies is acetate [52]. Acetate is a simple substrate and the end product of fermentation for many metabolic pathways based on the oxidation of complex carbon sources. For electricity generation, acetate has been reported to perform better than butyrate, propionate or glucose [50].

Generally, pure organic materials such as glucose, cysteine and acetate are used as substrate in the anode chamber. Since the use of pure substrates is not sustainable and economical, waste materials that are biodegradable and have a large amount of organic content can also be used as substrates [54]. In addition to domestic and industrial wastewater, bioenergy recovery can be realized by using waste and wastewater of different origins such as food industry wastewater, brewery wastewater [55], dairy wastewater [56], corn straw, cattle manure, composite food waste [57] and sewage sludge [2,4]. Domestic and industrial wastewater-based MFC studies have reported that final COD removal efficiency can reach up to 80% [1,58].

Zhang et al. [59] stated that corn straw and sulfide can be used to generate electricity in MFC with a maximum power density of 744 mW/m^2, a maximum sulfur removal of 91% and a maximum COD removal of 52%. Hydrolysis of the substrate improves the anaerobic degradation efficiency as well as increases the electricity production in MFC. Studies have been carried out on pretreatments such as ultrasound, alkali, ozonation, microwave assisted degradation and aerobic degradation in order to improve biogas production in the anaerobic degradation of organic materials [60].

ELECTRON ACCEPTORS IN MFC SYSTEMS

According to the results recorded in the MFC studies, the power generation rate is mainly affected by the following factors: (i) Electron generation rate from exoelectrogens grown in the biofilm on the electrode, (ii) the number of electrons transferred from the anode to the cathode, (iii) The efficiency of the electron acceptor to accept electrons transferred, (iv) Losses due to oxygen diffusion from the cathode to the anode [32,61]. In MFC systems, cathodic electron acceptor is an important parameter that affects

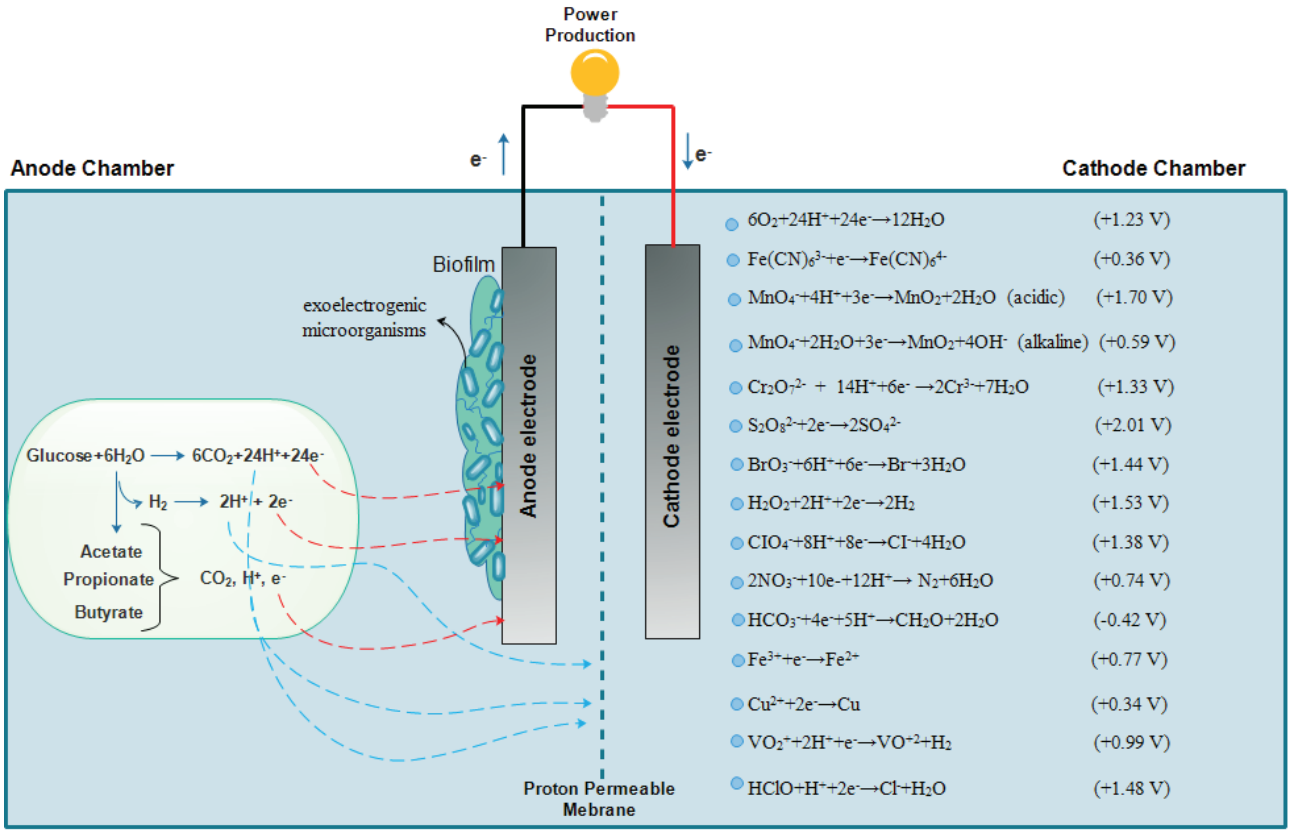

Figure 4. Generally used electron acceptors and their half-reactions.

MFC performance. By adding a chemical electron acceptor to the MFC system, the activation energy barrier is overcome and the cathodic activation loss is minimized. In MFC systems, the standard potential of an electron acceptor should be at least as much as the oxidation/reduction potential of the substrate oxidized by bacteria in the anode chamber, which is -320 mV. The electron acceptor must have a higher standard potential [62]. The characteristics of a good electron acceptor can be listed as having high redox potential, fast kinetics, affordability, sustainability and easy availability [63]. Oxygen is highly preferred electron acceptor in MFC systems due to its easy availability and oxidation potential. Due to the diversity of alternative electron acceptors and the expansion of MFC applications, the application of different electron acceptors has been evaluated in recent years [32]. Depending on the electron acceptor used, some environmentally harmful by-products may occur, thus limiting the commercialization applications of MFC technology [64]. Some electron acceptors and half-reactions generally used in scientific research are given schematically in Figure 4. In the continuation of the study, electron acceptors used in MFC systems will be discussed.

Oxygen (O_2)

Oxygen, the most commonly used electron acceptor in MFC systems, is considered a sustainable electron acceptor due to its low cost and availability in nature as well as its relatively high redox potential [63]. Oxygen can be used by giving water in the cathode compartment or by providing direct contact to the cathode in single-chamber MFC systems. Although oxygen is widely used, its poor contact with the electrodes and low reduction rate limits its use. Oxygen itself and the reaction product H_2O are both non-toxic, which makes O_2 the ideal electron acceptor [65]. But it has one important drawback: the reduction rate of O_2 is very slow, causing high overpotential, limiting the performance of [66]. Despite the wide variety of MFC configurations, only a few systems using oxygen as an electron acceptor were able to exceed 1.0 V cell voltage [33].

Different types of catalysts are used at the cathode to increase the oxygen reduction kinetics. Although the performance of the electrodes and thus the MFC performance can be improved by the catalyst coating, catalysts are often expensive and rare metals [32]. Among the catalysts, platinum (Pt) is the most widely used for oxygen reduction as it exhibits high catalytic performance and increased oxygen affinity. Pt-based catalysts can provide up to 5 times more power output than plain carbon cathode electrodes. In addition, less costly and more sustainable catalysts such as Fe/Fe_2O_3, PbO_2, MnO_2, Co, and activated carbon were also investigated [63].

Ferricyanide (K3[Fe(CN)6])

Ferricyanide is another electron acceptor commonly used in MFC systems. Unlike oxygen, the concentration of ferricyanide is not limited by solubility. In two-chamber MFC studies, it was determined that the power was increased by 1.5-1.8 times by replacing the oxygen electron acceptor with ferricyanide [67]. Although ferricyanide is an important electron acceptor in MFC systems due to its high system performance and stability, its use has been limited to laboratory applications because it is toxic, difficult to regenerate/recover chemically and is practically sustainable [63], [32]. The redox potential of ferricyanide is lower than that of oxygen, but due to its lower overpotential, it gives higher power output with a faster reaction rate. Zain et al. [61] obtained 0.589 V with oxygen and 0.833 V with ferricyanide in a continuous MFC system for nitrogen and carbon removal in their study. At the same time, carbon and nitrogen removal with ferricyanide was found to be 36% and 9% higher, respectively, than with oxygen operated MFC.

Permanganate

Permanganate is also widely used in MFC systems due to its relatively high oxidation capacity and being environmentally safe. It has been proven by previous studies that permanganate outperforms ferricyanide for power generation in MFC system [33]. As shown in Table 1, permanganate is reduced to MnO_2 by gaining 3 electrons in both acidic and alkaline conditions [68]. When permanganate is used as an electron receiver, no catalyst is needed, but like most electron acceptors it is depleted during power generation and must be constantly renewed. At the same time, pH control should be performed in the cathode to obtain stable power density. Eliato et al. [69] studied the performance of the MFC system using potassium permanganate as an electron receiver and glucose as a substrate. They found the current and maximum power densities as 0.030 mA/cm^2 and 93.13 mW/m^2 respectively, at 400 μM potassium permanganate concentration. Shorter lag time and higher power density were observed. However, with the depletion of permanganate and its rapid reduction to Manganese dioxide (MnO_2), brown precipitate is formed, which increases the internal resistance and causes a voltage drop. High pH with the use of permanganate will also have a negative effect on power generation.

In systems using biocathodes, reduction of Mn(IV) as well as oxidation of Mn(II) can be achieved by microorganisms [70]. A stable electricity generation can be achieved by reduction of Mn(IV) followed by oxidation of Mn(II) at the cathode. In the first step of the cycle, manganese dioxide is reduced to the hydrous manganite by taking an electron from the cathode electrode and again reduced to Mn^{2+} by taking another electron. This second step of the cycle can be performed by manganese oxidizing microorganisms [71].

Dichromate

Dichromate, which has high oxidation state chromium, has been proposed as an alternative electron acceptor [33]. When dichromate is used as the electron acceptor in the cathodic compartment, Cr^{6+} is reduced to Cr^{3-} as shown in Table 1. Guerro-Rangel et al. [72] evaluated three different

electron acceptors as potassium permanganate, potassium ferricyanide and potassium dichromate without pH adjustment at the cathode. As a result, the maximum open circuit voltage (OCV) and power densities found as 1.04 V and 7.29 mW/m² for $KMnO_4$, 0.71 V .92 mW/m² for $K_3[Fe(CN)_6]$, and 0.56 V and 0.79 for $K_2Cr_2O_7$. Pandit et al. [33] compared the performances of potassium permanganate, potassium persulfate, potassium dichromate, potassium ferricyanide electron acceptors in a dual chamber MFC system. Although potassium permanganate provides the best performance among the four electron acceptors with maximum OCV and power density, potassium persulfate was determined as it gives higher OCV and more stable power density. Among the four electron acceptors, the highest power density was obtained with potassium permanganate (116.2 mW/m²) and the lowest power density was obtained with potassium ferricyanide (40.6 mW/m²) .

Cr(VI) is a toxic chemical found in wastewater from electroplating, pigment, wood product and timber processes. In MFC systems by anaerobic biocathodes, Cr(VI) can be reduced to Cr(III) which is less toxic with electricity generation [73]. Cr(IV) reduction to Cr(III) under acidic conditions as shown in Table 1 [32].

Persulfate ($S_2O_8^{2-}$)

The persulfate anion has the strongest oxidation power among peroxygen compounds and can be applied as the cathodic electron acceptor in MFC since it has a high redox potential [32]. In aqueous solution, persulfate compounds can be activated in various ways to generate sulfate radicals with a standard redox potential of 2.6 V [74].

$$S_2 0_8^{2-} + activator \rightarrow 2SO_4^{-\cdot} \quad (3)$$

Sulfate radicals can degrade organic pollutants and high standard redox potential increases power generation in MFC systems. Although potassium persulfate is a strong electron acceptor due to its pH-regulating properties, its degradation rate is low [75]. Wang et al. [76] investigated a dual chamber MFC using iron activated $K_2S_2O_8$ as the cathode solution. As a result, the $K_2S_2O_8$–Fe^{2+} system has a maximum power density (MPD) of 401 mW/m², which is higher than the H_2O_2–Fe^{2+} (187 mW/m²) and $K_2S_2O_8$ (234 mW/m²) systems. Considering its high oxidizability according to Equations (4) and (5), potassium mono-persulfate can also be used as electron acceptor. Li et al. [75] studied potassium mono persulfate as an electron acceptor for the first time without using a catalyst in the MFC system. A power density of 16.37 W/m³ and COD removal of 99.4% were obtained.

$$HSO_5^- + 2H^+ + 2e^- \rightarrow HSO_4^- + H_2O \quad E^0 = 1{,}82\ V \quad (4)$$

$$HSO_5^- + H^+ + 2e^- \rightarrow SO_4^{2-} + H_2O \quad E^0 = 1{,}75\ V \quad (5)$$

Bromate (BrO_3)

Bromates are strong oxidizing compounds that are widely used in industrial applications. The bromate ion is a toxic pollutant classified as a carcinogen in nature (especially for humans) by the International Agency for Research on Cancer (IARC). It is important to remove bromate ions in a cost-effective and sustainable manner by converting them to non-toxic bromide ions that are naturally found in most water bodies [77,78]. As shown in Table 1, due to its relatively high redox potentials (1.44 V), it can be consider as electron acceptor in MFC systems. Dai et al. [62] evaluated sodium bromate as an alternative electron acceptor. They found that the performance of the MFC system was highly affected by pH and bromate concentration, and the OCV could reach 1.63 V by using 100 mM $NaBrO_3$. The MPD was determined as 1.490 W/m³. Adelaja et al. [77] used boramate solution as cathode and obtained bromate removal up to 79% and peak power density up to 6.75 mW/m².

Hydrogen Peroxide (H_2O_2)

Hydrogen peroxide (H_2O_2), a strong oxidant, is another electron acceptor that can be used in MFC systems. H_2O_2 can be an alternative electron acceptor to oxygen, especially in Pt-catalyzed cathodes [79]. The power density in MFC increased by about 200% than oxygen with the use of hydrogen peroxide as electron acceptor and showed high performance in long-term operation [80]. Tartakovsky and Guiot [80] compared oxygen and hydrogen peroxide electron acceptors in their study. They reported that the use of 300 mL/d of 0.3% H_2O_2 against aeration alone in the cathode chamber increased the power density by an average of 3 times. H_2O_2 can be used as electron acceptor as well as for Fenton reaction with in-situ production in cathode environment. In the case of using oxygen in the cathode chamber, the reduction of oxygen can occur via 2 or 4 electrons to form H_2O_2 (Equation (6)) or H_2O (Equation (7)) [81].

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (6)$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (7)$$

The two or four electron paths are highly dependent on the catalytic properties of the cathode material. The use of metal-based electrocatalysts catalyzes the 4-electron pathway, while the use of pyrolyzed graphite-based cathode electrodes catalyzes the 2-electron pathway that allows the formation of H_2O_2 [81]. Fu et al. [82] studied the degradation of azo dye with the MFC/Fenton hybrid system. H_2O_2 production was achieved by two-electron reduction of oxygen at the cathode. With this system, approximately 76.5% dye removal and 28.5 W/m³ MPD were achieved . Since H_2O_2 can be used and consumed as an electron acceptor in MFC systems, it can also be used for the removal of residual H_2O_2 formed as a result of reactions such as Fenton.

Zhang et al. [79] reported in their study a novel bioelectro-fenton system that can be operated as a microbial electrolysis cell (MEC) or MFC system. While methylene blue and H_2O_2 were removed in the MEC system, the remaining residual H_2O_2 was used as an electron acceptor by the MFC system. With this operating method, 50 mg/L of dye was removed and a maximum current density about 0.5 A/m^2 was obtained.

Perchlorate (ClO_4-) and Hypochlorite (HClO-)

Perchlorate is an important drinking water pollutant due to its inhibitory effect on thyroid functions [32]. The reduction reaction of ClO_4^- is as shown in Table 1. It is possible to treat perchlorate in groundwater by using perchlorate as an electron acceptor. However, since perchlorate is usually found in microliter in nature, it limits electricity generation with MFC. For this reason, its treatment with nitrate pollutant, which is commonly found in groundwater, has attracted attention. Jiang et al. [83] investigated the autotrophic denitrifying biocathode system to generate electricity by reducing nitrate and perchlorate in the MFC system. As a result, they showed that the maximum stable current density (3.10 A/m^3) is obtained when the effective molar ratio of NO_3^-/ClO_4^- is 1:1. They obtained 40.97% perchlorate and 86.03% nitrate removal under these conditions. Hypochlorite can be used as an electron acceptor in MFCs as a strong oxidant. In an MFC system, if the anode outlet is fed with hypochlorite in the cathode chamber, hypochlorite can also provide disinfection [64].

Momoh and Naeyor [84] investigated the treatment of high-strength slaughterhouse wastewater by using calcium hypochlorite powder (20 g/L) as an electron acceptor in the catholyte in a dual chamber MFC system with agar salt bridge. A MPD of 12.26 mW/m^2 has been achieved. Jadhaw et al. [64] compared NaOCl and O_2 as electron acceptors. The MPD (6.57 W/m^3) obtained with NaOCl was found to be 9 times higher than the power obtained using oxygen.

Nitrogenous Compounds

Nitrogenous aromatic compounds are on the priority pollutants list of many countries due to their persistence and mutagenic properties [63]. Due to the competitive redox potential of nitrate relative to oxygen, the denitrification process has attracted attention in MFCs for both wastewater treatment and electricity generation [63]. Fang et al. [85] investigated NO_3^- removal with carbon paper electrodes with and without Pt catalyst, in an abiotic cathode. In the experiments performed with the catalyst electrode, the NO_3^- removal rate and the maximum power densities were 3.5 and 16 times higher, respectively. The MPD was obtained as 7.2 mW/m^2 and nitrate reduction products were found mainly as ammonia (51.8%) and traces of nitrite (0.6%).

With the widespread use of biocathodes in MFC systems, the use of nitrate has attracted attention. With systems in which nitrate is used as an electron acceptor, nitrate is converted to N_2 gas by electrochemical denitrification [32]. Lefebvre et al. [44] reported a power density of up to 0.19 W/m^3, 65% COD removal and 84% nitrogen removal with a two-chamber MFC operated for more than 1.5 months. Although the use of nitrate as an electron receiver has been widely studied, nitrite formed as an intermediate has received less attention so far. Besides nitrate, nitrite has also been proven to be used as an electron acceptor in MFCs via autotrophic denitrification [63]. It has been reported that exoelectrogenic bacteria can reduce nitrate and nitrite to N_2 by interchangeably using them as electron acceptors [32]. The study of Cucu et al. [86] is a field study carried out for nitrate removal in recent years. In this system, which uses a inoculum taken from the Romanian Burtea river sediment, nitrate was used for electricity generation and as an electron acceptor. 97% COD and 96% nitrate removal efficiencies were achieved in a single chamber MFC with a power density of 88 mW/m^2. Oon et al. [87] investigated nitrate removal in a biocathode MFC. While they achieved 41.7% nitrate removal in the system they operated with open circuit, they achieved higher nitrate removal efficiency as 74.7% when operated in closed circuit. Their results showed that nitrate can be used as a terminal electron acceptor for cathodic reduction. Li et al. [88] reached a MPD of 0.069 W/m^2 with a nitrobenzene removal efficiency of 1751 g/m^3×day using a Pt-based cathode in their study. However, they reported that during nitrobenzene reduction, intermediates of nitrosobenzene and phenylhydroxylamine can accumulate at the abiotic cathode.

Carbon Dioxide (CO_2)

In an oxygen-free environment, other compounds present such as iron, sulfate, selenate, nitrate, manganese, selenate, urine, carbon dioxide and fumarate are used as electron acceptors [71]. The reduction potential of CO_2 has a very low oxidation-reduction potential of -0.420 V, so its use as an electron acceptor produces a low voltage. In order to generate electricity, the potential of the cathode chamber must be higher than the anode chamber potential. Therefore, CO_2 reduction requires external energy [32]. Cao et al. [89] used CO_2 as an electron acceptor in a sunlight catalyzed biocathode. According to the equation in Table 1, carbon dioxide is reduced by gaining electrons and biomass is formed.

Metals

By using metals as electron acceptors in MFC systems, both electricity can be generated and metals can be removed or recovered from wastewater [63]. In recent years, many studies have been carried out for the removal and recovery of metals such as copper, silver, chrome, manganese, vanadium and selenium in MFC systems [90]. Treatment of heavy metals from wastewater is important to prevent their toxic effects on ecosystem and human health [91]. In the next part of the study, some metals used in MFC systems are summarized.

Iron (Fe)

In MFC systems, iron can be used as both a mediator and an electron acceptor with Fe^{3+}/ Fe^{2+} redox couple. It can be reduced in the cathode as shown in Table 1. Fe^{3+} compounds at the cathode are reduced to Fe^{2+}, and Fe^{2+} is then reoxidized to Fe^{3+} by oxygen. With such a cycle, electrons are passed from the cathode electrode to an electron acceptor by Fe compounds acting as mediators [71]. $FePO_4$ in the sewage sludge, which is also important because of its orthophosphate content, has been studied as a potential electron receiver due to its Fe(III) content. $FePO_4$ can be reduced with the MFC system. When iron cations are reduced, Fe and PO_3^{4-} are separated and (PO_3^{4-}) is released into solution. The separated phosphate can be precipitated as magnesium Ammonium phosphate by adding $MgCl_2$ and NH_4OH. Fisher et al. [92] mobilized orthophosphate from iron phosphate ($FePO_4$) in sewage sludge by microbial fuel cell power. The process yielded orthophosphate recovery of up to 600 mg/l. They also obtained a power density of about 0.06 mA/m^2. Although the iron ion provides relatively high-power densities relative to other electron acceptors, a low pH is required to keep it soluble as iron tends to precipitate at high pH as hydroxides. It is reported that these precipitates that may form are harmful to the use of membranes. In addition, a mediator is needed to transport electrons and protons to Fe^{3+} [32].

Copper (Cu)

Copper is one of the common heavy metals in the soil and water environment, often emitted from the mining and metallurgical industries. Trace copper is an essential micronutrient for all plants and animals, but high levels of copper can become toxic to life. Therefore, the removal of copper is of great importance [47]. The use of copper (Cu) as an electron acceptor in MFC systems has been of interest due to the reduction of the soluble copper ion to its solid metallic form. Zhang et al. [90] investigated the reduction of complex copper compound ($Cu(NH_3)_4^{+2}$) in a double-chamber MFC. A MPD of 0.20 W/m^2 is achieved. Thermodynamic and cyclic voltammetry analyzes revealed that the compound decomposed into Cu^{2+}, then accumulated at the cathode as Cu and Cu_2O.

Mercury (Hg^{2+})

Mercury and its compounds are widely used in pulp and paper making, battery manufacturing industry, paint, pharmaceutical manufacturing and oil refining. Mercury can be considered as an alternative electron acceptor, with its redox potential (-320 mV), which is higher than the $NADH/NAD^+$ redox potential [93]. Wang et al. [93] investigated Hg^{2+} performance in cathodic chamber using anaerobic inoculum and synthetic wastewater in the anode chamber. In addition to 98% mercury removal efficiency, they achieved a MPD of 0.43 W/m^2. Kumar et al. [91] obtained an open circuit voltage of 778 mV and a power density of 32.6 mW/m^2 with MFC, which has only Hg^{2+} as the electron acceptor. In 24-hour tests, up to 98% Hg^{2+} removal efficiency was achieved at a rate of 0.4 mg/L/hr.

Vanadium (V)

Vanadium (V) is another example of using heavy metals as electron acceptors. Vanadium may arise from pentoxide processing activities and wastewater from vanadium mines. It has a high redox potential especially at low pH (Table 2) [32]. Zhang et al. [94] used V(V) as electron acceptor in the cathode chamber for electricity generation potential. In this study which sulfur and glucose were used as substrates at the anode, removal efficiency of approximately 82.2% and 26.1% for sulfide and V(V), respectively, and a MPD of approximately 614 mW/m^2 was reported. Qiu et al [95] investigated the production of bioelectricity with V(V) removal in a biocathode MFC. With an initial concentration of 200 mg/L, V(V) was almost completely treated in 7 days of operation. Besides, a maximum power density of 529 mW/m^2 was obtained.

Azo Dyes

Azo dyes are aromatic compounds containing one or more azo groups (-N=N-), widely used in the textile, cosmetic and paper industries. The discharge of azo dyes is undesirable both because of their color and the mutagenic and toxic properties of their degradation products. Azo dyes can be removed by MFC systems with exoelectrogen microorganisms in the anode chamber or through cathode chambers using lactase as a catalyst. Although there are many studies on the removal of azo dye in the anodic compartment in MFC systems, the use of azo dyes as cathodic electron acceptors is a relatively new field of study [82] [63]. Mani et al. [96] compared the dye removal in the anode chamber and the cathode chamber in terms of COD and electricity production for the removal of "acid orange 7" dye. While the average COD removal was 80% and the power density was 50 mW/m^2 in the cathode chamber, an average of 69% COD removal and 42.5 mW/m^2 power density were obtained in the anode chamber**.** Bakhshian et al. [97] investigated reactive dye removal at the cathode catalyzed by lactase. Molasses was used as a high strength and low-cost substrate in the anode chamber. They achieved 84% COD removal in the anode chamber and 87% color removal efficiency in the cathode. MPD increased by approximately 30% with enzymatic decolorization of the dye in the cathode chamber. The chemical structures of azo dyes significantly affect their removal performance. For similar structures of azo dyes, monoazo dyes can be removed more easily than polyazo dyes [98].

Chlorophenols

Chlorinated aliphatic hydrocarbons are important because of their carcinogenic and toxic properties. Some anaerobic microorganisms can use these pollutants by degrading them [32]. Studies with both mixed culture and pure culture of *Geobacter lovleyi* have shown that hydrocarbons can be degraded. Therefore, the use of chlorophenols in

biocathodes has attracted attention. Huang et al. [99] studied the mineralization and dechlorination of pentachlorophenol in MFC without mediator. Pentachlorophenol was dechlorinated at a rate of 6.3±1.2 g/m^3×day with a power density of 0.083 W /m^2 . Wen et al. [100] used 4-chlorophenol as an electron acceptor in the abiotic MFC cathode and obtained a MPD of 0.033 W/m^2 by dechlorination.

This review examines various alternative electron acceptors in MFCs. Since some pollutants also act as electron acceptors, their reduction in MFC systems is possible. The list of different electron acceptors used in MFCs is compiled in Table 1.

POTENTIAL AND CHALLENGES ON FUTURE APPLICATION OF MFC

In recent years, laboratory-scale studies of MFC have received great attention; numerous studies have reported that nanocomposites (metal/metal oxides) embedded on the anode surface increase bacterial adhesion, conductivity, electron transfer, and reduction of ohmic losses. Appropriate substrate selection for bacterial growth and cathodic electron acceptor also play an important role in MFC performance. Considering that most proposed electrode modifications increase the cost that is not possible for commercial applications, it is advantageous that the correct selection of the cathodic electron acceptor provides additional pollution reduction as well as performance enhancement of MFC [84]. In many cases, MFC technology has to compete with methanogenic anaerobic digestion technology, which can use the same biomass for power generation and has wide commercial applications [10]. Although there have been many laboratory-scale developments in MFC systems, there are still several limitations to the scale-up and commercialization of MFC. The high internal resistance of MFC systems, unstable voltage generation, and the cost-increasing conditions mentioned above make it difficult to scale up. At the same time, it should be taken into account that power production may decrease due to possible activation, ohmic, bacterial, metabolic and mass losses [10].

MFC operating in continuous flow mode and constructed wetland MFCs have been investigated as efficient systems at laboratory scale, but commercial scale applications to operate in real world conditions have not been satisfactorily reported [38]. Another issue to consider for large-scale system designs is periodic membrane replacement, which increases the cost of MFC as membrane fouling reduces proton transfer. To ensure long life, the MFC system must be resistant to corrosion, instability and biofouling. The use of oxygen in the cathode chamber is important for sustainability, but a continuous sprinkling of oxygen can diffuse through the membrane, affecting bacteria at the anode. At the same time, platinum, which is preferred for oxygen reduction reactions, is not economical and can be toxic by reacting with some substances in wastewater.

Table 1. Electron acceptors in MFC systems

Electron Acceptor	Anode chamber	OCV (V)	Maximum Power Density (MPD)	Reference
Oxygen	Anaerobic inoculum+Synthetic media	-	10.2 mW/m^2	[68]
Oxygen	Pre-treated anaerobic inoculum+synthetic media	0.67	17.43 mW/m^2	[64]
Oxygen	Domestic wastewater+ Synthetic media	0.589	-	[61]
Permanganate	Anaerobic inoculum+Synthetic media	1.33	115.6 mW/m^2	[68]
Permanganate	Anaerobic inoculum+Synthetic media	0.73	93.13 mW/m^2	[69]
Ferricyanide	Anaerobic inoculum+Synthetic media	0.78	40.6 mW/m^2	[33]
Ferricyanide	Domestic wastewater+ Synthetic media	0.833	-	[61]
Dichromate	Anaerobic inoculum+Synthetic media	0.56	0.79 mW/m^2	[33]
Hydrogen peroxide	Anaerobic inoculum+Synthetic media		22 mW/ m^2	[80]
Permanganate	Anaerobic inoculum+Synthetic media	1.11	116.2 mW/m^2	[33]
Persülfate	Anaerobic inoculum+Synthetic media	1.10	101.7 mW/m^2	[33]
Persülfate	Waste activated sludge+Synthetic media	-	234 mW/m^2	[76]
Fe^{+2} activated persulfate	Waste activated sludge+Synthetic media	-	401 mW/m^2	[76]
Calcium Hypochlorite	Slaughterhouse waste water	1.56	12.26 mW/m^2	[84]
Sodium Hypochlorite	Pre-treated anaerobic inoculum+synthetic media	1.06	148.4 mW/m^2	[64]
Nitrate	Domestic wastewater+ Synthetic media	-	9.4 mW/ m^2	[44]
Nitrate	river sediment inoculum+domestic wastewater	-	88 mW/ m^2	[86]
Fe^{+3}	İnoculum from another operated MFC+ Synthetic media	4.5	0.86 mW/ m^2	[101]
Cu^{2+}	İnoculum from another operated MFC+ Synthetic media	-	0.20 W/m^2	[90]

Therefore, it is important to investigate for alternative electron acceptors for large-scale systems [1].

There are still many issues to be investigated and many limits to be overcome before the MFC system can be used on a large scale. The power output obtained in MFC technology is low and can be increased with applications such as the use of genetically modified microorganisms, electrode design using nanoparticles, reactor designs to reduce internal resistance [43]. The hybrid system integrating nanotechnology for electrode material, genetic engineering for microorganisms, artificial intelligence for smart MFC, real-time adaptation and various applications will be an innovative integration for future MFC applications [8].

CONCLUSION

Although MFC systems have attracted intense interest in recent years, their practical applications are few due to many limitations and difficulties. Many operating conditions are tried to be optimized to improve the performance of MFC. In addition to maximum power density in MFC systems, effective removal of waste is one of the main objectives. For this reason, it is possible to increase the coulombic efficiency and COD removal by using the maximum energy of the waste with suitable electron acceptors.

Electron acceptors are one of the most important factors determining the performance and applicability of MFC systems. In this study, the performances and applicability of electron acceptors used in MFC systems were reviewed. Oxygen is a promising electron acceptor in terms of its availability and sustainability in nature, as well as the large-scale applicability of MFC systems. The cathode is not only limited to the oxygen reduction reaction it is also suitable for reducing biotic or abiotic way of pollutants.

Many studies in the literature have investigated the use of a single electron acceptor in the MFC system, since there are very complex wastewaters in nature, it is necessary to investigate the compositions of different electron acceptors and their interactions with each other. Although the use of oxygen as an electron acceptor in large-scale systems is considered sustainable, alternative electron acceptors with high redox potential are attracting attention to increase the power density. Especially since some electron acceptors are potential pollutants, MFCs are also used as a purification mechanism for these pollutants or valuable chemical recovery. In the commercialization of MFC systems, it is recommended to optimize the use of the most suitable electron acceptor or the combination of certain electron acceptors according to the presence of contaminants in the place where the system will be operated. Since there are many parameters affecting the MFC system, it would not be correct to dedicate the results of studies using different electron acceptors only to the electron acceptor used. Studies comparing different electron acceptors under the same operating conditions are limited. For this reason, the comparison of alternative electron acceptors and even their use together should be examined. At the same time, the determination of the by-products formed as a result of the reduction of the electron acceptors used is important for real-world use. The applicability of MFC systems in waste water plants can be evaluated by contributing to the system with partial oxidation as a pre-treatment rather than an ultimate treatment of organic material. It is recommended to carry out studies by developing the combined treatment systems to be established in this way.

AUTHORSHIP CONTRIBUTIONS

Authors equally contributed to this work.

DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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