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Comparison of complex effluent treatability in different bench scale microbial electrolysis cells

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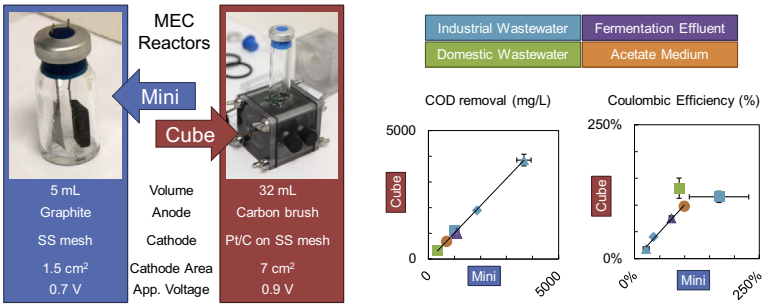
HIGHLIGHTS

- Mini and cube MECs were operated with various wastewaters and substrates.
- Organic treatment and current generation were compared between the reactor types.
- Organic treatment performance was consistent between mini and cube MECs.
- Mini MECs provide a suitable low cost platform for screening wastewater sources.

GRAPHICAL ABSTRACT



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ABSTRACT

A range of wastewaters and substrates were examined using mini microbial electrolysis cells (mini MECs) to see if they could be used to predict the performance of larger-scale cube MECs. COD removals and coulombic efficiencies corresponded well between the two reactor designs for individual samples, with 66–92% of COD removed for all samples. Current generation was consistent between the reactor types for acetate (AC) and fermentation effluent (FE) samples, but less consistent with industrial (IW) and domestic wastewaters (DW). Hydrogen was recovered from all samples in cube MECs, but gas composition and volume varied significantly between samples. Evidence for direct conversion of substrate to methane was observed with two of the industrial wastewater samples (IW-1 and IW-3). Overall, mini MECs provided organic treatment data that corresponded well with larger scale reactor results, and therefore it was concluded that they can be a useful platform for screening wastewater sources.

1. Introduction

The organic matter present in wastewater is an energy and nutrient rich resource that is currently under-utilized. Conventional aerobic wastewater treatment methods, such as activated sludge, can consume a significant amount of energy for treatment (~0.6 kWh/m^3), and typical treatment plants have limited energy recovery (McCarty et al., 2011). Microbial electrochemical technologies (METs), such as microbial electrolysis cells (MECs), have shown great potential for recovering energy from wastewater that can be used to offset treatment energy demands (Logan and Rabaey, 2012; Pant et al., 2012). In an MEC, a biotic anode, populated with exoelectrogenic microbes that oxidize organic material and produce electrical current, is coupled with a hydrogen-evolving cathode (Liu et al., 2005; Rozendal et al., 2006). The reaction is not spontaneous and requires an additional applied potential of ~0.11 V, although potentials greater than 0.5 V are typically required due to internal resistance and electrode overpotentials (Logan et al., 2008).

A variety of wastewaters have been used in MECs, including domestic, swine farm, winery, food processing, industrial, landfill, and refinery effluents (Cusick et al., 2010; Ivanov et al., 2013; Liu et al., 2005; Mahmoud et al., 2014; Ren et al., 2013; Tenca et al., 2013; Wagner et al., 2009). Solid biomass can also be used to

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generate hydrogen in a two-step process combining dark fermentation with electrohydrogenesis, with increased yields and conversion efficiencies compared to dark fermentation alone (Lalaurette et al., 2009; Lu et al., 2009; Wang et al., 2011). Hydrogen recoveries and current densities vary among these different wastewaters, as their compositions can be significantly different (Cusick et al., 2010; Tenca et al., 2013). Chemical and biochemical oxygen demands are typical measures of organic strength and degradability in wastewater, but these tests are based on either complete chemical oxidation or biodegradation under aerobic conditions. MECs are anaerobic systems, and therefore treatment results using these tests may not directly relate to MEC performance (Ren et al., 2013). As a result, direct measurements in MECs are necessary to evaluate their performance with complex substrates.

Mini MECs (5 mL) were recently developed as an inexpensive platform for conducting high throughput MEC experiments (Call and Logan, 2011). Test procedures using mini MECs are also relatively simple compared to those needed with larger reactors. Mini MECs have been previously used to evaluate treatment performance of industrial and domestic effluents (Ivanov et al., 2013; Ren et al., 2013), but the treatability of these wastewaters has not been directly compared to that obtained with larger-scale reactors. In this study, the performance of mini MECs was directly compared with larger cube-type reactors used in many other MEC tests (Ambler and Logan, 2011; Call and Logan, 2008; Cusick et al., 2010; Wagner et al., 2009) for a variety of complex wastewaters and simple substrates. The goal was to evaluate the utility of mini MECs for screening treatability of wastewaters using simpler and cheaper procedures than those required for tests with the larger, cube-type MECs.

2. Methods

2.1. Effluent samples

Industrial wastewater (IW) samples from a polymer and performance chemical production facility were collected and shipped in cooled containers overnight to Penn State. Three samples (IW-1, IW-2 and IW-3) were collected from different locations within the wastewater collection and treatment operations at the chemical production facility. Sample IW-1 was collected from the onsite wastewater treatment system just before pH neutralization and wastewater treatment. IW-2 was collected at a point further upstream before all process effluents within the facility were combined. IW-3 was collected after pH neutralization (and prior to onsite wastewater treatment).

Effluent from a dark fermentation process (FE), generated by *Clostridium thermocellum* fed 1191 medium with synthetic cellulose (Avicel, 5 g/L), was produced at the National Renewable Energy Lab (NREL, Golden, CO, USA) and shipped overnight to Penn State (Levin et al., 2006). Domestic wastewater (DW) samples were collected from the outlet of the primary clarifier at the Pennsylvania State University wastewater treatment facility (University Park, PA, USA). DW was evaluated in MECs and also served as a pre-acclimation substrate to enrich MEC anodes prior to tests with other samples. Acetate medium (AC), containing 1 g/L of sodium acetate dissolved in 50 mM PBS (PBS; 2.45 g/L $NaH_2PO_4{\cdot}H_2O$, 4.58 g/L Na_2HPO_4) with additional nutrients (0.31 g/L NH_4Cl, 0.13 g/L KCl) and BOD nutrient buffer (Hach Co., Loveland, CO, USA), was used as a positive control, as its composition does not vary. All samples were stored at 4 °C prior to use in the experiments.

2.2. Reactor construction

Mini MECs consisted of 5 mL borosilicate serum bottles (Wheaton, Millville, NJ, USA) sealed with butyl rubber stoppers and aluminum crimp caps (Call and Logan, 2011) (Fig. S1a). Anodes were made of 1.0 cm × 1.5 cm × 0.32 cm graphite blocks (Grade GM-10; GraphiteStore.com, Inc., Buffalo Grove, IL, USA) connected to titanium wire current collectors (0.032 gauge; Malin Co., Brookpark, OH, USA) that extended through the rubber stopper. Cathodes were made of stainless steel mesh (Type 304, 50 × 50 mesh size; McMaster-Carr, Elmhurst, IL, USA) cut to the same projected area as the anodes, and connected to stainless steel wire current collectors (0.032 gauge; Malin Co., Brookpark, OH, USA).

Cube MEC reactors were made from 4-cm long by 3-cm diameter cylindrical polycarbonate chambers (Lexan, 32 mL liquid volume) with a 1.6-cm diameter by 7-cm tall glass tube glued to the reactor top to provide gas headspace (Call and Logan, 2008) (Fig. S1b). Carbon fiber brushes (2.5-cm diameter, 2.5-cm length, Panex 35 polyacrylonitrile fiber; Zoltek, St. Louis, MO, USA) with twisted core, titanium wire current collectors were used as anodes. Brushes were heat treated at 450 °C for 30 min before use to remove contaminants and create more favorable surface conditions for electrically active microbes (Feng et al., 2010). Cathodes were made of stainless steel mesh (Type 304, 50 × 50 mesh size; McMaster-Carr, Elmhurst, IL, USA) cut into 2-cm diameter discs with a total projected surface area of 12 cm^2 with 7 cm^2 exposed to solution. A 0.5 mg/cm^2 platinum catalyst layer [10% (w/w) Pt on carbon black, Vulcan XC-72; Fuel Cell Store, College Station, TX, USA] was applied to the anode facing (solution) side of the cathodes using Nafion as a binder [5% solution (w/w), 33.33 μL/cm^2; Sigma Aldrich, St. Louis, MO, USA]. Gas bags (0.1 L capacity, Cali-5 bond, Calibrated Instruments Inc., Hawthorne, NY, USA) were connected to the headspace with plastic tubing and needles to collect additional gas and maintain atmospheric pressure in the headspace.

2.3. Operation and measurements

Mini MECs were operated in triplicate, and cube MECs in duplicate, in a 30 °C controlled temperature room. Electrodes were connected to a programmable power supply (Model 3645A; Circuit Specialists Inc., Mesa, AZ, USA) with an applied potential of 0.7 V for mini MECs and 0.9 V for cube MECs, consistent with previous tests (Cusick et al., 2010; Ren et al., 2013). A multimeter (Model 2700; Kiethley Instruments Inc., Cleveland, OH, USA) connected to a computer was used to record voltage measurements across a 10 Ω resistor placed in series between the positive terminal of the power supply and anode of each reactor. Current was calculated using Ohm's law ($U = IR$; A), where U (V) is the measured voltage, I (A) is current and R (Ω) is external resistance. Current density (j; A/m^2) was normalized to the projected cathode area and averaged over the time to reach 90% charge accumulation ($I_{avg\text{-}90}$), as previously described (Ivanov et al., 2013). The total charge recovered over a batch cycle was calculated by integrating the current over the cycle length ($C_T = \sum I{\cdot}\Delta t$; C). Coulombic efficiency (CE) was based on the total charge measured and change in chemical oxygen demand over a cycle (Ivanov et al., 2013).

Anode biofilms were pre-acclimated using DW as an inoculum and substrate, as this procedure has been shown to reduce startup time and improve subsequent performance (Ren et al., 2013). Mini MECs were fed DW until current profiles were repeatable for multiple cycles, and then switched to the individual samples. Cube MEC anodes were acclimated in microbial fuel cells (MFCs) fed DW before being transferred into clean MEC reactor bodies with new cathodes, and then switched to the individual samples. MFCs used for anode acclimation were 4-cm polycarbonate chambers, like the cube MEC bodies, with a 0.5 mg/cm platinum [10% (w/w) platinum on carbon black, Vulcan XC-72; Fuel Cell Store, College Station, TX, USA] catalyzed air cathode, prepared as previously