

Review

Microbial Fuel Cell Technology as a New Strategy for Sustainable Management of Soil-Based Ecosystems

Renata Toczyłowska-Mamińska ^{1,*} , Mariusz Ł. Mamiński ²  and Wojciech Kwasowski ³ 

¹ Institute of Biology, Department of Physics and Biophysics, Warsaw University of Life Sciences, Building No. 37, 159 Nowoursynowska St., 02-776 Warsaw, Poland

² Institute of Wood Sciences and Furniture, Warsaw University of Life Sciences, Building No. 34, 159 Nowoursynowska St., 02-776 Warsaw, Poland; mariusz_maminski@sggw.edu.pl

³ Institute of Agriculture, Department of Soil Science, Warsaw University of Life Sciences, Building No. 37, 159 Nowoursynowska St., 02-776 Warsaw, Poland; wojciech_kwasowski@sggw.edu.pl

* Correspondence: renata_toczyłowska@sggw.edu.pl

Abstract: Although soil is mainly perceived as the basic component of agricultural production, it also plays a pivotal role in environmental protection and climate change mitigation. Soil ecosystems are the largest terrestrial carbon source and greenhouse gas emitters, and their degradation as a result of aggressive human activity exacerbates the problem of climate change. Application of microbial fuel cell (MFC) technology to soil-based ecosystems such as sediments, wetlands, farmland, or meadows allows for sustainable management of these environments with energy and environmental benefits. Soil ecosystem-based MFCs enable zero-energy, environmentally friendly soil bioremediation (with efficiencies reaching even 99%), direct clean energy production from various soil-based ecosystems (with power production reaching 334 W/m²), and monitoring of soil quality or wastewater treatment in wetlands (with efficiencies of up to 99%). They are also a new strategy for greenhouse gas, soil salinity, and metal accumulation mitigation. This article reviews the current state of the art in the field of application of MFC technology to various soil-based ecosystems, including soil MFCs, sediment MFCs, plant MFCs, and CW-MFCs (constructed wetlands coupled with MFCs).



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1. Introduction

While soil is primarily seen as an environment for agricultural production, its importance is far more extensive. Beyond ensuring people's food security, soil is a critical component of environmental protection and climate change mitigation because it plays a role as a carbon sink, storing 2–3 times more carbon than the atmosphere and all living terrestrial plants [1–4]. Soil is the largest terrestrial carbon source, comprising organic and inorganic carbon, and soil-based ecosystems play an important role in carbon sequestration, e.g., 1 ha of grassland can store 0.1–8.7 t C/ha/year, depending on the soil type, climate, and land management [5]. Another soil-based ecosystem—peatlands—comprise only 3% of the global land surface, but they are capable of storing between 15% and 30% of global soil carbon [6,7]. The escalating utilization of peatlands for agricultural purposes over time has been documented in Poland, the United Kingdom, Germany, and Ireland [8–11]. As a result, carbon dioxide is released into the atmosphere when aerobic conditions mineralize C stored in peat [12,13]. The amounts released from these C sources have been estimated to be around 6% of global anthropogenic CO₂ emissions [14]. Despite the enormous importance

of soil in the environment, ca. one-third of the world's soils are now being degraded due to extensive industrial and agricultural activities, which has been found to significantly contribute to climate change [15,16]. Soil pollution with pesticides, heavy metals, and a wide range of other toxic organic and inorganic substances results not only in environmental risks but also affects the entire ecosystem balance [17–19]. Nowadays, when humanity is facing the urgency to reduce global warming, more attention must be paid to soil-based ecosystems and new possibilities of their management regarding the most favorable environmental and climate impacts. In this context, microbial fuel cell (MFC) technology can be a tool that opens the path to sustainable management of soil-based environments. Originally, MFC technology was developed to produce electricity by utilizing the metabolism of microorganisms [20]. MFCs require microorganisms that directly transport electrons outside the cell. Such transfer is possible in bacteria called exoelectrogenic, exoelectrogens, or electrogens, which are able to release electrons extracellularly [21]. From a chemical point of view, an MFC is an electrochemical cell in which electrogenic microorganisms catalyze electrochemical reactions (oxidation and/or reduction) [22]. These reactions subsequently lead to the production of electricity from organic matter [23–28]. In the anaerobic part of an MFC, the oxidation of organic substrates by microorganisms occurs at the anode, which is accompanied by extracellular release of protons and electrons (Figure 1). The electrogenic activity of exoelectrogens makes it possible to transfer electrons to the solid anode and then, through an external electrical circuit, to the cathode part. Protons reach the cathode through a proton-permeable membrane. In the presence of the cathode, protons and electrons react with oxygen, the final electron acceptor in the system, to form water [29]. The system's electric current is generated as the result of separation of the oxygen-free anode's environment (electron collector) from the cathode (electron acceptor). The separation forces the electrons to pass through the resistor (external circuit) to the electron acceptor. A wide range of substances have been used as fuel in MFCs, including simple organic compounds (e.g., carbohydrates and proteins) and complex mixture, such as lignocellulosic materials, various type of wastewater (e.g., municipal, brewery, and agricultural [30]), plant residues (e.g., corn straw) [31], and oils (e.g., crude oil) [32]. As reported by Bhattacharaya et al. [33], the carbon oxidation rates in MFCs achieved $0.105 \text{ mmol C/m}^{-2} \text{ d}^{-1}$ for organic matter and $0.689 \text{ mmol C/m}^{-2} \text{ d}^{-1}$ for glucose.

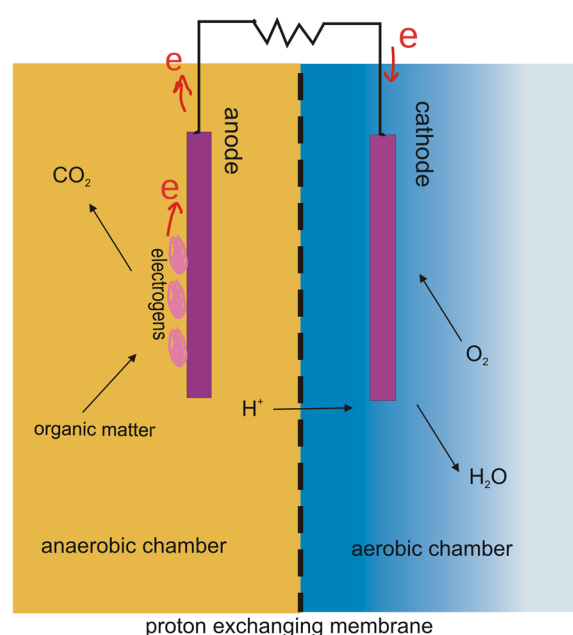


Figure 1. Schematic presentation of the principle of operation of MFCs.

In the early 2000s, MFC technology was firstly implemented in soil ecosystems, and it turned out that the potential difference naturally occurring in soil is favorable to electron flow and enables membrane-less MFC configurations [34]. A soil ecosystem-based MFC is typically composed of an anode buried in the anaerobic soil phase and a cathode placed in contact with air or in the oxygen-rich water phase (Figure 2). In laboratory experiments, the anode and cathode compartments can be separated by a proton permeable membrane, but membrane-less designs are most often used, especially in field tests. Soil microorganisms decompose organic matter present in soil, which results in the generation of electrons and protons. Electrons are transferred from the anode to the cathode through an external circuit, which is responsible for current generation in the system. Protons pass through the soil to the cathode where, with electrons, in the presence of oxygen, water is formed.

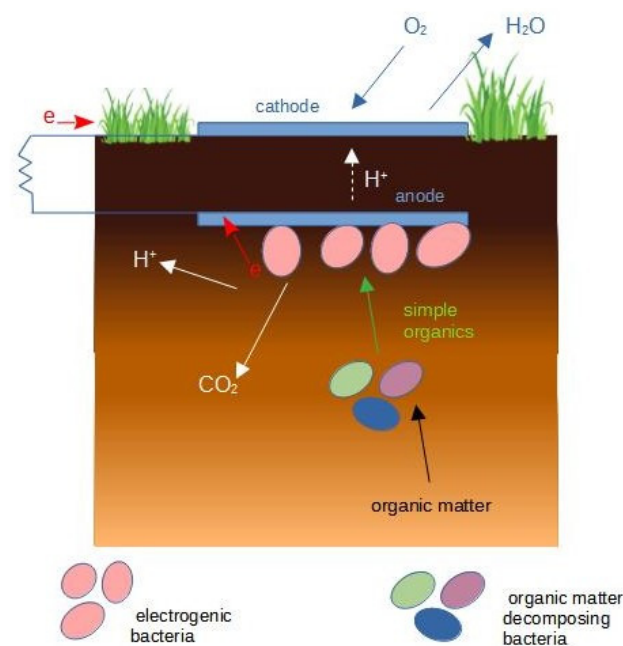


Figure 2. Schematic presentation of a soil MFC.

Until now, MFCs based on soil have been developed from different ecosystems, such as meadows, swamps, peats, wetlands, agricultural or forest ecosystems, and sediments from rivers, lakes, or seas. Among soil ecosystem-based MFCs, we can distinguish:

- (1) Soil MFCs—work in different types of soil, e.g., soil from farmland, swamps, meadows, peats, and forests; soil is the supporting matrix, separator between electrodes, and source of microorganisms and organic matter; in this type of MFC, soil is used without growing plants (in laboratory experiments) or the influence of plants growing in the soil is neglected (in field tests).
- (2) Sediment MFCs—work in sediments that are comprised of two phases: soil and water; soil function is the same as in the case of soil MFCs and the influence of possible growing plants is neglected.
- (3) Plant MFCs—work in the rhizosphere of living plants; soil is mainly a supporting matrix, source of microorganisms, and separator between electrodes.
- (4) CW-MFCs—MFC technology coupled with constructed wetlands (CWs), dedicated to wastewater treatment.

The research on soil ecosystem-based MFCs started in 2001, when Reimers et al. showed power production from marine sediment with the use of Pt and graphite electrodes [34]. The power produced was very low and reached only 10 mW/m^2 of anode area. However, the research proved that it was possible to produce electricity directly from a

soil-based ecosystem. This observation initiated further studies that showed that electricity can also be produced from other soil-based ecosystems, like farmland, meadows, forest soil, swamps, or peat bogs [35–37]. Through the years, power production efficiency of soil ecosystem-based MFCs has increased significantly, reaching over 300 W/m^2 (Figure 3). It turned out that anode electrogenic microorganisms during the conversion of organic matter to electric current cause soil bioremediation, making MFC technology an effective substitute for conventional remediation techniques that are devastating to soil ecosystems [38]. The discovery of electrotrophic microorganisms in soil-based ecosystems that are able to accept electrons from the electrode allowed for the reduction of inorganic soil pollutants on the cathode [39]. The phenomenon became the basis of soil bioremediation from heavy metals in MFCs [40]. Anodic oxidation in MFCs was also utilized for wastewater treatment in various wetland environments, allowing for an enhancement of wastewater treatment efficiency to even 99% [41,42].

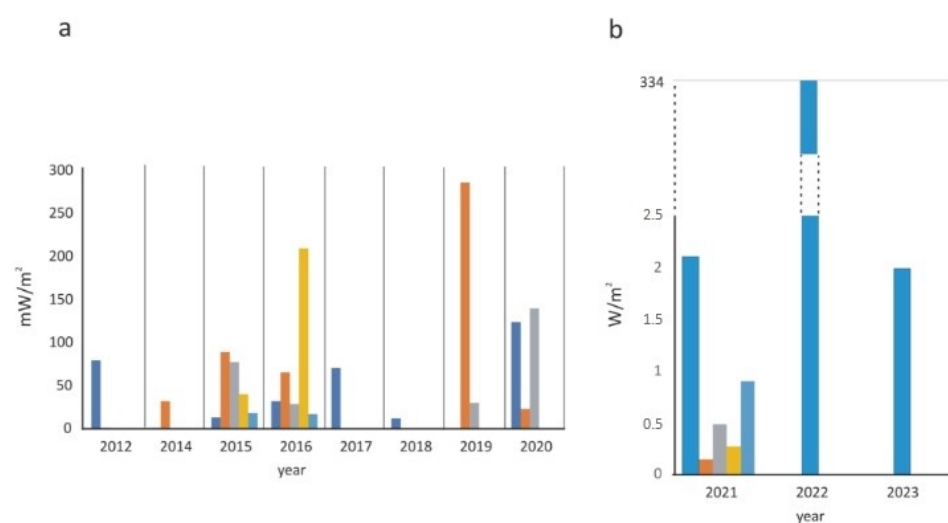


Figure 3. Increase in power production efficiency in soil MFCs through the years (a) 2012–2020 and (b) 2021–2023. Different colors of bars indicate different publications.

MFCs applied to soil-based ecosystems offer a range of ‘services’ and sustainable management in these environments. These include:

- (1) Direct production of electric current from different types of soils and sediments realized with the use of mainly soil MFCs, sediment MFCs, and plant MFCs;
- (2) Bioremediation from organic and inorganic pollutants contaminating soil-based ecosystems with the use of soil MFCs and sediment MFCs;
- (3) Effective wastewater treatment in wetlands realized by coupling constructed wetlands (CW) with MFC technology;
- (4) Greenhouse gas mitigation, soil salinity mitigation, and heavy metal accumulation mitigation with the use of soil MFCs and plant MFCs;
- (5) Wireless energy-neutral sensing with the use of soil MFCs, sediment MFCs, and plant MFCs.

This article demonstrates for the first time that MFC technology, when applied to soil-based ecosystems, provides numerous benefits. Therefore, it needs to be considered as a new strategy for sustainable soil management.

2. Soil as a Source of Microorganisms and Biomass

Soil is commonly known as the biologically active uppermost layer of the Earth’s crust, composed of minerals, soil organic matter, living organisms, gas, and water. It

is a three-phase medium consisting of solid, liquid, and gaseous phases [43]. The solid phase is composed of mineral grains of various shapes and sizes, soil organic matter, and organic-mineral particles [44]. The liquid phase is soil water containing dissolved organics and minerals, and the gas phase is the soil air, which is a mixture of gases and water vapor [44]. There is an antagonistic system between soil water and air because they can occupy the same volume of free interparticle space among soil grains; so, the more pores are filled with water, the less the soil is aerated [45]. Soil texture, pore size, and air–water relationships determine aerobic or anaerobic conditions for microorganisms and their distribution. Soil organic matter, apart from minerals, is the basic component of soil, significantly affecting a number of its chemical and physical properties. Soil organic matter is not a homogeneous substance but a mixture that includes the biomass (edaphon) (i.e., all living organisms inhabiting the soil, e.g., bacteria, fungi, protozoa) and organic remains in the form of undecomposed or partially decomposed plant and animal tissues and soil humus (i.e., organic soil matter that does not show the structure of the tissues of the organisms from which it was created and is a mixture of amorphous, dark-colored colloidal substances formed in the soil as a result of the humification process) [44]. The main source of soil organic matter is the dead remains of higher plants, microorganisms, and animals. In forest ecosystems, the basic source of organic matter is plant fallout (leaves, fruits, cones, needles, branches, etc.) and, to a much lesser extent, plant roots [46]. In meadow ecosystems, grassroots are the main organic matter and are able to effectively bind large amounts of CO₂, estimated at 3.4–10.2 billion t CO₂ equivalents per year (CO₂ e year^{−1}) [47–49]. In agroecosystems, a significant part of organic matter is carried away with crops; thus, the main sources of organic matter are crop residues, straw, and organic fertilizers. It is estimated that organic carbon resources amount to approx. 1500–2400 Pg C in soil and 1700 Pg C in permafrost [50]. Soil inorganic carbon, the second-largest sink of terrestrial carbon, is estimated at 695–940 Pg C and is restricted mainly to arid and semiarid soils [51]. These soils comprise CaCO₃, CO₂, HCO₃[−], and CO₃^{2−} and play an important function in carbon sequestration [4].

Soil is also the largest reservoir of microorganisms, including electrogens, and is perceived as the last bastion of biodiversity on Earth, as the variety of microorganisms living in soil is many times greater than that on the surface [52]. It is estimated that one gram of soil can contain from 2 to 8 million species of bacteria, which corresponds to 1 billion bacteria in 1 g of soil [53]. In the surface horizons of soils, the biomass of bacteria varies widely, from 0.4 tons/ha in poor habitats to 10 tons/ha in fertile ones. The number increases most often with increased soil acidity and can reach 5–10 tons per hectare [44]. The activity of soil organisms is the basis of life in the biosphere and determines many processes and interactions both in the worlds of plants and animals. A special role in this respect is played by the rhizosphere, the layer of soil adjacent to the roots of living plants, in which there are 1000–2000 times more microorganisms than outside its borders [54]. Soil organisms colonizing the rhizosphere enable plants to take up nutrients through the active transformation of organic and mineral components, which allows for plant growth [55]. The diversity and physiological activity of soil microorganisms are influenced by a number of factors, such as the type of soil system (e.g., farmland, forest, meadow, wetland, sediment), depth, humidity, plant type, fertilization method, and cultivation system [56].

Under aerobic conditions in soil, microbial aerobic respiration occurs during which ATP (adenosine triphosphate) is produced with the use of an electron transport chain, where oxygen is the final electron acceptor [57]. Under oxygen deficiency, electron transport is inefficient and under such conditions some bacteria have developed mechanisms that allow them to survive using alternative acceptors to oxygen, such as metals [58]. These bacteria use extracellular electron transfer and pass electrons to alternative metal acceptors

such as Fe or Mn [59]. Closure of the complete electron transport chain is facilitated through extracellular transport, which is the basis of the metal reduction mechanism by microorganisms known as electrogens. One of the best-known electrogenic bacteria used in many studies on MFC technology around the world is *Geobacter sulfurreducens*, which is a naturally occurring soil strain capable of reducing Fe(III), Mn(IV), and U(VI) in an anaerobic environment and was originally isolated from sediments from a contaminated ditch [60]. The transfer of electrons by *G. sulfurreducens* to iron takes place as a sequence of redox reactions due to the presence of cytochromes (electron transport proteins) in the outer membrane of the bacterial cell. Another representative of the *Geobacter* family isolated from soil, *Geobacter metallireducens*, was the first microorganism discovered to be capable of reducing insoluble iron(III) oxides in combination with the oxidation of short-chain fatty acids or alcohols [61]. The ability to reduce metals such as Fe(III), Mn(IV), and Co(III) under anaerobic conditions is also exhibited by *Shewanella putrefaciens*, isolated from river sediments. In this case, the transfer of electrons to metals takes place in two ways: employing a system of cytochromes in the outer membrane and through hair-like projections of the membrane, called pili, which have the ability to conduct electrons even over long distances from the bacterial cell [62]. In *Pseudomonas aeruginosa*, isolated from the rhizosphere, extracellular electron transfer is possible due to the secretion of redox mediators, mainly pyocyanins [63].

The limitation of electrogenic bacteria is that they are unable to decompose complex organic matter and can use only simple organic compounds, such as simple salts, acids, or simple sugars [64]. Thus, their presence in soil is inextricably linked to other non-electrogenic microorganisms of the soil microflora. Non-electrogenic bacteria and fungi living in soil decompose organic remains by humification and mineralization, transforming soil organic matter into simple compounds, which can be further used by electrogens to produce electricity [65]. Among mineralization bacteria, there are autotrophs and heterotrophs, which, as a result of their metabolic activity, transform numerous inorganic and organic compounds into simpler forms that are better absorbed by plants and other microorganisms [66]. Soil bacteria are known to be able to turn unassimilable molecular nitrogen into ammonia, which can be assimilated and metabolized in plant and animal cells [66]. The most popular nitrogen-fixing bacteria are from the genera *Rhizobium*, *Cyanobacteria*, and *Frankia*, known for their ability to assimilate molecular nitrogen from the air and convert it into ammonia [66]. As a result, nitrogen is incorporated into the biomass and enters the nitrogen cycle in the environment. Among autotrophs, there are also *Cyanobacteria*, which obtain energy from photosynthesis thanks to the presence of photosynthetic pigments in their cells. These bacteria are also responsible for fixing carbon dioxide and building soil biomass [67]. Sulfur bacteria, e.g., *Thiobacillus* or *Thiotrix*, oxidize elemental sulfur to water-soluble sulfates, making it more available to plants. Nitrifying bacteria of the genera *Nitrosococcus*, *Nitrosobacter*, *Nitrobacter*, and *Nitrospira* take part in the nitrogen cycle and oxidize ammonia to nitrates [68]. Methanogens (e.g., *Methanobacteria*, *Methanococci*) decompose organic matter under anaerobic conditions, and the product of their respiration is methane, which can be further used by methanotrophs under oxic or anoxic conditions, e.g., *Gammaproteobacteria* [66,69]. In soil, there are obviously a wide range of bacteria capable of decomposing of lignocellulosic plant residues, belonging to the four main phyla: *Firmicutes*, *Actinobacteria*, *Proteobacteria*, and *Bacteroidetes*, e.g., *Pedobacter* sp., *Mucilaginibacter* sp., *Ruminococcaceae* sp., or *Enterobacter* sp. [70,71]. Therefore, the diversity and richness of soil microorganisms, in addition to ensuring plant growth, enable the effective use of biomass and the development of electrogenic bacteria that can be utilized in MFC.

3. Production of Electricity from Soil-Based Ecosystems Using MFC Technology

3.1. Soil MFCs

A soil MFC is a special type of MFC designed for the production of electricity directly from various types of soil, which is used here as the substrate (source of organic matter and supporting matrix), a source of microorganisms, including electrogens, and in membrane-less configurations, as a separator between the anode and cathode [72]. A soil MFC is an environmental fuel cell in which soil is the medium, and the metabolic activity of endogenous soil microorganisms is used to convert the chemical energy stored in the organic matter contained in the soil directly into electric current. Thus, soil MFCs are perceived as attractive decentralized energy sources, independent of conventional energy networks. Additionally, contrary to solar and wind-based systems, they are not dependent on the weather conditions, making the technology more stable and accessible. Soil MFCs have a simple structure and are practically maintenance-free because there is no need to continuously supply substrate or oxygen to the system [73]. Usually, soil MFCs have an anode buried in the deeper layer of soil, to which organic matter is transported via diffusion (Figure 2) [74]. The cathode is placed at the top of the soil, where oxygen access is assured from the air. Sometimes proton-exchangeable membranes are used, but membrane-less configurations are preferable and are possible due to the naturally occurring gradient in soil, which creates the natural potential difference necessary for the flow of electrons [75]. The main disadvantages of soil MFCs are the complicated soil structure, changeable soil composition, high soil resistance, and low mass transfer [76]. Soil conductivity is related to the presence of cations and anions in the soil solution (liquid conductivity) and adsorbed charged particles on the surface of soil grains (solid conductivity). Common factors affecting soil conductivity include salinity, water content, ion concentration, temperature, and soil particle composition [77]. The high internal resistance of soil is a factor that inhibits the operation of MFCs, especially in the case of poorly conductive soils or sediments due to the high density of the solid phase of soil. Increasing the moisture content can improve the amount of capillary water and thus reduce the resistivity of soil. It was shown that when the soil moisture in the MFC increased from 23% to 28% and 33%, the internal resistance decreased, respectively, from 42.6 Ω to 10.8 Ω and 7.4 Ω , which improved the efficiency of the MFC [78].

Afsham et al. used soil soaked with groundwater taken from a depth of 30 m in a soil MFC in Iran. In the reactor, with a capacity of 2.3 L, electrodes of stainless steel, graphite, or Pt were used. A maximum power production of 64 mW/m² was achieved, which corresponded to a current density of 308 mA/m² [79]. Another study was conducted on a synthetic soil suspension, which was a biologically active mixture of sand, silt, and clay saturated with water [77]. For the investigations, two types of electrodes were used: carbon felt and stainless steel/epoxy/carbon black composite. A maximum power density of 251 mW/m² was achieved for composite electrodes and it was observed to persist for more than 60 days. Studies of the composition of the bacterial consortium at the anode biofilm showed the presence of strains from the family Geobacteraceae, known for their electrogenic activity. One of the most abundant groups contained species of the family Comamonadaceae, which are responsible for the removal of nitrates and show fermentation activity [77]. On the cathode, mainly aerobic bacteria were found, such as Trueperaceae and Burkholderiaceae. Interestingly, the power produced in an MFC with a carbon felt anode was much lower in comparison to that produced with composite electrodes, although the electrodes indicated similar conductivity. Carbon felt electrodes turned out to have higher charge transfer resistance and lower diffusion processes than composite electrodes. Also, the higher specific surface area for composite electrodes provided better conditions and

surface morphology for bacterial growth and metabolism, which showed that the electrode material characteristics are a crucial parameter to be taken into account when considering the power production efficiency of soil MFCs [77]. Power was also produced from soil taken from the surface layer (0–20 cm) of a meadow in a cylinder-type MFC with a capacity of 1 L and Pt electrodes—an anode placed at the bottom of the cylinder and a cathode at the top [80]. In this case, additional substrates for soil bacteria were introduced, glucose and straw, for which the maximum power production was 31 mW/m² and 10 mW/m², respectively, which corresponded to a current density of 100 mA/m² and 11 mA/m², respectively. In other studies, Dunaj et al. [81] investigated the influence of the type of soil sampled from agricultural and forest areas on the performance of soil MFCs. Forest soil from an area overgrown with deciduous forest and soil from a cultivated garden plot were used for the study. The tests were carried out in systems with a capacity of 1 L and electrodes made of carbon fabric. The results of the research indicated that the content of organic carbon in the soil, the rate of mineralization, and the composition of the bacterial consortium were the key factors determining the efficiency of electricity production in the soil MFC. It was observed that the power production for the MFC using garden soil (44 mW/m²) was significantly higher than that using forest soil (4.2 mW/m²). Simultaneously, the proportion of water-soluble polyphenols in the forest soil was approximately 10 times greater than in the garden soil, and the ratio of C/N for the forest soil was significantly higher than that of the garden soil, at 28.1 and 16.9, respectively. This indicated that the organic matter in forest areas exhibited a higher resistance to decomposition, resulting in lower nitrogen availability compared to agricultural soil. This was also confirmed by the higher rate of nitrogen respiration and mineralization in agricultural soil than in forest soil: the respiration rate measured in $\mu\text{mol CO}_2/\text{day}$ was, respectively, 0.29 and 0.033, and the rate of nitrogen mineralization measured in $\mu\text{mol NH}_4^+/\text{day}$ was 38.3 and -10.6 , respectively. Although the acetate level in forest soil was 8 times higher than that in garden soil, this did not correspond with MFC performance. Acetate is known to be an effective substrate for *Geobacter*, which was not found in the anode of the forest soil-based MFC. Meanwhile, the dominant genera identified in the anode of the garden soil-based MFC were *Clostridia* and *Geobacter*. This phenomenon was explained by the high content of polyphenols in forest soil, which may inhibit *Geobacter* development. In other studies where different types of soil were used (sandy loam and loamy sand with various C/N ratios), it was shown that the highest power production (68 mW/m²) was obtained for soil with the highest C/N ratio (14:1) [82]. This is contradictory to the research by Dunaj and co-workers [81], where a higher C/N ratio did not correspond with higher power production. Although the amount of organic carbon is an important parameter affecting MFC power production efficiency, its influence needs to be assessed individually for specific soil types.

Besides soil type (which relates to, e.g., differences in organic matter content, soil conductivity, and type of microorganisms), there are other factors that influence the power production efficiency of soil MFCs. Electrode configuration and placement in soil is also an important aspect, as optimal electrode spacing allowed for increased power production by 58–158% and cathode immersion showed a negative effect, causing 68% voltage decay [83]. Until recently, power production in soil MFCs did not exceed 100 mW/m². However, recent studies show a significant increase in this field (Figure 3), mainly due to the development of new electrode materials, especially for anodes, as attracting electrogens to the anode in a solid medium such as soil is much more problematic than in the aqueous media used in conventional MFCs [84]. So far, the highest power production in a soil MFC was 334 W/m² when Fe³⁺ supplementation was applied [85]. Thus, a question about the efficiency of MFCs in iron-rich soil arises (Table 1).

Table 1. Soil MFCs designed for electricity production.

MFC Configuration	Soil Type	Additional Substrate	Max Power	References
Portable, with carbon nanotube-based electrodes and floating air cathode	Rice paddy soil	no	70 mW/m ²	[86]
Dual chamber	Farmland soil and sediment	Fe ³⁺	334 W/m ²	[85]
Single chamber, carbon black electrodes with PTFE, PVA, epoxy, and PVDF * binders	Topsoil with garden compost	no	500 mW/m ²	[77]
Stainless steel mesh/carbon black electrodes	Soil	Synthetic urine medium	271 mW/m ²	[77]
Membraneless MFC with air cathode, carbon felt electrodes	Muddy soil, sandy soil	Household rice washing wastewater	485.2 mW/m ² 112 mW/m ²	[87]
Dual and three-chamber MFC, carbon felt anode, stainless steel cathode	Contaminated soil	Citric acid	40 mW/m ²	[88]
porous carbon electrodes	Farmland soil	Urine	85 mW/m ²	[76]
Stainless steel/epoxy/carbon black composite	Synthetic soil	Synthetic urine	251.5 mW/m ²	[77]
Graphite fiber felt electrodes	Soil from ground level 3 m	Glucose, yeast extract	2122 mW/m ²	[89]
Bamboo charcoal anode, activated carbon cathode	Peat soil	Bamboo waste, fluvic acid	2011.9 mW/m ²	[90]

* PTFE—poly(tetrafluoroethylene); PVA—poly(vinyl acetate); PVDF—poly(vinylidene fluoride).

Such an increase in the power production efficiency of soil MFCs allowed for consideration of their application potential as an energy source to power small devices. The first implementation of soil MFCs in field tests showed that, despite different soil compositions and parameters, the power produced in lab-scale experiments was lower than that in field tests [91]. However, a stack of soil MFCs (maximum power production of 6.5 mW) was able to power a commercial electrolytic water treatment reactor in field tests for several months, proving its ability to ensure a decentralized, renewable energy source [91]. In practical applications of soil MFCs, the power output seems to be more effectively increased by stacking multiple reactors than by increasing the electrode size or chamber volume. Thus, electrically stacking soil MFCs should be the strategy for scaling up this technology [92]. A soil MFC was also applied as a self-powering portable soil water content sensor, which could be used for the management of irrigation schedules to reach high productivity in agriculture [93]. The sensor was based on activated carbon electrodes with Nafion and the cathode was additionally modified with carbon nanotubes. The experiments indicated that the sensor was effective for measuring water content in soil in the range of 36–48%, which is the normal humidity for many crops. A soil MFC with carbon felt electrodes was also applied as a heavy metal (Cd²⁺, Zn²⁺, Pb²⁺, or Hg²⁺) biosensor working in the range of 0.5–30 mg/L [94]. The sensor was batteryless and worked stably for four months. A similar application of soil MFCs was proposed by Olias et al. for the monitoring of dissolved oxygen in water. The authors demonstrated the applicability of the device up to 4.5 ± 1.2 mg/L of dissolved oxygen and a linear response range of 53.3 ± 22.6 mV/L/mg [95].

3.2. Plant MFC

Plant MFCs are MFCs that work in the rhizosphere, which is a thin layer of soil in the proximity of living plant roots, to a depth of 0.5–4 mm [96]. The rhizosphere is a unique environment, different from bulk soil, where rhizodeposition takes place [97]. The released rhizodeposits are composed of water-soluble root exudates (wide range of sugars and oligosaccharides, amino acids, proteins, organic acids, enzymes, and sterols) and mucilage, sloughed-off tissues and root cells [98]. In the rhizosphere, H^+ and OH^- ions, CO_2 , O_2 , H_2 , and CH_4 have also been observed to be released [96,99]. Such a wealth of nutrients stimulates microbial growth and activity and results in an enhanced number of bacteria in the rhizosphere in comparison with bulk soil and a different microbial diversity, called the root microbiome. One of the most well-known representatives of the root microbiome is *Rhizobium* sp., known from atmospheric nitrogen fixation to ammonia [100]. There is also an abundance of other microorganisms, including bacteria able to decompose lignocellulosic matter, e.g., *Ruminococcaceae* sp., *Enterobacter cloacae*, fermentative species like *C. sporosphaeroides*, and a wide range of electrogens, e.g., *G. sulfurreducens*, *G. metallireducens*, or *G. hydrogenophilus* [70].

In plant MFCs, electrogenic rhizosphere microorganisms colonize the anaerobic anode, where root exudates are oxidized, generating carbon dioxide, electrons, and protons (Figure 4). Separation of the anaerobic anode from the aerobic cathode causes electron transport to the cathode through the external electric circuit. Due to potential gradient in soil, protons pass through the soil to the cathode, where with oxygen and electrons, water is formed. Electrons are also produced in the rhizosphere as a result of non-electrogenic bacteria activity, e.g., oxidation of ammonia to nitrate. Such electrons also transferred to the anode and support electricity production in the system [70].

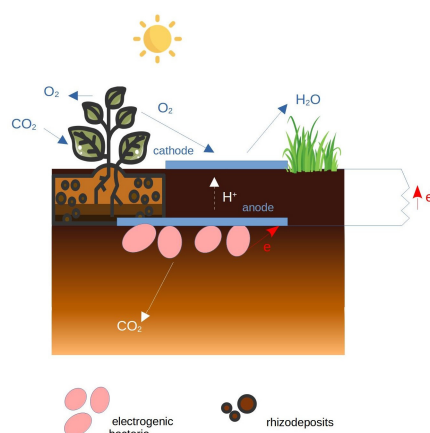


Figure 4. Schematic presentation of a plant MFC.

In the literature, plant MFCs are sometimes considered to be the same as soil MFCs and described as such. Indeed, both soil MFCs and plant MFCs work in different types of soil to produce electricity and they both use soil organic matter as a substrate and soil microorganisms as catalysts. However, the main difference between them is that the substrate for soil MFCs is soil organic matter while for plant MFCs it is rhizodeposits, which are constantly produced by living plants [99]. It needs emphasizing that soil utilized in soil MFCs is usually without living plants or their influence is neglected, while plant MFCs work in the rhizosphere of living plants, and their influence is predominant. As plants use sunlight to produce organic matter, it is sometimes stated that sunlight is converted into electric energy in plant MFCs. However, the maximum power conversion efficiency here is estimated at 0.92%, which does not allow plant MFCs to compete with photovoltaics, where efficiencies reach over 26% [101]. In plant MFCs, mainly hydrophytes, wetland

plants, and vascular plants are used as they are water tolerant, with high solar energy conversion rates and biomass production [72]. Power production in plant MFCs is often low, not exceeding 100 mW/m^2 (Table 2). However, there are many factors that influence power production efficiency, such as plant species, soil type and its microbial composition, and other factors connected with electrode and reactor characteristics that are typical for MFCs [70]. The species of plant used is one of the most important factors influencing power production efficiency in plant MFCs, e.g., utilization of *Wachendorfia thyrsiflora* instead of *Cyperus papyrus nanus* allowed for a 2-fold increase in power production [102]. Similarly, over a 3-fold increase in power production, from 69 mW/m^2 to 222 mW/m^2 , was observed when *Canna stuttgart* was used instead of *Brassica juncea* [103]. That is because plants with fast root growth systems or high production of root exudates favor increased power production [72]. The addition of organic substrates to the soil of plant MFCs can also increase their power production efficiency. Adding compost to the soil of a plant MFC resulted in a 3-fold increase in power density and when waste activated sludge was added, power production reached a maximum value of 1036 mW/m^3 [102,103]. Recent research on plant MFCs shows the possibility of electricity production from agriculturally cultivated plants like lettuce [104]. This points out a new direction for modern agriculture, where cultivation of crops could be coupled with electricity production. Plant MFCs were also investigated for their potential as decentralized energy sources for low-power devices, e.g., a bryophyte-based MFC for remote sensor, radio power supply [105] or an opuntia-based MFC as a biobattery in semi-arid environments [106]. It was also proposed to use plant MFCs in the concept of a floating garden for powering remote environmental sensors [107]. In this approach, *Oryza sativa* was grown in sediment, resulting in a power production density of $22\text{--}28 \text{ mW/m}^2$ and the system was able to operate for a year without the need for maintenance.

Table 2. Power production in plant MFCs above 10 mW/m^2 limit.

Plant	Anode	Cathode	Power Production	References
<i>Vallisneria natans</i>	Carbon felt	Carbon felt	45.3 mW/m^2	[108]
<i>Glyceria maxima</i>	Graphite felt	Graphite felt	12 mW/m^2	[109]
<i>Epipremnum aureum</i>	Carbon rod	Stainless steel	73.7 mW/m^2	[110]
<i>Oryza sativa</i>	Carbon felt, maple wood biochar granules	Air cathode	41.4 mW/m^2	[111]
<i>Oryza sativa</i>	Carbon cloth	Carbon cloth	28 mW/m^2	[107]
<i>Puccinellia distans</i>	Carbon felt	Air cathode	83.7 mW/m^2	[112]
<i>Cyperus papyrus nanus</i> <i>Wachendorfia thyrsiflora</i> Control (no plant)	Granular activated carbon	Carbon paper	$510 \pm 92 \text{ mW/m}^3$ $1036 \pm 59 \text{ mW/m}^3$ $392 \pm 67 \text{ mW/m}^3$	[102]
<i>Brassica juncea</i> <i>Trigonella foenum-graecum</i> <i>Canna stuttgart</i>	Carbon brush	Carbon brush	69.3 mW/m^2 80.2 mW/m^2 222.5 mW/m^2	[103]
<i>Spartina anglica</i>	Graphite rod	Graphite felt	222 mW/m^2 of plant growth area	[113]

Table 2. Cont.

Plant	Anode	Cathode	Power Production	References
<i>Spartina anglica</i>	Graphite felt	Graphite felt	679 mW/m ² of plant growth area	[114]
<i>Aglaonema commutatum</i> <i>Epipremnum aureum</i> <i>Dranacaena braunii</i> <i>Philodendron cordatum</i>	Carbon felt	Carbon felt	12.5 mW/m ²	[115]

3.3. Sediment MFCs

Sediments refer to the matter lying on the bottom of water reservoirs as a result of sedimentation. They include mineral elements such as clays, silts, sands, and gravels, as well as organic matter formed from the remains of plant and animal organisms [29]. The chemical composition of sediments depends on natural factors such as the type of soil cover, topography, and climatic conditions [116–120], as well as on anthropogenic activity, including land use, urbanization, and industrial and agricultural activities [121–123]. The idea of using MFCs to produce electricity from sediments is relatively obvious and allows for the use of energy stored in the biomass deposited in sediment. The concept assumes the use of bacteria naturally living in sediments, decomposing the organic matter in sediment [124]. Sediments from waterbodies such as rivers, seas, and lakes have been the most frequently used in MFCs. Typically, a sediment MFC consists of an anode buried in the sediment (anaerobic environment) and a cathode placed in water containing dissolved oxygen, connected by an external circuit (Figure 5) [125]. This allows for harvesting energy from the naturally occurring potential difference at the sediment–water interface, which is also influenced by the microbiological composition of the MFC working environment. Previous research indicates that the generation of electricity in sediment MFCs is the result of the chemical oxidation of microbial reductants (humic acids), Fe²⁺ or sulfur compounds at the anode, and microbial oxidation of organic compounds, or S⁰ [126]. The electrons released are passed to the anode and, through an external circuit, to the cathode, which results in an electric current flowing through the system. The main bacteria involved in current production in sediments are *Desulphuromonas* sp., *Desulfobulbus* spp., *Desulfocapsa* spp., *Geothrix* spp., and *Geobacter* sp. [34,127].

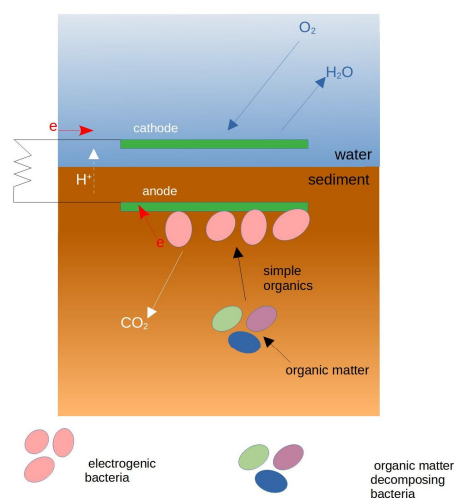


Figure 5. Schematic presentation of a sediment MFC.

Marine sediment MFCs have been applied in many field tests to produce electric current on the seabed, allowing them to power marine research devices for oceanographic and military measurements or environmental monitoring [34,128]. MFCs working on marine sediments were shown to power wireless sensors for wave motion, temperature, migration of marine organisms, salinity, monitoring of various pollutants from anthropogenic activities, and pH or oxygen levels in sea water [129]. The typical power production obtained in field tests from sediment MFCs is low, usually not exceeding 20 mW/m², but significant progress has been made in this field (Table 3).

Table 3. Power production from sediment MFCs.

MFC Configuration	Substrate	Maximum Power mW/m ²	Volume L	References
Laboratory experiments				
Carbon brush electrodes	Lake sediment	2	121	[130]
Graphite fiber felt electrodes,	Sediment enriched with glucose	2.1	n/a	[89]
Graphite electrodes	Marine sediment	8	0.55	[131]
Carbon felt anode modified with surfactants, Ti cathode	tidal flat sediment	600	0.6	[132]
Carbon felt anode modified with humic acid	Marine sediment	165	0.7	[133]
Single-chamber MFC with carbon fiber electrodes	Marine sediment	1400	2	[134]
	Fluvial sediment	700	2	
Field tests				
Circular tube from PEM, granular graphite anode	Marine sediment	4	4.5	[135]
Ti/Ir/Ta anode and stainless steel cathode	Marine sediment with acetate	20	0.6	[136]
Carbon felt anode modified with 3-aminopropyl-triethoxysilan or composite with Fe ³⁺	Marine sediment	203.8	n/a	[137]
Pt mesh or graphite fiber electrodes	Marine sediment	10	n/a	[34]
Fine carbon fibers	Marine sediment	380	9.6	[138]
Modified graphite anodes, ceramic-graphite composite anodes with Mn ²⁺ and Ni ²⁺	Marine sediment	105	n/a	[133]
Graphite rod anode, graphite plate cathode	Marine sediment	34	n/a	[139]

Assuming that marine sediments typically contain 2–3% organic carbon (dry weight), it has been estimated that sediment MFCs powered by such substrates could theoretically sustain a production of 50 mW per square meter of cathode surface virtually indefinitely. High-capacity sediment MFCs (167 L) were applied in field tests in water off the coast of the United States, where sediments contained 4–6% organic carbon [140]. The systems used for the tests contained graphite electrodes in the form of discs, and, depending on the location of the tests, the power output was from 11 to 32 mW/m². Analysis of the bacterial consortium working in sediment MFCs showed that the dominant species, depending on the location, were bacteria *Desulfobulbus* spp. or *Desulfocapsa* spp., the main substrates

of which for the production of electricity were iron sulphides [141]. Field studies were also carried out with the use of an MFC made of an anode in the form of a graphite rod placed in the sediment layer on the seabed and a cathode made of carbon fiber or a titanium brush [139]. In this case, a power production of 34 mW/m^2 was obtained, but only for a month, after which a decrease in cell power was observed due to uncontrolled precipitation of sulfur on the anode surface. The concept of a floating sediment MFC was applied in field tests to power remote environmental sensors in marine sediments, where the floating MFC produced power of 6 mW/m^2 [142].

Due to the low power densities obtained from sediments, recent research has focused on improving power production efficiency. The main reasons for low power efficiency in sediment MFCs are: (1) low current density at the anode; (2) limited mass transfer at the anode; (3) limited cathode performance (oxygen availability); and (4) fast depletion of organic substrates in sediments [141]. Overcoming these limitations may be realized through redesigning reactor and electrode architecture, increasing the electrode surface area, selection/modification of electrode material and properties, selection of sediment type, or adding biodegradable substrates to sediments [141]. In the case of marine sediments, the high conductivity of seawater is a significant advantage compared to typical MFC systems that operate on electrolytes with much lower conductivities. Because sediment MFCs must use cathode-dissolved oxygen, cathodes with huge surface areas have been designed [142]. To increase the efficiency of anodes, they are modified, e.g., with mediators that facilitate the transport of electrons to the anode, which allows for a significant increase in power production compared to unmodified electrodes [133]. Modifying the graphite anode with Mn^{2+} resulted in an increase in sediment MFC power production in field tests from $20\text{--}40 \text{ mW/m}^2$ to 105 mW/m^2 . Modification of the anode with humic acid resulted in an over 6-fold increase in power density produced in a sediment MFC [143]. Humic acid can chelate metal ions such as Fe and Mn, which enhances the electron transfer mechanism. This effect is strengthened by the quinone group of humic acid, which is redox active and serves as an electron transfer mediator. A large influence of pH on the efficiency of power production was also observed. An increase in pH from 8.5 to 12.5 resulted in a 100-fold increase in MFC power production [144]. The efficiency of power production in sediment MFCs is also strongly limited by the content of organic matter and the rate of its decomposition by bacteria. This effect was observed in sediment to which biodegradable materials such as chitin and cellulose were added [145]. Although higher power production values were obtained compared to sediment without additives, as could be expected, power production dropped sharply after the substrates were exhausted. Therefore, the use of slowly degrading compounds should be treated more like a kind of bio-battery that works until the substrates are exhausted.

So far, the highest power density has been obtained from fluvial and marine sediments in Mexico with the use of single-chamber MFCs [134]. The research indicated that electricity production from sediments was highly influenced by the type of sediment and the season of the natural hydrological cycle. When marine sediments were used during the dry season, a power density of 1.4 W/m^2 was obtained, while for the rainy season it was only 0.1 mW/m^2 . The highest power density for fluvial sediments was 700 mW/m^2 during the rainy season and 350 mW/m^2 during the dry season. Sediments collected during the dry season had higher contents of organic matter and ions, which influenced voltage production in the MFC. Microbial analysis revealed the presence of *Clostridium* species in fluvial sediments and *Vibrio* species in marine sediments, which resulted in different power production efficiencies.

4. MFC Technology as a Tool for Soil Bioremediation

Soil-based ecosystem contamination as a result of human activity has a huge impact on soil fertility, plant growth, grain quality, and human health. Taking into account that soil is contaminated with ca. 30 million tons of pesticides and chemicals from anthropogenic sources (e.g., electroplating, pigment application, painting, landfill leakage, excessive use of pesticides, herbicides or fertilizers, and stainless steel or solid waste seepage), the situation is serious, as the pollution of soil has direct and indirect impacts on human health and the ecosystem [146]. Each year, 3 million individuals are admitted to hospitals as a result of pesticide poisoning, and the same phenomenon results in a quarter of a million premature deaths [147]. It is estimated that between 1 and 2.5 million tons of pesticides are used annually, of which 40% are herbicides [148]. As Latino et al. reported, the half-life of pesticides in soil can vary from 3 days to 1000 days; thus, the residues of many pesticides are found in soil, groundwater, and even surface water [149]. Environmental analyses indicated that on 64% of farming land, pesticide concentrations exceeded “no-effect levels” declared by suppliers, while the concentrations on nearly one-third of farmland were reportedly high, with 1000 times the “no-effect” level [150]. Therefore, it is apparent that removing exogenous pesticides from the environment is a matter of the utmost urgency. The reclamation of soil contaminated organically with compounds such as antibiotics, polycyclic aromatic hydrocarbons (PAHs), and phthalates is also an urgent concern. Soil contaminated with petroleum hydrocarbons containing toxic and harmful components is a serious threat to the whole environment (air, water, fauna, and flora) and adversely impacts human health [151].

Among all soil-based ecosystems, special attention should be paid to sediment bioremediation. Sediments play an important role in both water and soil ecosystems because sediments are the environments in which chemical reactions take place with the participation of many compounds present in water [152]. Moreover, they are an important warehouse for a wide range of pollutants, keeping them away from water and preventing their toxic influence on the environment. In sediments, there are stored especially difficult organic pollutants (e.g., PAHs (polycyclic aromatic hydrocarbons), hexachlorobenzene) and heavy metals (e.g., P, Zn, Cd, Cr, As) [153]. By establishing an equilibrium between the water and the sediment, toxic substances are “trapped” in the sediment, which protects the water from pollution. Disruption of this balance, as a result of human activity or natural processes, leads to the release of pollutants from sediments, which is a serious threat to aquatic organisms and humans. The large amounts of heavy metals entering aquatic ecosystems as a result of industrial and agricultural human activities, as well as municipal sewage and car exhaust, have become a global threat, since heavy metals are included in the food chain as a result of biological and geochemical processes [129]. Therefore, in recent years, there has been increased interest in the remediation of sediments, e.g., through ozonation, dredging (mechanical removal of sediments from the bottom of water reservoirs), or electrochemical methods [154]. In the case of soil, conventional techniques of remediation include landfilling, chemical reduction, oxidation, stabilization/solidification, soil leaching, and electrokinetic remediation [155]. However, all of these conventional methods have many disadvantages, such as high cost, secondary pollution, soil infertility, and soil erosion [156]. For example, the chemical reduction of soil contaminated with Cr(VI) involves introducing FeSO_4 and results in the formation of iron hydroxide in soil [157]. Compared to physical and chemical agents, bioremediation is recognized as a green, cost-effective, and applicable technology, encompassing basic bioremediation, biostimulation, and bioaugmentation. Primary bioremediation is considered environmentally friendly and economically reasonable, but it usually takes a long time (as it follows the pace and course of natural processes of biodegradation of pollutants in soil) and is ineffective when the concentrations of heavy

metals and pollutants exceed certain limits [156]. Naturally occurring bioremediation processes are very slow, mainly due to the lack of appropriate electron donors and acceptors in the environment [156]. The essence of bioaugmentation is the introduction of additional microorganisms into soil that have the ability to remove a given type of pollution, while biostimulation is achieved by modifying the soil environment, for example, by aerating the soil or introducing nutrients for specific types of microorganisms to increase their number and activity. From the point of view of ecological safety and costs, bioaugmentation is worse than biostimulation, which increases the activity of native microorganisms in soil and makes it more efficient at turning organic substrates into carbon dioxide. However, the lack of electron acceptors, the scarcity of functional microbes, and the inefficiency of electron transfer limit the effectiveness of biostimulation in contaminated soil [158]. Heavy metals in soil are bioremediated in different ways. Microorganisms either immobilize or solubilize them, which eases their transport *ex situ* [159].

MFC technology simultaneously solves these problems by recovering energy (generating electricity) from polluted soil and, because of that, has recently received great attention as an energy-saving bioremediation approach [160–162]. Remediation in MFCs belongs to the category of bioelectrochemical remediation, which is a biostimulation technology [158]. MFCs have many advantages, such as environmental friendliness, low cost, safety, cleanliness, easy operation, and sustainability. The resulting electric current stimulates the growth and activity of functional microorganisms and symbiotic microflora, which accelerates the biodegradation of organic pollutants. The coupling effect of soil cleaning with electric current production increases the transfer of free electrons, which accelerates the rate of oxidation–reduction reactions in soil [156]. Subsequently, the MFC method of synchronous energy production from soil is the opposite of electrokinetic remediation, which requires energy input. MFC technology does not cause secondary contamination of soil and is more suited to the removal of low-concentration pollutants [163]. At the same time, the use of MFC for bioremediation is associated with a high-energy conversion rate and the ability to work under various weather conditions. Biodegradation in soil-based ecosystems can be realized in two ways: in the anode through the oxidation of organic pollutants with the use of electrogens, and in the cathode through the reduction of inorganic pollutants with the use of microorganisms capable of accepting electrons from the electrode, called electrothrophic organisms or electrotrophs. A value-added offshoot of the soil bioremediation process in MFCs is electricity production. Contaminated soil can be considered as a bioelectrochemical system in which oxygen is chosen as the electron acceptor to reduce the cost of remediation due to its infinite quantity and availability.

Application of MFC technology allows for efficient removal of a wide range of toxic substances from soil-based ecosystems (Table 4). For instance, Huang et al. reported an air cathode MFC in a study of the stimulated degradation of a model organic pollutant—phenol [164].

Table 4. Bioremediation in soil ecosystem-based MFCs.

MFC Configuration	Soil Ecosystem Type	Removal of Soil Contamination	Power Production During Bioremediation	References
Cathode bioremediation				
Graphite felt electrodes	Farmland soil	Total Pb 14.7% Total Zn 22.3%	21.7 mW/m ²	[165]
Three-chamber MFC	Soil	Total Cu 36.7% Total Cr 52.3% Total Pb 19.6%	n/a	[160]
Wetland plant MFC	Constructed wetland	Cr ⁶⁺ 99%	n/a	[38]
Graphite brush anode, graphite felt-activated carbon cathode	Soil from university campus	Pb ²⁺ 21%	n/a	[166]
Granular activated carbon electrodes	Farmland soil	Cu ²⁺ 36.9%	65.7 mW/m ²	[37]
Carbon felt electrodes	Soil	Cu ²⁺ 94.7%	n/a	[167]
Graphite felt electrodes	Sandy loam soil	Total Cd 130%	22.7 mW/m ²	[168]
Carbon felt electrodes	Soil	Total Cu 69.2%	n/a	[156]
Carbon brush anode, carbon cloth cathode	Soil	Cr 36%	200–300 mW/m ²	[169]
Anode bioremediation				
Single-chamber MFC with graphite felt electrodes	Soil from petrochemical industrial area	Anthracene 61.6% Pyrene 55.9% Total petroleum hydrocarbon 59.1%	24 mW/m ²	[166]
Anode: macroporous corn stem modified with carbon nanotubes; cathode: carbon felt	Soil from university campus	Petroleum hydrocarbon 42.2%	n/a	[170]
Dual-chamber MFC	Sediment	PAH (naphthalene 69.9%, acenaphthene 55.6%, pyrene 46.8%)	25 mW/m ²	[171]
Granular activated carbon electrodes	Soil	Herbicide atrazine 91.7%	n/a	[172]
Graphite felt electrodes	Soil	Benzo[a]pyrene 72.5%	n/a	[173]
Carbon electrodes	Waterlogged soil from paddy field	Phenol 90.1%	29.45 mW/m ²	[164]
Carbon electrodes	Aged saline soil	n-Alkanes (C8–C40) 29%	n/a	[174]
Granular activated carbon electrodes	Farmland topsoil	Pesticide hexachlorobenzene 71.1%	77.5 mW/m ²	[175]
Graphite felt anode, active carbon cathode	Soil from university campus	Tetracycline 64.5%	8.8 W/m ³	[176]

Both cathodes and anodes are mainly made of carbon-based materials, such as carbon cloth, carbon mesh, carbon felt, graphite rod, or granulated carbon. Fabric (GORE-TEX) is also used as the air cathode and porous carbon felt as the anode in MFCs introduced into the ground. Under closed-circuit conditions, 90.1% of the phenol was removed after 10 days, while the degradation rate was only 27.6 and 12.3% under open-circuit conditions and without the MFC, respectively. At the same time, a maximum power density of

29.45 mW/m² (projected cathode area) was obtained for an external resistance of 100 Ω. In other studies, a U-type air cathode MFC showed a 120% increase in the petroleum hydrocarbon removal rate after 25 days [177]. The alkane (C8–C40) and PAH removal rates were 79% and 42%, respectively. Studies using microMFCs to remove dibenzothiophene showed that the rate of removal was increased more than three times compared to the natural rate of purification due to the stimulation of electrogenic microbial metabolism [178]. An air cathode column MFC removed 82.1–89.7% of diesel fuel after 120 days, accompanied by a current production of 70 mA/m² [179]. Another study compared two types of carbon anodes in a column-type MFC with an air and a ground cathode [174]. The net degradation rates of total petroleum hydrocarbons, PAHs, and total C8–C40 alkanes were only 18, 36, and 29% after 180 days, respectively. This was due to the use of soil with a high degree of salinity that was contaminated with petroleum hydrocarbons for a long time. Bioremediation of contaminated soil-based ecosystems may be enhanced by the addition of substrates to the polluted soil, e.g., the removal efficiency of the toxic, fire-resistant, organic pesticide hexachlorobenzene was improved after the addition of anaerobic sludge to the contaminated soil [175]. Employing electrotrophs such as *Geobacter sulfurreducens* allowed for soil bioremediation of heavy metals, e.g., removal of U(VI) was through its reduction to the insoluble form U(IV), which was adsorbed on the electrodes. In this way, it was possible to obtain U immobilized on the electrode, which could be easily removed by replacing the electrodes [39]. Representatives of the family *Geobacter* also have the ability to remove organic compounds from sediments, e.g., *G. lovleyi* can reduce tetrachloroethylene and trichloroethylene to cis-dichloroethylene and *G. metallireducens* can reduce nitrates to nitrites in sediments in the presence of an electron donor electrode [180].

5. MFC Technology Applied for Wastewater Treatment in Soil-Based Ecosystems

Wetlands include swamps, marshes, peat bogs, and areas where the water level is close to ground level. They perform extensive functions in ecosystems, such as providing habitats for many species of plants and animals, flood prevention, water retention, carbon dioxide storage, and water purification [181]. Due to the latter function, there is increasing interest in the development of constructed wetlands (CWs), which are built mainly to remove nitrogen, phosphorus, and other pollutants of agricultural origin that are found in surface runoff [155]. CWs are eco-friendly wastewater treatment systems designed to mimic natural water treatment processes. In CWs, plants, soil, and its microorganisms play important roles in providing symbiotic physical, chemical, and biological functions, including filtration, ion exchange, physicochemical adsorption, chemical precipitation and decomposition, bioabsorption, and microbial reactions such as ammonification, nitrification, denitrification, and biodegradation [182]. As a result of these processes, various types of organic and inorganic impurities are removed. CWs are characterized by natural stratification, where redox gradients change with height. These naturally occurring redox gradients are very beneficial for MFC technology, which is implemented in CWs. A typical CW-MFC system has anode and cathode areas that are separated by media (e.g., soil, sand, or gravel), fibrous materials, or proton exchange membranes (Figure 6) [146,183]. An anoxic region forms near the bottom of the CW, while an aerobic region is near the air–water interface. Soil microorganisms in the anode area, especially those living in the rhizosphere, catalyze oxidation under anaerobic conditions, which leads to the production of electrons, protons, and carbon dioxide. Both electricity generation and wastewater treatment are based on the microbial oxidation of organic and inorganic matter in wastewater.

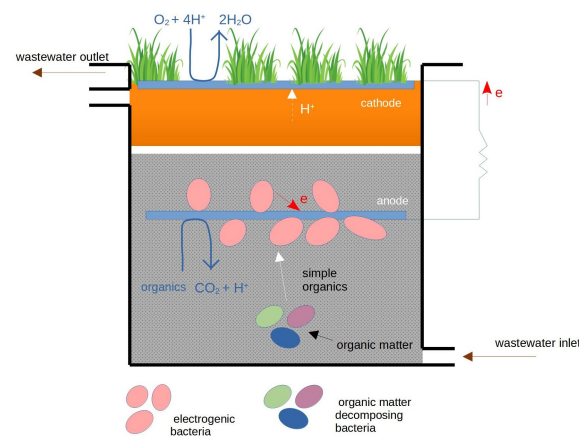


Figure 6. Schematic presentation of a CW-MFC system.

In some studies, CW-MFCs are assigned to plant MFCs due to the strong influence of plant metabolism in both systems [184]. However, in plant MFCs, electricity production is the primary goal, while in CW-MFCs, the primary function is wastewater treatment while electricity produced during the wastewater treatment process can be considered as a bonus. The integration of CWs with MFCs results not only in electricity production during the treatment process but also allows achieving higher wastewater treatment efficiency than in the case of using CWs or MFCs individually.

For example, Srivastava et al. reported a 49% higher wastewater treatment efficiency in a CW-MFC system than in a CW alone, and the treatment process was accompanied by electricity production, with a maximum power density of 320.8 mW/m^3 , corresponding to a current density of 422.2 mA/m^3 [185]. The COD removal efficiency in CW-MFCs can reach nearly 100%, as shown in an investigation with synthetic wastewater [41]. CW-MFCs were also successfully applied for the treatment of domestic, swine, and municipal wastewater in pilot-scale and semi-pilot scale studies with a COD removal efficiency of up to 87% and a maximum power density of 0.9 W/m^3 [186]. Of particular importance is the ability to remove N and P in CW-MFC systems. Investigations in this field showed that CW-MFC systems achieved an NH_4^+ removal efficiency of 88–97%, nitrate removal efficiency of 93%, and total P removal efficiency of 72–97%, depending on the plant species used [187,188]. A CW-MFC was also found to successfully remove pollutants such as azo dyes, antibiotics, or heavy metals, with efficiencies of up to 99%, with a simultaneous power production of up to 198.8 mW/m^2 [186]. Numerous factors influence the performance of CW-MFCs, e.g., aeration, type of plant used, electrode material and configuration, temperature, and pollutant load [186,189].

The type of soil parent rock used was also found to have a great influence on the efficiency of treatment. In an investigation of three materials, sand, zeolite, and volcanic slag, it was proven that the best conditions were provided by zeolite, for which the purification efficiencies were 92% for COD, 93% for NH_4^+ , and 96.7% for total P [190]. Zeolite provided microorganisms with the best conditions for the production of enzymes that were necessary for the degradation of organic substances and the transfer of electrons. Since zeolite is a porous rock with a rough surface, its specific surface area was much larger than that of the other two rocks studied. Natural zeolite contains aluminosilicate in which aluminum atoms are replaced with silicon. This structure gives zeolite a negative charge that attracts NH_4^+ , which is adsorbed on clays and is chemisorbed by humic substances. The large surface of the zeolite possesses numerous active sites for the chemisorption of organic matter in the process of ion exchange and creates suitable conditions for microorganisms.

It was also found that the electricity production process during wastewater treatment in CW-MFCs affects the CW ecosystem, as it changes the microbial consortium composi-

tion. Wang and co-workers investigated a CW-MFC with water wolf (*Ipomoea aquatica*) intentionally planted in the vicinity of the cathode to help remove impurities and increase the efficiency of oxygen delivery to the cathode [191]. Synthetic wastewater containing from 24.8 to 87.6 mg/L NH_4^+ and 21.6 to 94.6 mg/L NO_3^- was introduced into the wetland, which resulted in the removal of NH_4^+ and NO_3^- up to 98.8%. A maximum power production of 300 mW/m³ was observed, corresponding to a current density of 1 A/m³. Studies of the composition of the bacterial consortium at the anode showed that the dominant species were Anaerolineaceae, Nitrosomonadaceae, Nitrospira, and Tamera [191]. The bacterial composition of the anode consortium was found to be significantly different from the composition of the consortium of the raw wetland, which proved that the current production conditions affected the CW microbial community and the phenomenon needs in-depth research.

6. Soil Ecosystem-Based MFCs as a Strategy for Methane Mitigation, Soil Desalination, and Mitigation of Heavy Metal Accumulation

Although the largest amount of greenhouse gases is accounted for by CO_2 , the global warming potential of CH_4 and N_2O is 20–310 times more effective per molecule than that of CO_2 [192]. Meanwhile, the methane concentration in the atmosphere is increasing at a higher rate than CO_2 , which imposes the necessity to pay special attention to preventing methane emissions to the atmosphere [193,194]. Generally, methane is produced during organic material decomposition under anoxic conditions in the presence of CO_2 as an electron acceptor. The process is realized by bacteria decomposing waste and sewage, bacteria realizing fermentative digestion, and decomposing organic matter in wetlands [193,195]. However, methanogenesis takes place in various anaerobic environments as a terminal step of organic matter decomposition, so the monitoring of methane emissions has been introduced in various soil-based ecosystems containing organic matter [196].

Among them, the largest natural methane emitters are wetlands, which account for only 6–8% of the earth's land surface, but they are responsible for 63% of natural methane emissions [197]. Various methods have been proposed to suppress methane generation in sediments, e.g., chemical treatment (acid/base), heat treatment, or ultrasonication [198]. In wetlands, the addition of external inorganic electron acceptors such as SO_4^{2-} , Fe^{3+} , or Mn^{4+} was applied, and in soil, various agrotechnical treatments were tried, e.g., soil amendment and cultivar selection [199,200]. Recent investigations strongly suggest that MFCs applied to soil-based ecosystems can play a significant role in methane mitigation, as microorganisms working in MFCs oxidize organic matter present in the soil environment, which acts as an electron donor for electricity production. It was proved that organic matter decomposition in soil is enhanced due to current generation in MFCs [201]. Electricity production from organic matter limits the availability of this substrate for methanogens, which suppress methane generation in soil environments [146]. It was shown that applying CW-MFCs allows for effective regulation of CH_4 and N_2O emissions from wetlands. Moreover, the amount of current produced during the methane mitigation process is enhanced by the presence of living plants in soil ecosystems [202]. The available power production was estimated at 1.6–3.2 W/m² of plant growth area [203]. Liu et al. described that greenhouse gas emissions were strongly influenced by the material of the cathode, influent C/N ratio, and Ni addition [146]. Application of a carbon fiber felt cathode resulted in a 5-fold decrease in N_2O emissions and over a 2-fold decrease in methane emissions in comparison to other studied cathode materials. The addition of Ni caused a further CH_4 emission reduction from 0.8 to 0.2 mg/(m²h) and N_2O emission reduction from 100 to 15 µg/(m²h). It was also observed that a low C/N ratio reduced methane emissions, while a high C/N ratio inhibited N_2O emissions. In another study, a CW-MFC with Mn ore as the matrix

allowed for the suppression of methane emissions by 55% when compared to a CW, with a simultaneous COD removal efficiency 99.85% [204].

Next to wetlands, rice paddy fields are large methane emitters, accounting for 26% of global anthropogenic emissions of CH₄ [205]. According to a model assuming zero-order kinetics proportional to the produced electricity, the application of MFC technology could reduce the amount of methane emitted by paddy fields by 28% [205]. However, these assumptions changed when a plant MFC was applied in the paddy field [206]. In the research, an improved White Ponni variety of paddy rice was used. The maximum power produced was 46 mW/m² when a double cathode was applied, internal and floating, together with biochar amendment. It was shown that methane emissions from a paddy field were reduced by 57% when compared to a paddy without an MFC. In this way, field studies showed higher methane mitigation efficiency of MFCs when applied to paddy fields than the previous model suggested. As the application of MFC technology as a greenhouse gas mitigation strategy is a relatively new direction, the driving factors and mechanisms of the process are not well known yet. However, the high potential of this innovative strategy should be the driving force for intensifying research in this field in the near future.

MFC technology may also be helpful in mitigating soil salinity, which has turned into a huge problem connected with environmental damage and reduces crop yield by even 58% [207]. In the research on MFCs, there have been many trials of their application in saline and hypersaline environments [208]. It was shown that an increase in substrate salinity did not damage the anode community of MFCs but also resulted in an increase in power production. Liu et al. reported an enhanced power output from 720 to 1130 mW/m² when the NaCl concentration increased from 0.1 to 0.4 M [209]. The resistance of MFC technology to high-salinity environments opens new possibilities for its application to the desalination of soils. Such an attempt was undertaken with the use of a plant MFC in saline-sodic soil, where high MFC desalination efficiency was observed [210]. The soil conductivity was reduced by 83%, which was accompanied by a power production of 34 mW/m². Despite the soil desalination potential of MFCs, not much research has been conducted in this area, which needs intensified efforts in this field.

MFCs are relatively well proven as being zero energy, neutral to the environment, and as a very effective tool for bioremediation of soil polluted with heavy metals (Table 4). This aspect of MFCs can also be utilized in modern agriculture as a strategy for mitigating heavy metal accumulation in agricultural crops. Gustave et al. applied a soil MFC with carbon felt-based electrodes as a tool for mitigating heavy metal accumulation in rice [211]. The research was conducted in response to increasing contamination of paddy fields with heavy metals, leading to their accumulation in rice and resulting in health risks. The results of the study showed that applying a soil MFC significantly limited the uptake of heavy metals by rice plants. The accumulation of Cd, Cu, Cr, and Ni in rice grains was, respectively, 35.1%, 32.8%, 56.9%, and 21.3% lower than in controls. This effect was ascribed to the reduced bioavailability of heavy metals in the soil pore water. Such an idea may be implemented with other agriculturally important plants and enable the reduction of pollution of agricultural crops. It is also possible to restrict heavy metal absorption by plants through preventing metal migration in soil. It was observed that As mobility in paddy soils was strictly connected to the redox reactions of Fe minerals [212]. In flooded soil, Fe oxides were reduced to ferrous ions, and As was released into the pore water. Application of a soil MFC reduced As migration to the pore water by up to 47% by limiting Fe reduction [213]. This was possible due to the enhanced dissolved organic matter degradation in soil MFCs, which results in fewer electron donors being available to metal-reducing bacteria to reduce iron oxides. Thus, application of MFCs may become an arsenic mitigation strategy in soils.

On the other hand, application of MFCs in organic matter-rich wetlands polluted with As must be careful, as migration may be promoted when the amount of Fe-reducing bacteria is increased in MFCs [213].

7. Summary

As soil-based ecosystems have large impacts on the environment and climate change, they need much more attention than they are receiving right now. Aggressive and extensive agricultural operations and industrial activity lead to the degradation of soil-based ecosystem, which in turn exacerbates the problem of climate change. MFC technology has underrated potential to become a new strategy for sustainable soil-based ecosystem management with special care for environmental aspects. Soil ecosystem-based MFCs can be renewable, clean energy sources that work indefinitely, as they use natural microorganisms present in soil ecosystems and nutrients that are continuously supplied by plant and animal decay. Until recently, a barrier to the development of MFCs in soil environments was low power production, but research conducted in recent years has shown numerous factors affecting power production efficiency, so increasing this parameter is feasible and needs to be considered on many levels. The result of these investigations has been significant progress in power production efficiency, and currently the maximum power density obtained is up to 334 W/m^2 , which is a comparable efficiency to that obtained for MFCs fed liquid substrates such as wastewater, as well as to photovoltaic modules, which yield ca. 210 W/m^2 [214]. MFCs applied to soil-based ecosystems may be batteryless, maintenance-free, decentralized energy sources and field studies indicate that they can be effective for power devices working on the seabed or in other places far from power grids and they can be self-powering sensors for measuring soil quality.

Although power production from soil environments is a significant aspect, other possibilities of this technology make power production a secondary benefit. Especially attractive is the use of MFCs as a soil bioremediation technique that is not only economically beneficial but also non-invasive and non-degrading to soil ecosystems, contrary to currently used physical and chemical methods. In MFCs, the biodegradation efficiency of soil pollutants is significantly accelerated as a result of creating current conditions, which contributes to an increase in the rate of metabolism of microorganisms and the development of electrogenic bacteria. MFC systems achieve high efficiencies (often exceeding 90%) in soil removal of substances such as PAHs, diesel oil, antibiotics, and pesticides. In addition, the cleaning of soil can be accompanied by the production of electric current exceeding even 200 mA/m^2 . Particularly attractive is the removal of heavy metals from soil ecosystems, with a purification efficiency exceeding 90%, accompanied by a power production of 8.8 W/m^3 . MFCs coupled with CWs enable very effective treatment of wastewater, e.g., removing N and P compounds with efficiencies of up to 99% and an accompanying electricity production of even 1 A/m^3 . It was proven that wastewater treatment in a CW-MFC system was much more efficient compared to CW. Finally, application of MFC technology to soil-based ecosystems may become a new strategy for methane mitigation and soil salinity mitigation. The first studies in this field showed that application of MFC technology reduced metal emissions from soil-based ecosystems by even 57%. Recent research also opens the possibility of applying MFC technology to modern agriculture to reduce the pollution of agricultural crops by heavy metals. Although the first results are very promising and indicate the possibility of reducing metal accumulation by almost 57%, not enough attention has been paid to this technology so far.

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