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BIOENERGY AND BIOFUELS

Performance of a pilot-scale continuous flow microbial electrolysis cell fed winery wastewater

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Abstract A pilot-scale (1,000 L) continuous flow microbial electrolysis cell was constructed and tested for current generation and COD removal with winery wastewater. The reactor contained 144 electrode pairs in 24 modules. Enrichment of an exoelectrogenic biofilm required ~60 days, which is longer than typically needed for laboratory reactors. Current generation was enhanced by ensuring adequate organic volatile fatty acid content (VFA/SCOD≥0.5) and by raising the wastewater temperature (31±1°C). Once enriched, SCOD removal (62±20%) was consistent at a hydraulic retention time of 1 day (applied voltage of 0.9 V). Current generation reached a maximum of 7.4 A/m^3 by the planned end of the test (after 100 days). Gas production reached a maximum of 0.19±0.04 L/L/day, although most of the product gas was converted to methane (86±6%). In order to increase hydrogen recovery in future tests, better methods will be needed to isolate hydrogen gas produced at the cathode. These results show that inoculation and enrichment procedures are critical to the initial success of larger-scale systems. Acetate amendments, warmer temperatures, and pH control during startup were found to be critical for proper enrichment of exoelectrogenic biofilms and improved reactor performance.

Keywords Biohydrogen · Biomethane · Bioelectricity · Microbial electrolysis cell · Bioenergy

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Introduction

A microbial electrolysis cell (MEC) is an emerging technology capable of converting the soluble organic matter in wastewater to storable energy such as H_2 (Call and Logan 2008) or CH_4 (Clauwaert and Verstraete 2009; Cheng et al. 2009). MECs contain an anode, where microbes catalyze the release of electrons from organic matter, and a cathode, where electrons are consumed in the hydrogen evolution reaction (Liu et al. 2005b) or by methanogenesis (Cheng et al. 2009). The open circuit potential of an MEC anode (ca. −0.3 V at standard conditions) (Liu et al. 2005a) cannot overcome the minimum potential for hydrogen evolution (−0.4 V) under normal operating conditions. As a result, hydrogen production from an MEC requires supplemental voltage from an external power source (Liu et al. 2005b). In MECs, methane generation can occur via hydrogenotrophic methanogenesis (Prathap et al. 2009) or the direct conversion of protons, CO_2, and electrons with a methanogenic biocathode (Cheng et al. 2009). The direct conversion of electrical current into methane requires an applied voltage more negative than −0.7 V (Cheng et al. 2009).

Advances in MEC reactor design and electrode materials have lowered material costs and improved hydrogen production rates and electrical efficiency. The use of a single-chamber MEC design increased hydrogen production from 0.02 L/L/day (Rozendal et al. 2006) to 1.5± 0.02 L/L/day at an applied cell voltage (E_{ap}) of 0.5 V (Call and Logan 2008). Electrical efficiencies have reached as high as 406±6% (E_{ap}=−0.3 V) in fed batch, single-chamber MECs with acetate (Call and Logan 2008). MEC cathode costs have been significantly reduced by replacing Pt catalyst-loaded carbon cloth with high surface area (650 m^2/m^3) stainless steel (SS) brushes (Call et al. 2009a) or woven SS mesh (Zhang 2010). Using SS brush cathodes hydrogen (1.7±0.1 L/L/day) and current (188± 0.1 A/m^3) were generated in a membrane-less single-chamber MEC at high electrical efficiencies (221±8%, E_{ap}=−0.6 V) (Call et al. 2009a). When SS mesh (#60 mesh) was used as a cathode in a single-chamber MEC, specific surface area of the cathode per volume of reactor was lower than with brushes, but hydrogen production (2.1±0.1 m^3/m^3/day), current density (188±19 A/m^3), and electrical efficiency remained relatively high (173±14%, E_{ap}=−0.9 V) (Zhang 2010).

Investigations of energy recovery from actual wastewaters using MECs have been limited to laboratory-scale experiments (liter or milliliter volumes) and relatively optimal operational conditions. Most tests have been conducted with specific chemicals such as acetate (Call and Logan 2008) and glycerol (Selembo et al. 2009) serving as electron donor, and only in a few instances MECs have been tested with actual wastewaters such as potato chip (Kiely et al. 2011), swine (Wagner et al. 2009), domestic (Ditzig et al. 2007), and winery wastewaters (Cusick et al. 2010). Optimized conditions for maximizing hydrogen production include running tests at higher temperatures (30°C), using carbon cloth cathodes with a Pt catalyst, and choosing operational conditions that help to limit methane production such as air exposure of the cathode after each fed batch cycle (approximately every 1 or 2 days).

The development of bioreactors that can operate under highly dynamic conditions of variable wastewater flow and composition requires the use of larger-scale systems. Based on the success of the laboratory tests with wastewaters, and the need to better understand how reactor performance might be translated from the laboratory to practical applications, it was decided that a pilot-scale test would be conducted to better explore limits of current MEC designs and materials. A single-chamber MEC (0.03 L) fed winery wastewater showed reasonably good performance in laboratory tests under fed batch conditions, producing 17 A/m^3 and hydrogen gas at a rate of 0.17 L/L/day (Cusick et al. 2010). Since the winery had available space and a good location for a pilot-scale reactor, it was decided to test a larger MEC at this site. The reactor was designed to have the best performing architecture and the most promising low-cost materials known at that time (January, 2009). Therefore, we used a single-chamber MEC equipped with graphite fiber brush anodes (Logan et al. 2007) and SS mesh cathodes (Zhang 2010) under continuous flow conditions, even though this architecture and these operating conditions had not been tested together with this wastewater in the laboratory. The operation of the winery limited our time to conduct tests beforehand, as most wastewater production occurs during the latter months of the year (see below). This production cycle also limited the duration of field tests to ~100 days, a period of time consistent with other economic constraints for conducting field tests.

The main engineering goal of the pilot test was to determine whether current densities typically obtained in the laboratory with wastewaters could be obtained in the field from a scaled up version of the laboratory architecture. Notable differences between the laboratory and pilot reactor architectures were: (1) the electrodes needed for the larger reactor were much longer than those used in the laboratory, (2) multiple electrodes in module configurations had not been tested, (3) insulators were needed to prevent electrodes from short circuiting due to the water flow, (4) SS cathodes had not previously been tested with a winery wastewater, and (5) the wiring and connections were all much different from those used in laboratory-scale systems. Although hydrogen gas production was the ultimate goal for the MEC, it was realized that a single-chamber architecture and operational conditions could lead to methane production (Chae et al. 2009; Rader 2010). However, given all the other uncertainties about scale up, the need to move this technology forward took precedence and it was decided to test this larger architecture to evaluate performance parameters relative to current production per total electrode surface area, COD removal, and operational stability. We therefore describe here the first ever tests using a 1,000 L, single-chamber MEC fed an actual wastewater, and the conditions that were needed to ensure reactor startup, operation, and current production.

Materials and methods

Field site Field tests were conducted at the Napa Wine Co. (NWC), in Oakville, CA, USA. The NWC crushes 6.4×10^6 kg (7,000 tons) of grapes annually and produces approximately 5.1×10^4 m^3 (13.5 MG) of wastewater per year, the majority of which is produced during the harvest season (August–November). On site wastewater treatment (via aerobic biological oxidation) consumes approximately 654,000 kWh/year of electricity.

Pilot-scale MEC reactor design A water storage tank and the MEC reactor vessel were fabricated from steel-reinforced, high-density polyethylene by Fabtech Plastic & Metals (Ramsey, MN, USA), and shipped to the test site. The rectangular reactor was 0.7 m (28 in.) in height, 0.64 m (24 in.) in width, and 2.3 m (8 ft, 8 in.) in length, and contained 24 electrode modules (Fig. 1). The reactor lid was bolted to the reactor and sealed with 7.6 cm of water to prevent gas leakage. The total reactor volume was 1,000 L, with a working liquid volume of 910 L (90 L of electrode displacement). The raised lid added an additional 280 L of volume. To ensure a water seal at the lid–reactor junction as well as minimize headspace, the water level was maintained 2 cm below the top of the lid resulting in a total liquid volume of ~1,100 L and a headspace volume of 47 L. The pilot-scale MEC reactor was constructed and operated in an outdoor area near a wastewater collection sump.

Wastewater from the facility all flows to a central sump, where it is then pumped to the aeration ponds for treatment. Wastewater fed to the reactor was pumped from the wastewater collection sump to a storage tank (0.5 m^3) prior to being pumped into the reactor (1 m^3; Fig. 2a). During continuous flow operations, a peristaltic pump (Cole Parmer, Vernon Hills, IL, USA) fed wastewater from the storage tank into the reactor through flexible polypropylene tubing (1.9 cm I.D.) at a continuous rate (1 m^3/day) to maintain a 1-day hydraulic retention time (HRT). The reactor design included diffusion and baffle plates to promote more uniform flow through the reactor and the electrode modules. A diffusion plate (0.6 cm diameter holes, 30% open area) was installed 15.2 cm into the flow length to achieve more uniform flow prior to the module region of the reactor. Flow passed through 24 electrode modules, each oriented perpendicular to the flow path, along the 2.1 m of flow length. To reduce short-circuiting flow through a 3-cm space between the bottom of the electrode modules and the reactor floor, five baffle plates of increasing height (20, 31, 41, 51, and 56 cm) were installed at distances from the inlet of 50, 91, 132, 173, and 214 cm. Reactor mixing, chemical additions, and enhanced substrate distribution were accomplished through a recirculation line installed on the sidewall of the reactor that withdrew water from the end of the tank and returned it to the midpoint and influent regions of the reactor. Substrate recirculation was maintained throughout the field study at an approximate rate of 0.82 m^3/day (9.5 L/min).

Twenty-four electrode modules were operated in parallel within the MEC, with each electrode module containing six anodes and six cathodes for a total of 144 electrode pairs. The electrodes were positioned on opposite sides of a 0.7× 0.6 m perforated plastic frame (Fig. 1). Strips of glass fiber matting (1 mm×5 cm×0.7 m, Nippon Sheet Glass Co, Ltd., Japan) were placed between the anode and plastic frame to prevent short circuiting between electrode pairs. Anodes were made of graphite fiber brushes (D= 5.1 cm, L=66 cm, Panex 35/titanium wire, Gordon Brush, CA, USA), and cathodes were made of SS 304 (mesh #60, W=7.6 cm, L=66 cm, McMaster-Carr, OH, USA). Prior to

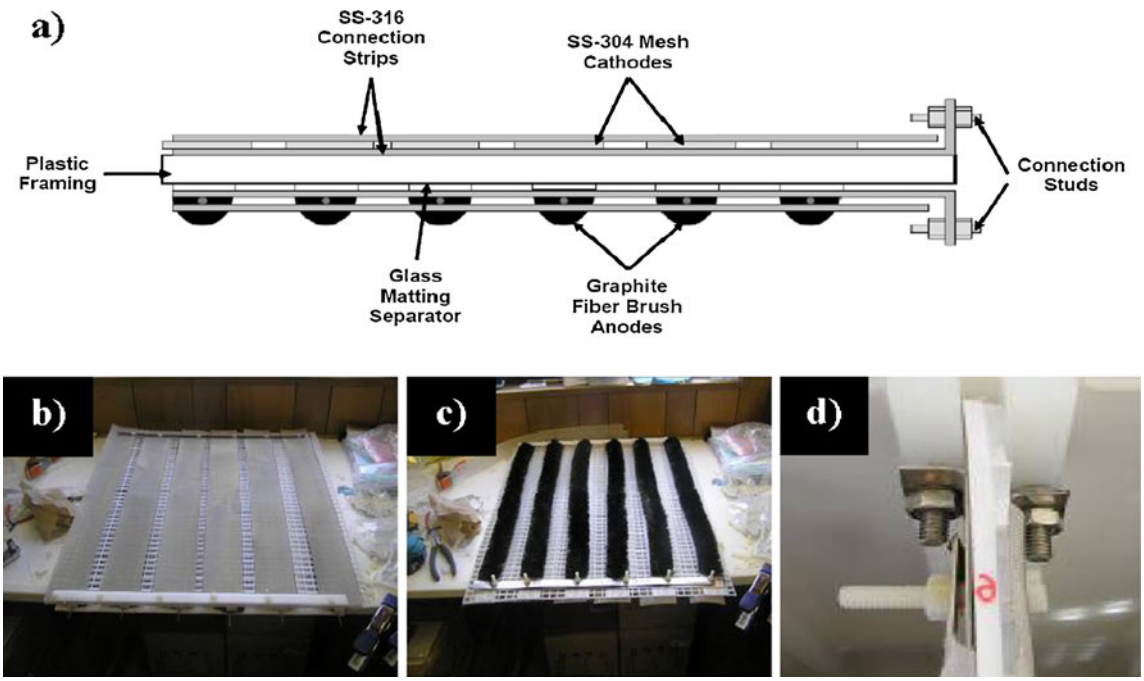

Fig. 1 **a**) Schematic of constructed electrode modules and pictures of **b**) cathode side and **c**) anode side of a module as well as **d**) bolting within the reactor

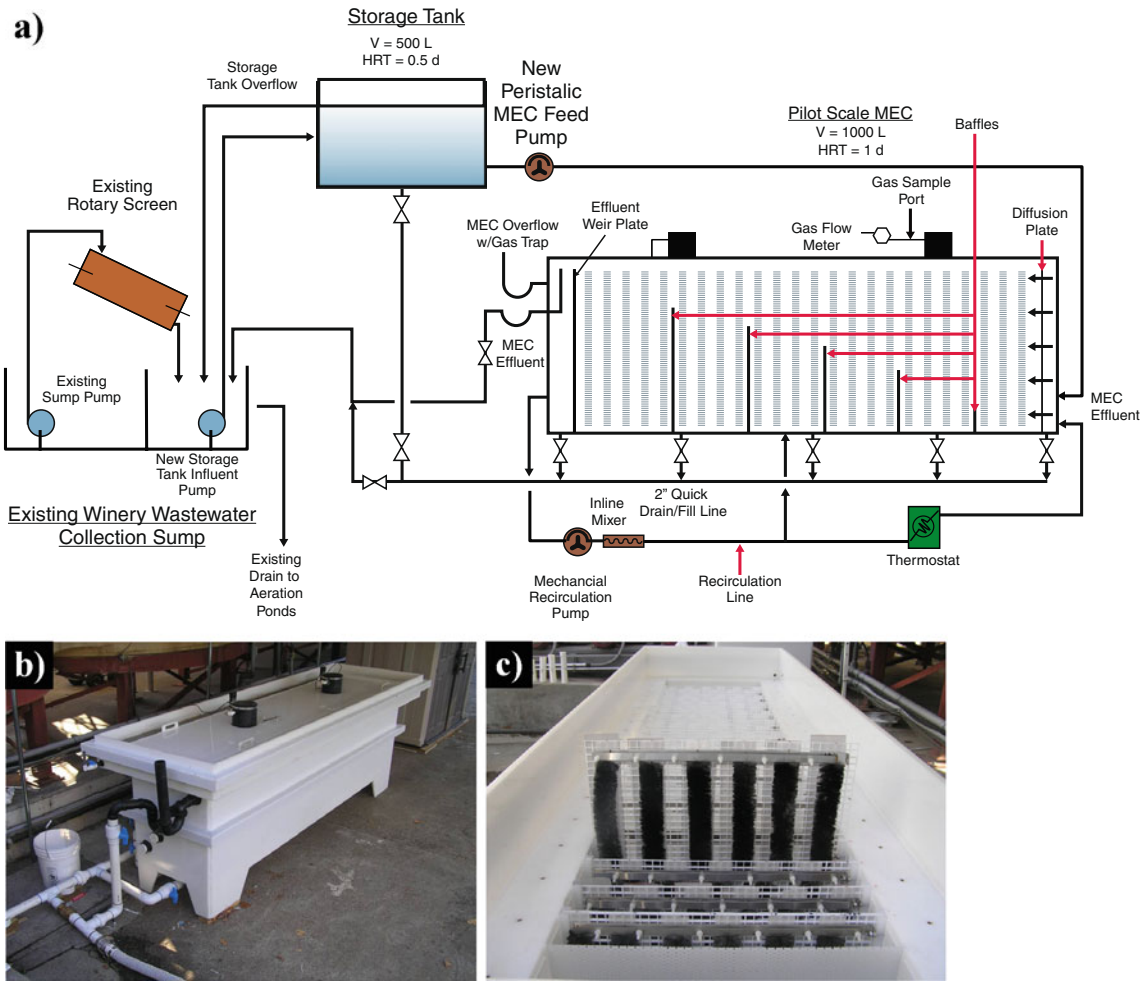

Fig. 2 **a**) Process flow schematic of pilot-scale MEC, **b**) overview picture of reactor, and **c**) module orientation within reactor

use, all 144 anodes were heat treated. Optimal heat treatment in the laboratory for the brush anodes was reported as 450°C for 30 min (Wang et al. 2009). Due to time constraints and the size the brushes, heat treatment was conducted in a conventional oven at 290°C for 1 h (maximum possible for this oven).

The anodes and cathodes of each module were electrically connected in series (Fig. 1) by pressing individual electrodes between two solid strips of SS 316 that functioned as current collectors (0.2×1.3×61 cm). This electrode arrangement resulted in a projected cathode area 0.050 m^2 per module, with a total of 24 modules, for a total of 7.2 m^2 for the entire reactor. The actual specific cathode surface area, estimated from the mesh size, wire diameter, and pore size (Zhang 2010) was 18.1 m^2/m^3 of total reactor volume. Electrodes were secured by attaching the current collection strips to the top of the plastic framing and plastic strips at the bottom of the module framing with plastic bolts (Fig. 1d). Following construction, modules were inserted into individual slots within the reactor. The anode and cathode current collectors were then bolted to the reactor wall using 1.3 cm (0.5 in.) stainless steel studs (Fig. 1d) to secure the modules in place and to provide an electrical connection between the electrodes and external power sources.

Reactor inoculation In laboratory tests, successive transfers from one MEC or MFC to another are often used to reduce startup time of a reactor (Liu et al. 2008; Logan et al. 2008). However, there was no reactor of sufficient size to provide an inoculum for this reactor. Therefore, various inocula and feed adjustments were used to add or enrich exoelectrogenic bacteria during the startup period for the reactor. The original inocula were raw wastewater (day 0, September 11, 2009) followed by sludge from the first aeration pond at the winery (300 L, day 4) and activated sludge from the local wastewater treatment plant (500 L, days 8 and 15). Research has shown that *Geobacteraceae*, which have previously dominated mixed culture MEC anode communities (Cusick et al. 2010; Kiely et al. 2011; Call et al. 2009b), can be grown using acetic acid and fumarate. We therefore developed an additional inoculum in a smaller tank

(210 L barrel) to stimulate the growth of *Geobacteraceae* by incubating wastewater with fumarate (8 g/L) and acetic acid (1.4 g/L; in $NaHCO_3$, 5 g/L) for 7 days, and adding the drum contents to the reactor on day 15.

Analytical procedures Each module was connected to a single power source, forming 24 independent circuits, with each module separately measured for current generation. Power supplies (1665; BK Precision, USA) were used to apply a constant voltage of 0.9 V across each module. The voltage (E) of each module was measured across an external resistor (0.01 Ω) every 20 min using a multimeter (2700; Keithly, USA) connected to a computer. Current (I) was calculated using $I=E/R$, where R is external resistance.

Biogas production (L/min) was initially measured using two thermal mass gas flow meters (McMillan, USA) that transmitted a pre-calibrated voltage reading to the multimeter. Biogas was not cleaned or dried prior to measurement, and as a result the flow meter eventually corroded and malfunctioned. The meters were replaced on day 71 with a 50-mL bubble flow meter (20136; Restek, USA). Biogas samples were collected from two sampling ports on top of the reactor, with composition determined as previously described (Call and Logan 2008). The energy content (Wh/L/day) of biogas was determined by first converting gas composition and production to specific gas production (L_{H2}/L/day, L_{CH4}/L/day) and then converting to energy density with the lower heating values (NIST 2008) of hydrogen (3.0 Wh/L_{H2}) and methane (10 Wh/L_{CH4}). Energy content (Wh/L/day) was converted to energy density (W/m^3 reactor) for comparison with energy input. Energy input was determined from the added voltage as previously described (Call and Logan 2008). Multiparameter probes (Pro Plus; YSI, USA), installed in the storage tank and effluent region of the reactor, were used to measure solution temperature, pH, and conductivity every 15 min.

Liquid samples were collected daily from the sump, storage tank, and the reactor (influent and effluent). Soluble chemical oxygen demand (SCOD) was measured (duplicate samples) using standard methods (TNT plus COD Reagent; HACH Company). Volatile fatty acids (VFA), residual sugars (fructose/glucose) and ethanol were determined daily by winery staff. Ethanol was determined from an IR spectrum (Anton PAAR, Alcolyzer, VA, USA), VFA was measured by acidic distillation (Astoria II, Astoria Pacific, OR, USA), and residual sugars were quantified with an enzymatic analyzer (Awareness Technology Inc, Chemwell, FL, USA). A recirculation rate of 9.5 L/min was used to produce well-mixed conditions within the MEC reactor, evaluated on the basis of SCOD, VFA, residual sugars, and ethanol, of daily samples from the influent and effluent regions of the reactor. SCOD removal was calculated as the difference between SCOD in the storage tank and reactor effluent.

Theoretical hydrogen gas production was calculated on the basis of stoichiometric conversion of electrical current to hydrogen. Theoretical methane production was based on the conversion of 8 mol of electrons and protons and 1 mol of CO_2 to methane by either hydrogenotrophic methanogenesis or electromethanogenesis.

Results

Current generation during reactor startup Reactor startup under field conditions was much slower than in the laboratory (Cusick et al. 2010), and several steps were taken to improve operational conditions. Inoculation of the reactor with wastewater, sludges and enrichments did not produce a current of more than 0.4 A/m^3 for the first 20 days when the reactor was operated in fed batch mode. Laboratory reactors have operated well with these types of inocula, and thus a lack of suitable bacteria was not considered to be a factor. Continuous flow operation was initiated on day 21 and maintained for the remainder of the field study. Following inoculation, two factors were thought to limit performance: pH and temperature. MFCs operated at a pH below 6 produce little current (Gil et al. 2003), and no studies have examined the effect of pH on startup. Therefore, on day 21, we added a buffer (Na_2HPO_4) to maintain pH>6 (days 21−37). Due to economic constraints, phosphate buffer addition was then discontinued and pH was controlled by diluting wastewater with boiler water to stabilize reactor pH at >6 (days 38 to 45). This also lowered the SCOD to a range used in laboratory experiments with this wastewater (1–2 g COD/L; (Cusick et al. 2010)). Current production ranged from 0.1 to 0.3 A/m^3, suggesting that pH and organic load were not limiting startup. Warmer temperatures (20–30°C) are required during startup of laboratory MFCs in order to obtain good performance (Cheng et al. 2010). Therefore, on day 43, a thermostat and heater were installed on the recirculation line to increase wastewater temperatures from frequently low and highly variable (14–22°C) to a more constant temperature (31±1°C). However, these steps did not appreciably increase current (Fig. 3).

Current was successfully increased from 0.3 to 2 A/m^3 (days 52 to 65) through amendment of the wastewater with diluted vinegar (acetic acid; Fig. 3). Based on various tests with wastewater, in which the microbial communities were shown to be dominated by various *Geobacter* species, we reasoned that the reactor performance could be improved by adding acetate to stimulate *Geobacter* sp. growth. The wastewater produced during harvest contained a high organic load (4–7 g SCOD/L), but low volatile fatty acids

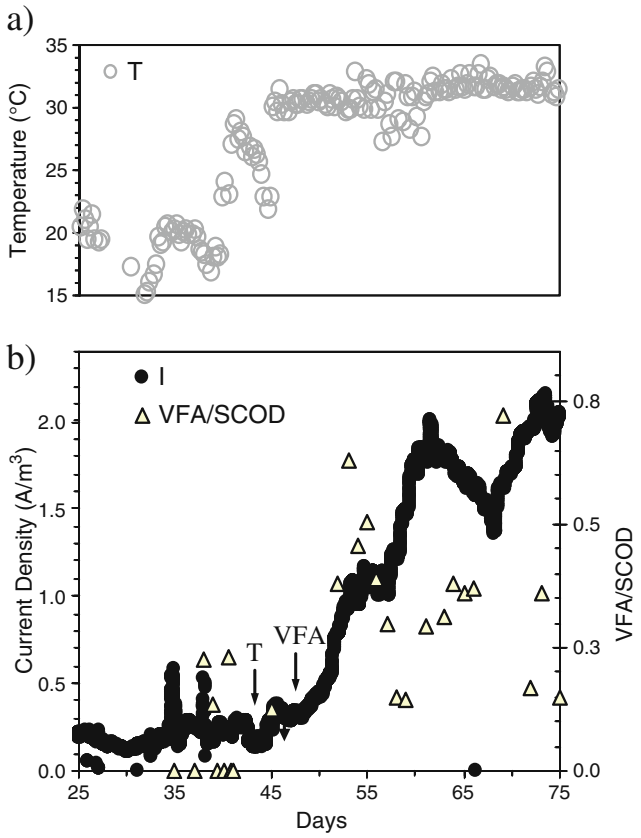

Fig. 3 Effect of **a** temperature and **b** VFA on inoculation. *Arrows* denote installation of thermostat and switch from wastewater to dilute vinegar

(0.05–0.21 g VFA/L, Fig. 4a). After day 65, harvest operations ended at the winery and the wastewater contained a much higher proportion of VFAs from washing operations and bottling, and thus no further acetate amendments were needed. These results provided valuable evidence that acetate amendments to the field reactor were essential for reactor startup with this wastewater, and that the MEC could not be otherwise enriched with sufficient exoelectrogenic bacteria without this acetate addition.

Current generation after enrichment Operation after day 65 resulted in a steady increase in the current to 7.4 A/m^3 on day 91 (Fig. 4a). At the peak, average current generation per module was 299±72 mA (range of 121 to 445 mA; Fig. 1). During this period (day 66 and thereafter) the reactor was fed wastewater diluted with boiler water to keep the pH ≥6 and maintain the SCOD within a desired range of 0.7−2.0 g/L. Wastewater (150±50 L) was drawn twice a day (once in the morning and once in the evening) from the sump into the storage tank and diluted with boiler water (350±50 L). Diluted wastewater was continuously pumped from the storage tank through the reactor at a rate of 1 m^3/day.

Conductivity, pH, and temperature The solution conductivity, pH, and temperature were continuously monitored after day 24 using a dedicated probe. The average pH was maintained at 6.4±0.3 (Fig. 5a) by buffer addition (days 0−40) or dilution with water (days 40−100). During buffer addition, solution conductivity was maintained at 1.8±0.5 mS/cm. When using boiler water for dilution, the average conductivity was 0.7±0.3 mS/cm (Fig. 5a). This difference in solution conductivity did not result in an observable effect on current generation or gas production between periods of buffer addition and dilution.

The average solution temperature within the reactor was maintained at 31±1°C until a thermostat malfunction on day 95, resulted in a temperature drop from 31°C to 15°C. The drop in temperature caused current density to decrease to 2.5 A/m^3 (Fig. 5b). The thermostat was non-operational for the final 5 days of the field study. This shows that once acclimated, the MEC could produce current at lower

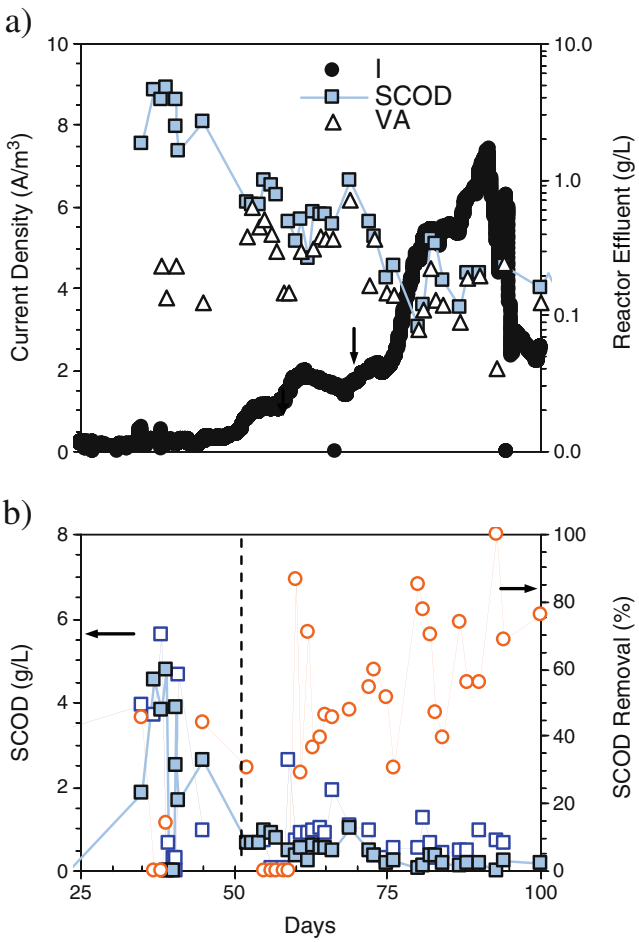

Fig. 4 **a** Pilot-scale MEC reactor current density and effluent composition and **b** SCOD removal based on difference between storage tank and reactor SCOD. *Arrow* (**a**) indicates end of harvest. *Dashed vertical line* (**b**) indicates start of influent wastewater dilution with boiler water

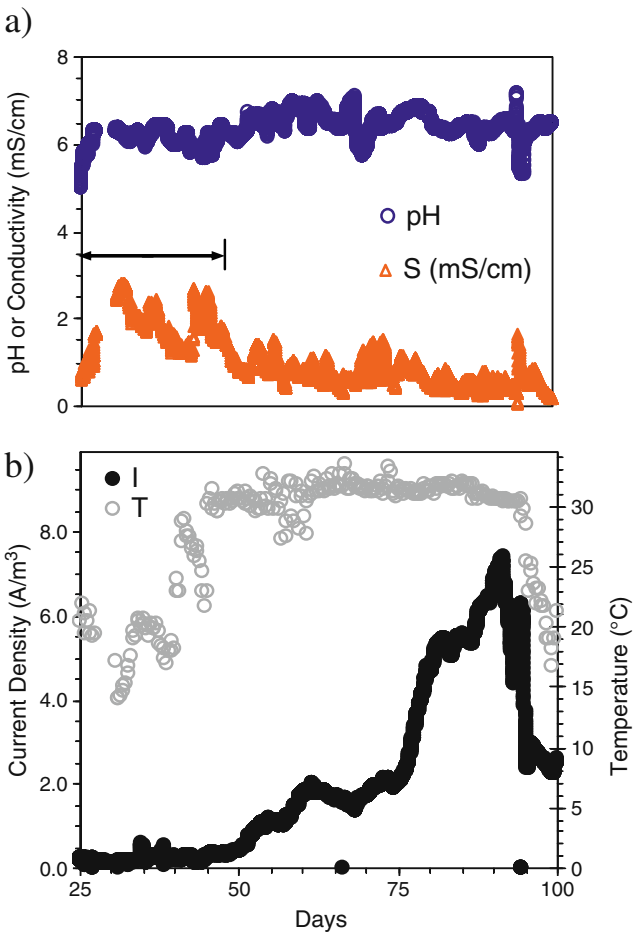

Fig. 5 **a** pH and conductivity (mS/cm) and **b** temperature (°C) on the MEC and current density over the duration of the pilot study. *Arrows* indicate period of buffer addition

temperatures, consistent with finding regarding temperature in MFCs (Cheng et al. 2010). The study was concluded on day 100 due to low wastewater flow rates and economic constraints.

COD removal As current density increased from 2.0 to 7.4 A/m^3, the average SCOD removal increased from ~50% to ~70% (Fig. 4a, b). The extent of SCOD removal during the inoculation period (days 0−60) was limited by insufficient microorganisms and exoelectrogenic activity, but later on it was also related to influent substrate concentrations (0.76±0.5 g SCOD/L) as reflected by measured current densities. As the reactor effluent SCOD concentration decreased from 0.46 to 0.15 g SCOD/L, current density increased 2.0 to 7.4 A/m^3 (Fig. 4a). Once enriched, SCOD removal averaged 62±20% (days 60 to 100, n=30 points).

Gas production and composition Biogas production was first observed on day 22, ranging from 0.002 to 0.28 L/L/day (Fig. 6b). Gas production at sub-mesophilic (15–22°C) temperatures (days 22–43) was low (0.09±0.04 L/L/day), with the gas composed primarily of H_2 (33±22%) and CO_2 (51±21%). Sub-mesophilic biogas production also coincided with low MEC current production. Once the thermostat was installed and temperatures were held more constant in the mesophilic temperature range (31±1°C), biogas production significantly increased (0.19±0.04 L/L/day). An increase in VFA concentration after day 52 may have contributed to the observed increase in gas production. Biogas production remained high at 0.21±0.04 L/L/day as current densities increased to 5 A/m^3. As current increased to 7.4 A/m^3 (days 85–91), biogas production decreased from 0.28 to 0.16 L/L/day, likely as a result of conversion of H_2 into CH_4. The percentage of CH_4 in biogas samples increased with temperature and current density from 21±12% (days 0−51) to 86±6% (days 52−97) after thermostat installation and MEC inoculation (Fig. 6a). H_2 was not present in biogas samples after thermostat installation except at trace concentrations.

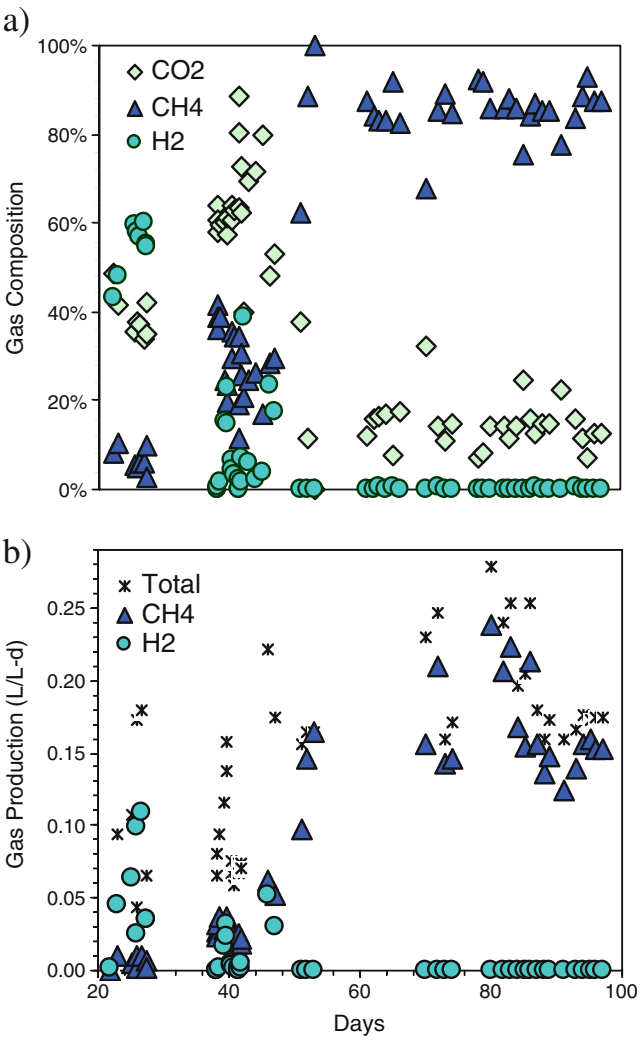

Fig. 6 Pilot-scale MEC biogas **a** composition and **b** production

Measured and maximum possible rates of hydrogen gas production H_2 was recovered at appreciable rates (0.07± 0.04 L/L/day) during days 22–43 (Fig. 7a), at a time when the MEC was fed sugar-rich wastewater during the harvest period, at sub-mesophilic temperatures. Part of the hydrogen recovered could therefore have been produced by sugar fermentation as well as electrohydrogenesis. If all measured current was converted to H_2, the peak rate of hydrogen production would have been 0.074 L/L/day (day 94), well below the highest measured hydrogen production rate.

The hydrogen produced at the cathodes or by fermentation was converted to methane. Conditions established in the reactor that can stimulate the growth of current generating exoelectrogens (mesophilic temperatures, high VFAs, and near neutral pHs) are the same as those that promote growth of methanogens. In laboratory MEC experiments, oxygen exposure between batches is used to suppress methanogenic growth (Call and Logan 2008; Cusick et al. 2010). The pilot-scale MEC was operated with a continuous flow, which prevented periodic oxygen exposure and likely contributed to conversion of hydrogen production into methane, as has been seen in other continuous flow MEC studies (Clauwaert and Verstraete 2009; Rader and Logan 2010).

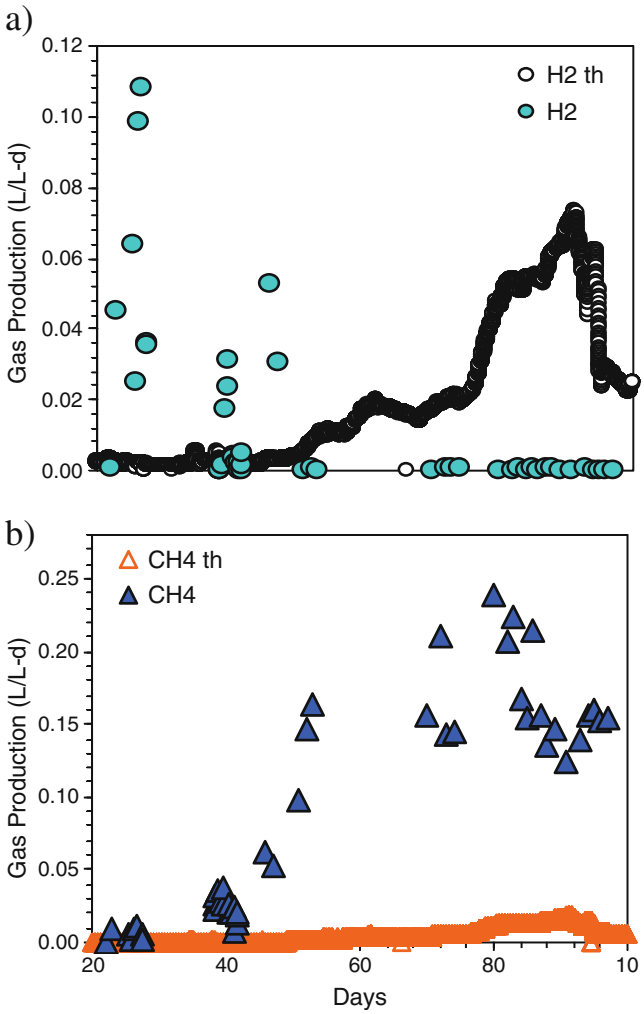

Fig. 7 Comparison of theoretical and measured gas production rates for **a** hydrogen and **b** methane

Methane gas production Measured methane production from the pilot-scale MEC (0.24 L/L/day) was much greater than possible from stochiometric conversion of current into methane (0.02 L/L/day; Fig. 7b). The disparity in these values implies that methane production proceeded independently of the generated current, although it cannot be ruled out that current generation helped to stimulate methane production. However, peak methane production was less than reported for winery wastewater when optimized for methane production using anaerobic digesters. Methane production rates in digesters fed winery wastewater range from 1.7±0.4 L/L/day (Moletta 2005) at a full scale plant with multiple constantly stirred tank reactors to 3.6±0.2 L/L/day in laboratory up-flow anaerobic sludge blanket reactors (Kalyuzhnyi et al. 2000).

The percentage of CH_4 (86±6%, Fig. 6b) in the biogas produced by the MEC was much higher than that typical of anaerobic digestion when acetoclastic methanogenesis accounts for 75% of methane production (Parkin and Owen 1986). Acetoclastic methanogenesis produces one molecule of CO_2 for every molecule of CH_4, resulting in biogas with a large fraction of CO_2 (30–35%) (Parkin and Owen 1986). The relative purity of biogas produced by the MEC suggests that hydrogenotrophic methanogenesis primarily contributed to methane production in the pilot-scale MEC, although supersaturation of the CO_2 cannot be discounted here due to the short HRT and lack of mixing.

Net energy production The energy contained in the biogas produced by the MEC was larger than the energy applied to the electrodes. At an applied voltage of 0.9 V, and a current of 7.4 A/m^3, the energy input was only 6.0 W/m^3. Based on the lower heating values of hydrogen and methane, the energy production by the MEC peaked at 99.1 W/m^3 on day 80 (due primarily to methane gas production). Therefore, although hydrogen was not recovered as originally intended, electrical energy input (to maintain cathode potential) was exceeded by energy content of produced gas. If biogas were converted to electricity with a microturbine at an efficiency of 28% (EPA 2007), the peak electrical output (27.7 W/m^3) energy would still exceed the electricity consumed by maintaining a voltage difference (0.9 V) between electrodes.

Discussion

Scalability of the MEC based on cathode surface area Previous studies have suggested that many MECs and MFCs are limited by cathode performance and electrode spacing (Call et al. 2009a; Cheng et al. 2006a, b). This suggests that one way to evaluate MEC performance for different size reactors is to evaluate performance on the basis of current density for the amount of cathode surface area in the reactor. Peak reactor performance was 7.4 A/m^3, or 0.41 A/m^2 based on the cathode surface area (18.1 m^2/m^3). The maximum current produced by a single module (#12) was 0.445 A (day 94). If the current produced by this module been achieved for all 24 modules, the maximum MEC current density would have been 10.7 A/m^3 (0.59 mA/m^2 based on cathode surface area).

This maximum current density for the best performing module is slightly lower than a current density of 0.72 A/m^2 (17 A/m^3) obtained in the laboratory using a 0.030 L MEC fed winery wastewater (shipped on ice from California to Penn State) (Cusick et al. 2010). Multiplying the cathodic current density of the laboratory MEC (0.72 A/m^2) by the specific surface area of the pilot-scale reactor (18.1 m^2/m^3) suggests that the volumetric current density of the pilot-scale reactor could have reached 13.1 A/m^3 (546 mA/module). The measured current density of 7.4 A/m^3 is therefore ~44% less than that estimated to be possible based on differences in cathode specific area and module performance.

The lower current density of the pilot reactor than the laboratory reactor was due to several differences between these systems in terms of reactor geometry, electrode materials, inclusion of glass fiber separators, possible connection resistances, and microbiological factors that resulted in relatively slow startup of the reactor. The cathodes used in laboratory MECs were made of Pt-loaded carbon cloth (23.3 m^2/m^3). It has been found that cathodes made of SS 304 mesh (the same as used here) produced 50% lower current densities (Zhang 2010) than Pt/carbon cloth cathodes in MECs lacking a separator (E_{ap}=0.6 V) (Call and Logan 2008). Thus, on the basis of the type of cathodes alone, this suggests that the 44% less current density obtained with the field reactor is primarily due to the reduced cathode performance of SS compared to the Pt/carbon cathodes. However, there are other differences in the systems as well. In the pilot reactor, the anodes and cathodes in each module were held between two stainless steel strips that functioned as current collectors. Poor electrical connections could have resulted in appreciable ohmic losses, producing differences in current densities among modules (Fig. S2). It is recommended in the future that the electrode connecting strips be welded to the electrodes to minimize contact resistance. Strips of glass matting were used to prevent short circuiting between electrode pairs may have hindered proton transport from anode to cathode. Additional tests conducted in the laboratory following field trials have shown that current density is reduced using glass fiber matting compared to systems lacking a separator (Yimin Zhang, personal communication). Proper enrichment of the reactor consumed the majority of time allotted for the field test (60 of 100 days), limiting the time available for current generation to reach steady state.

Outlook The pilot study has provided needed insight for researchers on issues that are important for scaling up MECs. Challenges associated with the slow startup and system performance led to other laboratory tests conducted in concert and after these field tests to better understand reactor performance. There are at least three important findings. First, we found that we had reasonable agreement between current densities obtained in the field in a reactor with 144 electrode pairs and a volume of 1,000 L and tests conducted in the laboratory using substantially smaller reactors of 0.03 L with the winery wastewater when the use of different cathode materials was considered. Second, system startup was unexpectedly slow with the larger reactor due to the absence of acetate, a pre-acclimated reactor inoculum, low and varying temperatures, and low pH. Our results showed that the critical step for enrichment of exoelectrogens in the pilot-scale reactor was increasing the concentrations of VFAs (VFA/SCOD≥ 0.5), along with maintaining a constant temperature (31±1°C) and pH above 6. Subsequent experiments have shown that once an MFC is enriched and producing power at higher temperatures (20°C to 30°C), power can be produced in proportion to temperature (Cheng et al. 2010), but no power is produced when the MFC is first enriched at low temperatures. Field tests described here had to be stopped before the effect of temperature could be more fully investigated, but a failure of the heater showed that significant current production was still obtained once the reactor was enriched with exoelectrogenic bacteria. The effects of pH and VFAs on reactor startup need to be further investigated. The use of a pre-acclimated inoculum may also be important for large reactor inoculation. In the laboratory it is common practice to inoculate reactors with solutions from operating MFCs or MECs (Zhang et al. 2009) as it is well known that serial transfer (Liu et al. 2008) and long acclimation times can improve reactor performance (Rabaey et al. 2003). A serial transfer from another reactor was not possible due the absence of substantial wastewater flow before the harvest, and lack of a suitable-sized reactor relative to the 1,000-L reactor volume. In the future it is recommended that better methods are found to develop pre-acclimated cultures for these larger reactors.

A third challenge for MECs, where hydrogen production is desired, are better methods to achieve hydrogen recovery. In laboratory tests with the winery wastewater in smaller reactors we achieved good hydrogen recovery (Cusick et al. 2010), but in the pilot-scale system most of the gas was composed primarily of methane (86±6%). As a result of our findings with the pilot-scale reactor, we conducted additional continuous flow laboratory tests using only acetate as a substrate (Rader and Logan 2010). Tests with this 2.5 L MEC that had eight pairs of graphite fiber and stainless steel brush anodes also showed that hydrogen produced in the system was rapidly converted to methane after only 14 days of operation. Thus, it is clear that the single-chamber design used here will have to be modified to better isolate the cathode from the wastewater solution to prevent hydrogenotrophic methanogenesis.

The use of MECs continues to be a promising technology for combining energy recovery and wastewater treatment. Overall there was a COD removal of 62±20% from the wastewater once the reactor was acclimated for current generation. This COD removal would greatly decrease the energy needed for aerobic decomposition of the organic matter in downstream aerated lagoons. Despite a lack of recovery of hydrogen gas recovery here, energy recovery from the system was still larger than that added as energy from the electrical current input making this process potentially useful for net energy recovery.

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