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Short Communication

Transformation of dissolved organic matters in landfill leachate–bioelectrochemical system

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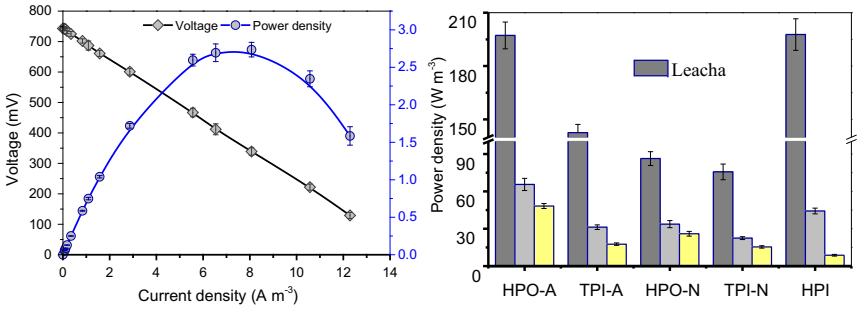
HIGHLIGHTS

- Bioelectrochemical system reactor and anoxic/oxic reactor treated leachate.
- BES removed 84–89% COD and 94–98% NH_4^+-N, much higher than A/O reactor.
- Dissolved organic matters in effluents from BES and A/O reactor were compared.
- BES converted hydrophilic fraction of the fed DOM to CO_2 and excess humin.
- Electric fields at cathode assists ammonium removal by BES.

GRAPHICAL ABSTRACT



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ABSTRACT

A membraneless bioelectrochemical system (BES) reactor and an anoxic/oxic (A/O) reactor of identical configurations were applied to treat the landfill leachate (20,100 mg l^{-1} chemical oxygen demand (COD) and 1330 mg l^{-1} NH_4^+-N) at 24-h hydraulic retention time and 3 kg chemical oxygen demand m^{-3} d^{-1} volume loading. The BES with maximum power density of 2.77 ± 0.26 W m^{-3} and internal resistance of 47.5 ± 1.4 Ω removed 84–89% COD and 94–98% NH_4^+-N, 11% and 47%, respectively, higher than the A/O reactor. The dissolved organic matters (DOM) in effluents from the BES and the A/O reactor were for the first time characterized and compared. The MFC preferentially degraded hydrophilic fraction (HPI) of the fed DOM and yielded excess humin with high aromaticity. The electric fields by bioelectrochemical reactions occurred at cathode stimulate the activities of COD degraders and nitrifiers in biofilms to enhance ammonium removals by BES reactor.

1. Introduction

Landfill leachate is heavily polluted wastewater with complex dissolved organic matter, inorganic macro-components, heavy metals and xenobiotic compounds (Kjeldsen et al., 2002). Microbial fuel cells (MFC) were devices to convert energy in organic or inorganic substances into electricity (Garner et al., 2012; Chou et al., 2014; Lee et al., 2014; Zhang et al., 2015a). This device was applied for pollution removal and energy generation from landfill leachate (You et al., 2006; Zhang et al., 2008; Greenman et al., 2009; Gálvez et al., 2009; Puig et al., 2011; Tugtas et al., 2013; Özkaya et al., 2013; Ganesh and Jambeck,

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2013; Vázquez-Larios et al., 2014; Damiano et al., 2014). These MFC studies noted 28–74% removal of chemical oxygen demand (COD) and 23–43% removal of NH_4^+ in the leachate feed. To enhance cell performance, these mentioned studies commonly adopted noble metal catalysts to accelerate reaction rates on cathode and to separate the anode and cathode compartments by an ion exchange membrane to minimize backmixing of protons in the solution. However, application of noble catalyst or ion exchange membrane increases the installation costs of the leachate–MFC.

The tested leachate–MFC has low ammonium removal rates. Zhang et al. (2015b) proposed the use of a 3.5-L membraneless MFC with biocathode, a bioelectrochemical system (BES), as a cost-effective device for leachate treatment. At 3 kg COD m^{-3} d^{-1} loading and 24-h hydraulic retention time (HRT), the tested membraneless BES could remove 90% of fed COD and 99% of NH_4^+ in the leachate feed. Additionally, these authors aerated the solution around the cathode to produce anoxic/oxic local environment for removing nitrate to nitrogen gas. This newly proposed MFC presents an attractive alternative for landfill leachate treatment, particularly on the almost complete removal of nitrogenous compounds that cannot be easily reached in conventional wastewater treatment process. The reasons for the supreme nitrogen removal capability by the tested BES remain unclear.

This study started up a membraneless BES as proposed by Zhang et al. (2015b) and an anoxic/oxic (A/O) reactor of identical geometry with the same operational protocol. The dissolved organic matters (DOM) in the effluents from both reactors were characterized for the first time based on their hydrophobicity and acidity. We noted a low Columbic efficiency of the tested BES, as commonly noted for other liter-scale BES being reported. The possible mechanisms corresponding to the noted high ammonium removal by the BES were discussed.

2. Methods

2.1. Reactor setup and test

The BES and the A/O reactor were of the same geometry as proposed by Zhang et al. (2015b). Briefly, both the BES and A/O reactor were consisted of a cylindrical anode compartment of diameter of 10 cm and height 20 cm, and a cathode compartment as the space outside the cylinder embraced by a cone of diameter 14 cm (bottom) and 25 cm (top) and of height 18 cm. Carbon fiber brushes embedded in graphite granules were filled up the cathode and anode compartments for both reactors. The only difference between these two reactors is the former has an external circuit with a fixed resistance of 100 Ω while the latter was free from any external loading.

Landfill leachates were collected from a landfill site at Taiyuan, China, with the following mean characteristics (in mg l^{-3}): COD_{cr} of 20,100, BOD_5 of 9035, total organic carbon (TOC) of 7450, NH_4^+-N of 1330, total nitrogen (TN) of 1500, alkalinity of 6720, and pH 7.4. The leachate was fed to the inner cylindrical compartments at volume loading of 3 kg COD m^{-3} d^{-1}. All experiments were conducted at room temperatures. The cone compartment was intermittently aerated at 500 ml min^{-1} in 30 min aeration + 90 min no-aeration cycles.

2.2. Extraction and fractionation of DOM

The collected samples (original leachate and the effluents from A/O reactor and from MFC) were filtered by 0.45 μm cellulose nitrate membrane filter. The filtrate was diluted with 30 volumes of deionized water and then was acidified to pH 2 using HCl. The DOM in filtrates was fractionated using Amberlite XAD-8 and XAD-4 resins into five organic fractions: hydrophobic acid (HPO-A), hydrophobic neutral (HPO-N), transphilic acid (TPI-A), transphilic neutral (TPI-N), and hydrophilic fraction (HPI). Briefly, 3000 ml of acidified filtrate was passed through XAD-8 and XAD-4 resin columns at a flow rate of 10 bed volumes per hour with the HPI was the organic matter in the XAD-4 effluent. Each of the resin columns was eluted backward with 0.1 M NaOH at a flow rate of 2 bed volumes per hour, followed by 2 bed volumes of milli-Q water. The elute from XAD-8 was the HPO-A, and that from XAD-4 was TPI-A. The HPO-N and TPI-N were those being respectively adsorbed on XAD-8 and XAD-4 resins but were not eluted by NaOH. Detailed description of fractionation scheme is available in Wei et al. (2011).

2.3. Analytics and calculations

The potentials of the cathode and the anode were monitored with Ag/AgCl reference electrode (+0.197 V vs. standard hydrogen electrode (SHE)) (model RE-5B, BASi, Ningbo, China). The volumetric power density was normalized by the anode liquor volume. The polarization curves were obtained by measuring the stable voltage generated at various external resistances (maintained for 30 min at each resistance), from which the maximum power density (P_{max}) was estimated (Logan et al., 2006). The internal resistance (R_{int}) of cell was determined from the slope of polarization curves.

All DOM measurements were done in triplicate with the average and standard deviation being reported. 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. The total COD (TCOD), total nitrogen (TN), NH_4^+-N, and alkalinity contents were analyzed according to the Standard Methods (APHA, 1998). The apparent molecular weight distribution of DOM was characterized by high-performance size exclusion chromatography (HPSEC) with UV-detection at 254 nm. Weight-average molecular weight (M_w) and number-average molecular weight (M_n) were calculated from the HPSEC-UV results with molecular weight standards of polyethylene glycol (0.6 kDa, 1 kDa, 6 kDa, 20 kDa). Polydispersity (d) of molecular weights was calculated with the equation of $d = M_w/M_n$.

The fast Fourier infrared spectroscopy (FTIR) spectra (KBr, 1%) of samples were adopted by Spectrum 1B (Perkin Elmer, Waltham, MA, USA) between 4000 cm^{-1} and 400 cm^{-1}. 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 M KCl and acidified to pH 3 with 1 M HCl. A xenon lamp was the excitation source, and the excitation and emission slits were set to a 5 nm band-pass. Each EEM plot 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. Reactor performance

The tested membraneless BES yielded a power curve with P_{max} = 2.77 ± 0.26 W m^{-3} at 7.5 A m^{-3} (Supplementary materials). Correspondingly, the open circuit voltage (OCV) was noted high (743 ± 14 mV), correlating to the low R_{int} obtained (47.5 ± 1.4 Ω). These data suggested that the present BES was well operated with the fed leachate.