

# Production of hydrogen from domestic wastewater using a bioelectrochemically assisted microbial reactor (BEAMR)

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## Abstract

Hydrogen production from domestic wastewater was examined using a plain carbon electrode or graphite-granule packed-bed bioelectrochemically assisted microbial reactors (BEAMRs) capable of continuous or intermittent hydrogen release. When graphite granules were added to the anode chamber (packed-bed mode) current density was increased when the domestic wastewater had a high initial chemical oxygen demand (COD > 360 mg/L), and produced a maximum Coulombic efficiency of 26% (applied voltage of 0.41 V) and a maximum hydrogen recovery of 42% (applied voltage of 0.5 V). The packed-bed system successfully treated the wastewater, with removal efficiencies of biochemical oxygen demand (BOD), chemical oxygen demand (COD), and dissolved organic carbon (DOC) in the range of 87–100%. The final BOD of the treated wastewater was always reduced to less than  $7.0 \pm 0.2$  mg/L. Overall hydrogen production based on COD removal was a maximum of 0.0125 mg-H<sub>2</sub>/mg-COD (154 mL-H<sub>2</sub>/g-COD versus a maximum possible conversion of 0.126 mg-H<sub>2</sub>/mg-COD), with an energy requirement equivalent to 0.0116 mg-H<sub>2</sub>/mg-COD, producing an 8% net yield of H<sub>2</sub>. These results demonstrate that a wastewater treatment based on a BEAMR reactor is feasible, but improvements are needed in hydrogen recoveries and Coulombic efficiencies to increase the overall hydrogen yield.

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## 1. Introduction

In a microbial fuel cell (MFC), bacteria oxidize organic matter, producing protons and electrons. Protons diffuse through the electrolyte towards the cathode. The electrons travel around a circuit to the cathode, producing current. At the cathode, a species, such as oxygen, reacts with the electrons and protons to form a reduced compound, such as water. In a bioelectrochemically assisted microbial reactor (BEAMR), hydrogen is evolved at the cathode according to



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by eliminating oxygen at the cathode, and adding a small voltage to the circuit [1,2]. The potential at pH = 7 that is required to produce hydrogen is theoretically  $-0.61$  V ( $V_{\text{Cat}}$ ; versus Ag/AgCl) [3]. The anode potential produced by the oxidation of the organic matter by the bacteria is approximately  $V_{\text{an}} = -0.50$  V, so the minimum theoretical applied voltage is 0.11 V ( $V_{\text{app}} = V_{\text{an}} - V_{\text{Cat}}$ ). In practice, the minimum applied voltage to produce hydrogen from the bioelectrolysis of acetate has been found to be more than  $\sim 0.25$  V due to ohmic resistance and electrode overpotentials [1,2]. However, this is still substantially less than the 1.8–2.0 V needed for hydrogen production via water electrolysis (alkaline conditions; [4]).

The BEAMR and MFC systems share many similar characteristics, and therefore many findings for improving electricity generation in MFCs should be applicable for increasing hydrogen production in the BEAMR system. There are important differences between the systems, however, that can affect system performance relative to hydrogen recovery. First, in the

BEAMR process, hydrogen can be lost due to its diffusion from the cathode chamber through the cation exchange membrane (CEM) into the anode chamber. Second, in the BEAMR process there is no potential for loss of substrate due to aerobic growth of bacteria due to oxygen diffusion into the anode chamber from the cathode chamber. This could allow higher Coulombic efficiencies (CEs) in the BEAMR than in the MFC, but it could also affect redox conditions in the anode chamber (and the development of the bacterial community), and therefore the performance of the system. The CE of a BEAMR, for example, can be as large as  $92 \pm 6.3\%$  with acetate [2], while in MFCs the CEs range from 10% to 78% using mixed cultures and acetate [5,6]. Third, it cannot be predicted based on MFC tests what the minimum applied voltage will be for hydrogen generation in a BEAMR process for different substrates, or how current density might be affected by the applied voltage in these systems.

In this study, we examined hydrogen production using domestic wastewater as the fuel in the BEAMR process, and evaluated system performance in terms of hydrogen recovery, CE, and the effectiveness of treatment (BOD, COD, and DOC removal). The BEAMR process is new, and so far only acetate has been examined as a substrate for hydrogen production. It is reasonable to expect that domestic wastewater could be used to make hydrogen in the BEAMR process as either acetate or wastewater can be used to generate electricity in an MFC. However, the amount of hydrogen that could be recovered and the required voltage needed to make the BEAMR process work cannot be predicted, and must be tested. In tests conducted previously with MFCs, maximum power densities and CEs with wastewater have been consistently lower than those achieved using acetate. For example, a maximum power density of  $661 \text{ mW/m}^2$  was produced in a single chamber MFC using acetate, but only  $146 \text{ mW/m}^2$  was achieved using domestic wastewater [5,7]. The recovery of hydrogen based on the measured current in the BEAMR has varied, from 90–100% [1] to  $57 \pm 0.1\%$  [2]. Previous BEAMR tests have only examined hydrogen production via intermittent gas release, but it has been shown in hydrogen fermentation tests that continuous gas release can increase overall hydrogen yields [8]. To examine the potential for hydrogen generation from domestic wastewater, we examined hydrogen production in a reactor with a plain carbon electrode versus a system with the anodic chamber filled with a bed of conductive graphite granules, and the effect of intermittent or continuous gas release.

## 2. Methods

### 2.1. Reactor construction

Previous research with MFCs has shown that performance can be improved by reducing electrode spacing [9]. A two-chambered reactor was therefore constructed so that the chambers were directly adjacent to each other with a cation exchange membrane (CEM; Nafion<sup>TM</sup> 117; Dupont Co., USA; projected surface area of  $11.4 \text{ cm}^2$ ) held between the two faces using an O-ring, and rubber gaskets (Fig. 1). Each rectangular chamber (292 mL capacity filled to either 192 or 256 mL) of the reac-

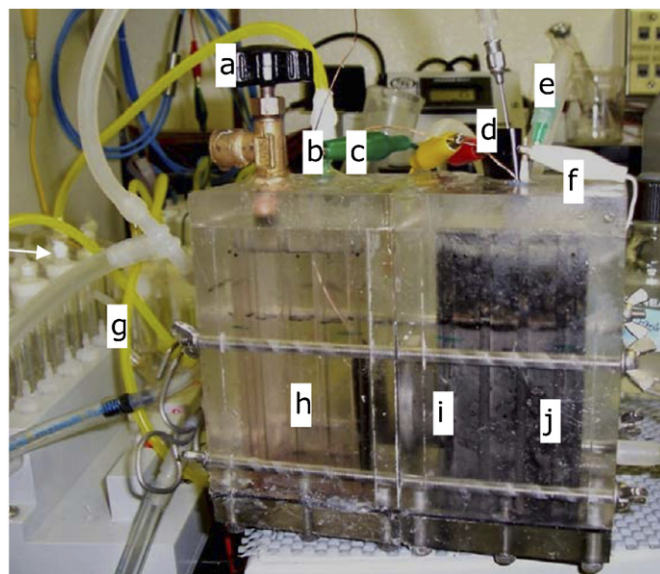


Fig. 1. Two-chambered acrylic BEAMR reactor shown with the anode chamber filled with granules. (a) Tube to respirometer, (b) headspace sampling valve, (c) wire to anode, (d) wire to cathode, (e) nitrogen sparge, (f) reference electrode, (g) bubble meters, (h) cathode chamber, (i) Nafion membrane, (j) anode chamber.

tor contained an electrode (projected surface area of  $26.5 \text{ cm}^2$ ) placed 1.8 cm from the CEM (Fig. 2). Experiments were conducted using reactor headspace volumes of 100 or 36 mL (as indicated). This reactor is larger than our previous BEAMR system [1]. The larger liquid and gas volumes used for the reactor made it easier to sample the reactor and not alter reactor conditions. The anode was nonwet-proofed carbon paper (Phosphoric Acid Fuel Cell Electrode, Toray Carbon Paper; De Nora North America, Somerset, NJ, USA) and the cathode was carbon paper with a Pt loading on the membrane facing side of  $0.5 \text{ mg/cm}^2$  (A-3 EFCG; De Nora North America, Somerset, NJ, USA). Copper wire was attached to the electrodes and all exposed metal surfaces were sealed with a nonconductive epoxy (Dexter Corp., NJ, USA). In some tests the anode chamber was filled with graphite granules (total volume of 131 mL; particle size of 2–6 mm ( $\frac{1}{4}$  in  $\times$  #10 mesh; Product 100, Graphite Sales, Inc., Chagrin Falls, OH, USA)) to increase the surface area of the anode and proximity of the anode to the CEM (packed-bed mode), reducing the liquid volume to 135 mL. The total anode surface area increased to  $1041 \text{ cm}^2$ , assuming a specific surface area of  $A_s = 6\theta/d$  [10] where  $d = 4 \text{ mm}$  is the granule diameter and  $\theta = 0.53$  is the bed porosity [11].

When operated in BEAMR mode, a resistor ( $11.5 \Omega$ ) was connected in series with a power source (model 3645 A DC Power Supply; Circuit Specialists, Inc., Mesa, AZ, USA) in order to allow measurement of the current in the circuit. Since the measured voltage drop across the external resistor is only about 2% of the total applied voltage, the voltage applied to the reactor was not corrected for this loss. The power source positive lead was connected to the anode and the negative lead connected to the resistor and then to the cathode. A multimeter (model 2700, Keithley Instruments, Inc.; Cleveland, OH,

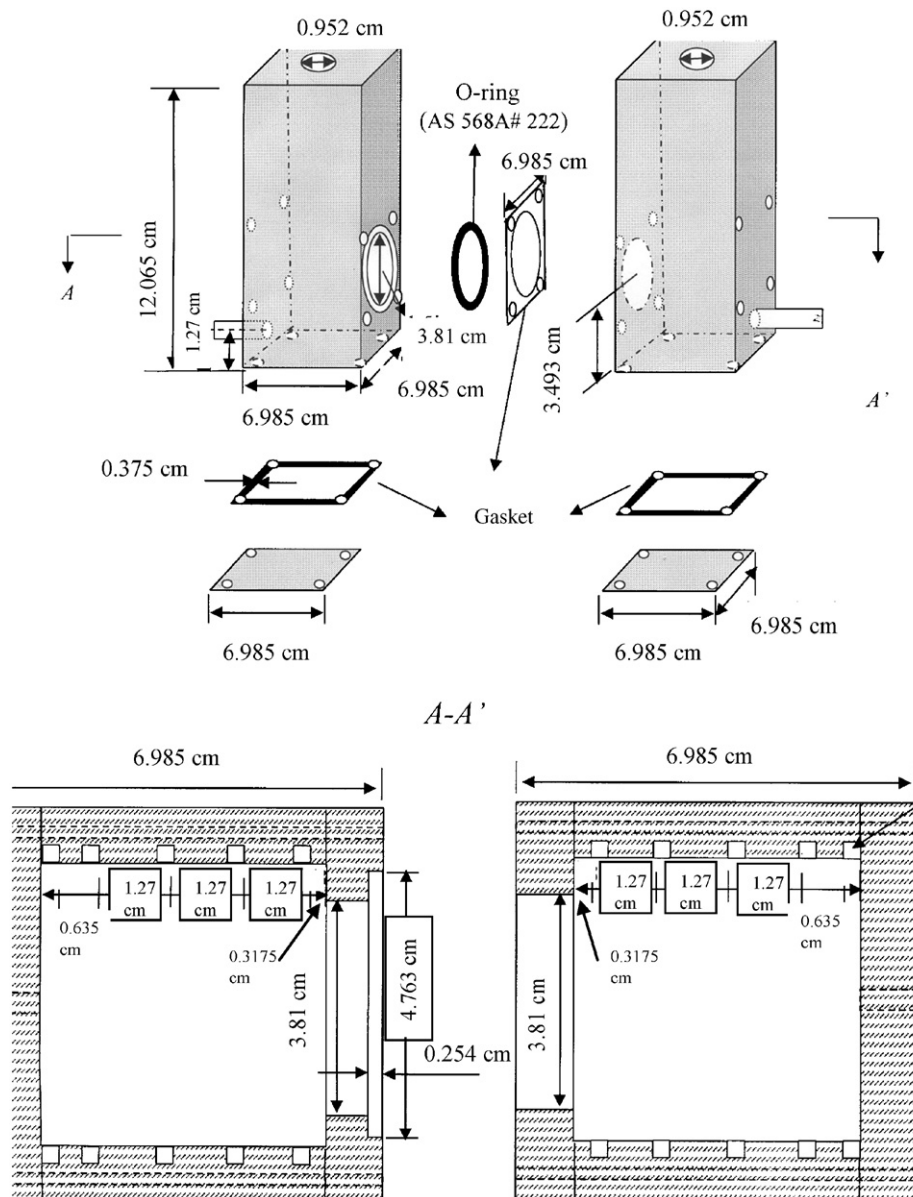


Fig. 2. Schematic of BEAMR reactor.

USA) was used to measure the voltage drop across the resistor ( $11.5\ \Omega$ ) and record the voltage between the anode and the reference electrode.

## 2.2. Experiments

Five applied voltages were examined with the reactor operated in BEAMR mode (0.23, 0.32, 0.41, 0.5 and 0.59 V), with experiments done in duplicate at each voltage (i.e. a total of 10 batch cycles).

Following the above tests, the reactor acclimated to wastewater was operated as an MFC in order to determine its internal resistance and to assess its performance relative to other MFCs used to produce electricity. The anode chamber was filled either with wastewater or 1 g/L sodium acetate (720 mg/L acetate) in

a mineral salt and vitamin solution [7]. The circuit load was fixed at  $1400\ \Omega$  resistor (except as noted) with air bubbled in the cathode chamber containing PBS. The reactor was cycled once on domestic wastewater and then switched for two cycles to the acetate solution.

## 2.3. Media

The anode chamber was filled with domestic wastewater and operated in MFC mode for one cycle of power generation (see below) with nitrogen gas sparging to maintain anoxic conditions so that bacteria would develop on the anode. Wastewater was obtained from the effluent of the primary clarifier of the Pennsylvania State University Wastewater Treatment plant, and amended with phosphate buffer solution (PBS)



Table 1  
Summary table of experiments performed with granules in the anode chamber (36 mL headspace) and primary findings

Order of experiments	Applied voltage (V)	COD <sub>i</sub> (mg/L)	COD <sub>e</sub> (mg/L)	Hydrogen recovery (%)	Coulombic efficiency (%)	Overall efficiency (%)
1	0.32	229	11	3.3	10.4	0.34
2	0.41	219	12	1.8	12.0	0.22
3	0.50	204	13	10.5	16.8	1.76
4	0.59	460	15	37.5	26.4	9.82
5	0.23	481	18	4.2	10.4	0.44
6	0.41	440	20	19.0	25.8	4.89
7	0.32	387	19	3.5	19.4	0.67
8	0.50	368	38	42.7	23.2	9.90
9	0.23	391	20	2.8	9.6	0.27
10	0.59	371	18	32.5	26.1	8.50

containing: 4.09 g/L Na<sub>2</sub>HPO<sub>4</sub> and 2.54 g/L NaH<sub>2</sub>PO<sub>4</sub> (pH=7.1). The initial condition ranges for the wastewater used in the experiments with granules were: BOD, 86 ± 4 to 270 ± 9 mg/L; COD, 204–481 mg/L; DOC, 56.8 ± 1.1 to 90.0 ± 1.0 mg/L. The order of the experiments, and the initial COD values, are summarized in Table 1. The cathode was filled with PBS, and it was replaced before each experiment with fresh solution sparged with nitrogen to remove oxygen. Once operated in BEAMR mode, the gas sparger in the cathode chamber was turned off.

#### 2.4. Analytical methods

Gas production was measured by continuous sampling, except as indicated. A needle valve fit with a septum (6514; Alltech Chromatography, Columbia, MD) was tapped into the top of the cathode chamber (Fig. 1). Continuous gas production was measured using a respirometer (AER-200; Challenge Environmental Systems, Fayetteville, AR). The concentration of hydrogen in the headspace of the reactor was determined by intermittent sampling the headspace gas (250 µL) using gas-tight syringes (Hamilton Samplelok Syringe used; Reno, NV) using a gas chromatograph (GC; model 310; SRI Instruments, Torrance, CA) equipped with a thermal conductivity detector and a molecular sieve column (Alltech Molesieve 5A 80/100) with nitrogen as the carrier gas. Methane and carbon dioxide were analyzed at the end of one batch cycle using the same sampling procedure and GC. The end of a batch cycle was determined when the voltage dropped to 25% or less of the maximum batch voltage. All experiments were conducted in a constant room temperature at 30 °C. In some tests, the reactor was sampled by intermittent release of gas production with GC analysis and measurement of hydrogen production as previously described [8]. The frequency of the gas release was dependent upon the rate of gas production. The reactor was checked at ≤ 10 h intervals for gas production using the gas-tight syringe. If gas was collected in the syringe then the concentration of hydrogen in the headspace was measured and the gas produced was recorded. If no gas was collected during the entire batch, then the beginning and final headspace hydrogen concentrations were used to determine how much hydrogen was produced.

Total chemical oxygen demand (COD), biochemical oxygen demand (BOD) and dissolved organic carbon (DOC) of the anode chamber solution at the beginning and end of each batch run were measured following standard methods (Methods 5220, 5210 and 5310 B, respectively; [13]). DOC was measured using a total organic carbon analyzer and autosampler (TOC-V<sub>CSN</sub> analyzer with ASI-V autosampler; Shimadzu Corp., Torrance, CA).

Reactor performance was evaluated in terms of CE and hydrogen recovery. The CE is the percent of COD, evaluated in terms of moles of electrons captured as current based on COD removal [12]. Hydrogen recovery ( $R_{H_2}$ ) was calculated as

$$R_{H_2} = \frac{n_{H_2}}{n_{Th}}, \quad (2)$$

where  $n_{H_2}$  is the moles of hydrogen recovered in the experiment, calculated as  $n_{H_2} = V_{H_2}/(RT)$ ,  $R$  is the gas constant (0.08206 atm-L/mol-K), and  $T$  the absolute temperature (303 K).  $n_{Th}$  is the moles of hydrogen that could theoretically be recovered based on the measured current, calculated as

$$n_{Th} = \frac{\int_{t=0}^t (I) dt}{2F}, \quad (3)$$

where  $F$  Faraday's constant (96,485 C/electron equivalent), and  $I$  the current calculated as previously described [10–13] integrated over the time of the batch test. Current densities (mA/cm<sup>2</sup>) were calculated on the basis of the projected surface area of both sides of the cathode (53 cm<sup>2</sup> total; each side 26.5 cm<sup>2</sup>).

The hydrogen yield,  $Y_{H_2}$  (mg-H<sub>2</sub>/mg-COD) was calculated as

$$Y_{H_2} = \frac{n_{H_2} M}{V_L (COD_i - COD_e)}, \quad (4)$$

where  $M$  is the molecular weight of hydrogen,  $V_L$  the volume of liquid in the anode chamber (0.135 L), and COD<sub>i</sub> and COD<sub>e</sub> the COD concentrations of the wastewater at the beginning and end of the batch test.

COD removal was calculated as the average from two batch tests. BOD and DOC removals were obtained for batch tests at each applied voltage with measurements performed in triplicate. All removals are calculated based on percent removals.

For example, for BOD removal was  $A = [1 - (\text{BOD}_e/\text{BOD}_i)] \times 100\%$ , where  $\text{BOD}_e$  is the average removal obtained in each batch test, and  $\text{BOD}_i$  is the average initial BOD concentration. Because an error term was known for the initial and final BOD and DOC concentrations, the propagation of error method was used to calculate the uncertainty of BOD and DOC removal. Again using BOD as an example,  $\delta(\text{BOD}_t - \text{BOD}_i) = \sqrt{\delta\text{BOD}_t^2 + \delta\text{BOD}_i^2}$  and

$$\delta A = A \sqrt{\left[ \frac{\delta(\text{BOD}_t - \text{BOD}_i)}{(\text{BOD}_t - \text{BOD}_i)} \right]^2 + \left[ \frac{\delta\text{BOD}_i}{\text{BOD}_i} \right]^2},$$

where  $\delta$  is the uncertainty on measurements (1 S. D.).

Anode potentials are reported versus an Ag/AgCl electrode. The reference electrode was located approximately 1.9 cm from the anode. The anode potential was continuously recorded throughout each batch experiment. The anode potential decreased immediately at the beginning of each batch cycle to the minimum potential (reported as the anode potential), and then gradually increased during the remainder of the batch cycle as the substrate was consumed. The minimum anode potential was therefore not recorded at a specific current density.

#### 2.4.1. Analytical methods for reactor operated as an MFC

Electrical impedance spectroscopy (EIS) was used to determine the internal resistance of the reactor. EIS scans were performed with the reactor operating at its maximum power output determined using a potentiostat (PC4/750<sup>TM</sup>, Gamry Instruments, Warminster, PA) and associated software (Gamry Framework Version 4.30 and Echem Analyst Version 1.30).

Polarization curves were used to determine the maximum power density of the fuel cell using acetate versus domestic wastewater using the single cycle method [12,7]. This method is based on varying the resistance of the MFC circuit (between 50 and 1400  $\Omega$ ) during a single batch run operating at its stable voltage.

### 3. Results

#### 3.1. Hydrogen production

Hydrogen was produced in the cathode chamber at applied voltages  $\geq 0.23$  V when the reactor was operated on domestic wastewater in the BEAMR mode with only a plain carbon paper electrode in the anode chamber (Fig. 3). However, the current density was low and did not consistently increase with the applied voltage. Methane and carbon dioxide were not detected in the gas produced in the cathode chamber. When graphite granules were added to the anode chamber the current density increased in proportion to the applied voltage ( $R^2=0.82$ ; Fig. 3A) for high COD values (350–500 mg/L), suggesting that the reactor was substrate limited. By adding more COD at an applied voltage, the current density increased. However, at low initial COD ( $< 230$  mg/L), the result was similar to that found in tests lacking granules: there was a low current density, which did not consistently increase with the applied voltage. CEs and elec-

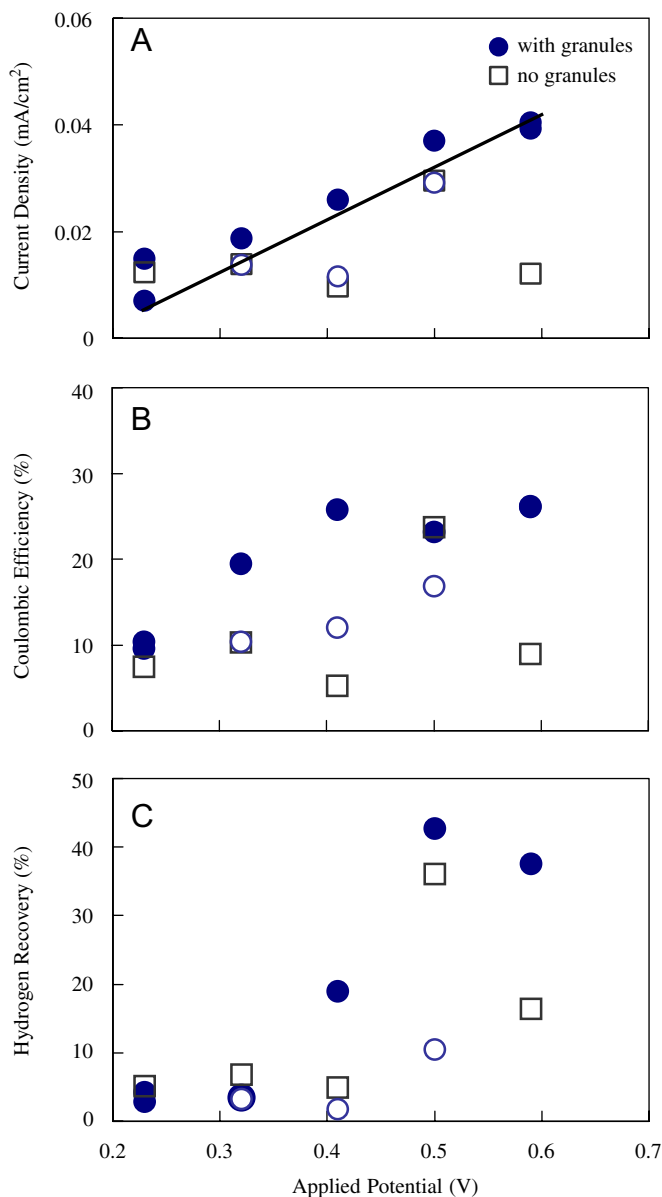


Fig. 3. (A) Current density, (B) Coulombic efficiency, and (C) hydrogen recovery for the reactor operated in BEAMR mode as a function of applied voltage with (circles) and without (squares) granules in the anode chamber. Continuous method of gas release used. Filled circles are used for high COD values ( $> 360$  mg/L), while open circles indicate a low initial COD ( $< 230$  mg/L).

trons recovered as hydrogen with and without graphite granules were similar. CEs ranged from 9.6% to 26.2% with granules and from 5.2% to 23.7% without granules (Fig. 3B). Electrons recovered as hydrogen ranged from 1.8% to 42.7% with granules and from 4.9% and 36.1% without granules (Fig. 3C). The maximum overall hydrogen recovery was 0.0125 mg-H<sub>2</sub>/mg-COD when the BEAMR was operated with granules at an applied voltage of 0.5 V. At this applied voltage, the hydrogen recovery was 42.7% and the CE was 23%. Dividing the overall hydrogen recovery by these two efficiencies results in the maximum theoretical yield, which is 0.126 mg-H<sub>2</sub>/mg-COD.

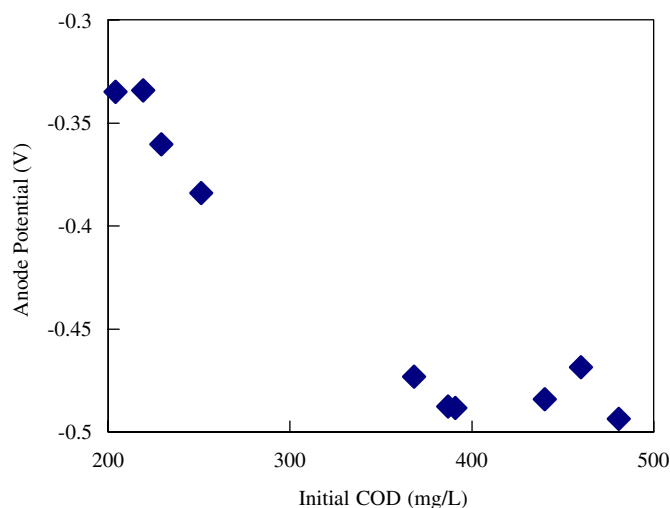


Fig. 4. Effect of wastewater initial COD concentration on the minimum anode potential (applied circuit voltages range from 0.23 to 0.59 V) with the reactor filled with graphite granules (36 mL headspace).

The erratic nature of the CEs and the variability of the strength of the wastewater samples (204–481 mg-COD/L) led us to suspect that the initial COD was affecting reactor performance. A comparison of the anode potentials measured in the reactor containing graphite granules indicated a good correlation of the initial COD of the wastewater with anode potential (Fig. 4). At low COD values (< 230 mg/L), the minimum anode potentials ranged from  $-0.335$  to  $-0.384$  V while at higher CODs (368–481 mg/L) the anode potential decreased to  $-0.468$  to  $-0.494$  V and we observed increased reactor performance (applied voltages varied from 0.23 to 0.59 V; data not shown). The decrease in the anode potential likely reflects a lower redox potential in the biofilm near the electrode, perhaps as a result of more substrate available at the anode. The performance of the reactor containing granules was therefore re-examined on the basis of the initial COD concentration, and there appeared to be a trend of increased CE, hydrogen recovery and current density with increasing initial COD (Fig. 5).

The detention time needed to complete a batch cycle in general decreased with increased applied voltage due to the increased current density and therefore the rate of consumption of substrate by the microorganisms. The detention time for one complete cycle decreased from  $108 \pm 11$  h ( $n = 2$ ) at an applied voltage of 0.23 V to  $30 \pm 5$  h ( $n = 2$ ) at an applied voltage of 0.5 V for the reactor containing graphite granules (Fig. 6). The detention time increased slightly at an applied voltage of 0.59 V versus 0.50 V, likely as a result of the higher initial CODs for the 0.59 V tests (460 and 371 mg-COD/L, versus 204 and 368 mg-COD/L at 0.5 V). Thus, the energetic cost of increasing the applied voltage was offset by an increase hydrogen recovery and a decrease in the required reactor detention time.

### 3.2. Treatment efficiency

Although the initial wastewater strength varied, consistent and effective treatment of the wastewater was achieved in

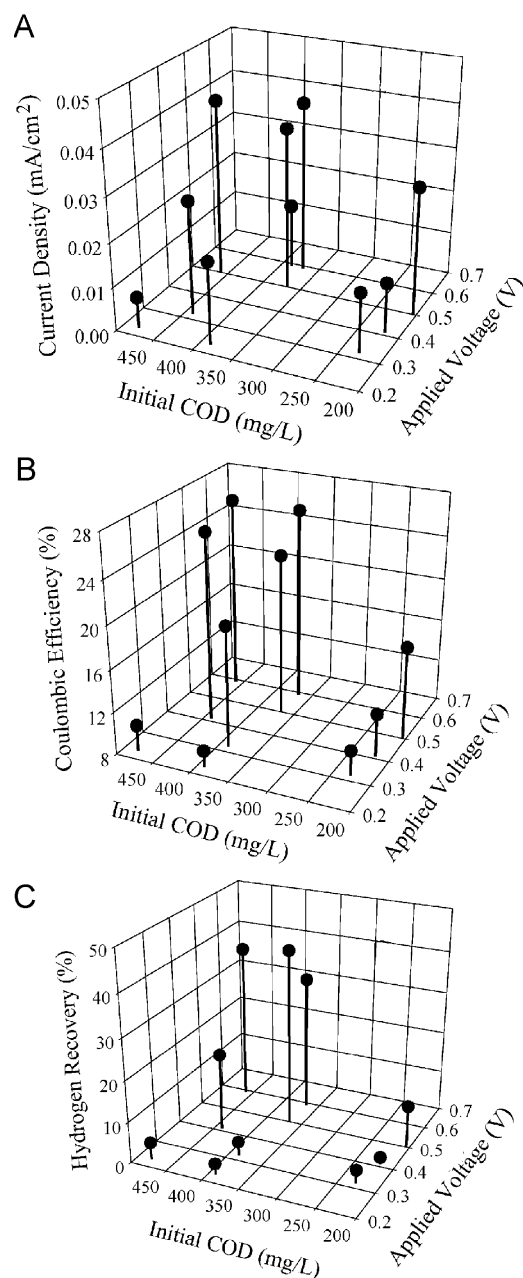


Fig. 5. Current density (A), Coulombic efficiency (B) and hydrogen recovery (C) for the reactor filled with graphite granules (36 mL headspace) as a function of wastewater initial COD concentration and applied voltage.

all tests. The initial condition ranges for the wastewater were: BOD,  $86 \pm 4$  to  $270 \pm 9$  mg/L; COD, 204 to 481 mg/L; DOC,  $56.8 \pm 1.1$  to  $90.0 \pm 1.0$  mg/L. The average BOD concentration ( $BOD_5$ ) at the end of a batch cycle was  $4.5 \pm 1.5$  mg/L ( $n = 8$ ) with a maximum of  $7.0 \pm 0.2$  mg/L and was not a function of the initial wastewater strength [14]. Overall removals (graphite granule tests) were: BOD,  $97 \pm 2\%$  ( $n = 8$ ; range 90–100%); COD,  $95 \pm 2\%$  ( $n = 10$ ; range 89–97%); and DOC,  $92 \pm 2\%$  ( $n = 5$ ; range 89–95%) (Fig. 7).

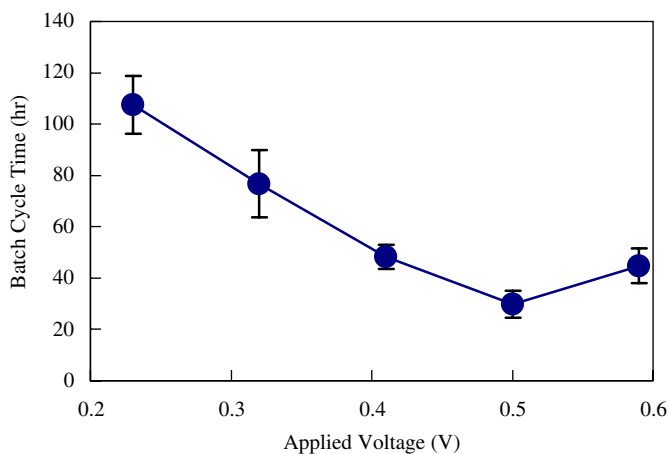


Fig. 6. Effect of applied voltage on the batch cycle time. Reactor with 36 mL cathode headspace and graphite granules in the anode chamber. Error bars represent standard deviation ( $n = 2$ ).

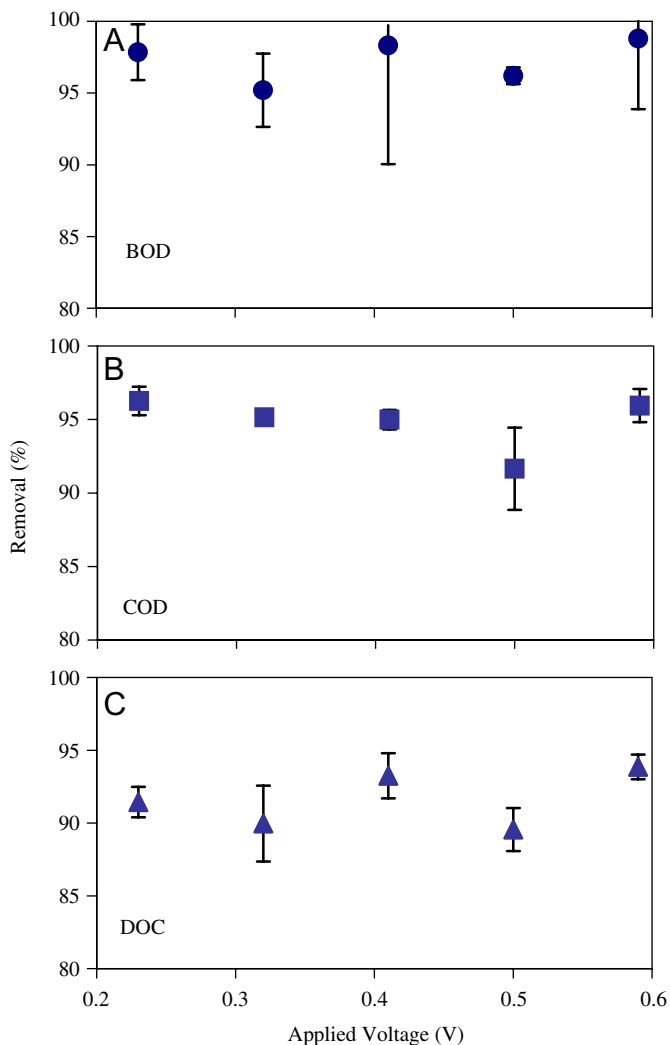


Fig. 7. Batch removal efficiencies of biochemical oxygen demand (A), chemical oxygen demand (B) and dissolved organic carbon (C) in domestic wastewater using graphite granules in anode chamber (and 36 mL headspace).

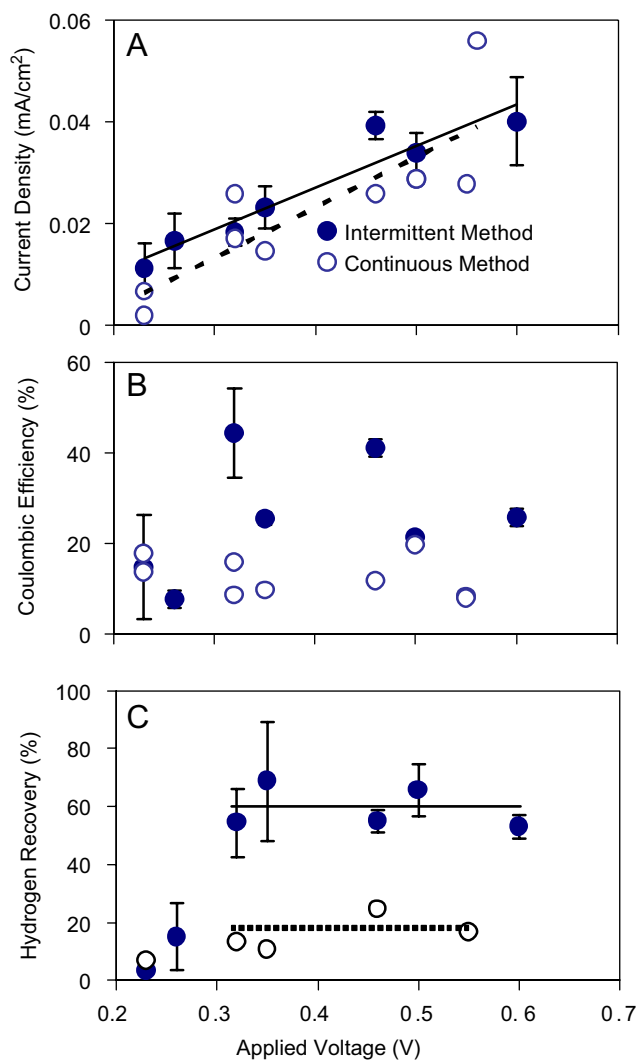


Fig. 8. Current density (A), Coulombic efficiency (B) and hydrogen recovery (C) (lines represent the averages 59% and 16%) as a function of applied potential for two different methods of releasing gas pressure with a head space of 100 mL and no granules added to the anode chamber. Error bars represent standard deviation of two batches run at the same applied potential.

### 3.3. Intermittent gas release

In one series of tests, intermittent gas release (versus continuous gas release) was also examined in reactors using a plain carbon anode (no granules). There was greater hydrogen production and CEs with intermittent gas release ( $R_{H_2} = 59 \pm 11\%$ ;  $n = 10$ ) than continuous gas release ( $R_{H_2} = 16 \pm 6\%$ ,  $n = 4$ ) for applied voltages ranging from 0.32 to 0.6 V (Fig. 8). The overall hydrogen produced was a maximum of 0.031 mg- $H_2$ /mg-COD-removed (382 mL- $H_2$ /g-COD), which is higher than 0.0125 mg- $H_2$ /mg-COD (154 mL- $H_2$ /g-COD) using continuous gas release with granules in the anode chamber. We suspect the main reason for the low hydrogen recovery was appreciable gas loss via diffusion through the tubing under conditions of relatively low hydrogen production. This same tubing has been previously used in tests of hydrogen production by bacteria due to fermentation of glucose, but rates

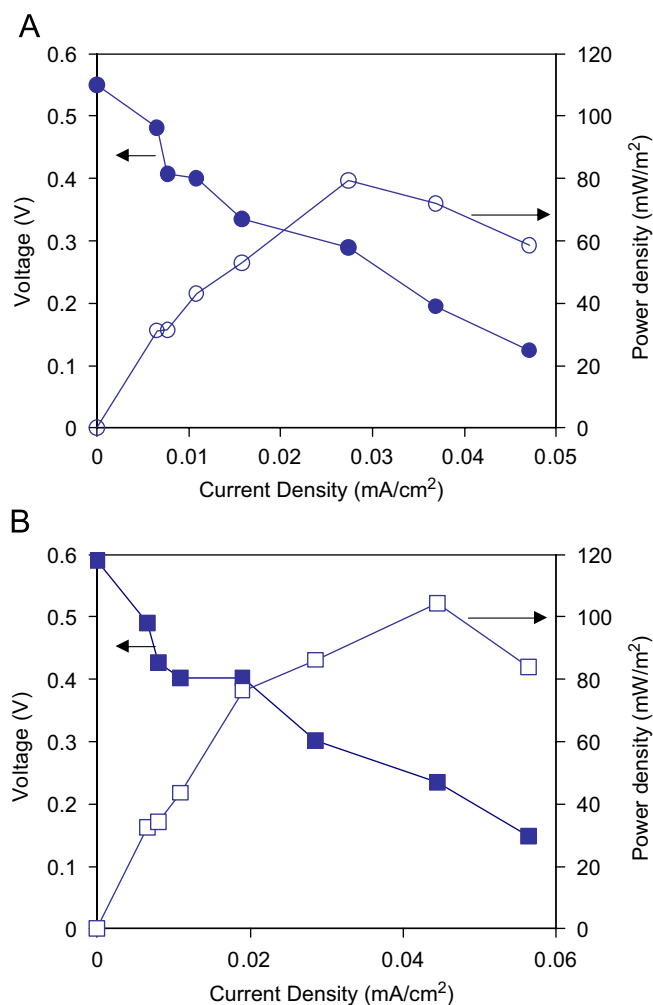


Fig. 9. Performance of the reactor when operated as an MFC using domestic wastewater (A) and acetate (B). Voltage (closed symbols) and power density (open symbols) measured at the maximum voltage of a batch test using a  $1400\ \Omega$  resistor by using the single cycle method [12] with an initial wastewater COD of 439 mg/L or an initial sodium acetate COD of 1000 mg/L.

of hydrogen production here are lower than in those tests [8]. However, the reasons for this increase are not well understood, and will need to be further explored in future tests with more efficient hydrogen gas capture designs.

### 3.4. Reactor performance in MFC mode

The reactor was also operated in MFC mode (graphite granules; headspace volume of 36 mL) in order to determine its performance for electricity generation relative to that achieved with other reactor designs. The maximum power density obtained from polarization curves was  $104\ \text{mW/m}^2$  using acetate, and  $79\ \text{mW/m}^2$  using domestic wastewater (Fig. 9). These power densities are higher than those found using a previously constructed dual chamber MFC ( $36 \pm 1\ \text{mW/m}^2$  using 29.5 mg/L acetate and  $38 \pm 1\ \text{mW/m}^2$  using domestic wastewater [14]). However, using a single chamber MFC, higher power densities have been achieved ( $661\ \text{mW/m}^2$  using 800 mg/L acetate

and  $146\ \text{mW/m}^2$  using domestic wastewater [5,7]). The internal resistance of the reactor was  $44\ \Omega$ . The maximum current density using sodium acetate was 19.7% higher than using domestic wastewater ( $0.0563\ \text{mA/cm}^2$  versus  $0.0471\ \text{mA/cm}^2$ ). The CE using acetate was lower than found using wastewater (12.2% compared to 15.1%).

## 4. Discussion

Hydrogen was successfully produced from the biodegradation of organic matter in domestic wastewater, while at the same time accomplishing wastewater treatment. In order to assess the energy needed to make hydrogen, versus the value of the produced hydrogen we examined the energy needed for the power source in terms of equivalent number of moles of hydrogen based on energy content, compared to the number of moles of hydrogen produced in an experiment. The energy required by BEAMR system ( $E_{\text{ps}}$ ) is obtained by converting the recorded voltage added by the power source ( $V_{\text{ps}}$ ) taken over time intervals  $\Delta t = 0.5\ \text{h}$  for  $n$  intervals using

$$E_{\text{ps}} = \sum_1^n (I)(V_{\text{ps}})\Delta t \left( \frac{1\ \text{kWh}}{1000\ \text{Wh}} \right),$$

where  $I$  is the current in the BEAMR circuit ( $I = V/R$ ),  $V$  the potential between the cathode and the anode recorded by the data logger, and  $R$  the circuit resistance. Note that the efficiency of the power source is not included in this calculation as the power needed for the BEAMR process could be supplied by an MFC. The energy required for the BEAMR reactor is converted to the equivalent number moles of hydrogen needed ( $n_{\text{req}}$ ) based on the energy content of hydrogen ( $121\ \text{kJ/g-H}_2$ ). For example, in one experiment where the maximum amount of hydrogen produced was  $n_{\text{ac}} = 2.757 \times 10^{-4}\ \text{mol H}_2$  (applied voltage 0.5 V), the energy required was  $E_{\text{ps}} = 1.73135 \times 10^{-5}\ \text{kWh}$  or  $n_{\text{req}} = 2.5506 \times 10^{-4}\ \text{mol H}_2$ . The energy requirement relative to hydrogen production for this experiment is therefore calculated to be  $R_E = n_{\text{req}}/n_{\text{ac}} = 0.925$ . This calculation shows that a net amount of hydrogen was produced as  $R_E$  was less than unity. However, the maximum net gain of hydrogen is low (8%) compared to values previously found using acetate. For example, in BEAMR tests using acetate, Liu et al. found hydrogen recoveries of  $0.091\ \text{mg-H}_2/\text{mg-COD}$  ( $2.9\ \text{mol-H}_2/\text{mol-acetate}$ ) for an energy input equivalent to  $0.016\ \text{mg-H}_2/\text{mg-COD}$  ( $0.5\ \text{mol-H}_2/\text{mol-acetate}$ ), or a net gain in hydrogen of 570% [1].

The low efficiency of hydrogen recovery using domestic wastewater, compared to that of acetate, is a result of a low hydrogen recovery (i.e. a loss of hydrogen that was formed) and a low electron recovery (failure to convert organic matter to current, i.e. a low CE). As shown in Fig. 8, hydrogen recoveries averaged only 16% with continuous gas release, but were larger by a factor of 3.7 with intermittent gas release (59%). Percent recoveries of hydrogen in intermittent gas release tests were comparable to that found by Rozendal et al. [2] ( $57 \pm 0.1\%$ ), but less than those measured by Liu et al. [1] (90–100%). The possible reasons for low gas recoveries are hydrogen losses



through the tubing used to record gas production, and hydrogen gas consumption by bacteria in the anode chamber. A detailed analysis of the mass transfer losses of H<sub>2</sub> through the membrane suggest that < 4% of the gas could be lost via diffusion [15]. Thus, loss of the gas through the tubing seems a much more reasonable explanation for low hydrogen recoveries. If we assume that hydrogen recoveries could be improved to 59%, then our net gain of hydrogen calculated in the above example would have improved from 7.5% to 33%.

The maximum CE observed here with domestic wastewater was 26%, compared to CEs of 60–78% [1] and 92 ± 6% [2] in previous BEAMR tests with acetate. The low CE indicates substantial COD removal without current production, but this is consistent with observations that CEs are higher in MFC tests with nonfermentable compounds than with fermentable sugars or complex wastewaters. For example, CEs were 50–65% in MFC tests using acetate and butyrate [16,5], but only 14–21% in a flat plate MFC using glucose, dextran or starch. In tests with domestic wastewater in an upflow MFC, CEs ranged from 0.7% to 8.1% [17]. Low CEs with wastewater have been attributed a loss of substrate due to bacterial utilization of alternative electron acceptors (such as sulfate or nitrate), fermentation, methanogenesis, and diffusion of organic matter from the anode chamber into the cathode chamber [7,12]. Sulfate, for example, is known to diffuse through Nafion, with a measured diffusivity of  $4.53 \times 10^{-7} \text{ cm}^2/\text{s}$  (80 °C, 3.0 M NaCl solution; [18]). In MFC tests using wastewater it was found that COD removal occurred due to sulfate reduction, resulting in low CEs [19]. While we did not examine sulfate as a part of this study, we did notice a sulfide-like odor from the water in the cathode chamber at the end of a batch cycle suggesting sulfate reduction was occurring in our system.

## 5. Conclusions

It has been observed in this study, and other BEAMR and MFC studies, that these processes can be used to treat wastewater. The BOD concentration was always reduced to less than  $7.0 \pm 0.2 \text{ mg/L}$ , and the average DOC removal was  $91.6 \pm 1.9\%$ , with final DOC concentrations of  $6.4 \pm 0.1 \text{ mg/L}$ . These levels of treatment are better than that required for standard secondary treatment effluent (BOD < 30 mg/L) [20]. However, improvements will be needed in H<sub>2</sub> production to make the BEAMR process a practical method for hydrogen generation. Although H<sub>2</sub> yields were low, they increased with wastewater strength, suggesting that wastewaters with high organic matter concentrations, such as food processing and animal wastewaters and septic tank waste, could still be useful in more immediate applications of the BEAMR technology. While the BEAMR process is quite new, improvements in this MFC-based technology are rapidly being made and therefore it may soon be possible to economically apply the technology for the simultaneous treatment of wastewater and hydrogen generation on both dilute and concentrated wastewaters.

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## References

- [1] Liu H, Grot S, Logan BE. Electrochemically assisted microbial production of hydrogen from acetate. *Environ Sci Technol* 2005;39:4317–20.
- [2] Rozendal RA, Hamelers HVV, Euverink GJW, Metz SJ, Buisman CJN. Principle and perspectives of hydrogen production through biocatalyzed electrolysis. *Int J Hydrogen Energy* 2006;31:1632–40.
- [3] Madigan MT, Martinko JM, Parker J. Brock biology of microorganisms, 10th ed. Pearson Education, Inc. 2003. p. 103, 114.
- [4] Kim HJ, Park HS, Hyun MS, Chang IS, Kim M, Kim BH. A mediatorless microbial fuel cell using a metal reducing bacterium, *Shewanella putrefaciens*. *Enzyme Microbiol Technol* 2002;30:145–52.
- [5] Liu H, Cheng S, Logan BE. Production of electricity from acetate or butyrate using a single-chamber microbial fuel cell. *Environ Sci Technol* 2005;39:658–62.
- [6] Oh SE, Min B, Logan BE. Cathode performance as a factor in electricity generation in microbial fuel cells. *Environ Sci Technol* 2004;38:4900–4.
- [7] Liu H, Logan BE. Electricity generation using an air-cathode single chamber microbial fuel cell in the presence and absence of a proton exchange membrane. *Environ Sci Technol* 2004;38:4040–6.
- [8] Logan BE, Oh SE, Kim IS, Van Ginkel S. Biological hydrogen production measured in batch anaerobic respirometers. *Environ Sci Technol* 2002;36:2530–5.
- [9] Liu H, Cheng S, Logan BE. Power generation in fed-batch microbial fuel cells as a function of ionic strength, temperature and reactor configuration. *Environ Sci Technol* 2005;39:5488–93.
- [10] Logan BE. Environmental transport processes. New York: Wiley; 1999.
- [11] Rabey K, Clauwaert P, Aelterman P, Verstraete W. Tubular microbial fuel cells for efficient electricity generation. *Environ Sci Technol* 2005;39:9077–82.
- [12] Heilmann J, Logan BE. Production of electricity from proteins using a microbial fuel cell. *Water Environ Res* 2006;78(5):531–7.
- [13] American Public Health Association, American Water Works Association, Water Pollution Control Federation. Standard methods for the examination of water and wastewater, 19th ed. Washington, Dc. American Public Health Association, 1995.
- [14] Min B, Cheng S, Logan BE. Electricity generation using membrane and salt bridge microbial fuel cells. *Water Res* 2005;39(5):942–52.
- [15] Heilmann J. Microbial fuel cells: proteinaceous substrates and hydrogen production using domestic wastewater. University Park, PA: The Pennsylvania State University; 2005.
- [16] Min B, Logan BE. Continuous electricity generation from domestic wastewater and organic substrates in a flat plate microbial fuel cell. *Environ Sci Technol* 2004;38:5809–14.
- [17] He Z, Minteer SD, Angenent LT. Electricity generation from artificial wastewater using an upflow microbial fuel cell. *Environ Sci Technol* 2005;39:5262–7.
- [18] Herrera A, Yeager HL. Halide and sulfate ion diffusion in nafion membranes. *J Electrochem Soc* 1987;134:2446–50.
- [19] Rabaey K, Ossieur W, Verhaege M, Verstraete W. Continuous microbial fuel cells convert carbohydrates to electricity. *Water Sci Technol* 2005;52(1–2):515–23.
- [20] EPA, EPA onsite wastewater treatment systems manual (<http://www.epa.gov/ordntrnt/ORD/NRMRL/pubs/625r00008/html/html/625R00008chap3.htm>) (Table 3–27), 2002, Accessed October 24, 2005.