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

MEC Reactors

Mini
Cube

5 mL
Graphite
SS mesh
1.5 cm²
0.7 V

Volume
Anode
Cathode
Cathode Area
App. Voltage

32 mL
Carbon brush
PVC on SS mesh
7 cm²
0.9 V

COD removal (mg/L) Coulombic Efficiency (%)

Industrial Wastewater
Fermentation Effluent
Domestic Wastewater
Acetate Medium

0 5000
0%
250%

6 mL Volume 32 mL
Graphite Anode Carbon brush
SS mesh Cathode Pt/C on SS mesh
1.5 cm² Cathode Area 7 cm²
0.7 V App. Voltage 0.9 V

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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/m³), 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...
generate hydrogen in a two-step process combining dark fermentation with electrohydrogenogenesis, with increased yields and conversion efficiencies compared to dark fermentation alone (Lalauvette 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 (Ren 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; Cusick 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 cellu-lose (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 NaH2PO4, H2O; 4.58 g/L Na2HPO4) with additional nutrients (0.31 g/L NH4Cl, 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 x 1.5 cm x 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 x 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 dia-ter cylindrical polycarbonate chambers (Lexan, 32 mL liquid vol-ume) 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 x 50 mesh size; McMaster-Carr, Elmhurst, IL, USA) cut into 2-cm diameter discs with a total projected surface area of 12 cm² with 7 cm² exposed to solution. A 0.5 mg/cm² 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/cm²; Sigma Aldrich, St. Louis, MO, USA]. Gas bags (0.1 L capacity, Call-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; Keithley 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/m²) was normalized to the projected cathode area and averaged over the time to reach 90% charge accumulation (Iavg, 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 (Ci = ∑j(t)dt). 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/cm² platinum [10% (w/w) platinum on carbon black, Vulcan XC-72; Fuel Cell Store, College Station, TX, USA] catalyzed air cathode, prepared as previously
described (Cheng et al., 2005). A 1000 Ω load was used as the external resistance during MFC operation.

Substrate was typically replaced in the MECs when the current in at least one reactor (two for mini MECs) in a replicate set decreased to less than 0.02 mA for the mini MECs and less than 0.2 mA for the cube MECs. After each batch cycle with mini MECs, effluent was removed, replaced with fresh substrate, and headspaces were sparged for 2 min with an 80:20 N2/CO2 gas mixture to remove oxygen and residual hydrogen and methane. After cube MEC batch cycles, gas concentration and composition was analyzed, effluent was removed, replaced with fresh substrate, and headspaces were sparged for 20 min with ultra-high purity N2 gas. Gas bags used with the cube MECs were sparged by filling with ultra-high purity N2 gas and vacuuming empty three times in succession.

A gas chromatograph (GC) (Model 310; SRI Instruments, Torrance, CA, USA) with argon as a carrier gas and a 6-foot molecular sieve packed 5A column was used to measure gas concentrations of H2, CH4 and N2 after cycles in cube MECs. A GC with helium as a carrier gas and a 6-foot Porapak Q column was used to measure CO2 concentrations. Gas composition was determined by taking duplicate samples from the cube reactor headspace and gas bag with an airtight syringe (0.5 mL Gastight syringe; Hamilton Co., Reno, NV, USA) and injecting into the GCs (Ambler and Logan, 2011). Gas quantity was determined using the known headspace volume (10 mL) and a gas bag method based on initial nitrogen gas concentrations (Ambler and Logan, 2011). Cathodic and overall gas conversion efficiencies for methane and hydrogen combined and hydrogen only were calculated as previously described (Wagner et al., 2009).

Influent and effluent chemical oxygen demand (COD) was measured using a standard chromic acid colorimetric method (Hach Co., Loveland, CO, USA). A three-day headspace biochemical oxygen demand (HBOD3) test was used to determine influent and effluent biochemical oxygen demand (BOD) (Logan and Patnaik, 1997). The HBOD3 test has been shown to provide results that are consistent with a conventional five day BOD test with less labor, time and without sample dilution (Logan and Patnaik, 1997; Min et al., 2004). Primary clarifier effluent was used to provide an adequate microbial seed in all HBOD3 vials, and it was added in a 50:50 (v/v) ratio to the samples. COD and HBOD3 were measured once stable and repeatable current profiles were observed for consecutive batch cycles. Sample pH and conductivity were measured using a probe (Orion Versastar; Thermo Scientific, Waltham, MA, USA; SB90M5 SympHony; VWR, Radnor, PA, USA).

2.4. Calculations

Measurements from mini and cube MECs were compared using statistical methods to determine the relationship between the two reactor types. Organic treatment, current generation, cycle length and efficiency were compared between the two reactor types using a two-sample Student’s t-test, assuming unequal variances. A significance level of α = 0.01 was used to determine if the means of the measurements were different between reactor types for each substrate sample. Linear regression using the least squares method was used to relate the means of COD removal, CE, I(avg-90) and effluent COD measurements in mini and cube MECs. Linear regression was also used to compare the mean hydrogen recovery to HBOD removal for each substrate sample in the cube MECs.

3. Results and discussion

3.1. Wastewater characteristics

Initial organic concentrations of the fermentation effluent (FE), industrial wastewater (IW), domestic wastewater (DW) and acetate (AC) samples were 450–7200 mg/L of COD (Fig. S2). The raw fermentation effluent had the highest COD concentration of 7180 ± 100 mg/L, and it was therefore diluted in 50 mM PBS to 1230 ± 70 mg/L before being used in MEC tests to shorten the cycle length, as well as provide buffering capacity and solution conductivity. Although PBS addition is not practical for wastewater treatment applications, it was used to dilute the FE sample to provide an intermediate condition between a more ideal fuel (AC) and actual wastewaters (IW, DW) by simulating the organic complexity of real wastewaters with the buffering capacity and conductivity of an ideal substrate. Sample IW-2 also had a high initial organic concentration of 6750 ± 100 mg/L of COD, it produced little current, and it had long cycle times in MEC tests (Fig. S3). After ~40 days of reactor tests, IW-2 was diluted in a sodium chloride solution to 1450 ± 40 mg/L of COD in an effort to reduce cycle time, while maintaining solution conductivity. Sodium chloride solution was prepared to match the conductivity of the full-strength IW-2 sample (3:1 ratio of NaCl:IW-2, v/v).

Initial pH for the IW-3, FE, DW and AC samples ranged from 7.0–8.2. Samples IW-1 and IW-2 had an initial pH below 5.5 (Fig. S4a), which was outside the optimal range for exoelectrogentic microbes (He et al., 2008). To ensure that MEC performance was not inhibited by low pH, IW-1 and IW-2 were neutralized to pH 7.3 with 0.3 M NaOH before tests in MECs. Solution conductivity, measured after pH and organic concentration adjustments, ranged between 0.7–1.9 mS/cm for the non-buffered wastewater samples (IW-1, IW-2, IW-3, DW) and 3.7–4.0 mS/cm for the FE and AC samples (Fig. S4b).

Influent COD and HBOD3 concentrations of the samples as they were used in MECs ranged between 450–4500 mg/L of COD and 230–790 mg/L of HBOD3 (Fig. 1). Of the six samples tested, the three industrial wastewater samples (IW-1, IW-2, IW-3) had the highest influent COD concentrations, all exceeding 1400 mg/L. The COD/HBOD3 ratios provided insight into the aerobic biological degradability of the organic material in each sample, with lower values indicative of a more easily degradable substrate. IW-1 and IW-3 had COD/HBOD3 ratios greater than 5, meaning a significant portion of the COD was not readily degradable under aerobic conditions within 3 days. AC, which contained organic matter that was readily degraded, had a COD/BO D3 of 1.3, and all other samples had ratios below 3.

3.2. COD removal and coulombic efficiency

Between 66–92% of the influent COD was removed in mini MECs, and 74–90% in cube MECs over a fed-batch cycle with each sample (Fig. 2a). Average cycle length varied between samples and
was generally 2–11 days (Fig. 2b). Effluent COD concentrations from MECs fed the IW samples ranged from 360–780 mg/L, which was higher than the rest of the samples tested (Fig. 2c). IW-2 and IW-3 had significantly lower effluent COD concentrations in cube MECs than mini MECs, while FE and AC were significantly lower in mini MECs (T-test, p < 0.01). IW-1 and DW effluent COD concentrations were not significantly different between mini and cube MECs. The differences in COD removals between the mini and cube MECs with the IW-2 and IW-3 samples could have been a result of gas buildup in the headspace of the mini MECs. Increased gas pressures could have inhibited gas production and COD removal compared to cube MECs that had gas bags to maintain atmospheric headspace pressure. MECs fed the AC sample had the lowest effluent COD concentration and highest overall removal, which was expected because acetate is readily degraded by exoelectrogens. IW-3 had the highest influent COD concentration and COD/HBOD3 ratio, but had the second highest COD removal of 82 ± 5% in the mini and 86 ± 2% in the cube MECs.

Average coulombic efficiencies (CE) varied significantly between reactors fed different samples, ranging from 23–169% in the mini MECs and 18–132% in the cube MECs (Fig. 2d). Coulombic efficiencies with IW-1 and IW-3 were 38 ± 3% and 23 ± 6% in mini MECs and 41 ± 2% and 18 ± 3% in cube MECs. The low CE with these samples indicates that a large portion of COD removal was not due to current generation, but instead it was due to reactions other than anode respiration. Open circuit cycles confirmed significant COD removal in the absence of current generation for the IW-1 and IW-3 samples (Fig. S5). The CEs for IW-2 in the mini and cube MECs exceeded 100% (169 ± 60% and 115 ± 11%), suggesting that microbial hydrogen oxidation at the anode was contributing to the measured current density. Oxidation of hydrogen evolved at the cathode by exoelectrogenic microbes on the anode, also known as hydrogen cycling, is an issue in single chamber MECs since there is no physical separator (such as a membrane) between the anode and cathode (Lee and Rittmann, 2010). The average CE with the DW sample was also greater than 100% in cube MECs (132 ± 19%), but was 89 ± 7% in the mini MECs. Current was unstable at the end of later DW-fed cube MEC cycles, while current in mini MECs fed DW was stable (Fig. S6). Erratic current production in the cube MECs fed DW likely contributed to the difference in CEs between mini and cube reactors, although it is not known why this was only observed with DW-fed MECs.

### 3.3. Current generation

Average current densities, calculated over the time to 90% charge accumulation ($I_{\text{avg-90}}$), varied between wastewater samples and reactor types. $I_{\text{avg-90}}$ current densities were higher in cube
MECs for all samples (except IW-1), which could be partially attributed to the platinum catalyst layer used on the cathodes in the cube MECs (Fig. 3a). The time to achieve 90% charge accumulation ($t_{90}$) in mini MECs was also longer than those in the cubes with IW-2, IW-3, and FE, which could have contributed to the difference in average current density between mini and cube reactors (Fig. S7). AC and FE samples produced the highest current densities of the samples tested in both mini and cube MECs. IW-1, IW-2, and IW-3 average current densities in both mini and cube MECs were significantly less than AC, but still greater than DW.

The energy required for organic treatment, which was based on the additional energy added to the MECs through the external power supply, was highest in MECs fed IW-2 and DW (Fig. S8). The high treatment energy observed in these samples was likely due to hydrogen cycling, which generates current without oxidizing organic material. The energy requirements for the IW-1, IW-3, FE, and AC samples varied between substrates, but were generally slightly higher in cube MECs due to the difference in applied potential. Total charge recovered, normalized to the reactor liquid volume, also varied between individual samples, but was reasonably consistent between cube and mini MECs fed IW-1, IW-2, FE, and AC (Fig. 3b). There was no significant difference (T-test, $p > 0.03$) in total charge normalized to the liquid volume between mini and cube MECs for samples IW-2, IW-3, FE, and AC.

Charge accumulation, which is the coulombs transferred through the circuit at a given time expressed as a percentage of the total coulombs recovered over the cycle, was consistent between reactor types with ideal substrates, but different for the real wastewater samples. AC and FE, which were buffered and contained easily degradable organic material, exhibited similar profiles in both mini and cube MECs, with a nearly linear initial period followed by a plateau (Fig. 3c). DW fed reactors showed reasonable agreement between charge accumulation profiles, but the charge profiles did not exhibit a pronounced plateau like those observed with AC and FE solutions (Fig. S9). Charge accumulated faster in the cube MECs fed IW-2 and IW-3 than in the mini MECs, but the opposite was observed for IW-1 with faster charge accumulation in the mini MECs (Fig. 3d). Cube and mini MECs fed IW-2 and mini MECs fed IW-3 also showed a non-linear response at the beginning of cycles, indicating that there was some lag time before the maximum charge accumulation rate was obtained. This would suggest that the organic material in the

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**Fig. 3.** (a) Current density averaged over the time to 90% charge accumulation ($I_{avg-90}$) and (b) total charge recovered (normalized to the reactor liquid volume) over batch cycles with various substrates in mini and cube MECs. Representative plots of charge accumulation in triplicate mini and duplicate cube MEC reactors as a percentage of the total coulombs measured over a cycle for each substrate are shown for AC, which exhibited a similar response in both mini and cube MECs, and IW-3, which was not similar.
IW-2 and IW-3 samples was degraded at a slower rate than other samples. The different profiles for the mini and cube MECs with complex substrates indicated that performance differences between reactor types are primarily due to the substrate, but the reactor design is also a factor.

3.4. Comparison of mini and cube MEC treatment performance

Treatment performance and efficiency in mini and cube MECs was examined using a linear regression to determine if there were significant performance correlations between the two reactor designs. Total COD removal and CE were significantly related \((R^2 > 0.99, p < 0.01)\) for the reactor types (Fig. S11a). Average current density with AC was significantly higher in both mini and cube MECs than the FE, IW, and DW samples. When AC was not included in the regression, the relationship for average current density was no longer significant \((R^2 < 0.6, p > 0.12)\), indicating that the trend was disproportionately influenced by the AC values. Effluent COD with the IW samples was lower in the cube MECs than the mini MECs, while effluent COD with the DW, AC, and FE samples was lower in the mini MECs. The values for effluent COD concentration were reasonably well distributed, but the residuals showed a trend with organic strength, indicating that COD removal efficiency in the mini MECs may have been influenced by the organic concentration of the substrate (Fig. S10b).

The difference in effluent COD concentration between the mini and cube MECs could also be due to other characteristics of the wastewater samples since only a small number of samples were examined in this study, and because the IW samples all came from the same facility.

3.5. Gas recovery in cube MECs

Measurable concentrations of hydrogen and methane were observed in cube MECs with each individual sample. Total measured biogas volume was greatest in the IW fed MECs, although more methane than hydrogen gas was measured with IW-1 and IW-3 (Fig. 5a). Cube MECs with IW-2 generated 24 ± 10 mL of hydrogen over batch cycles, which was similar to AC (22 ± 3 mL), but cycle time was significantly longer at nearly 8 days with IW-2 versus ~2 days with AC. There was a significant \((R^2 = 0.90, p < 0.01)\) relationship between HBOD\(_5\) removal and volume of hydrogen gas recovered, but the measured gas volume was inconsistent over multiple cycles with some samples (Fig. 5b). Measured hydrogen gas volumes with MECs fed IW-1, IW-2, and DW were the most inconsistent over time, as exhibited by large standard deviations relative to the average.

The energy contained in the recovered hydrogen and methane gas, based on the heat of combustion \((\Delta H_{H_2} = 285.8 \text{ kJ/mol}, \Delta H_{CH_4} = 891 \text{ kJ/mol})\), exceeded the energy that was added through the power supply with all samples, except DW (Fig. S12). When the efficiency was computed using just the recovered hydrogen, only the MECs fed AC exceeded 100%, although this does not account for hydrogenotrophic methanogenesis, which would reduce the hydrogen yield. The energy efficiency also does not account for the energy in the substrate. Using the heat of combustion to estimate the energy content of the gas also assumes that the gas is converted into energy, but hydrogen is a valuable product that can be used for other processes.

Cathodic hydrogen recovery \((r_{H_2, cat})\) represents the fraction of current that was recovered as hydrogen gas, while the overall hydrogen recovery \((r_{H_2, COD})\) is based on the total COD converted to hydrogen. Cathodic hydrogen recovery was less than 40% for all samples except AC, which had a 67% hydrogen gas recovery (Fig. 6a). The combined cathodic recovery for both hydrogen and methane \((r_{H_2, cat} + r_{CH_4, cat})\) was 96% for the FE and AC samples, indicating that nearly all the generated current went into gas production (Fig. 6b). Most of the methane generated in IW-1 and IW-3 fed MECs was likely from direct methanogenesis of the substrate since combined cathodic recoveries were well over 100%, and substantial methane production occurred in open circuit controls (Fig. S13). Hydrogen gas cycling between the anode and cathode for the DW and IW-2 samples, which results in current generation without net gas production, most likely contributed to low cathodic gas recoveries of 37% and 74%. Nearly all the COD removed in cube MECs for IW and AC samples was converted to gas, with an overall gas recovery \((r_{H_2, CH_4, COD})\) of 84–94% (Fig. 6b). Overall gas recovery
was 72% with FE and only 48% with DW fed MECs. Alternative electron acceptors, like oxygen, nitrate, and sulfate, could have contributed to the low overall gas recoveries for these samples, but these species were not analyzed in this study as the focus was on treatment efficiency.

Current, COD removal and gas production in an MEC should be proportional to each other if alternate electron acceptors are not available for substrate removal. This was observed here for MECs fed AC, as nearly all of the electrons generated from organic oxidation at the anode were measured as current through the external circuit and recovered as gas, with coulombic efficiencies, cathodic gas recoveries, and overall gas recoveries between 94–99%.

Results for MECs fed domestic and industrial wastewater were less consistent. In MECs fed IW-1 and IW-3, electrons recovered in the gas exceeded those measured as current due to direct substrate methanogenesis. Hydrogen cycling in MECs fed IW-2 and DW resulted in current generation that did not translate to gas production. Therefore, while COD removal was consistent with current generation and gas production in MECs fed ideal substrates, real wastewaters were more complex and the relationship between these performance parameters was less predictable.

4. Conclusions

Organic removal and treatment efficiency in mini MECs corresponded well to performance in cube reactors despite differences in materials and applied potentials. COD removal and coulombic efficiency for individual samples were significantly correlated between reactor types. Average current density was related between mini and cube MECs, although the cathode catalyst layer and higher applied potential contributed to generally higher current density in cube MECs. Current recovery was similar between mini and cube MECs fed well-buffered samples, but significantly different with industrial effluents. Mini MECs were useful for evaluating substrate performance and provide a simpler, cheaper procedure for screening wastewater samples.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2014.08.028.

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