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Plant microbial fuel cells for recovering contaminated environments

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ABSTRACT

Plant Microbial Fuel Cells (PMFCs) are bioelectrochemical systems able to convert solar energy into bioelectricity with the support of rhizosphere microbial populations. The simultaneous bioelectricity and biomass production makes PMFCs an interesting nature-based solution for promoting not only energy production, but also soil decontamination. This review reports the main bacterial groups involved in microbial fuel cell systems and key factors influencing their performances in plant presence. In detail, to implement PMFCs for remediation of contaminated soils, it is firstly necessary to know chemical characteristics of pollutants, their concentrations, soil physico-chemical characteristics and soil microbial community structure and functioning. Then, based on characterization data of the contaminated soil, a plant species able to resist pollutant toxicity and promote soil phytoremediation processes (e.g. phyto-extraction, phyto-stabilization, phyto-degradation) can be selected, also based on the climatic characteristics of the study area. Finally, electrode materials and their configurations need to be designed to ensure an efficient plant growth, adequate electron transfer and the best possible generation of bioelectricity and at the same time promoting the degradative activity of microorganisms.

1. Introduction

Soil contamination is a serious global problem causing numerous treats to natural ecosystems and human health. Due to the rapid global increase in industrialization, urbanization, and intensive agriculture, soil quality has been seriously compromised by the presence of potentially harmful wide-ranging contaminants such as heavy metals and persistent organic pollutants [1,2].

Heavy metal (HM) soil pollution can exert several toxic effects on biota at different trophic levels, including plant species [3]. In a similar way to HMs, persistent organic contaminants can be toxic to terrestrial organisms, including plants and microorganisms and limit drastically plant development and yield [4]. Restoring polluted lands is crucial to recover biodiversity and ecosystem services for achieving Sustainable Development Goals (United Nations - Agenda 2030) and implementing concrete actions for the ecological transition promoted by the EU GREEN DEAL. Innovative and sustainable remediation strategies using plants for soil recovery have been developed over the last decade. Phyto-technologies for requalification of contaminated areas have been tested in several experimental studies and applied in the field [3] showing capacity to promote environmentally friendly solutions compared to traditional physico-chemical soil treatments. Plants and their associated microorganisms interact synergically in the rhizosphere and promote contaminant removal and degradation. Microorganisms are able to adapt promptly to pollutant presence and show a wide and often unexplored metabolic capacity which makes it possible to use contaminants as sources of nutrients and energy or to detoxify them. For this reason, various decontamination processes driven by the presence of specific plants (e.g. rhizodegradation, phytostabilization, phytoextraction) can generally be termed "phyto-assisted bioremediation" [5–11].

Recently, bioelectrochemical systems such as terrestrial microbial fuel cells (MFCs) have gained great attention for their capabilities to use organic matter and simultaneously achieve soil decontamination and energy production [12–18]. Aiming at combining the potential of phyto-assisted bioremediation and MFCs, a novel technology named Plant Microbial Fuel Cell (PMFC) has been developed.

PMFCs represent a particular configuration of MFCs, in which the

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electrolyte is water or sediment/soil (under saturated conditions) and the presence of plants can support an increase in electrical output and contaminant removal and/or organic matter degradation [15,19]. In fact, plants release root exudates, which are a carbon substrate for microorganisms, promoting the growth of electroactive bacteria (EAB) [20, 21]. EAB are natural microorganisms able to generate electricity through various metabolic processes [15]. They can develope a biofilm on cathode (biocathode) and anode (bioanode). In particular, under anaerobic conditions, EAB develop a biofilm on the anode and catabolize (oxidize) organic compounds (including various contaminants), producing and releasing protons (H^+), electrons (e^-), and carbon dioxide (CO_2). In both MFCs and PMFCs, an organic source/waste is transformed into electricity through microbial electrochemical reactions [15]. Electrons released by bacteria are transferred to the anode, and then, through an external circuit, to the cathode, where oxygen acts as the electron acceptor and form water as the final product [22,23]. Protons flow from the anode to the cathode through the electrolyte (soil/sediment) [15].

PMFCs have the advantage to provide the EAB with both organic substances in form of rhizodeposits, root exudates, and root border cells, as well as oxygen at the final electron acceptor (cathode), [15,24,25]. Plants supply significant amounts of carbon, and up to 60% has been estimated to be used as an energy source for microorganisms. A key factor in ensuring that a PMFC is operating in the best conditions is the development of a root system in the anode compartment under submerged and anaerobic conditions [26]; the latter favour oxidation of rhizodeposits and other organic compounds by microorganisms [20]. However, although an anode electrode needs to be close to rhizosphere for a high power generation, if the roots completely surround it, the efficiency can decrease in terms of electrical outputs [27].

A schematic diagram of PMFC is illustrated in Fig. 1.

In PMFCs, plants use nutrients from soil/water for their growth and metabolism, decreasing the overall nutrient load and pollutant concentration, and contributing to the degradation/transformation or bioaccumulation of contaminants. PMFC performance depends on several factors, including plant species selection, rhizodeposits, physico-chemical and microbiological properties of an environmental matrix (soil/sediment), MFC setup and configuration, electrode properties, etc. [20].

Although PMFCs capabilities to generate power using microorganisms for oxidation of organic matter present in wastewater have been widely studied, only few studies have evaluated PMFC efficiency for soil remediation. In several cases, PMFC systems work as a “black-box” because it is unclear if the degradation/removal of contaminants is achieved by electrochemical bacteria or specific contaminant degraders; moreover, the role of plants in contaminant degradation is only explained in few cases [26]. In this framework, the main factors to be considered for customizing PMFCs for contaminated soil remediation and bioenergy production are here described and discussed.

1.1. Physico-chemical soil characteristics and intrinsic pollutant chemical properties

Soil texture, mineralogy, nutrient content (e.g. carbon, nitrogen, phosphorous), redox potential and pH influence contaminant persistence and soil microorganism activity. In a soil, electrons are produced through transformation of inorganic and organic compounds, such as sulphur species, humic acid, and iron(II) [23]. Recently, it has been shown that soil pH in PMFCs set up with metal-contaminated or in agricultural soils amended with compost or biochar, tended to be higher at the cathode than at the anode during long-term operation [25,28,29]; this was presumably due to a rapid H^+ consumption for oxygen reduction reactions occurring at the cathode.

Soil texture, mineralogy and moisture influence oxygen presence. It is known that saturated soils are anaerobic and this is a key condition for the proper functioning of electrogenic activity at anode in microbial fuel cells [13].

Moreover, during PMFC operation, a decrease in electrical conductivity (EC) can be observed due to the root ion absorption and to the bioelectrochemical processes that drive PMFC electro kinetics mechanisms [28]. High EC values, that can be registered in the presence of saline soils, can reduce plant growth, and therefore limit bioelectrochemical capabilities of anodophilic soil microrganisms, leading to lower electricity production [29].

The evaluation of physico-chemical properties and toxicity of pollutants is a key aspect, which allows knowledge of the behaviour of a pollutant in a soil (e.g. absorption/adsorption) and its toxicity. This information makes it possible to select the plant species to be used that

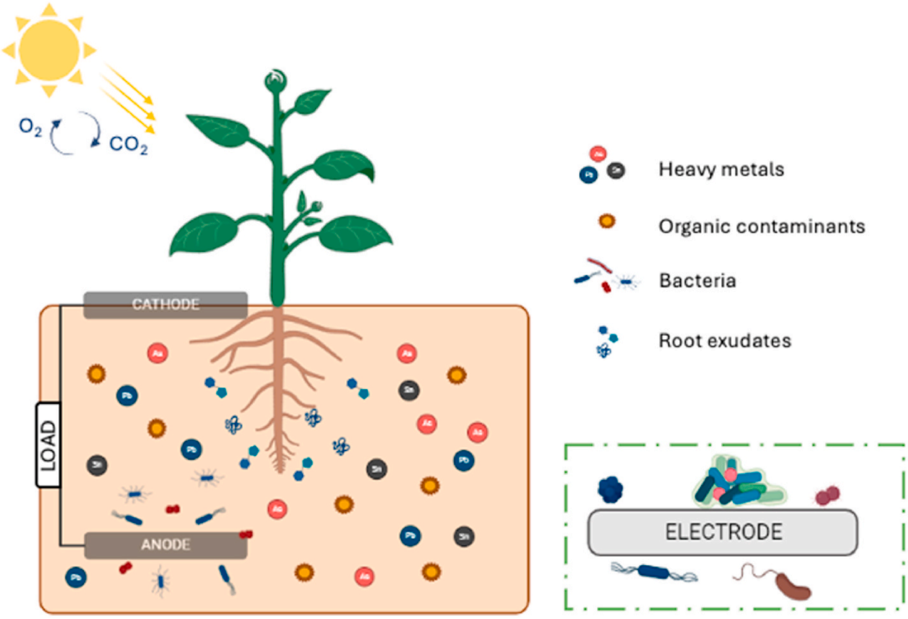


Fig. 1. Schematic diagram of a Plant Microbial Fuel Cell (PMFC). The pollutant removal occurs by the anaerobic oxidation of microorganisms, which generate electrons in this process. These electrons pass through an external circuit, which allows electricity to be generated.

are most tolerant to a specific soil contamination. For example, polycyclic aromatic hydrocarbons, due to their intrinsic chemical characteristics tend to be adsorbed by organic matter or bing to clay minerals [30] and can have a low bioavailability that hampers their biodegradation [30,31]. Persistent organic contaminants, such as polychlorinated biphenyls (PCBs), show high molecular stability, low solubility in water and high tendency to adsorb to particulate phase, which strongly limit their removal from soil [32].

Heavy metals can have different behaviour depending on the soil characteristics such as texture, mineralogy, microorganism activity and most importantly organic matter content.

1.2. Microorganisms in plant-microbial fuel cells

The rhizosphere is a microhabitat comprising roots and the soil immediately (a few millimetres) surrounding them, where intense chemical interactions occurs between plants and microorganisms [33]. The rhizosphere offers a variety of carbon-rich micro-environments, which are colonized by beneficial bacterial populations using these substrates. Microorganisms communicate between each other and with plants through chemical messages (i.e. production of exogenous molecules which act as a signals among different cells), develop synergistic actions (including contaminant removal and stress response) and influence plant functions and yield [33]. In the rhizosphere microbial communities of natural soil, electroactive bacteria such as *Anaeromyxobacter*, *Azospirillum, Bacillus, Bellilinea*, *Clostridium, Desulfuromonas*, *Geobacter*, *Longilinea* and *Phenylobacterium* have been identified [26]. Biofilm formation on anode is a key point for PMFC functioning and it can be influenced by soil characteristics, temperature, soil humidity, pH, dissolved oxygen, etc. Each of these abiotic factors is fundamental for PMFC performance and electricity generation. Although many bacterial species have been identified, there is a need to study several others that exhibit electrical activity and/or are able to promote contaminant bioremediation. However, in PMFCs, contaminant removal may occur if the microbial community has adapted to the presence of a contaminant (its concentration does not inhibit their vital activities) and has developed remediation capabilities [34].

Nitisoravut et al. [23] demonstrated in PMFCs the importance of plant-microorganism cooperation and rhizodeposit (e.g. mucigel and lysates) accumulation for several decontamination processes (phytoextraction, phytostabilisation, rhizodegradation, etc.) [35]. Root exudates change from plant to plant in terms of composition and concentration within and among species. Consequently, the diversity of microbial populations in the rhizosphere also changes depending on the chemical composition of a soil.

For example, the soil-plant-microbe species interactions occurring in PMFCs determine specific rhizosphere microbial activities and plant physiological responses that anable soil moisture regulation, nutrient retention, organic/inorganic ion transport and heavy metal immobilisation [36–38]. Overall, the most suitable soil-plant-microbiome combinations can act in a PMFC for obtaining electricity production (a carbon source for EAB is ensured by plant presence) over a long period of time and soil remediation with greater effectiveness than a simple MFC [20,26].

Logan et al. [39] reported that the extracellular electron transfer or the interactions of electroactive microorganisms with electrodes can be improved with catalysts or binders. Guang et al. [40], observed that the rate of substrate oxidation by electroactive bacteria is directly proportional to the power delivered; therefore, increasing the number of electroactive microorganisms using a plant species that provides them a favourable environment and rhizodeposit availability can increase PMFC power. Although it is expected that exoelectrogen bacteria and degrading bacteria work in cooperation, their specific functioning and relationships have not been thoroughly investigated so far.

The electroactive microorganisms associated with rhizosphere in PMFCs can be present on both the anode and cathode. Logan [39,41] highlighted the potential of a biocathode, not only for oxygen reduction, but also for nitrate reduction and hydrogen development.

The exoelectrogenic microorganisms (anodic microorganisms) identified in recent studies are listed in Table 1. These microorganisms have mainly been studied for their action mechanisms in MFCs. However, as noted by Nitisoravut et al. [23], this knowledge can be extended

Table 1

Main microorganisms and type of mechanisms (Direct: DT and indirect: IDT, see the text and Fig. 2) involved in electron transfer, substrate and function at anodes in MFCs and PMFCs.

ANODE				
Species	Electron transfer mechanism	Substrate	Function	References
Geobacter sulfurreducens	DT	acetate and H^+	Metal and sulphate reduction	[29,42]
Geobacter metallireducens	DT	acetate and H^+	Metal reduction	[29,42]
Geobacter grbiciae	DT	acetate and H^+	Fe(III) reduction	[29,42]
Geobacter hydrogenophilus	DT	acetate and H^+	Fe(III) reduction	[29,42]
Aeromonas hydrophila	DT		Fe(III), nitrate and sulphate reduction	[42]
Anaeromyxobacter	DT	acetate, lactate, pyruvate	Fe(III) reduction	[29]
Rhodoferax ferrireducens	DT	glucose	Acetate oxidation and Fe(III) reduction	[44,45]
Rhodopseudomonas palustris	DT	acetate, lactate, valerate, fumarate, ethanol, glycerol and yeast extract		[46,47]
Pseudomonas aeruginosa	IDT		Organic solvent metabolization	[22,48]
Pseudomonas putida			Organic solvent metabolization	[22]
Shewanella odeniensis	IDT		metal reduction	[29,42]
Bacillus tequilensis	*IDT*		*Cr(VI) reducing*	[22]
Shewanella putrefaciens	DT	lactate, pyruvate and formate	Fe(III) and Mn (IV) reduction	[29,42]
Bacillus tequilensis	IDT		Cr(VI) reduction	[22]
Actinobacillus succinogenes	IDT		succinic acid-production	[49]
Alcaligenes fecalis	IDT	glucose		[45]
Enterobacter cloacae	IDT	cellulose		[22]
Enterococcus gallinarum	IDT	glucose		[22]
Proteus vulgaris	IDT			[49]
Desulfubulbus propionicus	IDT	lactate, pyruvate, or ethanol	Fe(III)-nitrilotriacetic acid reduction	[50]
Desulfuromonas acetoxidans	DT	acetate or other organic compounds		[49]
Desulfovibrio desulfuricans	IDT	lactate	sulphate-reduction	[51,52]
Geothrix fermentans	IDT		Fe(III) reduction	[43]

to the PMFC system. Soil-plant-microbiome relationships can make microbial fuel cells more structured and performing. As above mentioned, they transfer extracellular electrons to the anode and thus produce current. Electroactive microorganisms described for performing extracellular electron transfer mainly include prokaryotic cells, but in some cases also fungi. Electron transfer occurs in various ways (Fig. 2), including direct and indirect mechanisms. Direct mechanisms consist of direct electrode contact with the formation of complex biofilms with a highly organised multi-cellular and multi-species structure. In biofilms, cells are linked together and embedded in a matrix composed mainly of proteins, nucleic acids, and carbohydrate polymers [39]. Another direct mechanism is the contact of a microorganism surface via membrane cytochromes or the formation of electrically conductive pili (nanopiles). On the other hand, indirect mechanisms can occur via released molecules or exogenous compounds, so-called electron transporters or mediators such as flavins, phenazines, hydrogen, eukaryotic metabolic shuttles [26,42,43].

Most common microorganisms that form biocathodes are electrotrophic microorganisms (cathodic microorganisms). Some examples are reported in Table 2. They comprise bacteria and archaea species. Bacteria on cathodes can be grouped into two types: aerobic microorganisms that use oxygen as an oxidant and assist in the oxidation of transition metal compounds, such as Mn(II) or Fe(II) to release electrons to the oxygen; anaerobic microorganisms that use compounds such as nitrate, sulphate, iron, manganese, selenate, arsenate, uranate, fumarate and carbon dioxide as terminal electron acceptors.

A different category of microorganisms, called interelectrode space microorganisms [22], can be present on plant root surfaces and surrounding electrodes. These microorganisms cooperate with the exoelectrogenic microorganisms, supplying them with simple compounds because of the decoupling of complex organic plant waste compounds and root secretions.

Evidence from various authors shows that electroactive microorganisms are species from all bacterial groups, including α-, β-, γ-, δ-*Proteobacteria* and *Firmicutes*, sulphate-reducers and acetogens.

The first bacterial genera identified, and the most recognised for potential application in PMFCs, are *Geobacter* and *Shewanella*, which are able to utilise minerals containing Fe(III), Mn(III) or Mn(IV) as terminal electron acceptors [22,26]. In these two genera, extracellular electron transfer is possible thanks to the direct involvement of multiheme cytochromes, which transfer electrons from the periplasmic proteins to the bacterial surface, and porin-type external membrane proteins, which physically transfer electrons directly to the minerals or electrode [26]. In addition, the outer membranes possess conductive nanowires that can mediate the transfer of electrons to minerals/electrodes (electron transfer could also be ensured over long distances of more than one cm at a rate of 10^9 electrons per second) [58] and make physical connections with neighbouring cells possible.

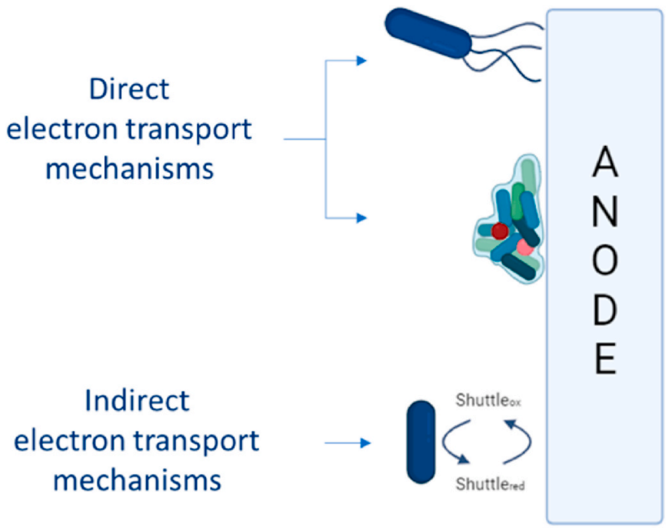


Fig. 2. Graphical overview of electron transfers of microorganisms at the anode through direct and indirect mechanisms.

Table 2
Main microorganisms and type of mechanisms (Direct: DT and indirect: IDT, see the text and Fig. 2) involved in electron transfer, substrate and function at cathodes in MFCs and PMFCs.

CATHODE				
Species	Electron transfer mechanism	Substrate	Function	References
Geobacter sulfurreducens	DT	acetate and H^+	metal and sulphur-reduction	[29,42]
Acidithiobacillus ferrooxidans	DT		sulphur and Fe (II) oxidation	[42]
Acidiferrobacter thiooxydans	DT		Fe-oxidation	[42,53]
Desulfovibrio vulgaris	DT		sulphate-reduction	[42,51,52]
Clostridium beijernicki	IDT	glucose, starch, lactate	Fe(III) reduction	[54]
Pseudomonas sp.	IDT			[42]
Acinetobacter calcoaceticus	IDT		nitrate and phosphate removal	[42,55,56]
Shewanella odeniensis	IDT		metal reduction	[42]
Shewanella putrefaciens	DT	lactate, pyruvate and formate	Fe(III) and Mn (IV) reduction	[29,42]
Dehalococcoides mccartyi	DT		reductive dehalogenation	[57]
Methanobrevibacter arboriphilus	DT		reductive dehalogenation	[57]
Methanobacterium formicicum	DT		reductive dehalogenation	[57]

There are other species identified as capable of producing high electricity in PMFCs, such as *Desulfobulbus* sp., *Anaeromyxobacter* sp. And *Geothrix* sp., *Pseudomonas* sp [35,36]. Other bacteria such as *Bacillus subtilis* and *Klebsiella aerogenes* are classified as weak exoelectrogens, as they produce rather low current densities in pure cultures [39].

Analysis of microbial communities in PMFCs shows a very diverse species composition, in which there is no single dominant microorganism, since more genera and species are involved in bioelectricity generation.

PMFCs have been used to reduce efficiently organic load of wastewater effluents and producing electricity, and they have also been used for removal contaminants such as hydrocarbons and heavy metals from soil or sediments [26].

1.3. Plant selection

Suitable plants for PMFC soil remediation need to exhibit an excellent capability to survive and develop in water-logged condition, to prevent oxygen interruption in anode chamber and consequently maintain the redox potential gradient [59]. High biomass production and photosynthesis rates are fundamental for ensuring appropriate PMFC performances [60]. Recently, Shaikh et al. [59] showed that marshy grasses can be intended as promising plants for PMFCs thanks to their capability to adapt to this system, high biomass production and salt tolerance. Recent studies reported the efficiency of several plants species for power generation using PMFC (Table 3) [37,61].

Several examples of PMFCs in which removal of contaminants occurs are listed in Table 3. Wareen et al. [62] explored the PMFC system

Table 3
PMFC applications for organic and inorganic contaminant removal using various plant species. Moreover, microbial community associated with the anode (MIC anode), treated matrices and experimental time, anode materials and contaminant removal efficiency are reported.

Plant species	MIC anode	Highest Power intensity/voltage/current	Experimental system and time	Anode materials	Contaminant concentration and removal	References
Lolium perenne	*Proteobacteria*	55 mA/m^2	water surface 120–200h	graphite granules	Cr (VI): 10–20 mg/L; 90%	[70]
Canna indica	*Geobacteraceae* *Anaerolinaceae* *Rhodocyclaceae* *Comamonadaceae*	50–80 mA/m^2	Sediment 90 days	graphite disk	Cr–Ni: 10 mg/L + 10 mg/L; Cr: 76.75% after 24h and 56.62% after 48h Ni: 83% after 24h and 29.12% after 48h	[71,72]
Phragmites communis	*Firmicutes* *Bacteroidetes* *Patescibacteria*	220 mV	Soil 96 days and 10 months	common carbon felts or graphite carbon felts	Cr (VI): 50–500 mg/Kg; 75% after 96 days and 78% after 10 months	[40]
Pennisetum alopecuroides	*γ-Proteobacteria* *Chloroflexi a-Proteobacteria* *Cynobacteria* *δ-Proteobacteria* *Acidobacteria* *Euryarchaeota*	220 mV	Soil 96 days and 10 months	common carbon felts or graphite carbon felts	Cr (VI): 50–500 mg/Kg; 75% after 96 days and decreases at 65% after 10 months	[40]
Typha orientalis	*Proteobacteria* *Actinobacteria*	137.12 ± 13.08 mv	Soil 150 days	Round shape carbon felts	Cd (II): 20 mg/kg; 30.2%	[26,29]
Oryza rufipogon	*Firmicutes* *Chloroflexi (Anaeromyxobacter, Geobacter, Phenilobacterium Azospirillum)*	350.50 ± 74.89 mV	Soil 150 days	Round shape carbon felts	Cd (II): 20 mg/kg; 22.8%	
Ipomoea acquatica	*Geobacter sulfurreducens* *β-Proteobacteria* *Firmicutes* *Calditrichaeota* *Synergistetes* *Acidobacteria* *Actinobacteria* *Bacteriodetes* *Archaea*	114 ± 5.89 mV	Sediment	carbon cloth	Cu: 200 mg/kg; 71.2%	[73]
Acorus Calamus	*Vogesella* *Pseudomonas* *Flavobacterium* *Rhizobium*	61.4 mV	Sediment 367 days	graphite felt	Pyrene: 3.2 mg/kg (87%) benzo[a]pyrene: 1.7 mg/kg: 75%	[64]
Acorus Calamus	*Longilinea* *Bellilinea* *Desulfobacca* *Anaeromyxobacter*	15.84 mW/m^2	Sediment	carbon cloth	Cr (VI) 18.21 mg/L; 94.1%	[65]
Vallisneria spiralis	*Firmicutes (Bacillus and Clostridium)* *Proteobacteria (Geobacter)* *Nitrospira* *Bacteroidetes* *Actinobacteria*	121.7 mW	Sediment	three pieces of modified polyacrylonitrile-based graphite felt	Pyrene + phenanthrene: 10 mg/kg; 88.2%	[74]
Hydrocotyle umbellate	*Geobacter sulfurreducens* *Shawanella putrefaciens* *Bacillus subtilus* *Azospirillum humicireducens* *Pseudomonas putida*	543.3 mV	Sediment 40 days	carbon plate	Zn (97.6%), Cr (89.4%), Cu (88.5%), Mn (51.2%), Mg (99.5%) Ni (95.7%)	[62]
Eichhornia crassipes		1120 mV	Sediment. 40 days	carbon plate	Zn (99.8%), Cr (94.3%), Cu (95.2%), Mn (96.7%), Mg (99.9%) and Ni (98.4%)	[62]

ability to generate energy from organic compounds in sediments through exoelectrogenic decomposition during wastewater and heavy metal treatment. As above mentioned, the PMFC technology can also accelerate organic pollutant degradation through two simultaneous phenomena: direct oxidation of organic substances at the anode and co-metabolism.

Yan et al. [63,64] and subsequently Liu et al. [65] used PMFCs with the *Acorus calamus* plant for evaluating possible degradation of various contaminants such as phenanthrene, pyrene, and Cr(VI). The highest removal efficiency values obtained were 99.47% ± 0.15 and 94.79% ± 0.63 for phenanthrene and pyrene, respectively. The mean voltage observed in these PMFCs was 17.1 ± 3.8 mV [63]. Yan et al. [64] observed that the degradation rates of pyrene and benzo[a]pyrene in a PMFC with *Acorus calamus* improved by almost 70% compared to a MFC without this plant. Finally, Liu et al. [65] reported a Cr(VI) removal efficiency of 98.92% at a concentration of 12.07 mg/L, achieving a maximum power density of 36.43 mW/m^2.

In another study, crude oil degradation was improved by 40% in the PMFC with plants compared to the same system without plants [66].

In general, higher availability of carbon sources are associated with higher electricity production and higher microbial abundances [22].

Organic compounds provided by roots of a PMFC can be converted into electricity, exploiting the syntropy between plants and electroactive bacteria, as shown in terms of good Coulombic efficiency [23]. Regard this aspect, power production can also be improved by an increased availability of organic matter, used as the source for the different process of the rhizosphere microorganisms [59]. In fact, adding organic matter, beneficial effects on both electric production and plant growth have been found by Moqsud et al. [67]. In the study by Liu et al. [68], different anode locations were investigated (always in anaerobic conditions). These authors showed that the anoxic environment at the anode and the presence of root exudates would promote the growth of electron acceptor bacteria on the anode, resulting in high electricity generation. In addition, the oxygen loss above the anode may have a positive effect on current generation by increasing the decomposition rate of the high molecular weight compounds exuded by roots and thus increasing the content of low molecular weight compounds available for EAB.

Moreover, Pamintuan el al [69]. showed that the enhanced current flow rates observed in PMFCs were correlated with plant growth and were attributed to the enhanced metabolic processes resulting in an accumulation of photosynthetic products.

Although promising results have been obtained so far in PMFC systems, there is a need to improve knowledge on their application, such as testing the potential of various plant species already used in phytoremediation of inorganic or organic contaminants and identifying new EAB for promoting bioremediation within this system.

1.4. Rhizodeposition characterization to unravel interactions between plant and soil microbial communities in PMFCs

The volume of soil with root system of plants (rhizosphere) is characterized by a wide variety of substances released from both growing plant species and microorganisms; most chemicals are organic compounds and basic plant constituents originated from photosynthesis and other plant processes [75]. The rhizosphere system modifies chemical, physical, and biological properties of soils in its immediate proximity. The rhizosphere along the axis of each root can be described in terms of longitudinal and radial gradients that develop as a result of root growth, nutrient and water uptake, rhizodeposition and subsequent microbial growth.

It is well known that root exudates play a key role in driving belowground interactions between microbes and plant root systems [76–78]. Based on their molecular weight, root exudates can be distinguished in two main groups: low and high molecular weight compounds (LMWCs and HMWCs, respectively). Carbohydrates, amino acids, amides, aliphatic acids, aromatic acids, miscellaneous phenolics, flavonoids and phytosiderophores belong to LMWC group while enzymes, vitamins and proteins are included into the HMWC group [6].

The direct neutralisation of unwanted elements in the rhizosphere through complexation to organic acids and other carbon-based compounds exudate by a plant's root system is considered as a first-step towards improved tolerance [79]. In accordance with Antoniadis et al. [80] the stability of these complexes is affected by the nature of the organic acids (higher molecular weight complexes persist insoluble in soil solution) and the soil pH conditions (lower pH causes H^+ competition for complexation), among other factors. It has been well documented that root exudates are important factors affecting plant capacities to absorb heavy metals. Under heavy metal stress, low molecular organic acids secreted by roots form complexes with metal elements, thus activating their activities in soil [81–83]. Chi et al. [84] demonstrated that an increase of malic and citric acids occurs in the rhizospheres of maize and *Brassica juncea* in an intercropping experiment with a cadmium contaminated soil. The organic acids released by the plant root favour the growth of maize and its resistance to Cd and may improve metal accumulation in *Brassica*.

The plant root system can exude degradative enzymes [85] that can act a key role in promoting degradation of persistent organic contaminants (e.g. nitroreductases, laccases, dehalogenase) as shown by several authors [86,87]. Moreover, plant roots can release allelopathic chemicals and compounds that can be usefully employed as co-metabolites by soil microorganisms in biodegradation of organic contaminants [82].

In PMFC technology used as a strategy for recovering polluted sites, it is fundamental to identify the chemical compounds released by plant species in the rhizosphere environment in order to understand how these can stimulate and activate soil microbial communities and, as a consequence, to comprehend the decontamination processes triggered by the synergistic actions of plant and microbes.

The assessment of root exudates can be performed by using targeted analytical approaches, such as the high-pressure liquid chromatography or gas chromatography coupled with tandem mass spectrometry (HPLC-MS/MS, GC-MS/MS). These methods can be strategic for studying modifications in plant exudation patterns, under different environmental conditions [6].

The assessment of rhizodeposition in terms of the amounts of compounds excreted by roots and their chemical identification, the release sites, their fate, and their impact still remains a relevant challenge faced by scientists [88,89]. Recently, Oburger et al. [90] developed a new rapid method for determining total carbon concentrations in root exudates of grass species by using spectrophotometry. Through this interesting approach it was possible to accurately quantify organic carbon in exudates with a minimum effort using a standard laboratory equipment (UV-photometer) and employing a low amount of sample. At the same time, this method was able to increase the amount of data sets, indicating C exudation rates by different plant species under different environmental conditions, providing increase of knowledge on C exudation dynamics. Fig. 3 reports an illustrative diagram on PMFC rhizosphere exudate role and methodologies for their identification.

1.5. Design of PFMCs

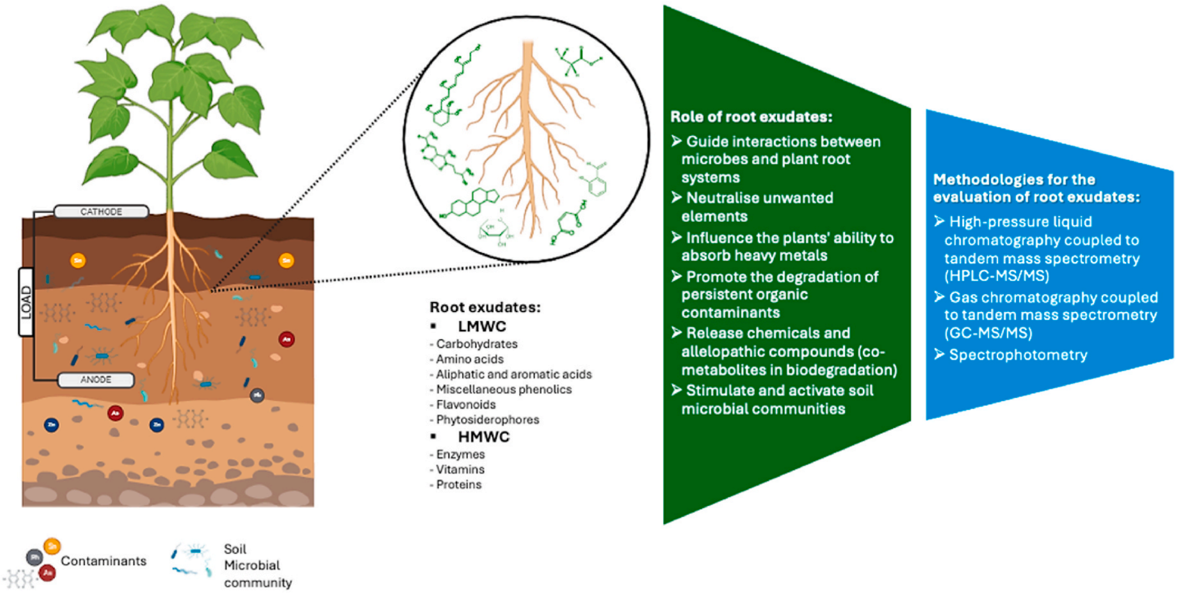
The main factors to be considered to design electrodes in a PMFC set up for soil decontamination are illustrated in Fig. 4. One of the key characteristics is the material biocompatibility for supporting both a good biofilm growth and current production. Only a non-toxic (for microorganisms) electrode, in anaerobic conditions, ensures microbial proliferation and an appropriate formation of an electroactive biofilm on its surface, thus enabling the electrons conduction. Furthermore, it should be considered that these units will operate in a highly corrosive environment, supporting the possibility of electrode oxidation. At the same time, these units need to be highly conductive to allow the mobility of electric charges through the circuit [91].

Finally, electrode porosity can have an impact on electrical performances, because microorganisms can better develop on a material with a high specific surface area [92].

Carbon based materials seem to be the most convenient choice because of their biocompatibility, good chemical stability, reasonable conductivity, and relatively low cost [93]. These properties make these materials preferable to metal ones which, apart from the stainless steel and titanium that are quite expensive, do not fulfil the above-mentioned non-corrosiveness condition. The most commonly used carbon based materials are graphite felts, fabrics, granules and rods, carbon felts and carbon fibers.

Recent experimental studies focusing on energy production, achieved in PMFC with different substrates (e.g. organic soil, wetland, garden, contaminated soil, etc.) are summarized in Table 4. Some researchers used the same electrode materials, obtaining efficient performances in terms of electron transfer and power density [29,94,95], although for other authors the use of different materials for the anode and cathode resulted in better performances [96,97].

Electrode configurations have a significant impact on the actual large-scale applications of PMFCs. Horizontal and vertical cells are characterized by an extremely simple and cost-effective construction process that allows for the effective remediation of refractory organic pollutant polluted soils without additional membranes [98]. On the



Role of root exudates:
- Guide interactions between microbes and plant root systems
- Neutralise unwanted elements
- Influence the plants' ability to absorb heavy metals
- Promote the degradation of persistent organic contaminants
- Release chemicals and allelopathic compounds (co-metabolites in biodegradation)
- Stimulate and activate soil microbial communities

Methodologies for the evaluation of root exudates:
- High-pressure liquid chromatography coupled to tandem mass spectrometry (HPLC-MS/MS)
- Gas chromatography coupled to tandem mass spectrometry (GC-MS/MS)
- Spectrophotometry

Fig. 3. Illustrative diagram of the characterisation of rhizodeposits in PMFC: role of root exudates and methodologies for their assessment. LMWC: low molecular weight compounds; HMWC: high molecular weight compounds.

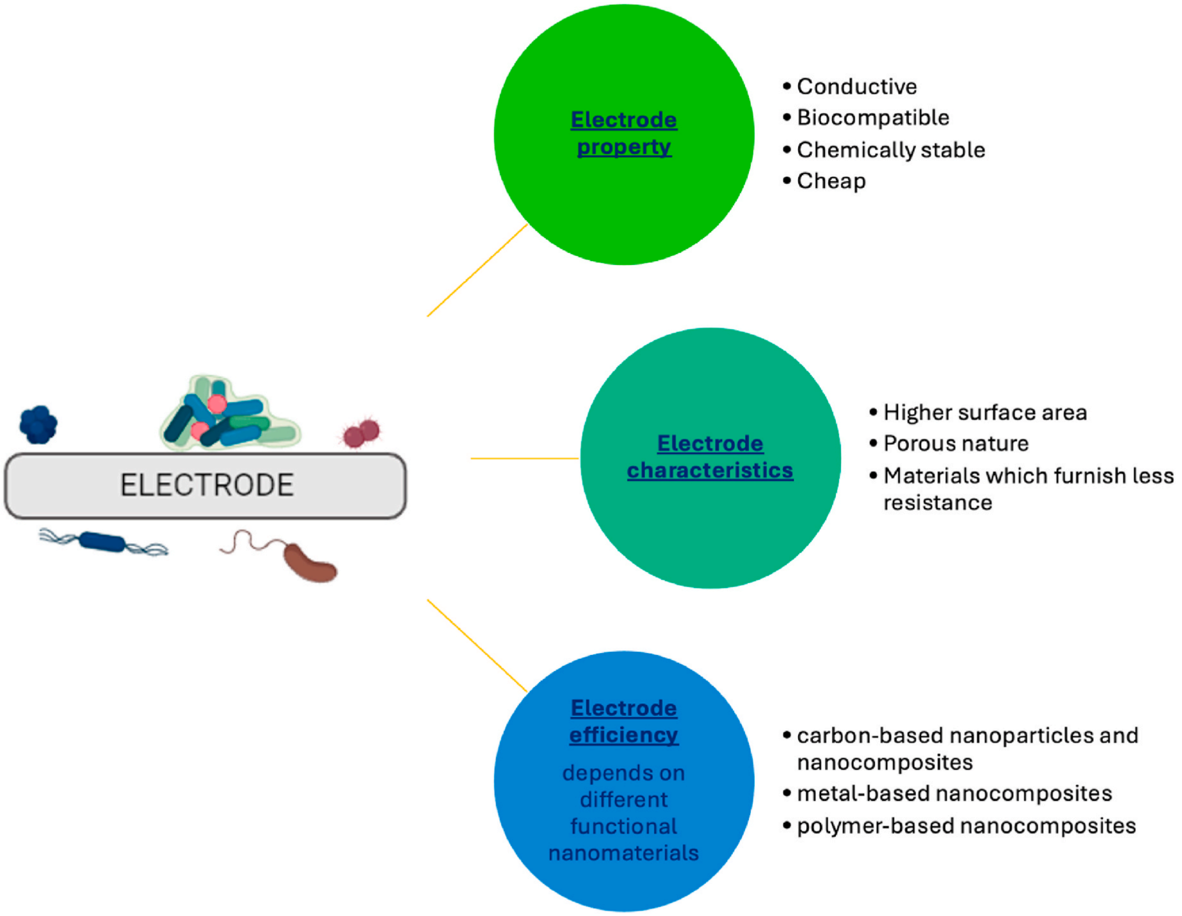


Fig. 4. Main factors to be assessed to customize electrodes in PMFCs set up for soil decontamination.

other hand, a more complex architecture, as a cylindrical configuration, can have a greater potential for system scalability.

Some contaminants can be difficult to remove because they are not bioavailable to microorganisms. However some authors reported that electrical potential differences in PMFC can improve pollutant degradation [99] by mobilising them into more bioavailable fractions and guiding them towards the roots, favouring their bioaccumulation [100, 101]. Moreover, low bioavailable persistent organic pollutants (e.g. PAH

Table 4
Studies on PMFCs energy harvesting potential. Material for electrodes, the plant species and substrate are specified.

Anode material	Cathode material	Plant Species	Substrate	Highest Voltage	Highest Power	Highest Current	Notes	Ref.
Graphite Fabric	*Graphite Fabric*	*Lactuca sativa* L.	*Panoponics-based PMFC*	30-50 mV				[35]
Graphite Felt	*Graphite Felt*			150 mV				
Stainless Steel Rods	*Stainless Steel Rods*		*Soil-based PMFC*	230 mV				
Carbons Bristle Brushes	*Stainless Steel Clip*	*Triticum aestivum*	*Garden soil + Bioslurry*	856 ± 26 mV				[103]
Carbon Felt	*Carbon Felt*	*Chinese pennisetum*	*Soil from natural wetland*	667.94 ± 128.65 mV	2.86 ± 1.03 mW/m^2			[104]
Graphite Granules	*Carbon Felt*	*Lolium perenne*	*Hoagland's solution*			55 mA/m^2	*Cr(VI) as pollutant*	[70]
Zinc	*Copper*	*Spathiphyllum patinii*		475 mV				[105]
Bamboo Charcoal	*Bamboo Charcoal*	*Zea mays*	*Organic Soil*	980 mV	320 mW/m^2		*Horizontal*	[95]
				620 mV	128 mW/m^3		*Vertical*	
Carbon Fiber	*Carbon Fiber*	*Oryza sativa* L.	*Soil + Compost (1%wt)*	700 mV	39.2 mW/m^2			[67]
Carbon Felt	*Carbon Felt*	*Oryza sativa*	*Paddyl + Compost(10% wt)*	894.39 ± 53.44 mV	34.78 mW/m^2			[29]
Granular Activated Carbon (GAC)	*Carbon Paper With 0.4 Mg/Cm2 Pt*	*Wachendorfia thyrsiflora*	*thickened Waste Activated Sludge*		1036 ± 59 mW/m^2			[97]
Stainless Steel Mesh	*Stainless Steel Mesh*	*Vigna radiata Wilczek*	*Garden Soil*		0.35 mW/m^2			[69]
Graphite Rods	*Graphite Rods*				0.12 mW/m^2			
Carbon Felt	*Carbon Felt*	*Pennisetum alopecuroides*	*Wetland Soil*	429.61 mV			*Cr(VI) as pollutant*	[40]
Zinc Mesh	*Spiral Copper*	*Cordyline fruticosa*	*Mix Soil + fertilizers*		3.5 mW/cm^2			[106]
Carbon Felt	*Carbon Felt*	*Oriza sativa* L.	*Soil*		9.6 mW/m^2		*maximum daily average generation*	[107]
Carbon Felt	*Carbon Felt*				8.5 mW/m^2		*average continous generation*	
Graphite Felt	*Graphite Felt*	*Oryza sativa* L.	*Sandy Loam*		6 mW/m^2			[108]
Graphite Felt	*Graphite Felt With Pt*	*Oryza sativa* L.	*Soil*		14.44 mW/m^2			[109]
Graphite Felt	*Graphite Felt With Pt (0.1 Mg/cm^2)*	*Oryza sativa* L.	*Rice Paddy field Soil*		19 mW/m^2			[110]
Graphite Felt	*Graphite Felt*	*Spartina anglica*	*Salt Marsh*		82 mW/m^2		*salt marsh PMFC*	[94]
Graphite Felt	*Graphite Felt*	*Phragmites australis*	*Peat Soil*		22 mW/m^2		*peat soil PMFC*	
Graphite Felt	*Graphite Felt With Pt (0.1 Mg/cm^2)*	*Oryza sativa* L. *cv.*	*Rice Paddy field Soil*		140 mW/m^2			[96]
Graphite Felt	*Graphite Felt*	*Aglaonema commutatum*	*Uncontaminated Soil*	184.9 mV			*PAHs and crude oil as pollutants*	[66]

and crude oil) can be degraded better in presence of surfactants. In this regard some bacteria or plants able to produce biosurfactants can significantly favour hydrocarbon degradation [102]. Indeed, Zhao et al. [66] report that the charge-transfer resistance values in the PMFCs studied were significantly reduced with the addition of plants, glucose and the β-cyclodextrin surfactant.

2. Conclusions

The Plant microbial fuel cells technology is an innovative and promising approach for recovering contaminated environments and simultaneously produce electricity thanks to the positive interactions established between plants and microbial communities. However, knowledge about plants and its associated rhizosphere microbiome is still inadequate for fully exploit all possible positive synergic interactions for this purpose. Further studies are needed for identifying, selecting and stimulating the most appropriate plant-microorganism associations for the removal each specific class of contaminants. Moreover, innovative PMFCs have to be developed and designed for ensuring suitable electrical performances in specific contaminated environments. Only with a close collaboration between different scientific disciplines such as environmental chemistry, microbial and plant ecology, energy and electrical engineering can new progresses in PMFC application be achieved.

CRediT authorship contribution statement

Valeria Ancona: Conceptualization, Writing – original draft, Writing – review & editing. **Cristina Cavone:** Writing – original draft, Writing – review & editing. **Paola Grenni:** Writing – original draft, Writing – review & editing. **Gabriele Gagliardi:** Writing – original draft, Writing – review & editing. **Carlotta Cosentini:** Writing – original draft, Writing – review & editing. **Domenico Borello:** Writing – original draft, Writing – review & editing. **Anna Barra Caracciolo:** Conceptualization, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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