Electricity generation from swine wastewater using microbial fuel cells

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Abstract

Microbial fuel cells (MFCs) represent a new method for treating animal wastewaters and simultaneously producing electricity. Preliminary tests using a two-chambered MFC with an aqueous cathode indicated that electricity could be generated from swine wastewater containing 8320 ± 190 mg/L of soluble chemical oxygen demand (SCOD) (maximum power density of 45 mW/m\textsuperscript{2}). More extensive tests with a single-chambered air cathode MFC produced a maximum power density with the animal wastewater of 261 mW/m\textsuperscript{2} (200 Ω resistor), which was 79% larger than that previously obtained with the same system using domestic wastewater (146 ± 8 mW/m\textsuperscript{2}) due to the higher concentration of organic matter in the swine wastewater. Power generation as a function of substrate concentration was modeled according to saturation kinetics, with a maximum power density of $P_{\text{max}} = 225$ mW/m\textsuperscript{2} (fixed 1000 Ω resistor) and half-saturation concentration of $K_s = 1512$ mg/L (total COD). Ammonia was removed from 198 to 3 to 4 mg/L (83% removal). In order to try to increase power output and overall treatment efficiency, diluted (1:10) wastewater was sonicated and autoclaved. This pretreated wastewater generated 16% more power after treatment (110 ± 4 mW/m\textsuperscript{2}) than before treatment (96 ± 4 mW/m\textsuperscript{2}). SCOD removal was increased from 88% to 92% by stirring diluted wastewater, although power output slightly decreased. These results demonstrate that animal wastewaters such as this swine wastewater can be used for power generation in MFCs while at the same time achieving wastewater treatment.

Keywords: Microbial fuel cell; Electricity; Swine wastewater; Animal wastewater; Power generation

1. Introduction

Large volumes of high-strength wastewaters are produced annually from industrial and agriculture operations. For example, it is estimated that 5.8 × 10\textsuperscript{7} tons of animal manures are generated each year in the US alone (Dentel et al., 2004). The animal wastewater must be treated to meet discharge regulations prior to being released into the environment (Suzuki et al., 2002; Maekawa et al., 1995) to avoid water contamination and odor problems (Luo et al., 2002; Westerman et al., 2000). High concentrations of nitrate (NO\textsubscript{3}\textsuperscript{-}) and phosphate in wastewater can also contribute to water pollution through eutrophication of surface water (Luo et al., 2002; Ra et al., 2000). Many treatment techniques have been proposed to remove inorganic or organic pollutants from wastewater, but these processes...
entail high operational costs or large amounts of land for treatment (Sevrin-Reyssac, 1998).

One approach to offset the costs of industrial and animal wastewater treatment is to generate useful amounts of bioenergy, such as hydrogen or methane gas, from the organic matter in the wastewater while at the same time accomplishing treatment (Logan, 2004; Angenent et al., 2004; Rabaey and Verstraete, 2005). Food processing wastewaters have been tested for biological hydrogen production using fermentative bacteria in several types of processes (Das and Veziroğlu, 2001; Yu et al., 2002; Oh and Logan, 2005; Van Ginkel et al., 2005). However, these processes have not been widely used due to low energy recovery from the organic matter (1.4–2.5 mole of hydrogen per mole of hexose) and high operational costs (Logan, 2004; Angenent et al., 2004; Oh and Logan, 2005).

Microbial fuel cells (MFC) have been developed that can generate electricity directly from marine sediments, anaerobically digested sludge, food wastewaters, and domestic wastewater. The amount of power produced varies depending on the type of reactor and the specific source of the organic matter. In laboratory and field tests, 10–25 mW/m² (power normalized to the projected surface area of the anode) is produced with sediment fuel cells when the anode is placed into an anaerobic marine sediment and the cathode is in the overlying seawater containing dissolved oxygen (Reimers et al., 2001; Bond et al., 2002; Delong and Chandler, 2002; Tender et al., 2002). Using a single-chambered MFC configuration (Liu et al., 2004; Liu and Logan, 2004; Min and Logan, 2004), up to 26 mW/m² (maximum power density) was generated using domestic wastewater (initial chemical oxygen demand (COD) of 200–300 mg/L) while at the same time removing up to 80% of the COD (Liu et al., 2004). A flat plate MFC generated 72 ± 1 mW/m², but under conditions that achieved only 42% COD removal (Min and Logan, 2004). Liu and Logan (2004) generated a maximum of 146 ± 8 mW/m² using wastewater with a single-chambered air-cathode MFC operated in batch mode operation. In only a few cases has there been a direct comparison of a single wastewater with different types of MFCs. For example, it was shown using a food processing wastewater that power could be increased from 81 ± 7 to 371 ± 10 mW/m² by using a single-chambered MFC instead of a two-chambered MFC (Oh and Logan, 2005).

Animal wastewaters should provide a good source of organic matter for electricity production using an MFC, but so far this type of wastewater has not been examined for electricity production (Logan, 2004). Potential problems that could interfere with electricity generation in a MFC relate to those that can affect other anaerobic processes such as methane production: toxicity due to the high concentrations of ammonia in the wastewater or to volatile acids produced during hydrolysis and fermentation of the substrates (Rittmann and McCarty, 2001). In this study, we demonstrate for the first time that it is possible to produce electricity directly from swine wastewater using a MFC, while at the same time accomplishing wastewater treatment. Preliminary tests were conducted using an aqueous cathode, two-chambered MFC to demonstrate the feasibility of treatment and for comparison of power densities achieved using other substrates. More extensive tests were then conducted using an air-cathode, single-chambered MFC that is known to produce more power than the two-chambered system (Liu and Logan, 2004; Oh et al., 2004). Power output was examined as a function of circuit load (resistance), wastewater strength, and pretreatment by sonication of the wastewater. In addition, we examined ammonia and phosphate concentrations in the raw and treated wastewater.

2. Materials and methods

2.1. Animal wastewater

Swine wastewater was collected from the Pennsylvania State University Swine Farm (University Park, PA) and kept in a refrigerator at 4 °C before use. The wastewater was used as the inoculum for all MFC tests without any modifications such as pH adjustments or addition of nutrients or trace metals. Tests were conducted using full-strength wastewater, except as indicated, when the wastewater was diluted using ultrapure water (Milli-Q system; Millipore Corp., New Bedford, MA), autoclaved, or sonicated (Sonifier 450; Branson Ultrasonic Co., CT; output control = 7, duty cycle = 40%).

2.2. MFC configuration and operation

All experiments were conducted using MFCs operated in fed-batch mode in a temperature-controlled room (30 °C). A two-chambered MFC was used in initial tests that contained two electrodes (anode and cathode), each in a separate bottle (310 mL capacity, Corning Inc. NY, USA). Each bottle was filled to 250 mL with wastewater for the anode and phosphate buffer solution (pH = 7; 2.75 g/L Na2HPO4 + 4.22 g/L NaH2PO4 · H2O) for the cathode as previously described (Min et al., 2005). The two bottles were connected with a glass tube (total length = 8 cm; inner diameter = 1.3 cm) with a proton exchange membrane (Nafion™ 117, Dupont Co., Delaware, USA) held by a clamp in the middle of the tube. The electrodes (2.5 × 4.5 cm each) were made of a carbon paper (E-Teck) and connected via an external circuit containing a single resistor (R = 1000 Ω, except as noted). One side of the cathode was coated with a catalyst (0.35 mg-Pt/cm²). The cathode chamber was
continuously aerated at 30 mL/min to provide dissolved oxygen at the cathode.

Most tests were conducted using a single-chambered MFC containing an air cathode, with liquid contained inside a cylinder 4 cm long and 3 cm diameter chamber (28 mL empty bed volume) as previously described (Liu et al., 2004). The anode and cathode electrodes were located on the opposite sides of the chamber, and the reactor lacked a proton exchange membrane (PEM). The electrodes were made of the same materials as those used in the two-chambered system except a stainless steel wire was used for connecting the electrodes (by compression) to an external circuit. In some experiments, the side of the cathode facing the air was coated with polytetrafluoroethylene (designated as a PTFE cathode) in order to reduce evaporation of water through the cathode. This electrode was prepared by applying a PTFE solution (50% by weight), drying at room temperature for 10 min, and then heating for 10 min at 380 °C.

2.3. Analysis

Total and soluble (filtered) COD of wastewater were measured in duplicate (except as noted) using Standard Methods (method 5220; HACH COD system, HACH Company, Loveland, CO.; American Public Health Association, American Water Works Association, Water Pollution Control Federation, 1995). All samples for soluble COD (SCOD) were filtered through a 0.45 μm pore diameter syringe filter, while total COD (TCOD) measurements were conducted without treatment. Measurements on inorganic compounds were made in duplicate using procedures based on Standard Methods (American Public Health Association, American Water Works Association, Water Pollution Control Federation, 1995) for ammonia (Salicylate method), phosphate (PhosVer 3 method), nitrate (Cadmium reduction method), and nitrite (Diazotization chromotropic acid method) (HACH).

The cell voltage across a resistor was measured using a multimeter, and all data were automatically recorded by a computer and a data acquisition system (2700, Keithly). Power density, $P$ (W/m²), was obtained according to $P = IV/A$, where $I$ (A) is the current, $V$ (V) is the voltage, and $A$ (m²) is the projected surface area of the anode. The Coulombic efficiency (CE) was calculated based on current generation and the amount of substrate removal during a MFC operation (Liu et al., 2004; Oh et al., 2004; Min and Logan, 2004). The maximum power density was determined by adding fresh substrate to the MFC and establishing constant power, and then varying the external resistance over a range of 2–400 KΩ and recording the voltage (typically 5–10 min per resistor). The power was then calculated for each resistance as a function of the current.

3. Results and discussion

3.1. Power generation from swine wastewater using a two-chambered MFC

Preliminary experiments conducted using a two-chambered MFC demonstrated that electricity could be generated using swine wastewater, and that the bacteria needed were already present in the wastewater. When non-diluted swine wastewater was added into the two-chambered MFC, a circuit voltage of 20 ± 2 mV (±SD, $n = 90$; 8–53 h) was immediately generated within only a few hours (Fig. 1A). This initial voltage might have been due to both chemical and biological factors based on the difference of the potential between the two chambers. Thereafter, the voltage rapidly increased due to biological activity, and stabilized at 126 ± 1 mV ($n = 114$) over the following 47 h period (83–140 h), resulting in a power density of 7.1 ± 0.2 mW/m² ($R = 1000 \Omega$) for this first inoculation of the MFC with wastewater.

![Fig. 1. Voltage generation (A) with full-strength animal wastewater in a two-chambered MFC (1000Ω). Voltage and maximum power generation (B) as a function of current density obtained by varying the external circuit resistance from 4Ω to 400KΩ.](image-url)
After replacing the anode chamber solution four times, we obtained a consistent and repeatable cycle of power generation with non-diluted swine wastewater. By varying the circuit resistance, it was determined from a polarization curve that the maximum power that this system could produce was 45 mW/m² (141 mA/m²) at 1000Ω (Fig. 1B). This maximum power output is similar to that obtained using this same two-chambered system in several other studies using acetate (38 mW/m², Min et al., 2005; 43 mW/m², Oh et al., 2004; 40 mW/m², Kim et al., 2005) or cysteine (39 mW/m², Logan et al., 2005). The observation that a similar maximum power output was achieved with several different substrates is consistent with previous findings that power generation in this two-chambered MFC used by our research group is limited by internal resistance and not by the power that can be produced by bacteria with specific substrates (Min et al., 2005).

3.2. Power generation using a single-chambered MFC

To demonstrate the potential for greater power densities using animal wastewater, all further tests were conducted with a single-chambered MFC. Acclimation required more time with the single-chambered MFC (114 h) than the two-chambered MFC (data not shown). After two cycles of replacing the wastewater over 80 h, the voltage reached a stable value of 357 ± 1 mV (1000Ω), producing a maximum power density of 182 ± 1 mW/m² with the swine wastewater (Fig. 2A). Over a period of 44 h, the SCOD decreased by 27%, or from 8320 ± 190 to 6090 ± 60 mg/L (triplicate measurements). The CE for this measured COD removal was 8%. This CE is quite low, even compared to a value of CE = 20% obtained in tests with domestic wastewater for this MFC (Liu and Logan, 2004).

The maximum power density for the single-chambered MFC was 261 mW/m² (200Ω, 1.4 A/m²; Fig. 2B). This maximum power density is nearly 6 times that obtained using the two-chambered system. The observation that power density is much larger using the single-chambered than a two-chambered MFC (data not shown) suggests that the type of substrate can affect power output in this type of MFC. In previous tests using the same MFC, maximum power densities of 494 and 506 mW/m² were obtained using readily biodegradable substrates of glucose and acetate (Liu and Logan, 2004; Liu et al., 2005a). However, power output was lower using butyrate (305 mW/m²), and decreased further for domestic wastewater (146 mW/m²). These results demonstrate that the substrate, and perhaps the bacterial community that developed during acclimation, affected microbial kinetics and therefore the maximum power density achievable with the swine wastewater.

3.3. Power generation as a function of wastewater concentration

Power generation was measured as a function of wastewater concentration to determine if the concentration of organic matter in the wastewater was limiting power generation. The TCOD concentration of the wastewater was varied by dilution from 494 ± 1 to 4470 ± 440 mg/L (SCOD range of 359 ± 3–2840 ± 50 mg/L). The maximum power density obtained with a fixed external resistance (1000Ω) showed a saturation-type
relationship with respect to wastewater concentrations (Fig. 3). The maximum power density at this resistance was \( P_{\text{max}} = 225 \text{ mW/m}^2 \), with a half-saturation concentration of \( K_s = 1510 \text{ mg/L (TCOD)} \). The finding of a saturation-type relationship for power output as a function of substrate concentration is consistent with other studies using acetate or butyrate as a substrate in this single-chambered MFC (Liu et al., 2005a).

The CE of substrate removal was determined by measuring the TCOD and SCOD of the solutions after the voltage decreased to less than 100 mV (\( \sim 14 \text{ mW/m}^2 \)). The CEs measured at each substrate concentration decreased from 26% to 10% with an increase in wastewater concentration (Fig. 3). This inverse relationship between CE and substrate concentration is similar to that observed by Liu et al. (2005a). They found that the CE decreased from 28% to 13% (\( R = 1000 \Omega \)) using acetate in the same type of MFC, when substrate concentration increased from 80 to 800 mg/L. It is thought that part of this relationship between CE and substrate concentration is due to the effect of oxygen transfer into the system through the cathode. The higher the substrate concentration the longer the period of time needed to fully degrade the substrate. As the time period increases, more oxygen can leak into the system causing aerobic removal of the substrate, and lowering the overall CE. Substrate can also be removed using alternate electron acceptors, for example through sulfate reduction, heterotrophic denitrification, and methanogenesis.

3.4. Other factors affecting power generation

Several other factors were examined with respect to power output, including wastewater pretreatment by sonication or autoclaving, and stirring the wastewater. It was hypothesized that there would be relatively less electricity generation from the particulate organic matter than from the soluble organic matter due to slower degradation kinetics for particulate material (Bougrrier et al., 2004) and the limited diffusion of the particulate material into the biofilm to the electrode surface, where the electrochemically active bacteria are located. For example, sonication has been shown to increase biogas production in anaerobic digestors (Tiehm et al., 2001; Bougrrier et al., 2004). To decrease the time needed to fully degrade the biodegradable material in the sample during an experiment, the wastewater was diluted (1:10).

Sonication (20 min) increased the SCOD of diluted wastewater by 19%, or from 1300±40 to 1550±80 mg/L, but did not change the total COD (1940±80 mg/L). The increase in the SCOD came from the solids, as indicated by a decrease in TSS from 250±50 to 74±25 mg/L. When the sonicated and original diluted wastewaters were used in MFC tests, there was essentially no change in the maximum power density. The sonicated wastewater produced a maximum power density of \( 105±5 \text{ mW/m}^2 \) (8–29 h), while the untreated wastewater produced \( 101±4 \text{ mW/m}^2 \) (5–32 h) (Fig. 4). COD removals using the sonicated animal wastewater were 85% for the TCOD and 91% for SCOD (after 72 h operation; final TCOD = 290±20 mg/L and SCOD = 140±20 mg/L), while those for the untreated wastewater were 89% and 90% (final TCOD = 220±40 mg/L; SCOD = 130±10 mg/L), respectively. The CE for the sonicated wastewater was 6.8%, while that for the untreated wastewater was 7.2%. Given that these differences are in general quite small, wastewater sonication
alone does not appear at this time to be a useful way to increase power densities or COD removals in MFCs.

Autoclaving the wastewater was also examined as a method of treatment to increase power generation in the MFC. Autoclaving the wastewater can kill anaerobic bacteria, such as methanogens, that can result in a loss of organic matter in a manner that does not generate electricity. The maximum power density with the autoclaved wastewater (82 or 84 mW/m²) in two tests was not appreciably different than that obtained with raw wastewater (77 or 79 mW/m²) (Fig. 5). The CE with the autoclaved wastewater was slightly lower (17%), but not substantially different from that with the raw wastewater (20%). Thus, autoclaving alone is insufficient to appreciably alter power generation in the MFC.

The average power density of 110±4 mW/m² (3–30 h) for the sonicated and autoclaved diluted wastewater was significantly higher (p value<0.001, t-test) than that of raw wastewater (96±4 mW/m²; 5–26 h) (Fig. 6). Thus, the combined pre-treatment of autoclaving and sonicating the wastewater increased power generation by 16%. The reasons for this increase could include changes in biodegradability of the organic matter, and changes in the molecular weight or particle size spectra of the organic matter. While power densities can be increased by these two processes, however, it is not likely that such pretreatment could be economical due to the high energy input needed for both processes.

Another factor that was investigated to improve reactor performance was stirring the wastewater. It has been shown that slow proton transfer between the anode and cathode can limit power generation (Liu et al., 2005b). It was therefore speculated that stirring the water might increase power density due to enhancing proton transport to the cathode, and substrate transport to the anode. It was found, however, that power generation decreased as a result of stirring. The maximum power density was significantly (p<0.001, t-test) larger in the system without stirring (128±3 mW/m²; 8–27h) than in the system with stirring (118±2 mW/m²; 8–26h) (Fig. 7). While the reason for this change is not known, stirring may have decreased the concentration gradient of volatile acids in the biofilm produced from hydrolysis and fermentation of the organic matter. Alternatively, stirring might also have increased...
the oxygen flux into the reactor by affecting the resistance to oxygen mass transfer at the cathode, resulting in an increase in the redox potential of the anode chamber, but this situation was not examined further. Consistent with this explanation, COD removal was increased when the solution was stirred (90% TCOD and 92% SCOD removal with stirring; 89% TCOD and 88% SCOD removals without stirring; Fig. 7) while the CE with stirring (5%) was also less than that (8%) without stirring.

3.5. Nitrogen and phosphate concentrations during MFC treatment

Ammonia, nitrite, nitrate and phosphate concentrations were examined to determine the effect of MFC treatment on these parameters. After 100 h operation using diluted (1:10) wastewater, ammonia was removed by 83 ± 4% (from 198 ± 1 to 34 ± 0 mg NH₄-N/L) when the SCOD was reduced from 1240 ± 20 to 120 ± 30 mg/L (86 ± 6% removal). The high removals observed here for a reactor operating under anaerobic conditions was surprising. Nitrite and nitrate concentrations increased from 0.4 ± 0.1 to 2.9 ± 0.1 mg NO₂-N/L and 3.8 ± 1.2 to 7.5 ± 0.1 mg NO₃-N/L. This increase in oxidized nitrogen suggests that nitrification was occurring, likely as a result of oxygen diffusion through the cathode. Oxygen diffusion through the cathode is known to result in a loss of carbonaceous substrates to aerobic degradation, as evidenced by low CE in MFCs (Liu and Logan, 2004). The total amount of ammonia removal (164 mg NH₄-N/L) was much larger than the corresponding increases in nitrite (2.5 mg NO₂-N/L) and nitrate (3.7 mg NO₃-N/L). The low CE and low concentrations of nitrate and nitrite suggest additional nitrogen removal through several possible routes including denitrification, anaerobic ammonia oxidation (anammox) (Rittmann and McCarty, 2001; Dong and Tollner, 2003), nitrite reduction by lithotrophic ammonia oxidizers (Zart and Bock, 1998), or by some previously unobserved method of ammonia oxidation coupled to electricity generation. Further work is needed to better understand the process by which nitrogen is removed in this MFC.

Orthophosphate concentrations (PO₄-P mg/L) did not decrease, and may have slightly increased (41 ± 1–48 ± 1 mg/L) during the reactor test cycle. The increase in orthophosphate concentration could have been a result of the low redox potential in the MFC which would stimulate the release of stored phosphates in the bacteria (Luo et al., 2002), or the conversion of organic phosphorus in the wastewater to orthophosphate.

4. Conclusions

Electricity was generated using swine wastewater, at a power density that depended on the type of MFC. The maximum power density using a two-chambered MFC was 45 mW/m², while 6 times more power (261 mW/m²) was generated using a single-chambered system, although the CE was low (8%). Power generation showed a saturation-type relationship with wastewater concentration, with a half-saturation concentration constant of $K_s = 1510$ mg/L (TCOD). The combined pre-treatment of sonication and autoclaving the wastewater generated 16% more power (110 ± 4 mW/m²) than that produced using a raw diluted wastewater (96 ± 4 mW/m²). Stirring the wastewater in the MFC reduced the power density. Electricity generation was accompanied by 86 ± 6% removal of COD and 83 ± 4% removal of NH₄-N. However, phosphate concentrations increased by 17% during treatment. These results demonstrated the feasibility of using MFC technologies to generate electricity and simultaneously treat swine wastewaters, although additional studies are needed to scale up and optimize the process.

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References


