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Simultaneous sulfide removal and electricity generation with corn stover biomass as co-substrate in microbial fuel cells

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HIGHLIGHTS

- Sulfide and corn stover filtrate (CSF) acts as combined substrates in MFCs.
- Sulfide and organics removals with energy recovery are realized.
- CSF concentrations and electrolyte conductivities affect the performance.
- Sulfide related complex pollutants are treated in MFCs for the first time.
- MFC technology is promising for multiple contaminations treatment.

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ABSTRACT

Microbial fuel cells (MFCs), representing a promising method to treat combined pollutants with energy recovery, were utilized to remove sulfide and recover power with corn stover filtrate (CSF) as the co-substrate in present study. A maximum power density of 744 mW/m^2 was achieved with sulfide removal of 91% during 72 h operation when the CSF concentrations (mg-COD/l) and the electrolyte conductivity were set at 800 mg/l and 10.06 mS/cm, respectively, while almost 52% COD was removed due to the microbial degradation of CSF to the volatile organic carbons. CSF concentrations and electrolyte conductivities had significant effects on the performance of the MFCs. Simultaneous removals of inorganic pollutant and complex organic compounds with electricity generation in MFCs are reported for the first time. These results provide a good reference for multiple contaminations treatment especially sulfide containing wastewaters based on the MFC technology.

1. Introduction

Combined pollutant in wastewaters is widely produced throughout the world, bringing serious challenges and constrains on conventional wastewater treatments (Starostin and Sorokhtin, 2011; Velvizhi and Mohan, 2011). Sulfide is a typical kind of toxic, corrosive and malodorous pollutant which is commonly found all around the word, particularly in various wastewaters (Omri et al., 2011). It can be treated by physicochemical and biological processes (Zhang et al., 2008; Kumar et al., 2010a), while the coexisted substances in sulfide containing wastewaters may affect the process efficiency. Microbial fuel cells (MFCs) that can recover electrical energy from pollutants with bacteria as catalysts in mere one step (Logan et al., 2006; He et al., 2008; Zhuang et al., 2010; Zhang et al., 2012b), are demonstrated to effectively remove sulfide by oxidizing it to elemental sulfur (Rabaey et al., 2006; Zhang et al., 2009a). However, little attention has been focused on the effects of degradable organics on sulfide removal in MFCs in previous studies (Zhao et al., 2008; Sun et al., 2009). Zhang et al. (2009a) advocate it for the first time that the addition of glucose, which serves as the carbon source of sulfur-relating microbes, has enhanced the performance of the MFCs in electricity generation as well as sulfide removal. Lee et al. (2012) test the excessive application of lactate in MFCs to avoid any carbon limitations on microbes for sulfide removal. These results indicate that MFC technology is an effective method to treat combined pollutants relating sulfide, while only simple organics have been involved in these previous studies. Behaviors of complex organic compounds as well as

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interactions between sulfide and organics should be further investigated due to their competitions as electron donors and associations for pollutants removals in MFCs (Dutta et al., 2010).

In another aspect, organic carbon sources utilized by exoelectrogenic bacteria in MFCs vary from single carbohydrates to complex organics that commonly existed in wastewaters (Clauwaert et al., 2007). Corn stover is a sugar enriched biomass consisting of a mixture of cellulose, hemicelluloses and lignin, and reasonable to be broken down by microbes. Zuo et al. (2006) and Wang et al. (2009) have proved that steam exploded corn stover as the sole electron donor can be utilized by microbes to generate electricity in MFCs, respectively, while these studies are carried out without the consideration of any other co-substrates.

In this study, sulfide-related combined pollutant was explored for the first time, as complex organics of corn stover filtrate (CSF) was employed as co-substrate in MFCs. The performance characteristics of the co-substrate MFCs system, including power output, sulfide removal and corn stover degradation were monitored. Effects of initial CSF concentrations and electrolyte conductivities on power outputs as well as sulfide and corn stover removals were also examined to optimize the operating conditions. Compositions of the initial filtrate and their degradations in the effluents were detected respectively. Effects of CSF on the sulfur-relating exoelectrogenic bacteria activities and sulfide removals were also investigated.

2. Materials and methods

2.1. Construction of MFCs

Four cubic single-chamber MFCs were constructed according to a novel design reported in our previous study (Zhang et al., 2012a), with an effective volume of 125 ml (5 × 5 × 5 cm). The carbon fiber felt anode (1 cm thickness, 4 cm length and width, Beijing Ever Grow Resources Co. Ltd., Beijing, China) was laid in the middle of the chamber. The cathode made of plain carbon paper (with 0.5 mg/cm^2 of Pt on one side) was placed on the opposite site of the anode, with a projected surface area of 16 cm^2. The electrodes were connected to the external resistance of 1000 Ω using copper wires with all exposed surfaces sealed with non-conducting silicone. The MFCs were then attached to a data acquisition system (PMD1208LS, Measurement Computing Corp., Norton, MA, USA) to record voltage at an interval of 5 min (Zhang et al., 2009b).

2.2. CSF and electrolyte preparations

Dry corn stover was harvested from a farm in Changping district (Beijing, China) and stored for 1 year. Corn stover was converted into powder (0.5 mm) by crushing and grinding, and then dried at 40 °C for 48 h (Yoo et al., 2011). The corn stover powder was filtered to collect the organic derivatives, and about 1000 mg/l COD was obtained from the 2.5 g powder washed for three times with 400 ml water.

The electrolyte contained the following components (per liter): NH_4Cl (0.31 g); KCl (0.13 g); $NaH_2PO_4{\cdot}H_2O$ (4.97 g); $Na_2HPO_4{\cdot}H_2O$ (2.75 g); vitamin solution (1.25 ml) and 12.5 ml trace mineral element solution (Lovley and Phillips, 1988). Sulfide (100 mg/l) was added to the anode solution of the MFCs in the form of $Na_2S{\cdot}9H_2O$. The initial pH of the electrolyte was about 7 as the function of added phosphate buffer solution (50 mmol/l).

2.3. Operation of the MFCs

The MFCs were inoculated with 25 ml anaerobic sludge obtained from an up-flow anaerobic sludge blanket reactor treating high-sulfate wastewater. MFCs were initially domesticated with glucose (800 mg-COD/l) and sulfide (100 mg/l) at the fixed external resistance of 1000 Ω under 30 °C circumstances, with fresh nutrient buffer solution (NBS) mentioned above. The MFCs were operated in 72 h fed-batch mode as most of sulfide was removed within that time. After several batch cycle operations, the system was considered to be under steady-state conditions when the maximum voltage output was reproducible in two or more cycles. Then the substrate was switched to a medium of CSF with NBS as before, and operated for similar maximum voltages in two or more consecutive cycles (72 h for each). When stabilized, experiments were conducted to investigate the effects of different initial CSF concentrations (400, 800, 1200, 1600 mg/l) and electrolyte conductivities (4.85, 7.25, 10.06, 15.27 mS/cm, adjusted by NaCl) on electricity productions and sulfide removals, respectively. The experiments were carried out in duplicate and only the mean values were reported.

2.4. Chemical analytical methods

Measurement of COD was based on digestion with potassium dichromate in concentrated sulfuric acid for 2 h at 150 °C, and sulfide is not counted as a composition of the COD except where stated otherwise. Sulfide was determined according to the methylene blue method (n = 665 nm). The indication of "sulfide" described all species (H_2S, HS^-, and S^{2-}). pH was measured by using a pH meter (Mettler Toledo S02, USA). Electrolyte conductivity was monitored by a conductivity meter (DDS-11A, Shanghai Lei Yun test equipment Manufacturing Co. Ltd., Shanghai, China). Samples were taken at 12 h intervals to measure the residual sulfide, COD, and pH over the course of the whole experiment. Gas chromatography/mass spectrometry (GC/MS) was used to analyze the organic components presented in the CSF influent and the effluent of the MFCs system. The CSF of 500 ml was divided into two parts with 250 ml serving as the influent sample and the other 250 ml as the effluent sample after a complete cycle of 72 h in the MFCs. The samples were extracted using 10 ml ethyl acetate for three times and then dried under nitrogen before injected into a 6890 N/5973 GC/MS system (Agilent, USA) equipped with a DB-5 capillary column. The GC process was programmed at 40 °C for 0.5 min, then increased at 10 °C/min to 300 °C, and finally held at isothermal for 10 min. The injector temperature was 250 °C, and the injection size was 1 μl. The flow rate of the carrier gas (helium) was 0.6 ml/min. The ion source temperature was 230 °C for the mass-selective detector (Lei et al., 2009). Analysis was undertaken with reference to the NIST02 mass spectral library database.

2.5. Electrochemical monitoring and data presentations

The MFCs were continuously monitored using a data acquisition system connected to a computer. The circuit was operated under a fixed external load resistance of 1000 Ω except where stated otherwise. The open circuit voltage (OCV) and voltage measurements were taken at 5 min intervals throughout the test. The polarization curves were obtained by measuring voltages at various external resistances (ranging from 10 to 5000 Ω) to evaluate the relationship between voltage and current. For each point on the polarization curves, voltage readings were taken when the voltage stabilized.

To calculate the current (I) in amperes (A) by Ohm's law, $I = U/R$, where U is the potential drop in volts (V) across the external load resistor in Ohms. To calculate the power output P in watts (W) and the power density (PD, W/m^2) were calculated according to $P = I \times U$ and PD = $I \times U/S$ respectively, where S (m^2) is the geometrical area of the anode. The coulombic efficiency (CE) was deduced as follows, CE = $C_P/C_T \times 100\%$, where C_P is the total number of coulombs calculated by integrating the current over time. C_T is the theoretical number of coulombs that can be produced from the used