Biosensors and Bioelectronics 85 (2016) 135–141

Contents lists available at ScienceDirect

Biosensors and Bioelectronics

journal homepage: www.elsevier.com/locate/bios

Carbon fiber enhanced bioelectricity generation in soil microbial fuel cells

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ARTICLE INFO

Article history:
Received 29 February 2016
Received in revised form
14 April 2016
Accepted 1 May 2016
Available online 2 May 2016

Keywords:
Microbial fuel cell
Soil remediation
Hydrocarbons degradation
Bioelectricity generation
Conductive carbon fiber
Internal resistance

ABSTRACT

The soil microbial fuel cell (MFC) is a promising biotechnology for the bioelectricity recovery as well as the remediation of organics contaminated soil. However, the electricity production and the remediation efficiency of soil MFC are seriously limited by the tremendous internal resistance of soil. Conductive carbon fiber was mixed with petroleum hydrocarbons contaminated soil and significantly enhanced the performance of soil MFC. The maximum current density, the maximum power density and the accumulated charge output of MFC mixed carbon fiber (MC) were 10, 22 and 16 times as high as those of closed circuit control due to the carbon fiber productively assisted the anode to collect the electron. The internal resistance of MC reduced by 58%, 83% of which owed to the charge transfer resistance, resulting in a high efficiency of electron transfer from soil to anode. The degradation rates of total petroleum hydrocarbons enhanced by 100% and 329% compared to closed and opened circuit controls without the carbon fiber respectively. The effective range of remediation and the bioelectricity recovery was extended from 6 to 20 cm with the same area of air-cathode. The mixed carbon fiber apparently enhanced the bioelectricity generation and the remediation efficiency of soil MFC by means of promoting the electron transfer rate from soil to anode. The use of conductively functional materials (e.g. carbon fiber) is very meaningful for the remediation and bioelectricity recovery in the bioelectrochemical remediation.

1. Introduction

Remediation of petroleum hydrocarbons contaminated soil has been paid more and more attention attributing to the incremental area of contaminated soil (Chen et al., 2015; Li et al., 2015, 2014a). The current remediation technologies include the physical, chemical, microbial and phyto-remediation. Both the physical and chemical remediation easily lead to the destruction of soil structure and properties and thus were gradually eliminated (Riser-Roberts, 1998; Zhou et al., 2005). Though the conventional microbial and phyto-remediation exert little influence on the soil original habitat, they are seriously restricted by the environmental factors and climate conditions (Tang et al., 2010; Zhou et al., 2011). All this time, the highly effective, widely applicable and low cost remediation technologies have been sought by environmental scholars and engineers.

The bioelectrochemical approach, especially the microbial fuel cell (MFC) was demonstrated to effectively remediate the contaminated environment with the advantage of bioelectricity production (Logan et al., 2006; Lovley, 2006; Rabaey and Willy, 2005; Rabaey et al., 2010). Firstly, since the electron acceptor is non-exhaustible and passively applied (solid anode), the air-cathode MFC has its advantage in potential use in real remediation (Fig. S1). Secondly, the existence of anode accelerates the exoelectrogen to provide more electrons to promote the metabolic reaction rate of anaerobic bacteria (Cao et al., 2015). Thirdly, the pollutants (petroleum hydrocarbons) are biodegraded by the microbial catalysis as the electron donor while the oxygen is used as the electron acceptor with forming end-product water (Wang et al., 2012). Moreover, there is no addition of exogenous strains or chemical substances. Early the MFC was used to remediate the polluted wastewater (Liu et al., 2004; Rozendal et al., 2008), sludge (Jiang et al., 2009) and sediment (Yuan et al., 2010; Zhang et al., 2010). Recently the MFC was implemented to remediate the soil contaminated by phenol (Huang et al., 2011), petroleum hydrocarbons (Li et al., 2014a; Wang et al., 2012) and diesel (Lu et al., 2014a, 2014b) due to the stimulation from bio-current. In soil MFCs, the tested soil was hermetic, waterlogged or water-sealed which sustained the anaerobic condition of anode and thus

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http://dx.doi.org/10.1016/j.bios.2016.05.001
0956-5663/

safeguarded the running of remediation system (Zhao et al., 2009). Increasing moisture water of soil relatively reduced the internal resistance (Wang et al., 2012), yet the poor conductivity of soil seriously limited the performance of soil MFCs (Domínguez-Garay et al., 2013). The improvement of mass transfer (Li et al., 2015) and microbial activity (Li et al., 2016) enhanced the remediation efficiency of petroleum hydrocarbons in multi-anodes soil MFCs. However, the bioelectricity generation was still restrained by the tremendous internal resistance in soil MFCs (Morris and Jin, 2012).

In previous air-cathode soil MFCs, oxygen diffused actively was enough to supply the cathodic reaction and so the electrons collected by anode was the rate-limiting step (Li et al., 2016, 2014). There are two kinds of current including the electron transfer from substrate to soil and from soil to anode. The effective removal of contaminants simultaneously with low power production indicated that the electron transfer rate from soil to anode was key limiting step (Rezaei et al., 2007). Reducing distance between soil and anode undoubtedly results in the decrease of remediated medium quantity. Therefore, increasing the electrical conductivity of soil becomes an optimal approach to promote the power generation. In this study, the conductive carbon fiber was mixed with the petroleum hydrocarbons contaminated soil to improve power production in the constructed soil MFC.

2. Materials and methods

2.1. Tested soil and treatment

The petroleum hydrocarbon contaminated soil was collected near oil production platform in Dagang Oilfield (Tianjin, China). Soil properties were summarized in Table S1. After air-dried and passed through 2 mm sieve, the soil sample was marked as original soil (OS). Carbon fiber (1 cm of length, Jilin Carbon Factory, Jilin, China) was mixed with OS as 1% (*w*/*w*) of mass fraction (optimization) after cleaned by acetone (Wang et al., 2009) and marked as mixed carbon fiber original soil (MCOS). The slurry of soil to water as 10:3 (*w*/*w*) was artificially homogenized. The optimal content of mixed carbon fiber was demonstrated in Supplemental Information (Figs. S2 and S3).

2.2. Soil MFC configuration and operation

A soil MFC (6 cm × 6 cm × 20 cm) was assembled with an anode of graphite rod and an activated carbon air-cathode (Fig. S4). The graphite rods (0.5 cm of diameter, 23 cm of length) were washed for 24 h in 0.1 M HCl to remove metals from the surface (Freguia et al., 2007). The air-cathode was designed and installed as previous description (Li et al., 2014a; Zhang et al., 2014). Soil MFCs filled with 1000 g of OS and MCOS (mixed with 300 mL of distilled water) were marked as CK and MC, and the corresponding disconnected controls as CKOC and MCOC, respectively. All soil MFCs were operated in a 30 °C of incubator. On day 30, 50, 98 and 120, 50 mL of distilled water was injected every time to promote the mass transfer and microbial activity. In soil MFCs, soil samples between 0 and 5, 5–10, 10–15, 15–20 cm of distance from air-cathode were marked as MFC-5, MFC-10, MFC-15, MFC-20 respectively (Fig. S4).

2.3. Electrochemical analysis

The voltage (U) across the 100 Ω of external load (R) was recorded by a data acquisition system (PISO-813, ICP DAS Co., Ltd, Shanghai, China). Polarization and power density curves were measured by varying R from 5000 to 100 Ω. The electrochemical impedance spectrum was analyzed with a 10 mV of amplitude between 100 kHz and 100 MHz of frequency by a potentiostat (Autolab PGSTAT 302N, Metrohm, Switzerland) at the open circuit potential after installed (stabilization for 4 h). The air-cathode was used as the reference and counter electrode while the anode of graphite rod as the working electrode. Nyquist plots were simulated as an equivalent circuit (Fig. S5) using a fitting program (ZsimpWin 3.10).

2.4. Chemical analysis

The soil density, total porosity, soluble salt, organic matter, available N, P and K were measured as regular methods (Liu, 1996). The pH and electricity conductivity of soil were determined in a mixture of soil to distilled water as 1:5 (*w*/*v*). The soil particle size was evaluated using particle size analyzer (Malvern Instruments Ltd., US). The contents of hydrocarbons (total petroleum hydrocarbons, *n*-alkanes and 16 priority PAHs) were extracted as previous method (Wang et al., 2012).

2.5. Calculation

The current density (mA m^{-2}) and power density (mW m^{-2}) of MFCs were normalized to the project area of air-cathode ($A = 0.0036\ m^2$) as $I' = U/(R \cdot A)$ and $P' = U^2/(R \cdot A)$. The charge output was evaluated as $Q = \int_0^T (U/R)\mathrm{d}t$. The degradation rate was calculated as $\eta = (C_{OS} - C)/C_{OS}$, where C_{OS} and C are the hydrocarbon concentration in original soil and tested soil, respectively. The overall degradation rate of hydrocarbons based on the overall concentration, which was obtained by adding the contents of 16 kinds of PAHs (or 30 kinds of *n*-alkanes) (Li et al., 2014a).

3. Results

3.1. Bioelectricity generation of the soil MFC

The current densities of soil MFC mixed carbon fiber (MC) were significant higher than these of soil MFC without carbon fiber (CK) from beginning to end of experiment (Fig. 1(a)). The voltage generation of MC quickly rose (after 0.5 h) as soon as closed circuit, while CK exhibited a 19 h of stagnation. On 19th hour, the current density (69.4 mA m^{-2}) of MC was a factor of 24 higher than that (2.8 mA m^{-2}) of CK. After 39 h, the current density of CK reached the maximum value of 19.4 ± 0 mA m^{-2} (averaged over 12 h of peak current), with the corresponding voltage (across 100 Ω of resistor) of 7 ± 0 mV. The first peak current density (200 mA m^{-2}) of MC was observed after 3 days, then it was 35 times higher than that (5.6 mA m^{-2}) of CK. The maximum current density of 203.1 ± 0.8 mA m^{-2} (averaged over 24 h of peak current) was viewed for MC after 9 days, with the voltage of 73.1 ± 0.3 mV. The average current density (120.5 mA m^{-2}) of MC during 144 days was a factor of 16 as much as that (7.6 mA m^{-2}) of CK. The accumulated charge output (5398 C) of MC was 16-fold as much as CK (341 C) within the whole experiment of 144 days (Fig. 1(b)). The maximum power density of CK was 0.8 mW m^{-2} which was less than 5% of MC (17.3 mW m^{-2}) (Fig. 1(c) and (d)). When the external resistance is equal to the internal resistance of soil MFC, the power output reaches the maximum value. Observingly, the maximum power densities of CK and MC were received at the external resistors of 5000 and 700 Ω, suggesting that the mixed carbon fiber significantly lowered the internal resistance of soil MFC. The resistance (5000 Ω) of original soil was low due to the high salt content (2.8%) of contaminated soil sampled from the Binhai area close to Bohai Sea.