Research Progress on Degradation of Organic Pollutants By Soil Microbial Fuel Cells: Utility of Carbon-based Electrodes

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Abstract. Various organic pollutants in soil not only affect agricultural production and food safety, but also directly threaten human health and ecological environment. Microbial remediation is widely used, but its application is confined to the lack of electron acceptors, low efficiency, and poor broad-spectrum. Soil microbial fuel cell (SMFC) is a rising solution. The anode plays the part of an electron acceptor and conducts bioelectricity generated by microorganisms to decompose organic pollutants. While degrading pollutants, it can also generate bioelectricity to reduce energy consumption. In this paper, the research progress of soil microbial fuel cells and their carbon-based electrodes in recent years is reviewed, and the mechanism of bioelectrochemical reaction is introduced. Firstly, the structure and composition of carbon-based electrodes are compared and discussed, and the degradation rate is analyzed. Secondly, the electrochemical properties of SMFC systems composed of different carbon-based electrodes are described. At present, most of the research is concentrate on the modification of carbon-based electrodes to increase the degradation rates and electron conduction efficiency of pollutants. However, it is necessary to focus on the battery frame, multi-electrode SMFC and other directions, combined with nanomaterials, photoelectric technology to improve the degradation rate and power generation density. In the future research, the large-scale deployment of SMFC should be considered to put SMFC into practical application.

Keywords: E Microbial Fuel Cell, Soil, Organic Pollutant, Electrode.

1. Introduction

Organic pollutants in soil include pesticides, industrial chemicals, petroleum products, polycyclic aromatic hydrocarbons, etc. When the content of these organic pollutants in soil is too high, the quantity and speed of these organic pollutants exceed the purification speed of soil, which destroys the dynamic balance of nature and causes soil pollution. These pollutants can exist for a long time in the soil, causing damage to the soil ecosystem, affecting plant growth and threating to human health through the food chain [1]. Physical and chemical remediation technologies (such as heat treatment, chemical cleaning, photochemical degradation, etc.) have high cost and low efficiency, and may also cause secondary pollution [2]. Traditional microbial remediation methods (phytoremediation, microbial remediation and animal remediation) also have many shortcomings, such as long cycle and low abundance.

In this context, based on electro remediation and microbial remediation, soil microbial fuel cell (SMFC) technology, as a rising technology of renewable energy, shows extraordinary potential [3]. SMFC treats soil by using specific electroactive microorganisms, and produces bioelectricity while degrading organic pollutants through electrode action [4-6]. This technology can not only solve soil pollution, but also provide a new source of energy. SMFC generally consists of three parts: an anode buried in the soil, an external electrogenic microbial community attached to the anode, and a cathode in the water. When the external electric body is working, the anode plays the part of the electron acceptor, and the electrons flow from the anode to the load and finally to the cathode, and is usually a membrane-free MFC [7].

Based on the current research progress and the remaining knowledge gap, it is hypothesized that comprehensively summarizing recent progress of SMFC and pinpointing the development and future research directions of carbon-based electrodes are helpful to the removal of soil organic pollutants. Therefore, the objectives of this paper are: 1) Summarizing the structure of carbon-based electrodes in SMFC and comparing the removal efficiency of pollutants; 2) summarizing the electrochemical properties of different carbon-based electrodes; 3) proposing future research on carbon-based electrodes of SMFC.

2. The mechanism of action of SMFC

The SMFC utilizes naturally occurring microorganisms in the soil to attach to the anode to degrade organic pollutants, producing electrons and protons at the anode at the same time. The electrons are transferred from the anode to the cathode, and flow in a circuit with a load to form a current. The proton moves from the anode chamber to the cathode through the proton exchange membrane (PEM), and forming water after react with electrons and oxygen at the cathode [8].

Taking glucose as an example (Figure.1) [9], the oxidation reaction of the anode is:

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

And the reduction reaction of the cathode is:

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

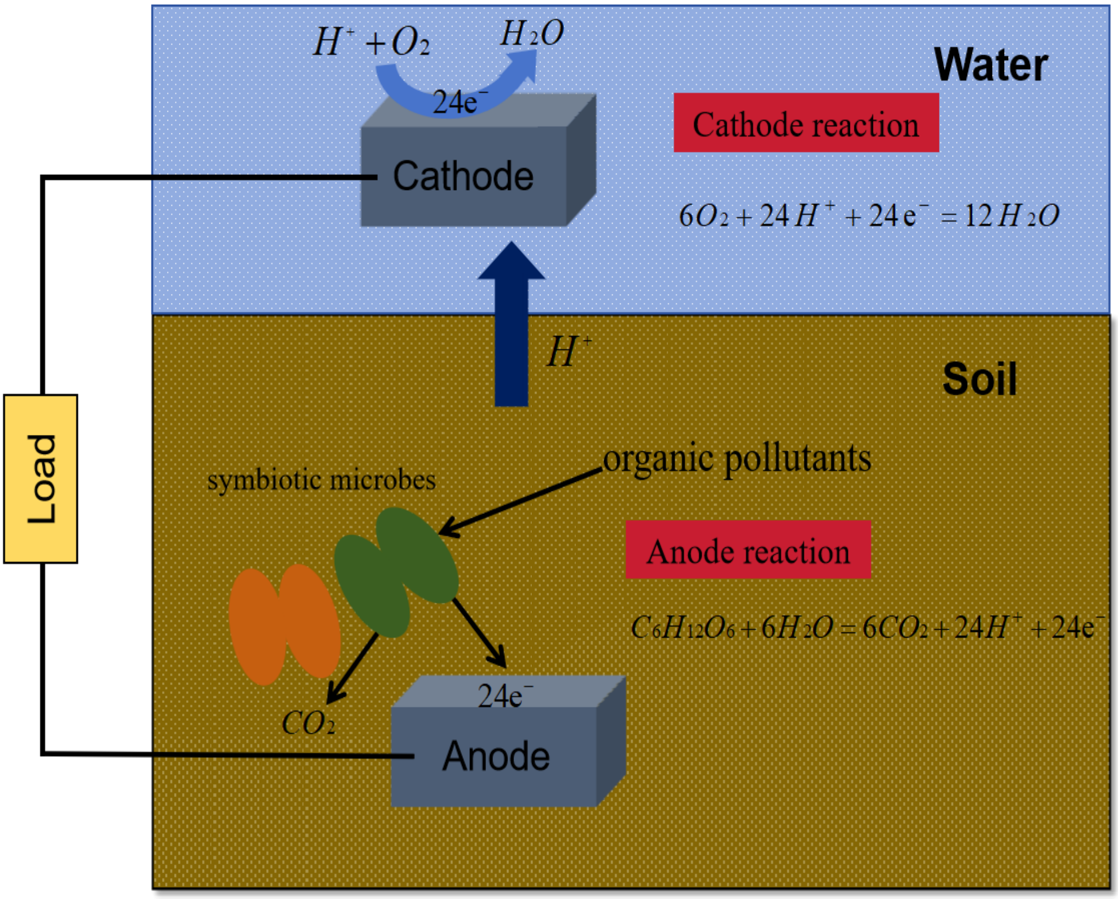

Figure 1. Microorganisms degrade organic pollutants near the anode that is buried in the soils.

The anode plays the part of the electron acceptor to undergo an oxidation reaction. The electrons are transferred from the anode to the cathode through the wire, and the cathode in the water undergoes a reduction reaction.

In this paper, some SMFC systems and their organic pollutant removal rates in recent years are illustrated (Table.1). For example, the degradation rate of phenol was nearly 99% after seven days under the start concentration of 80mg/ml (Table.1) [11]. Although SMFC has good prospects, there are still many defects: low degradation efficiency and power generation efficiency, single SMFC degradation of organic pollutants is single, short action distance, high mass transfer resistance.

Table 1. Examples of SMFC used in degrading organic pollutants.

Type of BES	Pollutants	Start concentration	Reaction time	Removal rate(%)	Reference
SMFC	Sulfadiazine, Di-2-ethylhexyl phthalate	10 mg/kg SDZ, 200 mg/kg DEHP(D_{200}+S); 10 mg/kg SDZ, 20 mg/kg DEHP(D_{20}+S); 200 mg/kg DEHP(D_{200}+S)	30 days	93.84±2.32(SDZ) 91.58±1.00(DEHP)	[10]
Natural hematite SMFC	Phenol	80 mg/ml	Seven days	1.5-mmNH-SMFC(close to 99) 2.0-mmNH-SMFC(close to 99)	[11]
Solar cell-SMFC	Phenol	80 mg/ml	11 days	63.2(SMFC), 81.7(0.5 V), 95.7(1.0 V), 98.5(2.0 V), 48.9(open circuit)	[12]
SMFC	Petroleum hydrocarbon	18 g/kg	75 days	42.17(CS/$CNTs_{20}$) 27.22(CS/$CNTs_{10}$) 25.56(CS/$CNTs_{30}$)	[13]
SBES	Phenanthrene, Biphenyl	10(PHE), 10(BP) mg/L	27 days	PHE: 31.5(soil), 44.9(1% BC900), 53.4(3% BC900), 61.6(6% BC900), 73.9 (10% BC900); BP: 27.6 (soil), 75.7(10% BC900), 71.7(6% BC900),42.7(1% BC900),54.1(3% BC900),	[14]
SMFC	Dissolved organic matter, Benzo[a]pyrene	DOC:594.26±47.51 mg/kg BaP:8.59±1.03 mg/kg	100 days	DOC: 310.09±2.74(S_{1cm}), 326.96±8.44(S_{11cm}) BaP: 72.52±1.88(S_{1cm}), 68.50±4.34(S_{11cm})	[15]
SMFC	hexachlorobenzene	35.53mg/kg(Group 1) 35.53mg/kg(Group 2) 35.40mg/kg(Group 3)	56 days	34.02(Group 1), 17.00(Group 1), 5.31(Group 1)	[16]
SMFC	atrazine	112.21 mg/kg	-	87.70	[17]

3. Carbon-based electrodes of SMFC

Due to its electrical conductivity, biocompatibility and chemical stability, SMFC uses many carbonaceous materials as electrodes, such as activated biochar, activated carbon, carbon paper, carbon cloth, graphite felt [2]. Carbon nanomaterials, such as graphene, carbon nanotubes, are also a good choice. Table.2 illustrates the removal rates of organic pollutants in various carbon-based electrodes and their SMFCs. It can be found that the SMFC for phenol removal is made of carbon felt at the anode and cathode (Table.1) [11, 12].

Table 2. Examples of electrodes used in degrading organic pollutants.

Type of Anode	Type of Cathode	Pollutants	Removal rate(%)	Reference
contaminated soils, anaerobic sludge	granular activated carbon	Sulfadiazine, Di-2-ethylhexyl phthalate	93.84±2.32(SDZ) 91.58±1.00(DEHP)	[10]
circular sheet carbon felt	circular sheet carbon felt	Phenol	1.5-mmNH-SMFC(close to 99) 2.0-mmNH-SMFC(close to 99)	[11]
circular sheet carbon felt	circular sheet carbon felt	Phenol	63.2 (SMFC),81.7(0.5 V),95.7(1.0 V), 98.5(2.0 V),48.9(open circuit)	[12]
CS/CNT	round carbon felt	Petroleum hydrocarbon	42.17(CS/$CNTs_{20}$) 27.22(CS/$CNTs_{10}$) 25.56(CS/$CNTs_{30}$)	[13]
Biochar	Biochar	Phenanthrene, Biphenyl	PHE:31.5(soil), 44.9(1% BC900), 53.4(3% BC900), 61.6(6% BC900), 73.9 (10% BC900); BP:27.6 (soil), 75.7(10% BC900),71.7(6% BC900),54.1(3% BC900),42.7(1% BC900)	[14]
graphite felt	graphite felt	Dissolved organic matter, Benzo[a]pyrene	DOC: 310.09±2.74(S_{1cm}),326.96±8.44(S_{11cm}) BaP: 72.52±1.88(S_{1cm}),68.50±4.34(S_{11cm})	[15]
granular activated carbon	air	hexachlorobenzene	34.02(Group 1), 17.00(Group 1), 5.31(Group 1)	[16]
activated carbon and quartz sand	activated carbon and quartz sand	atrazine	87.70	[17]

3.1. Anode

In the anode, carbon felt is more commonly used, especially round carbon felt. Zhang et al. [11] studied the use of a carbon felt as the anode material and the shape is a circle with a diameter of 6 cm. For sake ensure the biocompatibility of the carbon felt electrode, the carbon felt electrode was immersed in 0.1 mol/L hydrochloric acid and 0.1 mol/L sodium hydroxide for 24 hours and more. The SMFC system was used to degrade phenol-contaminated soil, and the degradation rate was nearly 99% [11]. Similarly, Xie et al. [12] also used carbon felt as an electrode material to degrade phenol-contaminated soil. Combined with solar energy technology, the final removal rate reached 98.5% [12]. Graphite felt is also a commonly used electrode material. Liang et al. [15] used graphite felt with a diameter of 7 cm as an anode material, and the maximum degradation rate of dissolved organic matter in the SMFC system can reach 47.82% [15]. It can be seen that carbon felt is more common as an anode material and the SMFC system has a very good effect on removing organic pollutants.

In addition, it can also be directly filled with granular activated carbon as anode. For example, Cao et al. [16] filled 15 mm granular activated carbon in the anode layer, the SMFC system is used to remove hexachlorobenzene, and the final removal efficiency is 34.02 % [16]. In addition, Wang et al. [17] mixed the soil that is contaminated with some activated carbon, the SMFC system was used to remove atrazine, and the pollutant removal rate reached 87.70% [17]. Filling biochar is also a good choice. Cai et al. [14] used biochar to produce in a circular quartz tube at 900 °C and thermally decomposed with N^2 flow. The SMFC system removed phenanthrene and biphenyl, and the final removal rates could reach 73.9% and 75.7%, respectively [14], with high degradation efficiency.

In terms of carbon nanomaterials, such as graphene (GR), graphene oxide (GO) and carbon nanotubes (CNT) have better electrical conductivity and electrochemical ability. Li et al. [13] used

0.12 g of carbon nanotubes as the anode, and added the carbonized corn stem (CS).They added soil about 300 g that is oil-contaminated to the SMFC system, and the anode is horizontally buried in the soil about 3.0 cm from the bottom reaction system. After that, they add about 500 mL of tap water in the reaction system to ensure that the height of the water can reach at least 3 cm. Finally, the removal efficiency of sulfadiazine was 93.84 ± 2.32, and the removal efficiency of di-2-ethylhexyl phthalate was 91.58 ± 1.00% [13].

3.2. Cathode

In the cathode, similar to the anode, carbon felt is also more commonly used. As an air cathode, it is mostly placed near the soil surface or on the water-soil interface and is placed in parallel with the anode, and the size is generally consistent with the size of the anode carbon felt [11, 12]. In addition, activated carbon and biochar can also be used as cathode materials [10, 14].

The carbon-based material between the anode and the cathode is very flexible and has many possibilities. CNT can play a part of an anode and carbon felt as a cathode [13], both electrodes can also be carbon felt [11, 12], and both electrodes are graphite felt [15].

4. Electrochemical characteristics

4.1. Carbon felt

The carbon felt is made of carbon fiber. The SMFC system with carbon felt as the electrode material has good electrochemical performance, which significantly increases the clamping voltage and electric current density of the system. The clamping voltage and electric current density obtained by Zhang et al. [18] are 658 mV and 15.741 mA/m^2, respectively. In contrast, the electric current density of the prior SMFC system just had 8.48 mA/m^2 [18]. At the same time, the linear regression analysis about the polarization curve of the system was carried out, and a small internal resistance of 4136 Ω was obtained, indicating that the polarization performance was excellent. In addition, the maximum power densities of the system were obtained was about 2.467 mW/m^2 [11]. It should be noted that the power densities is great increasing in the system, which means more effective electrode reactions, double carbon felt as the electrode material, while boosting anode performance and improving the operating efficiency.

4.2. Graphite felt

The graphite felt is mainly made of graphite fiber. The manufacturing process is more complicated than carbon felt. With graphite felt as the electrode material, the electrochemical characteristics of SMFC are also good. The electric current density can be used as a real constant-time indicator of the emergence and increase of biological anodes [19]. Liang et al. [15] established the SMFC system, the electric current density increased promptly to 2.62 mA/m^2, this observation may lead to the reduction of the anode potential through the non-biological reduction of the ferric iron or other oxidizing inorganics, and then in the next 20 days, the electric current density immediately increased to 66 mA/m^2 and remained, indicating that the microbial community on the biological anode is in the mature phase. After five days, to the 30th day, the electric current density decreased immediately to 19.40 mA/m^2. Finally, after 15 days, the current density gradually increased, last reaching the peak about 47.85 mA/m^2. Over the past 45 days, the electric current density weakened gradually along with time. The continuous descension of current density may be due to the declination of organic matter of concentration. The total Coulomb is formed by integrating the electric current generated during the entire 100-day operation. On days 50 and 100, the total Coulomb can be up to 1995.92 C and 3673.90 C, respectively [15].

4.3. CNT

Carbon nanotubes have a larger specific surface area, which boosts the formation of biofilms, and also have excellent capacity of electron transmit [20]. When CS/CNTS electrode was used, the electrophilic microorganisms were continuously enriched to the anode, and the voltage of SMFC increased steadily, reaching a stable output voltage of 70.7 mV on the 25th day [13]. The internal resistance of CS/CNT was low. As the time of reactiong continues, this voltage slowly decreases in the later phase. Decreasing in electric power generation is due to the descension of concentration of organic pollutants. In addition, CS/CNTs20 has the larger reaction surface than others, so the output voltage of CS/CNTs20 excels that of other SMFC groups.

5. Conclusions and prospects

This paper first introduces the working mechanism of SMFC for the degradation of the organic pollutant. Then, the configuration of different carbon-based electrodes in anode and cathode as well as the removal rate of organic pollutants are summarized and discussed, which is beneficial to the future collocation of carbon-based electrodes. Finally, the electrochemical performance of SMFC composed of various carbon-based electrodes is analyzed.

In recent years, SMFC has been limited to laboratory scale and has not been deployed extensively because there are still many gaps to be filled in terms of degradation and electrode materials. For example, how to match various carbon-based materials in the two levels of anode and cathode and combine them with other materials can make the SMFC system degrade organic pollutants with diversity and efficiency, which requires the design of a large number of carbon-based electrode models and combination, and the establishment of more control experimental groups.

In the future research, for the degradation of the organic pollutants by SMFC, we should not only focus on the modification of carbon-based electrodes to boost the degradation rate and electron conduction efficiency of pollutants, but also pay attention to the battery framework, multi-electrode SMFC and other directions, combined with nanomaterials, photoelectric technology to improve the degradation rate and power density. Finally, SMFC is put into practical application.

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