Bioresource Technology 189 (2015) 87–93

Contents lists available at ScienceDirect

Bioresource Technology

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

Simultaneous degradation of toxic refractory organic pesticide and bioelectricity generation using a soil microbial fuel cell

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HIGHLIGHTS

- MFC was assembled in a simple method in topsoil.
- HCB remediation was accelerated by using soil MFC and the HCB degradation pathway was investigated.
- Use soil microbial fuel cell to recover energy from the polluted topsoil.
- The existence of the anode in soil MFC promoted growth of electrogenic bacteria.

ARTICLE INFO

Article history:
Received 19 January 2015
Received in revised form 30 March 2015
Accepted 31 March 2015
Available online 6 April 2015

Keywords:
Microbial fuel cell
Topsoil
Bioelectricity generation
Toxic refractory organic pesticide

ABSTRACT

In this study, the soil microbial fuel cells (MFCs) were constructed in the topsoil contaminated with toxic refractory organic pesticide, hexachlorobenzene (HCB). The performance of electricity generation and HCB degradation in the soil-MFCs were investigated. The HCB degradation pathway was analyzed based on the determination of degradation products and intermediates. Experimental results showed that the HCB removal efficiencies in the three groups (soil MFCs group, open circuit control group and no adding anaerobic sludge blank group) were 71.15%, 52.49% and 38.92%, respectively. The highest detected power density was 77.5 mW/m^2 at the external resistance of 1000 Ω. HCB was degraded via the reductive dechlorination pathway in the soil MFC under anaerobic condition. The existence of the anode promoted electrogenic bacteria to provide more electrons to increase the metabolic reactions rates of anaerobic bacteria was the main way which could promote the removal efficiencies of HCB in soil MFC.

1. Introduction

As refractory organic pesticide, hexachlorobenzene (HCB) is toxic to human beings and the environment. A range of remedial techniques have been developed to remove toxic refractory organics in soil. These included soil washing, land-farming, soil vapor extraction, ion exchanges, soil flushing, phytoremediation and ecological remediation (Zhou and Song, 2004; Kong et al., 2014). However, the in-situ application of these traditional methods is usually expensive and may cause new problems, such as soil erosion and fertility loss (Khan et al., 2004; Kumpiene et al., 2008).

The microbial fuel cells (MFCs) are an advantageous technology that can obtain renewable chemical energy from waste organic sources and convert it into electrical energy. The MFCs can promote significantly the removal of organics, such as glucose (Virdis et al., 2009; Freguia et al., 2008; Puig et al., 2012). Some new MFCs, such as sediment MFCs and plants MFCs, have been widely studied and used (Liu et al., 2014; Villaseñor et al., 2013). Meanwhile, some studies have reported that MFCs could promote greatly the removal of refractory organics (Galvez et al., 2009; Luo et al., 2009). In the MFC anode, co-substrates provide electrons for both the degradation of biorefractory compounds and electricity production. Therefore, both the electricity production and the degradation of biorefractory compounds are the focus of MFC study (Fang et al., 2015; Yong et al., 2014).

Lear et al. (2007), Probstein and Hicks (1993), Acar and Alshawabkeh (1993) reported the traditional electrokinetic remediation in soil, which had a great influence to the soil structure and microbial communities, would consume huge electric power. Few studies have been reported the construction of MFC in topsoil. However, the soil MFCs have several advantages, such as simple configuration, lower energy consumption, less damage to soil structure and less impact to microorganisms. In this study, we used the easily-assembled soil MFCs to accelerate HCB remediation. The performances of soil MFCs were described and

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http://dx.doi.org/10.1016/j.biortech.2015.03.148
0960-8524/

analyzed. The HCB removal and electricity generation were studied. The bacterial communities in topsoil were analyzed. The HCB degradation pathway, types and transfer processes of intermediate products in soil MFC were explored. The effect of the electrons created by electrogenic bacteria at the anode was investigated.

2. Methods

2.1. Inoculation and system construction

Hexachlorobenzene (HCB, purity >98%), was obtained from AccuStandard (USA).

The topsoil utilized in this study was sampled from 0 to 20 cm below the surface of a farmland along the shore of Yangtze River. Immediately after the sampling, the soil was dried, sieved (<2 mm) and stored at room temperature. The physicochemical properties of the soil were as the following: the moisture content was 1.79%, the pH was 6.71, the organic matter was 2.06%, the total nitrogen was 0.15%, the available phosphorus was 0.25%, and the available potassium was 1.79%.

After adding different milliliters of HCB acetone solution (1000 mg/L) into 1000 g dry soil, the soil were stirred thoroughly to obtain a uniform property. Then, the polluted soil was left in the fume hood for 48 h to evaporate acetone before it was stored finally in a sealed box in the dark at room temperature (Yuan et al., 2007).

The soil MFC was constructed in the polluted soil, with schematic diagram listed in Fig. 1. The reactors were made of a glass cylinder with an internal diameter of 35 mm and a length of 150 mm. From the bottom upward, there were four layers: soil layer with a depth of 10 mm, soil MFC anode layer with 15 mm depth of granular activated carbon (GAC, 3–5 mm in diameter with a specific area of 500–900 m^2/g), polluted soil layer with a depth of 100 mm, soil MFC air-cathode layer with 15 mm depth of GAC. The

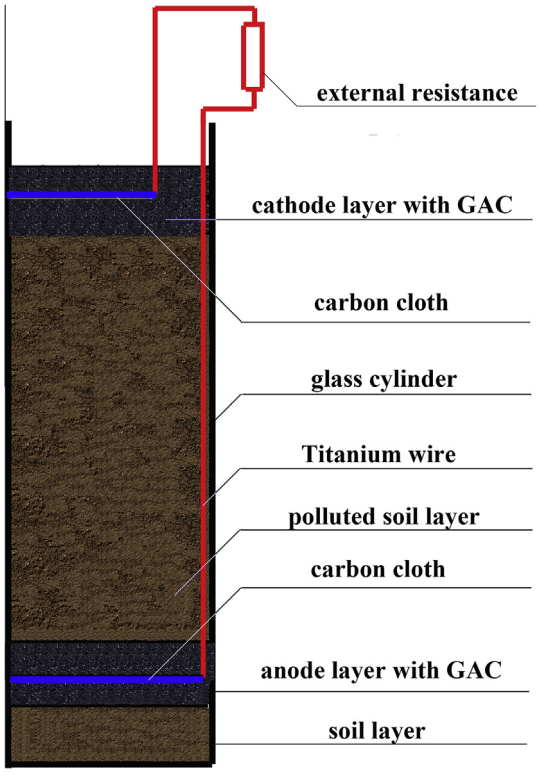

Fig. 1. Configuration of the soil microbial fuel cell.

volume of the whole container was 140 mL. Total mass of soil and GAC in soil MFCs system were 130 g (dry weight) and 20 g (dry weight), respectively.

In this experiment, 10 different groups of reactors were built, named as Group1 to Group10, in which, the anode and air-cathode embedding with carbon cloth (30 mm × 10 mm) were connected by titanium wires (1 mm in diameter). The external circuit was connected by titanium wires with different external resistances, and epoxy was used to prevent the Titanium wire from making a direct electrical contact with the cathode electrode.

The HCB initial concentration in the soil of Group1 was 40 mg/kg. Group2 was used as the control group, with the anode and air-cathode not connected. Both of Group1 and Group2 were connected with different external resistance of 10 Ω. The anaerobic sludge (MLSS: 50 g/L) sampled from the East City Municipal Wastewater Treatment Plant of Nanjing, China, was introduced into Group1 and Group2 group for microbial inoculation. The sludge (12 mL) was mixed with polluted soil in every reactors. Group3 has the same setup with Group2 except that the polluted soil in Group3 was not mixed with anaerobic sludge. Group4, Group5 and Group6 had the same configuration as Group1, with the external circuit connected with an external resistance of 2000 Ω, 1000 Ω, 510 Ω, respectively. Group7 and Group9 were the same as Group1. Only the HCB initial concentration in the soil of Group7 and Group9 were 80 mg/kg and 200 mg/kg, respectively. Group8 and Group10 were the same as Group2, while the HCB initial concentration of soil in Group8 and Group10 were 80 mg/kg and 200 mg/kg, respectively.

2.2. System operation

All the 10 groups were added with 45 mL nutrient solution with a composition as the following (per liter): 2 g of CH_3COONa, 0.31 g of NH_4Cl, 0.2 g of $MgSO_4{\cdot}7H_2O$, 0.13 g of KCl, 0.015 g of $CaCl_2$, 4.97 g of NaH_2PO_4, 2.75 g of Na_2HPO_4, 0.56 g of $(NH_4)_2SO_4$ and 0.1 mL concentrated trace element solution as reported by Klass (1998). Another 10 mL nutrient solution should be added when the voltage of soil MFC was less than 120 mV. The whole experiments were carried out in the dark at 30 °C. The experiments were conducted in triplicate and every sample was measured three times.

In the analysis of HCB concentration, the soil in every reactor was respectively completely mixed before freeze drying. Then 10 mL of hexane was added to every 0.5 g soil sample ahead of ultrasonic extraction (20 kHz) for 30 min and centrifugation for 10 min (5000 rpm). The supernatant was further filtered with 0.45 μm filtration membrane (GenerayBiotech (Shanghai) Co., Ltd.) (Oonnittan et al., 2010).

2.3. Analytics and calculations

The HCB concentration was measured with a Gas Chromatograph–Mass Spectrometer (GC–MS) (Thermo Fisher Scientific Co., Ltd., USA). The analysis used GC–MS choice ion pattern (SIM). Peak area of 84.00 and 286.00 were used to generate standard curve. The intermediates of HCB degradation were qualitatively determined by the GC–MS. The capillary column is DB-5MASS (inner diameter 0.25 mm, length 30 m). High purity Helium was employed as the carrier gas at a flow rate of 1 mL/min. The temperature of the gasification compartment was firstly set to 60 °C for 0.5 min, and then raised linearly to 235 °C at a rate of 25 °C/min. After maintaining at 235 °C for 2 min, it was further raised linearly to 250 °C at a rate of 2 °C/min and then maintained at 250 °C for 5 min. Finally, the temperature of gasification component was increased linearly to 280 °C at a rate of 15 °C/min and maintained at 280 °C for 5 min. The retention time and sampling