Effectiveness of domestic wastewater treatment using microbial fuel cells at ambient and mesophilic temperatures

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A B S T R A C T

Domestic wastewater treatment was examined under two different temperature (23 ± 3 °C and 30 ± 1 °C) and flow modes (fed-batch and continuous) using single-chamber air–cathode microbial fuel cells (MFCs). Temperature was an important parameter for treatment efficiency and power generation. The highest power density of 422 mW/m² (12.8 W/m³) was achieved under continuous flow and mesophilic conditions, at an organic loading rate of 54 g COD/L-d, achieving 25.8% COD removal. Energy recovery was found to depend significantly on the operational conditions (flow mode, temperature, organic loading rate, and HRT) as well as the reactor architecture. The results demonstrate that the main advantages of using temperature-phased, in-series MFC configurations for domestic wastewater treatment are power savings, low solids production, and higher treatment efficiency.

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1. Introduction

Conventional biological wastewater treatment processes, such as activated sludge, are energy demanding processes. Energy use for wastewater aeration can account for up to 50% of operating costs, with typical requirements of ~500 Wh/m³, or ~1 kWh for oxidation of 1 kg organic compounds removed during treatment (Rabaey and Verstraete, 2005). Aerobic treatment processes also produce large amounts of residual solids which are costly to treat and dispose (Ahn and Choi, 2004; Murray et al., 2008; Speece, 1996; Wei et al., 2003). The high energy requirements of these processes makes it important to investigate methods to reduce operational costs through process optimization or the use of more energy efficient anaerobic processes (Brischke et al., 2005; Cooper et al., 2007; Willis et al., 2007).

A microbial fuel cell (MFC) is a new bio-electrochemical process that produces electricity from the anaerobic oxidation of biodegradable organic substrates. Microbes in the anodic compartment produce electrons and protons from the oxidation of organic matter, with CO₂ and biomass as final products. There has been great interest in using MFCs for wastewater treatment (Habermann and Pommer, 1991), and power generation has been shown using a variety of wastewaters including both domestic and industrial wastewaters (Aelterman et al., 2006; Ghangrekar and Shinde, 2007, 2008; Liu et al., 2004; Min and Logan, 2004; Rodrigo et al., 2007). However, the main focus of these previous tests has been on the maximizing power densities, with less consideration of treatment efficiency or electrical energy recovery as a function of system operation. Many MFC tests on wastewaters and pure chemicals have been conducted under mesophilic conditions in order to control temperature in the laboratory, but lower ambient temperatures are more relevant for wastewater treatment applications. One of the first tests exploring domestic wastewater treatment using an air–cathode MFC with graphite rods demonstrated 26 mW/m² (Liu et al., 2004), with a total COD removal of about 50% and current recovery of 4%. A higher power density of 464 mW/m² (15.5 W/m³), with total COD removal of 40–50% and coulombic efficiencies of 20%, was achieved by flowing the wastewater through the carbon cloth anode (Cheng et al., 2006). While this flow scheme improved power output, such an approach would not be sustainable method as a practical method of treatment as the anode would foul over time. Temperature effects have only been considered in a few studies using synthetic defined substrates (Jadhava and Ghangrekar, 2009; Moon et al., 2006). All other cases treating real wastewaters were conducted under mesophilic conditions (30 °C), and have not examined effects of temperature on performance.

Nitrogen removal is another important aspect of wastewater treatment (Ahn, 2006). The nitrogen removals in MFCs may include both assimilatory nitrogen uptake, dissimilatory nitrate reduction, as well as physicochemical factors (such as ammonia volatilization...
at the cathode) that are increased in proportion to current generation (Kim et al., 2008).

An additional advantage of using MFCs for wastewater treatment is the potential for reduced solids production compared to aerobic processes (Logan, 2008). Aerobic growth yields are typically 0.4 g COD cell/g COD substrate, with yields of one tenth of this value for anaerobic growth (Speece, 1996). There is relatively little information on solids production in MFCs, and all tests have so far examined only single substrates. Cell yields in recent MFC tests were reported to vary widely from 0.07 to 0.22 g COD cell/g COD for glucose (Rabaey et al., 2003), and 0.24–0.31 g COD cell/g COD for acetate (Freguia et al., 2007). There are no data available on solids production in MFCs using domestic wastewater.

In this study, we examined domestic wastewater treatment at two different temperatures (23 ± 3°C and 30 ± 1°C) using both batch and continuous flow MFC systems. The efficiency of treatment was evaluated in terms of total and particulate COD removal, power production, energy recovery, and nitrogen removal. Examination of these factors will allow us to better explore the potential for using MFCs to produce power and reduce production of solids from the treatment systems compared to conventional aerobic processes.

2. Methods

2.1. MFC reactors and electrode materials

Single-chamber, air–cathode MFCs containing ammonia-treated graphite fiber brush anodes were constructed as previously described (Cheng and Logan, 2006; Logan et al., 2007). Each reactor consisted of a liquid chamber 4 cm long by 3 cm in diameter, with a liquid volume of 28 mL. Brush anodes were made of a core of two titanium wires with graphite fibers (PANEX 33 160 K, ZOLTEK) cut to 2.5 cm in outer diameter and 2.5 cm long. Each brush had an estimated surface area of 0.22 m² or 18,200 m²/m³-brush volume for the brush, with 95% porosity (Logan et al., 2007). The brush end was set into the chamber with its end 1 cm from the cathode. The cathodes (3.8 cm diameter, 7 cm² total exposed surface area) were made by applying a platinum catalyst (0.5 mg Pt/cm²; liquid side) and four diffusion layers (air side) on a 30 wt.% wet-proofed carbon cloth (type B-1B, E-TEK) (Cheng et al., 2006).

2.2. Inoculation and substrate

The MFCs were operated using effluent from the primary sedimentation tank (PST) as a substrate, under ambient (23 ± 3°C; laboratory bench) or mesophilic (30 ± 1°C; temperature-controlled room) temperatures. Three conditions for inoculation and microbial acclimation were examined: the PST overflow only (no external inoculation) at ambient temperature (P23); anaerobic sludge at ambient temperature (S23); and anaerobic sludge at a mesophilic temperature (S30). Reactor performance was evaluated under batch or continuous flow conditions (in duplicate). When operated in continuous flow mode, two MFCs were operated in-series, each reactor having a fixed external resistance (Reo) of 0.5 kΩ. The batch mode test was performed under a constant organic loading rate of 0.8–0.9 g COD/L-d. The organic loading rate of the continuous mode test was changed from 6 to 182 g COD/L-d with a change in HRT of 1.9 to 0.06 h for the first reactor, and from 0.35 to 1.75 g COD/L-d for changes in HRT of 20–4 h for the second reactor.

PST overflow and anaerobic sludges were obtained from the Pennsylvania State University Wastewater Treatment Plant and stored in a temperature-controlled room (4°C). Wastewaters were pumped (Masterflex, 7523-10, Cole-Parmer Inst. Co., USA; Micro210A, AVI Inc., USA) into the MFC reactors and used without any modifications or nutrient additions. Wastewater ranged in pH from 7.3 to 7.5, in chemical oxygen demand (COD) from 440 to 490 mg/L, and had in conductivity from 1.2 to 3.3 (1.80 ± 0.54) mS/cm. The ratio of soluble COD to total COD (sCOD/tCOD) was typically 0.52 g/g, and the readily biodegradable COD (as acetate) fraction of the wastewater was ~5.4% of tCOD.

2.3. Analyses

Cell potential (V) in the MFC circuit was monitored at 20 min intervals using a multimeter with a data acquisition system (2700, Keithly Instrument, Cleveland, OH). Current (I), power (P = IV), and Coulombic efficiency (CE) were calculated as previously described (Logan et al., 2007). Energy recovery was calculated based on electrical energy production per organics removed (Wh/g COD removed). Power density was calculated by dividing power by the projected surface area of one side of the cathode, consistent with previous studies and findings that the cathode (rather than the anode) limits power production in this reactor (Logan et al., 2006; Rismani-Yazdi et al., 2008). Volumetric power densities were based on the volume of the liquid media. Polarization data were obtained by varying the resistance in the circuit and measuring the voltage. In batch tests, data were collected over three complete cycles or more after the system demonstrated stable performance at each new external resistance. After batch mode polarization tests with domestic wastewater, comparative exoelectrogenic activities were evaluated using specific substrates (sodium acetate, propionic acid, or butyric acid). Each substrate (14 g COD/L) was spiked (1 mL) into the reactor to produce a similar initial concentration (COD 450–470 mg/L). This produced a slight increase in the conductivity that ranged from 1.80 ± 0.54 to 4.65 mS/cm. Stable cell potentials were recorded after the reactor was thoroughly acclimated to each substrate at a fixed resistance of 0.5 kΩ. For continuous flow tests, MFCs were operated for at least five to ten hydraulic retention times (HRTs) to ensure steady state conditions. In all experiments the systems were considered to be stable when there was less than a 10% variation in effluent characteristics and power production.

COD and nitrogen (Total nitrogen, ammonia, nitrite, and nitrate) were measured according to Standard Methods (APHA, 1998). Oxidation–reduction potential (ORP) and conductivity were measured using an electrode and meter (Mettler Toledo SevenEasy™ ORP meter with Mettler Toledo Inlab Redox Micro Electrode; Acorn CON 6 meter, Oakton Instrument). Volatile fatty acids (acetate, propionate, and butyrate) and alcohol (methanol, ethanol n-propanol, and n-butanol) were analyzed using a gas chromatograph (GC) (Agilent, 6890) equipped with flame ionization detector and a 30 m × 0.32 mm × 0.5 μm DB-FFAP fused-silica capillary column. Samples were filtered through a 0.45 μm pore diameter membrane and acidified using formic acid (0.65 M) prior to analysis. The temperature of the GC column was started at 60°C, increased at 20°C/min to 120°C, and then 30°C/min to a final temperature of 240°C for another 3 min. The temperatures of the injector and detector were both 250°C. Helium was used as the carrier gas at a constant pressure 103 kPa.

3. Results and discussion

3.1. Startup and acclimation

The time to maximum power output varied for the three different inocula, but after 25 fed-batch cycles the voltages produced by reactors were similar, with voltages ranging from 0.43–0.44 V (263–278 mW/m², 8.0–8.4 W/m², and 0.61–0.63 A/m²) with a 1 kΩ external resistor (Fig. 1). The voltage from the mesophilic
reactor reached the highest value after the first 9 cycles, but by cycle 12 the reactor with PST overflow only, that was operated under ambient conditions (P23), produced a higher voltage. After cycle 12, suspended biomass in the reactor was removed to limit the potential growth of methanogens and to stimulate growth of exoelectrogens. This change appeared to favor more rapid voltage production by sample P23.

### 3.2. Batch mode operation

Polarization and power density curves obtained after 25 fed-batch cycles show that the reactor operated under mesophilic conditions produced a slightly higher maximum power density than reactors operated at ambient temperatures (Fig. 2A). The mesophilic reactor (S30) produced 334 mW/m² (10.2 W/m³, 0.977 A/m²), or about 12% more power than the other two reactors (298 or 302 mW/m², 9.07 or 9.18 W/m³, for P23 and S23, respectively). CEs varied substantially for all reactors, with the highest CEs of 47–57% obtained at the lowest current densities (Fig. 2B).

Energy recovery was the greatest for MFCs operated under ambient temperatures, with a maximum of 0.69 Wh/g COD removal at the lowest current density, and 0.03 Wh/g COD removal at the highest current density (Fig. 2B). Energy recovery was slightly lower for mesophilic reactors with a maximum of 0.52 Wh/g COD removal. In all cases the current density (and therefore the circuit load) affected energy recovery more than the inoculum or reactor conditions.

COD removal was greater than 88% in all reactors at all current densities, except at the highest current density (~2 A/m²) at the lowest resistance tested (50 Ω) (Fig. 2C). Similarly, high particulate COD removals were achieved (>89%) except at this highest current density.

The ORP rapidly decreased in all reactors at the beginning of the cycle (~400 to ~500 mV (Fig. 3A and B)). Acetate was the main component of the VFAs. Other intermediate byproducts, including propionate, butyrate and ethanol were below the detection limit (Fig. 3C and D). COD degradation rates ($k_p$) for particulate COD (Fig. 3C and D) were higher under mesophilic conditions (69.3 mg tCOD/L-h, and 22.0 mg pCOD/L-h) than under ambient conditions (48.5 mg tCOD/L-h, and 12.5 mg pCOD/L-h). There were relatively little differences in the degradation rates ($k_p$) of the slowly biodegradable organic fraction in the wastewater under the two temperature conditions (9 mg tCOD/L-h for mesophilic, and 11 mg tCOD/L-h for ambient conditions) (Fig. 3C and D).

Total nitrogen removal in all cases of fed-batch MFCs was greater than 63%. Nitrogen was more effectively removed in mesophilic MFCs than in the reactors operated under ambient conditions. Total nitrogen (T-N) reduction was 74% for mesophilic (67% based on Org-N) MFCs and 63% for ambient reactors (55% based on Org-N) (Fig. 3E and F). Overall nitrogen removal rates were 2.9 mg T-N/L-h for MFCs under mesophilic temperatures, and 2.0 mg T-N/L-h for reactors under ambient temperatures. In all tests, there was very little nitrite (0–0.3 mg NO₂-N/L) or nitrate (0.9–1.1 mg NO₃-N/L) measured in the effluents.

### 3.3. Comparative power densities with pure compounds (batch mode)

More power was produced using acetate and butyrate than domestic wastewater, but less power was produced when using only propionate (Table 1). For acetate and butyrate, there was relatively little effect of temperature on maximum power densities, indicating the type of substrate was more important for these two chemicals than the temperature. However, there was a greater effect of temperature on propionate. Under mesophilic conditions, power densities for propionate were 27% higher than under ambient conditions.
3.4. Continuous mode operation

Overall, the operation of the MFCs in continuous flow mode resulted in increased power generation compared to reactors operated in batch mode (Fig. 4). Tests were also conducted in this case with a second reactor (in-series) to see if performance could be improved by varying organic loading and temperatures.

The HRT of the first reactor was varied from 112 min to 3 min, resulting in organic loadings that changed from 6 to 182 g tCOD/L-d. As expected, MFCs operated under the higher temperatures achieved better performance than those operated under ambient temperature conditions (as observed for batch mode tests). Maximum power generation under mesophilic conditions was 422 mW/m² (12.8 W/m³) at an HRT of 13 min (54 g tCOD/L-d), with a tCOD removal of 26%, CE of 1.7%, and energy recovery of 0.022 Wh/g COD removal. Ambient temperature MFCs showed a maximum power of 345 mW/m² (10.5 W/m³) for a HRT = 4.2 min (167 g tCOD/L-d), with a tCOD removal of 19%, CE of 0.7%, and energy recovery of 0.008 Wh/g COD removal. ORP was always low and therefore was not a factor in reactor performance, ranging from \(-500 \text{ to } -490 \text{ mV}\) in mesophilic conditions, and \(-430 \text{ to } -506 \text{ mV}\) under ambient conditions (data not shown).

There was less of a difference in power production between the ambient and mesophilic reactors for the second reactor at HRTs ranging from 20 to 4 h (0.35–1.75 g tCOD/L-d) (Fig. 4). For example,
at an HRT = 4 h (1.75 g tCOD/L-d), the power was 170 or 177 mW/m² (5.2 or 5.4 W/m³). However, COD removal was slightly larger at mesophilic temperatures (33% removal) than ambient temperatures (23% removal). The CE and energy recoveries were 26% and 0.214 Whr/g COD removal for mesophilic reactors, and 38% and 0.314 Whr/g COD removal for ambient reactors, respectively.

As also observed in fed-batch tests, acetate was the dominant VFA in all first reactors for tests at both temperatures, with the other measured byproducts near or below the detection limit (Table 2). All byproduct VFAs, including acetate, were below the detection limit in the effluent from the second reactors (Fig. 5). Even though maximum power generation in the system was produced under relatively high organic loading rates (as shown in Fig. 4), better effluent quality was achieved at lower organic loading rates. These results also showed that the MFCs had very low particulate organic concentrations in the effluents (<13 mg pCOD/L), implying low solids production from the system.

The operation of MFCs in continuous flow mode improved performance relative to power generation, compared to fed-batch conditions. For example, the maximum power densities at 30 °C were 26% higher than those in fed-batch tests. As expected, operation of the reactors under mesophilic conditions also increased power output, compared to those obtained under ambient conditions. Power densities were increased by 22% by operation at 30 °C compared to 23 °C under continuous flow conditions. This effect of temperature is different from those observed using acetate or butyrate as a substrate (Table 1). With acetate or butyrate there was little effect of temperature on power densities (0.7–1.4%). In contrast, there was an effect of temperature for propionate. Thus,
we see that temperature effects are dependent on the substrate, and that temperature changes are important for complex substrates such as domestic wastewater.

Total nitrogen was not effectively removed in continuous mode MFCs because the reactors were operated under high organic loading rates of 6.0–182 g COD/L-d for the first reactor, and 0.35–1.75 g COD/L-d for the second reactor (and therefore short HRTs of 0.06–1.82 h for the first reactor, and 4–20 h for the second reactor). There was only slight nitrogen removal (<5% based on T-N), and effluent concentrations of nitrite and nitrate were also very low in all tests (much less than <1 mg N/L). While total nitrogen removals were high in fed-batch tests, in continuous flow mode there was little nitrogen removal. This difference in performance likely resulted from the short HRTs examined when in continuous flow tests conducted at high organic loading rates, compared to the longer cycle times (50–120 h) used in previous fed-batch tests with animal wastewaters (Kim et al., 2008). Nitrogen removal via nitrification–denitrification can occur in air–cathode MFCs as ammonia-oxidizing bacteria such as *Nitrosomonas europaea* have been found on the cathode of single-chamber air cathode MFCs (Kim et al., 2008). The growth and contribution of anaerobic ammonium oxidizers in MFCs, however, are not proven in MFCs and *Anammox* bacteria have very unique physiological properties (Ahn, 2006). It appears at this time that ammonia is not directly used for electricity generation, and that physicochemical factors (such as ammonia volatilization) that are increased with current generation and HRT represent the main routes for ammonia removals in these systems (Kim et al., 2008).

3.5. Power densities with wastewater compared to other studies

Power densities obtained using brush anodes in these MFCs and domestic wastewater were generally higher than results previously reported using MFCs with different architectures (Ghangrekar and Shinde, 2007, 2008; Lefebvre et al., 2007; Liu et al., 2004; Min and Logan, 2004; Rodrigo et al., 2007). The maximum power generated here was only 10% lower, however, than that reported by Cheng et al. (2006). However, they used a reactor with closer electrode spacing (1 cm compared to 2-cm here), which is known to increase power. Additionally, they directed the wastewater flow through a carbon cloth electrode, which would likely foul the electrode over time due to clogging with particles in the wastewater. There are other reports of treating wastewaters using ferricyanide as an electron donor (e.g. Altermann et al., 2006), but these studies are not considered here with respect to power production as the power generated is due in part to the non-sustainable chemical energy in the chemical catholyte.

3.6. Process design

In general, lower organic loading rates (higher HRTs) showed higher energy recoveries. Therefore, optimal operating parameters (e.g. organic loading rate or HRT) will depend in part of the goals for treatment based on achieving either effluent discharge standards (i.e. maximizing treatment) or high energy recoveries.

The design conditions for maximizing energy production and organic removal were 6.4 g tCOD/L-d (HRT = 1.82 h, mesophilic) for the first reactor, and 0.35 g tCOD/L-d (HRT = 15.5 h, ambient) for the second reactor, corresponding to the overall organic loading rate of 0.67 g COD/L-d (HRT of 17.3 h). The overall treatment efficiency of this temperature-phased two-in-series reactor system was 83% removal of tCOD (94% of pCOD). Preliminary findings based on particulate COD (pCOD) reduction suggest that solids in effluent may be very low when using the temperature-phased two-in-series MFCs treating domestic wastewater. However, this will need to be further investigated as we did not measure total solids production using more conventional techniques (i.e. suspended solids and volatile suspended solids). The process achieved <13 mg pCOD/L in the reactor effluent over a six-month period. This solids fraction in effluent is so low that if this could be achieved in larger systems, MFCs could achieve a level of treatment...
that would meet secondary effluent standards for suspended solids (<20 mg/L) without the need for a clarifier. An additional polishing step would still be required, however, in order to meet secondary effluent limits of <20 mg COD/L and nutrient control.

4. Conclusions

In laboratory examinations using single-chamber air cathode MFCs containing graphite fiber brush anode, the results demonstrate that the main advantages of using a temperature-phased (mesophilic–ambient), in-series reactor configuration for domestic wastewater treatment are power savings, low solids production, and higher treatment efficiency. The highest power density (422 mW/m², 12.8 W/m³) was achieved under continuous flow, mesophilic conditions at an organic loading rate of 54 g COD/L-d, but COD removal was only 25.8%. Temperature was an important factor in treatment efficiency and power generation. Energy recovery depended on the operational conditions of flow mode, temperature, organic loading rate, and HRT.

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