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Short Communication

Long-term operation of manure-microbial fuel cell

Guodong Zhang [a,b], Qingliang Zhao [c,1], Yan Jiao [d], Duu-Jong Lee [b,e,*]

[a] Institute of Resources and Environment Engineering, Shanxi University, Taiyuan 030006, China
[b] Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 10617, Taiwan
[c] State Key Laboratory of Urban Water Resources and Environments (SKLUWRE), School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, China
[d] Applied Economic Research Institute, Shanxi University of Finance and Economics, Taiyuan 030006, China
[e] Department of Chemical Engineering, National Taiwan University, Taipei 106, Taiwan

HIGHLIGHTS

- Microbial fuel cell with biocathode is tested with dairy manure as fuel.
- The tested MFC can produce electricity stably for over 110 days.
- The anolyte DOM was monitored during MFC operation.
- MFC converted the hydrophobic acid and hydrophilic fractions as fuel.
- Degradable organic matters were converted to compounds with high aromaticity.

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ABSTRACT

Microbial fuel cell (MFC) is applied to produce electricity using dairy manure as a fuel. Since the way MFC utilizes manure as a fuel and the long-term operation stability of manure-MFC remains unclear, this study examined the evolution of dissolved organic matter (DOM) in anodic chamber and power generation by MFC in a 171 days test. The tested MFC can produce electricity over the entire testing period by single feed of manure, with stable power output and total chemical oxygen demand (TCOD) removal rate in the period of day 30–140. The hydrophobic acid (HPO-A) and hydrophilic (HPI) fractions of manure were the principal components of anolyte DOM, with the concentrations of both being reduced over MFC operation. The degradable organic matters were converted to compounds with high aromaticity.

1. Introduction

Large quantity of manure is produced by dairy farms. The dairy manure is commonly treated by anaerobic digestion (AD) process; however, the AD process typically has poor stability. Microbial fuel cells (MFCs) were used to produce electricity from organic matters (Logan, 2008). A few MFC studies were conducted for the use of dairy manure as the fuels.

Scott et al. (2007a) and Scott and Murano (2007b) reported peak power densities of 0.085 Wm^{-3} with a sediment MFC and 1.143 Wm^{-3} with a tubular MFC, when dairy manure was the fuel. Later, the MFC with air cathode was noted to yield maximum power density of 4.725 Wm^{-3} from dairy manure wastewater (Kiely et al., 2011). Lee and Nirmalakhandan (2011) considered the use of screened cattle manure as anode fuel. These authors reported a maximum power density of 0.2 Wm^{-3} with a single-compartment MFC combined with membrane-electrodes and of 0.3 Wm^{-3} with a twin-compartment MFC and brush-type anode electrodes. With revised structure and electrode material of MFC, Zhang et al. (2012) and Inoue et al. (2013) obtained power densities of 15.1 Wm^{-3} (biocathode MFC) and 16.3 Wm^{-3} (cassette-electrode MFC) respectively from a dairy manure-water mix. Wang et al. (2014) demonstrated that dairy manure with <80% moisture could also be used as MFC fuel.

The existing manure-MFC studies focused on maximizing power generation from dairy manure, with minimal notice having been paid to how the organic substances in manure are degraded in long term operation of MFC. This study aimed at characterizing the performance and the DOM evolution of biocathode MFC using dairy manure as a fuel during long term operation.

* Corresponding author at: Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 10617, Taiwan. Tel.: +886 2 232532; fax: +886 2 23623040.

E-mail addresses: qlzhao@hit.edu.cn (Q. Zhao), djlee@ntu.edu.tw (D.-J. Lee).

[1] Tel.: +86 451 86283017; fax: +86 451 86283017.

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2. Methods

2.1. MFC buildup and test

The biocathode MFC used in this study has been described (Zhang et al., 2012), which is consisted of a 100 mm × 90 mm cylinder anode compartment with two uniform cubes (80 mm × 80 mm × 50 mm), cathode compartment, linking with each other by a Plexiglas pipe (ϕ20 mm). Two proton exchange membranes (PEM) (Nafion™ 117, Dupont Co., Wilmington, USA) with the same geometry (80 mm × 80 mm) separated the single anode compartment and two cathode compartments. The cathode chambers were continuously aerated by air at 200 ml min^{-1} and the anolyte was stirred with a blade stirrer (300 rpm) for 3 min every h in the test. The graphite fiber brush made of carbon fibers (STS40 24 K, 650 ± 17 m^2 m^{-3}, average fiber diameter of 7.0 μm, 1.7 Ω cm^{-1}, Toho Tenax) were cut and twisted by two titanium wires. The brushes embedded in graphite granules (diameter of 1–5 mm, 55 m^2 m^{-3}, 0.5–0.6 Ω per granule, Jiuxin Carbon Goods Co., Jilin, China) made the cathode, with four brushes placed in the anodic compartment as electrodes. Ways of preparing PEM and electrodes were available in Liu and Logan (2004) and Zhang et al. (2012), respectively (Supplementary materials). The effective volume of the anodic chamber was 617 cm^{-3} and that of the cathodic chambers were 321 cm^{-3}.

Dairy manure was collected from a dairy farm in Xiangfang, Harbin, China. The manure had the following characteristics (pH and TS by wet basis, the others by dry basis): pH 6.97 ± 0.21; total solids (TS) 17.8 ± 1.6%; volatile solids (VS) 86.2 ± 3.1%; total carbon (TC) 41.3 ± 2.5%; cellulose content 34.7 ± 2.6%; hemicellulose content 22.5 ± 1.2%; lignin content 23.6 ± 4.7; total nitrogen (TN) 3.3 ± 0.2%; NH_4-N (ammonia nitrogen) 5874 ± 322 mg kg^{-1}; total phosphorus (TP) 1.57 ± 0.22%. The cathodes were fed by the medium contained (per liter of deionised water): 1.0 g NH_4Cl, 1.2 g K_2HPO_4, 0.5 g $MgSO_4$, 0.5g KCl, 0.14 g KH_2PO_4, 0.01 g $Fe_2(SO_4)_3{\cdot}H_2O$, 0.02 g yeast extract, and trace elements (Zhang et al., 2011), and inoculated with topsoil obtained from the turf at Harbin Institute of Technology, Harbin, China. The anodic chamber was directly filled with 2:5 (v/v) mix of dairy manure and distilled water. During the MFC test, the anode was fed initially and the cathode was fed periodically. All experiments were conducted at 30 ± 2 °C.

2.2. Extraction and fractionation of anolyte DOM

One hundred cm^3 of anolyte samples were collected on day 0 (initially), 75, and 171 respectively and their supernatants were collected by centrifugation at 4000×g (30 min). The obtained supernatants were filtered by 0.45 μm cellulose nitrate membrane filter, and were diluted with 60 vol. of deionized water. The diluted filtrates were acidified to pH 2 using HCl, and further the DOM in filtrates was fractionated into five fractions as described protocol by Wei et al. (2011) (Supplementary materials).

2.3. Analytical methods

The voltage drop data over 100 Ω resistors were recorded by multicenter voltage collection instrument (PISO-813, ICP DAS, Co., Ltd., Beijing, China). The potentials of anodic electrodes were monitored with Ag/AgCl reference electrode (+0.197 V vs. standard hydrogen electrode (SHE) (model RE-5B, BASi, Ningbo, Jiangsu province, China). The volumetric power density was normalized by the anodic liquor volume. The polarization curves were obtained by measuring the stable voltage generated at various external resistances (for 30 min at each resistance), from which the maximum power density (P_{max}) was estimated (Logan, 2008). Internal resistance (R_{int}) of cell is determined from the slope of polarization curves. The Coulombic efficiency (CE) of cell is calculated as described by Kim and Yu (2005).

All organic samples were filtered using 0.45 μm cellulose nitrate membrane filter and stored at 4 °C prior to analysis. All measurements were done in triplicate to report the average and standard deviation (SD) of collected samples. The dissolved organic carbon (DOC) in the filtrate was analyzed using TOC-5000 Total Organic Carbon Analyzer (Shimadzu, Kyoto, Japan). The ultraviolet absorbance of samples was measured at 254 nm with a Shimadzu UV-2550 UV/VIS spectrophotometer (Shimadzu, Kyoto, Japan). The specific ultraviolet light absorbance (SUVA) was calculated as (UV-254/DOC) × 100 to characterize the DOM aromaticity (Leenheer and Croué, 2003). The contents of TCOD of dairy manure were analyzed according to the Standard Methods (APHA, 1998). The contents of cellulose, hemicellulose, and lignin in dairy manure were measured using protocols by AOAC (1995).

FTIR spectra (KBr, 1%) of samples (HPO-A, HPO-N, TPI-A, TPI-N) were run on a Perkin Elmer (Spectrum 1B, Waltham, Massachusetts, USA) between 4000 cm^{-1} and 400 cm^{-1}. The spectra were baseline corrected and normalized to 1.0 for comparison.

The excitation-emission matrix (EEM) was measured in a 1-cm cuvette using a Jasco FP-6500 spectrofluorometer (Tokyo, Japan) at 24 °C. The organic samples were diluted to 1 mg l^{-1} of DOC using 0.01 mol l^{-1} KCl and acidified to pH 3 with HCl. A xenon lamp was the excitation source, and the excitation and emission slits were set to a 5 nm band-pass. Each EEM lot was generated by scanning excitation wavelengths from 220 nm to 400 nm with 5 nm steps and emitting fluorescence between 280 and 480 nm with 1 nm steps.

3. Results and discussion

3.1. Cell performance of MFC

The power curves for the present manure-MFC are shown in Fig. 1. After startup the MFC performance was continuously improved and peaked on day 30 and onward. The peak OCV of cell all above 800 mV and the maximum power densities were 14.11 ± 0.20 Wm^{-3} (Supplementary materials). This observation confirmed that the biocathode MFC yielded stable electricity using dairy manure as fuel with long-term stability.

The MFC power started to decline since day 140. The fed manure was depleted so the anode-respiring bacteria can have insufficient nutrients. On day 165 the P_{max} was only 39.7% of that on 140 day (Supplementary materials). The corresponding R_{int} was 229% of that on 140 d, likely being attributable to the increase in diffusional resistance (Fan et al., 2008) in later stage of tests.

3.2. Organic removal

The TCOD removals by MFC decreased with time; conversely, the CE efficiency was increased (Supplementary materials). The TCOD removal was 8302 ± 856 mg l^{-1} in the first 30 day operation, then it was stabilized to a rate of 4434 ± 667 mg l^{-1} during day 61–150). The average CE for cell in the first 30 day was 9.87 ± 2.48%. Restated, during early stage fraction of hydrolyzed organic matters were not converted into electricity, correlating with the experimental findings for a fed-batch system (Logan, 2008). The CE was increased to 14.91 ± 1.64% (d 61–90) and 18.65 ± 3.37% (d 121–150). Later, it dropped slightly to 16.9 ± 1.42% on day 151–171.

3.3. DOM in analytes

The HPI and HPO-A fractions were the principal components of anolyte DOM on day 0, representing 56.2% and 34.9% of the bulk