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Fermentation pre-treatment of landfill leachate for enhanced electron recovery in a microbial electrolysis cell

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HIGHLIGHTS

- Leachate pre-fermentation enhanced microbial electrolysis cell (MEC) performance.
- Current density and organic removal were significantly greater using pre-fermentation.
- Carbohydrates had the highest degree of fermentation, followed by protein and lipids.
- Acetate was the only organic acid detected in semi-continuous fermenters.

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ABSTRACT

Pre-fermentation of poorly biodegradable landfill leachate (BOD_5/COD ratio of 0.32) was evaluated for enhanced current density (j), Coulombic efficiency (CE), Coulombic recovery (CR), and removal of organics (BOD_5 and COD) in a microbial electrolysis cell (MEC). During fermentation, the complex organic matter in the leachate was transformed to simple volatile fatty acids, particularly succinate and acetate in batch tests, but mostly acetate in semi-continuous fermentation. Carbohydrate had the highest degree of fermentation, followed by protein and lipids. j, CE, CR, and BOD_5 removal were much greater for an MEC fed with fermented leachate (23 A/m^3 or 16 mA/m^2, 68%, 17.3%, and 83%, respectively) compared to raw leachate (2.5 A/m^3 or 1.7 mA/m^2, 56%, 2.1%, and 5.6%, respectively). All differences support the value of pre-fermentation before an MEC for stabilization of BOD_5 and enhanced electron recovery as current when treating a recalcitrant wastewater like landfill leachate.

1. Introduction

Recent reviews on microbial electrochemical cells (MXCs) highlight the growing interest in this technology as a means to gain value from organic waste streams (e.g., Logan and Rabaey, 2012; Pant et al., 2010; Rittmann, 2008). Most waste streams that are of interest for practical application of MXCs are comprised of complex organic substrates (Pant et al., 2010). Characteristics of the substrates influence MXC performance: organics removal, Coulombic efficiency (CE, the fraction of electrons recovered as electric current at the anode of an MXC compared to the electrons removed from the substrate), Coulombic recovery (CR, the fraction of electrons recovered as electric current at the anode of an MXC compared to the total influent electrons in the substrate), and current density (j, A/m^2 or A/m^3, the current produced normalized to the active surface of anode or to the reactor volume, respectively).

Landfill leachate is a possible feedstock for MXCs (Ganesh and Jambeck, 2013; Zhang et al., 2008; You et al., 2006). Leachates are liquid discharges from landfills, which dispose of around 95% of municipal solid wastes (MSW) worldwide (Renou et al., 2008). Leachate typically is a strong wastewater that contains high concentrations of organic matter (usually measured as chemical oxygen demand, COD), ammonium-nitrogen (NH_4^+–N), heavy metals, xenobiotic organic compounds (XOCs), humic compounds (HCs), and inorganic salts. Many factors affect the quality of leachate: the type of waste, age of the landfill, and the seasonal variations in the weather (Renou et al., 2008). Leachate composition changes as a landfill progresses through consecutive aerobic, acetogenic, methanogenic, and stabilization stages (Renou et al., 2008), and leachate can be classified into 3 groups based on the landfill age, i.e., young, intermediate, and mature. Table 1 summarizes typical characteristics of each group. Young leachate has significantly higher COD and biodegradability (based on the BOD_5/COD ratio, where BOD_5 is the 5-day biochemical oxygen demand), but the BOD_5/COD ratio for young leachates often is relatively low ($\sim$ 0.3).

Although leachate might be considered a good feedstock for MXCs because of its relatively high conductivity, buffering capacity, BOD_5, and minimal solids, studies show that j, CE, and CR are relatively low (Zhang et al., 2008; You et al., 2006), probably due

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to the large portion of poorly biodegradable organics in the leachate's COD. Previous research has shown that only 8–43% of the BOD_5 was removed in an microbial fuel cell (MFC) fed with diluted leachate (Greenman et al., 2009), while only 7% of the COD was converted to electricity in dual chamber, air–cathode MFCs fed with young landfill leachate (You et al., 2006). Recently, Ganesh and Jambeck (2013) investigated the performance of a single-chamber air–cathode, semi-continuously fed MFC for electricity generation from landfill leachate. They reported an average COD removal of 28% and current density of 26.8 mA/m^2. Moreover, CE was very low, ranging from 1 to 14% with an average value of 6.9%. Li et al. (2013) demonstrated the feasibility of treating food-waste leachate with 87% VFA removal, although with CE in the range of 14–20%.

MXC biodegradation of complex organic compounds, like those present in a landfill leachate, must occur through a series of anaerobic reactions. Anode respiring bacteria (ARB), the key microorganisms that colonize the anode of MXCs, are known to use only a few simple compounds as electron donors, in particular acetate and H_2 (Pant et al., 2010; Lee et al., 2008; Torres et al., 2007). Thus, fermentation reactions are necessary to produce the mixture of simple products that ARB can oxidize. However, fermentation products depend upon the organic sources, the microbial community, and operating conditions, such as pH and temperature (Lee et al., 2008; Ren et al., 2007).

Although fermentation and anode respiration can occur together in the anode of an MXC (Parameswaran et al., 2009; Ren et al., 2007), it may be advantageous to have some or most of the fermentation occur in an independent reactor that precedes the MXC. In this case, the MXC receives simpler organic compounds that can be oxidized more directly by ARB, thereby simplifying the structure and function of the ARB community in the biofilm anode and helping bring about higher current density (Torres et al., 2007). Separate fermentation reactors whose effluent is then fed to an MXC anode were evaluated for primary sludge (Yang et al., 2013), cellulose (Wang et al., 2011), and primary municipal wastewater (Nam et al., 2010). These studies showed increased performance compared to direct addition of raw complex substrate to the MXC anode.

Pre-fermentation treatment also might help to remove xenobiotic compounds that may be toxic to the ARB. Phenolics are a good example, and past studies have shown that phenolic compounds can be removed in anaerobic environments through syntrophic activities of phenol metabolizers, hydrogen-utilizers, and acetoclastic methanogens. For example, Tay et al. (2001) investigated the anaerobic biodegradation of phenol with different initial phenolic concentrations (105–1,260 mg phenol/L). They were able to achieve 88–98% phenol removal even at a high phenol loading rate (6 kg phenol-COD/L day).

In this study, pre-fermentation of landfill leachate was evaluated for whether or not it improved the performance of subsequent MEC treatment. First, the performance of the first-stage fermenter was characterized. Then, electron flows in biofilm anodes of MECs were evaluated with raw leachate versus fermented leachate.

Table 1
Classification of landfill leachate according to age and typical characteristics.[c]

	Young	Intermediate	Mature
Age (years)	<5	5 – 10	>10
pH-value	6.5	6.5 – 7.5	>7.5
COD (g/L)	>10	4 – 10	<4
BOD_5/COD	>0.3	0.1 – 0.3	<0.1
Organic composition	80% VFA[a]	5 – 30% VFA + HCs and FCs[b]	HCs and FCs

[a] VFA: volatile fatty acids.
[b] HCs and FCs: humic and fulvic acids, respectively.
[c] Sources: Renou et al. (2008).

2. Methods

2.1. Landfill leachate

The landfill leachate used in this study was collected from the Northwest Regional Landfill (Surprise, AZ) and kept refrigerated at 4 °C prior to use. The leachate was used as collected for all experiments: without pH adjustments, addition of nutrients/trace metals, or dilution. A specific methanogenesis inhibitor, 2-bromoethanesulfonate (BES), at 50 mM concentration was used as explained below (Parameswaran et al., 2010).

2.2. Anaerobic fermentation experiments

Batch anaerobic fermentation assays were performed using serum bottles with a working volume of 100 mL and a total volume of 160 mL. Anaerobic digester sludge from the Mesa Northwest Water Reclamation Plant (Mesa, AZ) was the inoculum and had total suspended solids (TSS) and volatile suspended solids (VSS) concentrations of 27.0 ± 10 and 23.2 ± 8 g/L, respectively. In these experiments, methanogenesis was inhibited by adding 50 mM BES. Once the inoculum (final concentration of 5 g VSS/L) and leachate were added into the serum bottles, the bottles were capped with rubber serum stoppers and aluminum caps after purging with N_2/CO_2 (80%:20%) gas for 30 min to remove O_2, placed in a 37 °C incubator shaker (175 rpm, C25KC, New Brunswick Scientific), and monitored (in triplicate) according to the batch biochemical methane potential (BMP) protocol (Parameswaran and Rittmann, 2012). The volume of gas produced was measured with a friction-free glass syringe of 10 or 50 mL volume (Popper & Sons, Inc., New Hyde Park, NY, USA).

In order to confirm the results from the batch fermentation experiments and to produce enough fermented leachate for MEC experiments, fermentation experiments were carried out with semi-continuous feed. The reactor was operated in a 37 °C incubator shaker, and leachate (with 50 mM BES) was fed once every 2 days. At the end of each HRT, the fermentation reactor contents were allowed to settle for 2 h, and the supernatant was centrifuged at 2000 rpm for 10 min. Although the hydraulic retention time (HRT) was 2 days, the solids retention time (SRT) was controlled at 44 to 50 days by regularly discharging a specified amount of sludge according to the definition of SRT (Rittmann and McCarty, 2001).

2.3. Microbial electrolysis cells

Dual-chamber, H-type MECs with a liquid volume of 320 mL in each chamber were as described elsewhere (Parameswaran et al., 2010; Lee et al., 2008; Torres et al., 2007). For anodes, approximately 270,000 graphite fibers (~ 8 cm length) were mounted on a stainless steel rod using plastic ties. The graphite-fiber anode was first treated by soaking it in 0.1 M HNO_3 for 4 h and then soaking it in pure acetone overnight, followed by ethanol (95%) for 3 h. Following the treatments, the graphite fiber anodes were washed three times with distilled water before placing them in the MEC. The cathodes were 0.8-cm outer diameter (OD) graphite rods, and the cathode pH was maintained at 12 by addition of 10 N NaOH. The cathode chamber was separated from the anode chamber with an anion exchange membrane (AMI 7001, Membranes International, Glen Rock, NJ), and an Ag/AgCl reference electrode (BASI Electrochemistry, West Lafayette, IN) was placed about 0.5 cm away from the anode to control the anode potential at –0.3 V vs. Ag/AgCl using a potentiostat (Princeton Applied Research, Model VMP3, Oak Ridge, TN). The temperature was controlled at