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Using Microbial Fuel Cells to Treat Raw Sludge and Primary Effluent for Bioelectricity Generation: Final Report

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Executive Summary

Improving energy recovery from wastewater is a sustainable approach for wastewater treatment and is also one of the Milwaukee Metropolitan Sewerage District (MMSD)/Veolia's interests to protect and improve the water environment in the Milwaukee area. This project is to build, operate and investigate microbial fuel cells (MFCs) for treating raw sludge or primary effluent (MFCs installed in the activated sludge system) to generate bioelectricity. Two sub-projects will be carried out simultaneously with different goals. First, we will investigate the performance of MFCs to treat raw sludge from MMSD wastewater treatment facilities. The specific objectives include: (1) examining the electricity generation from raw sludge in different types of MFCs; (2) determining the optimal parameters for system operation; and (3) revealing microbial communities and identifying dominant microorganisms. Second, we propose to install MFCs directly in aeration tanks and conduct the first onsite testing of MFCs in activated sludge system. The project will have significant scientific and practical contributions: (1) it aims to develop a cost-effective process for recovering energy from wastewater and improving oxygen use in aeration tanks; (2) implementation of the proposed technology does not require significant changes to the existing facilities; (3) the project has the potential to develop an online microbial sensor for monitoring organic concentration in wastewater; and (4) it will bring the expertise from MMSD/Veolia and UWM together to achieve mutual research goals and establish a close collaboration. The success of those projects will have a positive impact on the local water environment through application of novel technology, energy recovery from wastewater, and (possible) reduction of energy consumption by activated sludge systems. The research is carried out under the direction of Dr. Zhen He in a close collaboration with MMSD/Veolia.

The research has several significant findings: (1) MFC technology is not suitable for deployment in an aeration tank; (2) MFC technology may not be suitable for treating high-strength waste for energy recovery; (3) MFC technology can be a promising alternative for treating low-strength wastewater; and (4) energy production can be improved by using spiral spacers and other appropriate optimization of configuration and operation. Those results encourage us to continue MFC development with next task of demonstration of technical viability at a transitional scale (200-500 L).

This study has resulted in two joint journal publications and another two under revision/review.

1. Introduction

1.1 Treatment of Raw Sludge

It is well known that wastewater treatment consumes a significant portion of energy in the U.S. It is also well known that wastewater influent contains a large amount of energy contents in the form of organics. Thus, to maintain a sustainable society, it is clearly beneficial to efficiently extract energy from wastewater to compensate energy use of the treatment process. This can be realized by anaerobic processes to produce methane, hydrogen or bio-electricity. Here we will discuss a conventional approach—anaerobic digestion and a novel method—microbial fuel cell with the overarching goal to maximize bioenergy recovery from wastewater.

Anaerobic digestion (AD) is a well developed technology to generate biogas (mainly methane) from organic wastes through a series of microbial reactions. It has an established performance and is considered as an effective approach for wastes-to-energy. ***The main advantages of AD technology include***: 1) AD is a well developed and practiced technology; 2) AD can handle high strength wastewater at a loading rate of 10-20 kg COD/(m3 day); 3) Thermophilic AD can reduce pathogens in wastewater; and 4) Methane can be converted to useful electricity. ***The main disadvantages of AD technology include:*** 1) AD must be operated at (relatively) high temperature (>30 ºC) and thus requires heat input; 2) Biogas is difficult to store and needs to be treated because of components such as H2S; 3) Conversion of biogas to electricity requires an additional step and is at an efficiency of conventional combustion;and 4) The effluent of AD still contains high organic contents and requires post-treatment.

Microbial fuel cells (MFCs) are a new technology to directly produce electricity from organic wastes. MFCs are bio-electrochemical reactors in which bacteria oxidize various organic or inorganic compounds in the anode chamber and generate proton and electrons that transport to the cathode to reduce oxygen to water. Electron flow from the anode to the cathode generates an electric current or power if a load is connected (Figure 1.1). ***The main advantages of MFCs include***: 1) Direct generation of electricity; no additional conversion step is required; 2) MFCs can be operated at temperatures below 20 ºC, and are efficient at low substrate concentration levels, in terms of both electricity generation and organic removal; 3) Our previous studies and others' have found that MFCs can improve biodegradation of organics, even some refractory compounds; and 4) MFCs can be diversified with new functions such as hydrogen production, desalination, and heavy metal removal. ***The main disadvantages of***

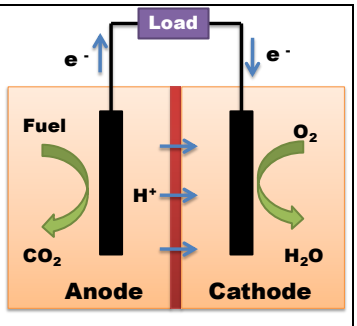

Figure 1.1 *Schematic of a microbial fuel cell.*

MFCs include: 1) MFCs are still in the development stage, yet the technology has advanced significantly in the past decade; 2) MFCs cannot efficiently treat high-strength wastewater; and 3) Construction cost could be high because of use of cathode catalysts.

1.2 Activated Sludge System

The activated sludge process is a widely applied method to treat municipal wastewater in the U.S. A key factor in the successful performance of activated sludge process is aeration, which consumes a considerable amount of energy and contributes significantly to operating expense in wastewater treatment plants. Moreover, the oxygen supplied by aeration cannot be efficiently used by microorganisms, resulting in wasted energy (via aeration). Efforts have been made to improve oxygen use by optimizing aeration systems. Here, we propose a solution to install MFCs directly into aeration tanks to increase oxygen use and recovery energy.

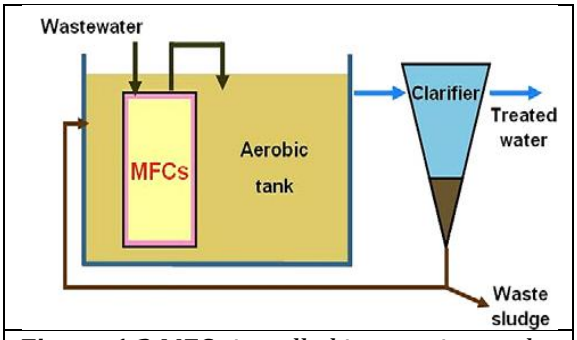

Figure 1.2 *MFCs installed in aeration tanks [1].*

The proposed process is shown in Figure 1.2. The anode of MFCs will be fed with the same raw wastewater as the influent to the aeration tanks; that is, part of the wastewater will be diverted into MFCs for anaerobic treatment with products of bio-electricity. By installing MFCs in aeration tanks, the excessive oxygen supply can be used by the cathode reactions of MFCs and part of the organic wastes can be converted into electricity directly. Although this idea has been previously investigated [1], the study missed important information on organic removal, and the experiment was conducted in small lab-scale reactors with poorly designed MFC and aeration systems. We propose to conduct onsite testing of this idea with an improved design of the MFC reactors in one of the MMSD's wastewater treatment facilities (e.g., Jones Island Water Reclamation Facility).

The significance and potential benefits of the proposed project include: 1) The first systematic study to integrate MFC technology with an activated sludge system and to conduct experiments in actual aeration tanks in a wastewater treatment plant; 2) The onsite experiment in the MMSD water reclamation facility will bring expertise from MMSD/Veolia and UWM together, thereby establishing a close collaboration; 3) The success of the project will generate a technology that can recover bioenergy and improve oxygen use in aeration tanks; 4) Implementation of the proposed process can be realized through simple upgrade without changing the existing facilities, which is advantageous for achieving better performance of the existing facility; and 5) The project may also make it

possible to use MFCs as an in situ microbial sensor for online monitoring COD concentration.

2. Improving Electricity Production in Tubular Microbial Fuel Cells through Optimizing the Anolyte Flow with Spiral Spacers

(This section has been published as: Zhang, F., Ge, Z., Grimaud, J., Hurst, J. and He, Z.* (2013) Improving electricity production in tubular microbial fuel cell system through optimizing the anode flow with spiral spacers. Bioresource Technology. Vol 134, pp 251-256)

2.1 Abstract

The use of spiral spacers to create a helical flow for improving electricity generation in microbial fuel cells (MFCs) was investigated in both laboratory and on-site tests. The lab tests found that the MFC with the spiral spacers produced more electricity than the one without the spiral spacers at different recirculation rates or organic loading rates, likely due to the improved transport/distribution of ions and electron mediators instead of the substrates because the organic removal efficiency was not obviously affected by the presence of the spiral spacers. The energy production in the MFC with the spiral spacers reached 0.071 or 0.073 kWh/kg COD in either vertical or horizontal installment. The examination of the MFCs installed in an aeration tank of a municipal wastewater treatment plant confirmed the advantage of using the spiral spacers. Those results demonstrate that spiral spacers could be an effective approach to improve energy production in MFCs.

2.2 Introduction

A microbial fuel cell (MFC) is a promising technology that can be applied to wastewater treatment for energy-efficient pollutant removal. In the past decade, researchers have made significant progress towards understanding fundamental issues of microbiology, electrochemistry and reactor architecture in MFCs [2]. However, MFC development is still hindered by challenges such as system scaling up and further improvement of electric energy. The power density > 1 kW/m^3 has been achieved in some studies with very small-scale MFCs [3], but large-scale MFCs (> 1 L) generally had low power output. Substantial efforts have been made to improve the power output in MFCs through modifying or pre-treating electrode materials, using high-efficiency separators, optimizing reactor configuration, and selecting efficient microorganisms [4-6].

Optimizing operating conditions is another important approach to improve MFC performance. Besides factors like temperature and pH, using mixing intensity to improve mass transfer could be an effective method to improve the performance in continuously operated MFCs. It was reported that a higher mixing intensity through applying a higher shear rate optimized biofilm formation and thus improved the activities of the electrochemically-active microbes in an MFC [7]. A study of a continuously operated liter-scale MFC found that the improvement of power production via adjusting the mixing intensity was affected by the substrate loading rates and higher recirculation rates might not be effective to increase electricity generation under some conditions [8]. Those results demonstrate the importance of the flow pattern of the anolyte to MFC performance and also reveal the problems of MFCs containing high surface area electrodes. The high surface area electrodes, such as carbon-fiber based brush electrodes, have been proved effective in improving electricity generation in MFCs [9]. Many studies that were conducted in small-size MFCs had good mixing of their anolytes and did not have obvious issues with the mass transfer of substrates and ions. However, in a large-scale MFC, substrates/ions could be unevenly distributed inside the anode compartment, thereby creating dead zones where substrates/ions supply is insufficient and electrode surface area is not efficiently used for electricity generation. For example, in a tubular MFC filled with high-density electrode materials, the anolyte will likely go from the inlet to the outlet through a pathway with less hydraulic resistance, which only occupies the part of the interior space of the anode compartment. Other parts of the anode space that do not receive an active supply of substrates/ions will have to rely on slow diffusion and may have microbes under a starving condition or higher electrolyte resistance, resulting in a low efficiency of microbial activity and electrode use. Therefore, it is necessary to optimize the flow of the anolyte as well as the substrates/ions' distribution in continuously operated MFCs containing high surface area electrodes.

The anolyte flow can be controlled by designing flow channels on the anode electrode [10], but it limited the application of high surface area electrodes. The recent development of spiral anodes in MFCs has aimed to optimize the anolyte flow for higher electricity generation. A spiral anode channel was created by using graphite-coated stainless steel mesh and this MFC achieved a good performance of both waste treatment and electricity generation from dairy wastewater [11]. Another study used an ion exchange membrane to create a spiral channel with carbon cloth as electrodes, which significantly improved power density compared with conventional two-chamber MFCs [12]. Both of those studies developed round-disk shape MFCs that present great challenges in being scaled up to a continuously operated system for practical wastewater treatment. A more detailed study of the anolyte flow pathway was reported in a tubular MFC containing a helical anode

electrode that created a helical flow channel [13]. Their results revealed that the flow pattern improved mass transfer, thereby resulting in more power output. However, the potential issue with this helical anode electrode is that its manufacturing procedure could be complicated and its surface area is limited by the carbon materials that are used.

In this study, the concept of a helical flow pattern and use simple spiral spacers to improve electricity generation in tubular MFCs were explored. Instead of creating spiral electrodes, those spiral spacers were adapted to the well-proven carbon brush electrodes; thus, they maintained the feature of a high surface area of the carbon brush while creating a helical flow pattern. The superior performance of the spiral spacers was demonstrated through comparison of the MFCs with and without spiral spacers in both laboratory tests and onsite investigation. The lab experiments examined the effects of recirculation rates, organic loading rates, and different installation positions (vertical and horizontal). In comparison, an MFC with a spiral anode electrode (carbon brush also was made into a spiral shape) was studied in the horizontal installation. The onsite test was conducted by installing two MFCs (with and without spiral spacers) in an aeration tank of a municipal wastewater treatment plant for treating primary effluent. The results were expected to provide a simple and feasible approach to produce more energy through optimizing the anolyte flow in tubular MFCs.

2.3 Materials and Methods

2.3.1 Lab MFCs setup and operation

Two tubular MFCs (MFC_{lab}-1 and MFC_{lab}-2) were constructed by rolling up a piece of cation exchange membrane (CEM, Membrane International Inc., Ringwood, NJ, USA） around a PVC tube with a 3.8-cm diameter that had a length of 70 cm and 1.0-cm holes throughout the tube. The PVC tube functioned as supporting material for the CEM tube that contained a 1-m long carbon brush as an anode electrode. The liquid volume of the CEM tube (anode compartment) was about 1.15 L. The carbon brushes were pretreated as previously before being used [14]. The spiral spacers were made of round-shape rubber plates with 4.5 cm in diameter and ~2 cm in distance between each plate (Figure 2.1 A). The rubber plates were connected with titanium wires, and the total number of spacers for one anode electrode was 35. The spiral spacers were installed to the anode electrode of the MFC_{lab}-1 (Figure 2.1 B), while the MFC_{lab}-2 acted as a control without the spiral spacers. The cathode electrode was a piece of carbon cloth (20 cm ×70 cm, Zoltek Corporation, St. Louis, MO, USA) containing 5 mg/cm^2 activated carbon powder (Thermo Fisher Scientific, USA) as a catalyst for oxygen reduction. The activated carbon powder was coated to the cathode electrode by using a 10% PTFE solution as a binder agent and heat-treated at 375 °C for half hour. For

vertical installation, each MFC was set up in a PCV tube that had a diameter of 7.6 cm and functioned as a cathode compartment with a liquid volume of 1.3 L. The cathode was aerated with the air at 100 mL/min. For horizontal installation, both MFCs were laid down with about 2° angles respective to the horizontal level and submerged in a tank with a liquid volume of 25 L that was aerated with the air at 200 mL/min. The anode and the cathode electrodes were connected to an external circuit across a resistor of 10 ohm, unless stated otherwise.

Both MFCs were continuously operated under the same condition at room temperature ~20 °C. The anodes were inoculated with the digested sludge collected from the MMSD's South Shore Water Reclamation Facility (Milwaukee, WI, USA). A synthetic solution was used as an anolyte containing (per liter of tap water): CH_3COONa, 1 g; NaCl, 0.5 g; $MgSO_4$, 0.015 g; $CaCl_2$, 0.02 g; KH_2PO_4, 0.53 g; K_2HPO_4, 1.07 g; $NaHCO_3$, 1 g; and trace element, 1 mL [15]. The anolyte feeding rate ranged from 0.6 to 2.4 mL/min, resulting in a hydraulic retention time (HRT) of 32 to 8 hours. Tap water was used as a catholyte in both MFCs and was fed at the same speed as the anolytes. The anolytes were recirculated at 50, 150 or 300 mL/min.

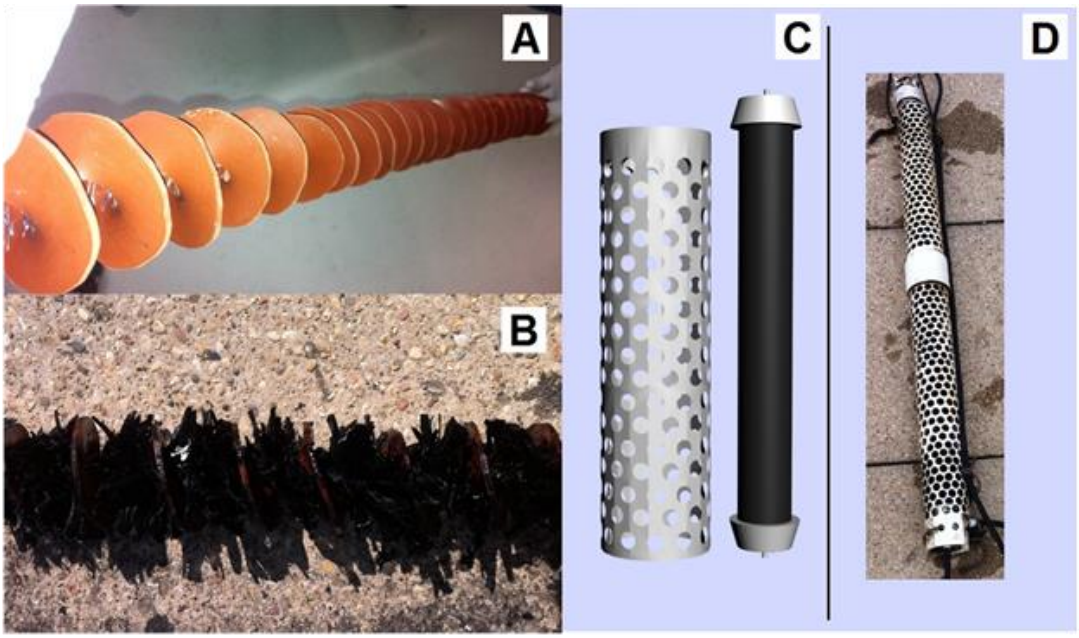

Figure 2.1 *Preparation of electrodes and the MFCs: A) spiral spacers made of rubber materials; B) spiral spacers installed onto a straight carbon brush; C) tubular MFC and porous PVC sleeve for the on-site test; and D) the assembled MFC for the on-site test.*

2.3.2 Onsite MFCs setup and operation

Two tubular MFCs (MFC_{onsite}-1 and MFC_{onsite}-2) were constructed using CEM tubes with a length of 100 cm and a diameter of 5 cm. No PVC tube was placed inside the CEM tube. The anode compartment that had a liquid volume of 2.0 L contained a 1-m long pre-treated carbon brush as the anode electrode. The cathode electrode was a piece of carbon cloth that wrapped the CEM tube and was coated with 5 mg/cm^2 activated carbon powder in the same procedure as the MFCs in the lab. The spiral spacers were installed in the anode of the MFC_{onsite}-1, while the MFC_{onsite}-2 acted as a control for comparison. The MFCs were placed in a PVC-tube sleeve that had a diameter of 7.6 cm and a length of 100 cm; the PVC tube contained 2.2-cm holes throughout (Figure 1 C and D). The completed MFCs were installed in an aeration tank (submerged in water) at the South Shore Water Reclamation Facility. The anodes of both MFCs were not particularly inoculated. The primary effluent pumped from a sample site was fed into the MFCs at 3 mL/min, resulting in an anolyte HRT of 11.1 h. Theanlytes were recirculated at 200 mL/min by a peristaltic pump. The MFCs took advantage of aeration in the aeration tank for the oxygen supply to their cathode electrodes.

2.3.3 Measurement and analysis

The MFC voltages were monitored by digital meters (2700, Keithley Instruments, Inc., Cleveland, OH, USA) every 5 min. The concentration of chemical oxygen demand (COD) was measured using a colorimeter (DR/89, Hach Company, Loveland, CO, USA) according to the manufacturer's procedure. Polarization tests were conducted by using a potentiostat (Reference 600, Gamry Instruments, Warminster, PA, USA) at a scan rate of 0.1 mV/S. Power density, current density, and COD loading and removal rate were calculated based on the liquid volume of the anode compartment. Columbic efficiency was calculated according to the following equation：

$$CE = \frac{Q_{output}}{Q_{input}} = \frac{\sum I \times t}{96485 \times COD_{total} \times 4}$$

Where CE is the coulombic efficiency based on organic substrate, Q_{output} is the produced charge, Q_{input} is the total charge available in the substrate that has been removed, and t (s) is the time. COD_{total} (mol) is the total COD removed by the MFC in the period of time t.

The theoretical power requirement for the pumping system was estimated as [16]:

$$P_{pumping} = \frac{Q\gamma E}{1000}$$

where P is the power requirement (kW), Q is the flow rate (m^3/s), γ is 9800 N/m^3, and E is the hydraulic pressure head (m). In this study, we estimated hydraulic pressure heads of 0.03 m and 0.05 m for the anolyte feeding and recirculation pumps. The energy consumption by aeration was estimated according to a previous publication [17].

2.4 Results and Discussion

2.4.1 Vertical installment

Vertical installation is commonly used in bioelectrochemical systems with a upflow configuration [8, 15, 18-21]. When the two MFCs were set up vertically, we examined the effects of the anolyte recirculation rates and the organic loading rates (or HRTs) on their performance of electricity generation and organic removal.

Three recirculation rates, including 50, 150 and 300 mL/min, were tested at a fixed HRT of 15 h. The corresponding upflow speeds at those recirculation rates are 1.9, 5.7 and 11.3 m/h. After the MFCs achieved stable electricity generation at an external resistance of 10 ohm, polarization curves were constructed to evaluate the overall power production (Figure 2.2). At 50 mL/min, the maximum power density and the maximum current density of the MFC_{lab}-1 were 4.9 W/m^3 and 43.1 A/m^3, respectively, higher than 3.1 W/m^3 and 24.7 A/m^3 of the MFC_{lab}-2, demonstrating that the spiral spacers improved electricity generation in an MFC (Figure 2.2 A). The advantage of the MFC_{lab}-1 became greater with an increased recirculation rate, and at 300 mL/min, the maximum power and the maximum current density of the MFC_{lab}-1 reached 7.1 W/m^3 and 62.6 A/m^3; at the same recirculation rate, the MFC_{lab}-2 produced 4.5 W/m^3 and 29.2 A/m^3 (Figure 2.2 C). The COD removal efficiency was not obviously different between the two MFCs at the same recirculation rate but a higher recirculation rate improved COD removal in both MFCs. For example, at 50 mL/min, the MFC_{lab}-1 removed 78.4±0.8% and the MFC_{lab}-2 removed 79.9±2.7% of the total COD; when the recirculation rate increased to 300 mL/min, the two MFCs removed 87.8±1.7% and 85.7±1.1%, respectively. Those COD results suggest that the spiral spacers might not improve the substrate supply to microorganisms, different from what we expected, although there is a chance that the helical flow promoted the substrate distribution to electrochemically-active bacteria but further evidence is needed. The improved electricity generation with the spiral spacers indicated that electricity production might not be directly limited by microbial activity, and the modified anolyte flow might have accelerated the transport of ions and chemicals that acted as electron mediators, both of which are key factors to electricity generation.

The effect of organic loading rates was examined through varying the influent flow rate from 0.6 to 2.4 mL/min, resulting in three HRTs of 32, 15 and 8 h, and the corresponding

loading rates ranging from 0.57 to 2.30 kg COD/m^3/day. A fixed recirculation rate of 300 mL/min was applied for the organic loading rate tests. Under the operation at an external resistor of 10 ohm, the MFC_{lab}-1 produced 14.9±0.8 mA and the MFC_{lab}-2 generated 9.8±3.7 mA at 0.57 kg COD/m^3/d (or HRT 32 h); both MFCs achieved almost 100% removal of the COD. When the organic loading rate increased to 2.30 kg COD/m^3/d (or HRT 8 h), the MFC_{lab}-1 produced 22.8±1.1 mA, much higher than 15.4±1.1 mA in the MFC_{lab}-2, while the COD removal was similar between the two MFCs (varied between 64-66%). The overall electricity generation in the MFCs was shown in the polarization curves (Figure 2.3). Clearly, the MFC_{lab}-1 had outcompeted the MFC_{lab}-2, confirming that the spiral spacers were beneficial to electricity generation. The power output increased with the increased organic loading rates (or decreased HRTs) because of more substrate supply. For instance, the maximum power density of the MFC_{lab}-1 increased from 4.0 W/m^3 at 0.57 kg COD/m^3/d (or HRT 32 h) to 8.2 W/m^3 at 2.30 kg COD/m^3/d (or HRT 8 h).

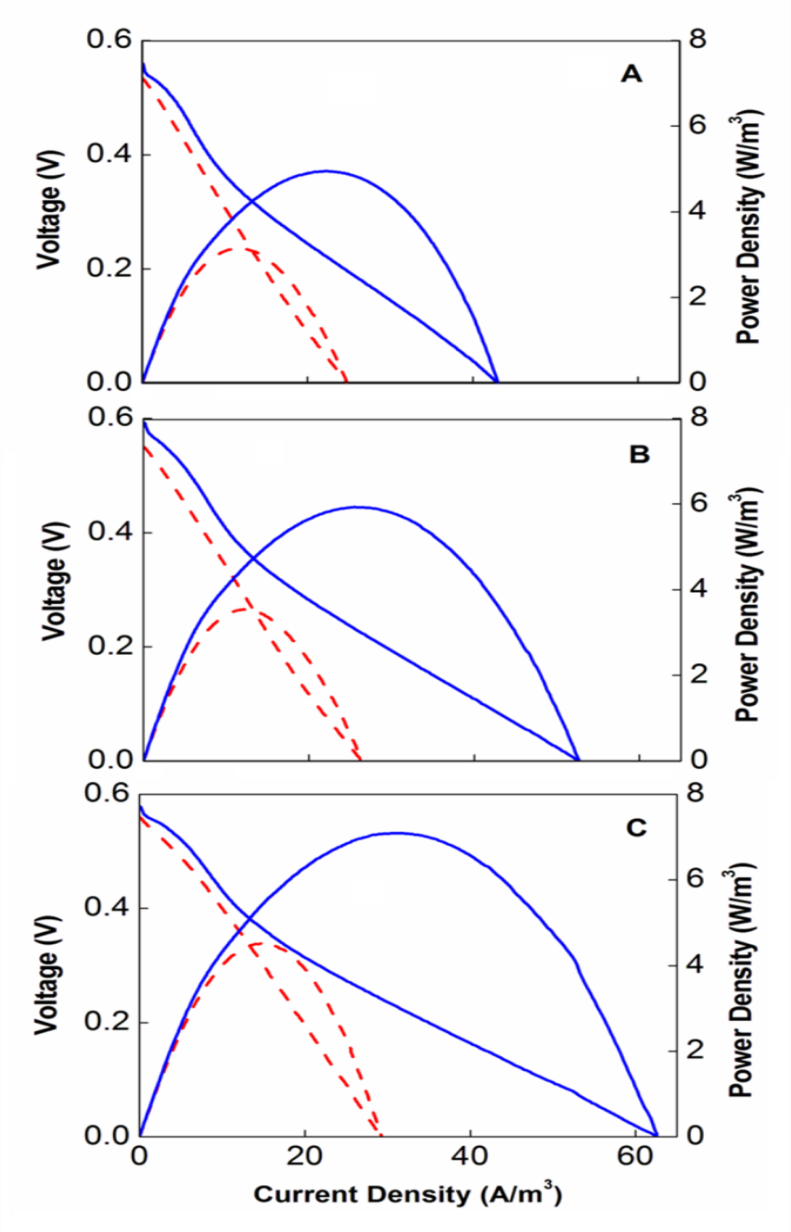

Figure 2.2 *The voltage and power curves of the MFC_{lab}-1 (blue solid line) and the MFC_{lab}-2 (red dash line) at different anolyte recirculation rates: A) 50 mL/min; B) 150 mL/min; and C) 300 mL/min.*

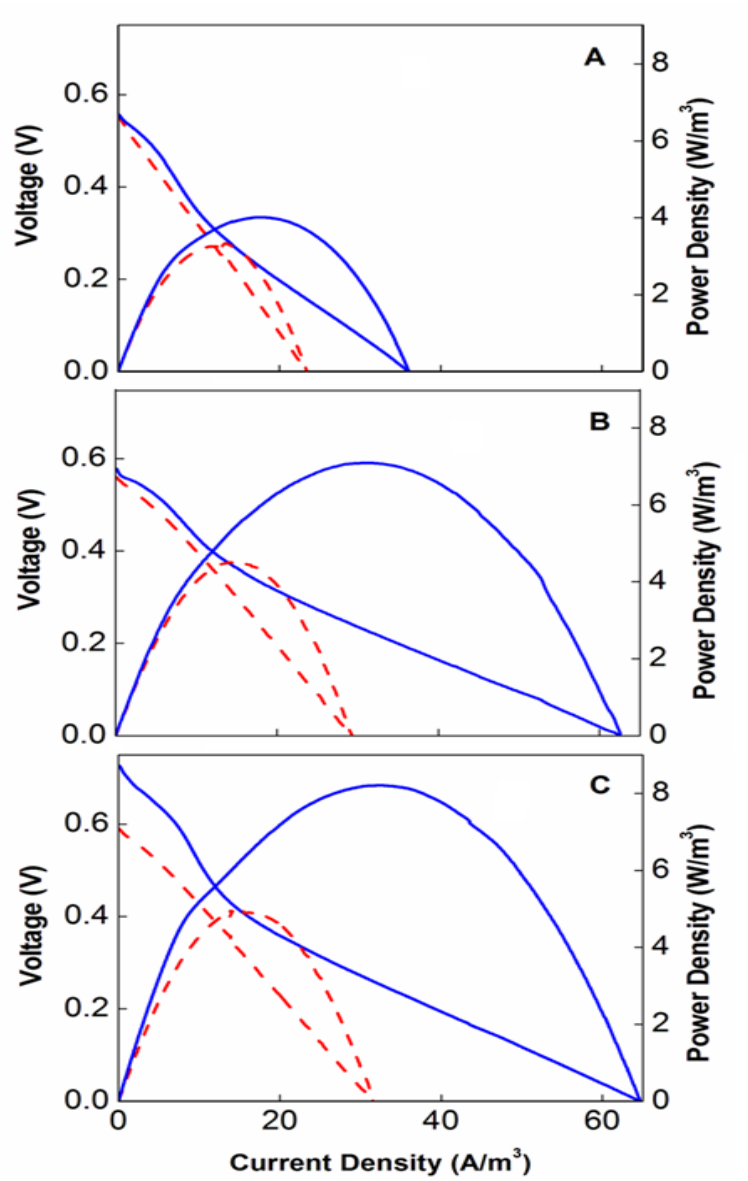

Figure 2.3 *The voltage and power curves of the MFC_{lab}-1 (blue solid line) and the MFC_{lab}-2 (red dash line) at different organic loading rates (or HRTs): A) 0.57 kg COD/m^3/d (33 h); B) 1.14 kg COD/m^3/d (15 h); and C) 2.30 kg COD/m^3/d (8 h).*

An effective approach to evaluate the electricity generation in an MFC is to establish an energy balance. Energy analysis has been missing in the MFC studies for a long time but is clearly important [22]. It was only recently that energy balances have been reported in MFCs [23-25]. In this study, energy balances were developed for both MFCs under sevaral conditions. In the vertical installation, the energy balance was analyzed at a recirculation rate of 300 mL/min and an organic loading rate of 2.30 kg COD/m^3/d (or HRT 8 h). The MFC_{lab}-1 produced an energy intensity of 0.071 kWh/ kg COD (or 0.036 kWh/m^3), while the MFC_{lab}-2 produced only 0.033 kWh/ kg COD (or 0.016 kWh/m^3) (Table 2.1). The overall

energy balances were negative for both MFCs, but the MFC_{lab}-1 had a less negative balance because of more energy production. The aeration accounted for 70% of the energy consumption; without aeration, the energy balances based on the pumping system would be positive for the MFC_{lab}-1 but still negative in the MFC_{lab}-2. Therefore, to achieve an energy-neutral (or surplus) treatment process using the MFC technology, aeration must be eliminated or maintained at a minimum. The non-aeration cathode can be accomplished through a passive air supply that was demonstrated in a previous tubular MFC [8].

Table 2.1 *Analysis of energy production and consumption in the MFCs under a certain conditions. The unit of energy is kWh/kg COD.*

		Production	**Consumption**			**Energy Balance**	
			Pumps	**Aeration**	**Total**	**Pumps only**	**Total**
Vertical Installment	**MFC_{lab}-1**	0.071	0.034	0.081	0.115	0.037	-0.044
	MFC_{lab}-2	0.033	0.035	0.083	0.117	-0.002	-0.084
	MFC_{onsite}-1	0.205	0.141	-	0.141	0.064	0.064
	MFC_{onsite}-2	0.053	0.130	-	0.130	-0.077	-0.077
Horizontal Installment	**MFC_{lab}-1**	0.073	0.035	0.084	0.120	0.038	-0.047
	MFC_{lab}-2	0.028	0.036	0.087	0.123	-0.008	-0.095
	New MFC_{lab}-2	0.043	0.036	0.087	0.124	0.007	-0.081

2.4.2 Horizontal installment

Some tubular MFCs were operated in a horizontal position [26-27]. Horizontal installation could be more advantageous over vertical installation when multiple MFCs are connected in a series and the produced biogas needs to be driven out of the tubular reactor. Therefore, we also compared the performance of the MFC_{lab}-1 and the MFC_{lab}-2 when they were horizontally installed in a water tank containing tap water as the catholyte. A fixed recirculation rate of 300 mL/min and an organic loading rate of 2.30 kg COD/m^3/d (or HRT 8 h) were employed for the test. At an external resistance of 10 ohm, the MFC_{lab}-1 produced 22.6±0.9 mA, higher than 13.7±0.7 mA in the MFC_{lab}-2, demonstrating that the spiral spacers were also effective to improve electricity generation in the horizontal installation. The COD removal was similar between the two MFCs, varying between 62 and 64%. The maximum power density of the MFC_{lab}-1 was 8.8 W/m^3, about 1.87 times the one of the MFC_{lab}-2 (4.7 W/m^3) (Figure 2.4). The energy production in the MFC_{lab}-1 was 0.073 kWh/kg COD, 160% higher than 0.028 kWh/kg COD in the MFC_{lab}-2. Similar to the vertical installation, the MFC_{lab}-1 achieved a less negative energy balance than the MFC_{lab}-2 (Table 1).

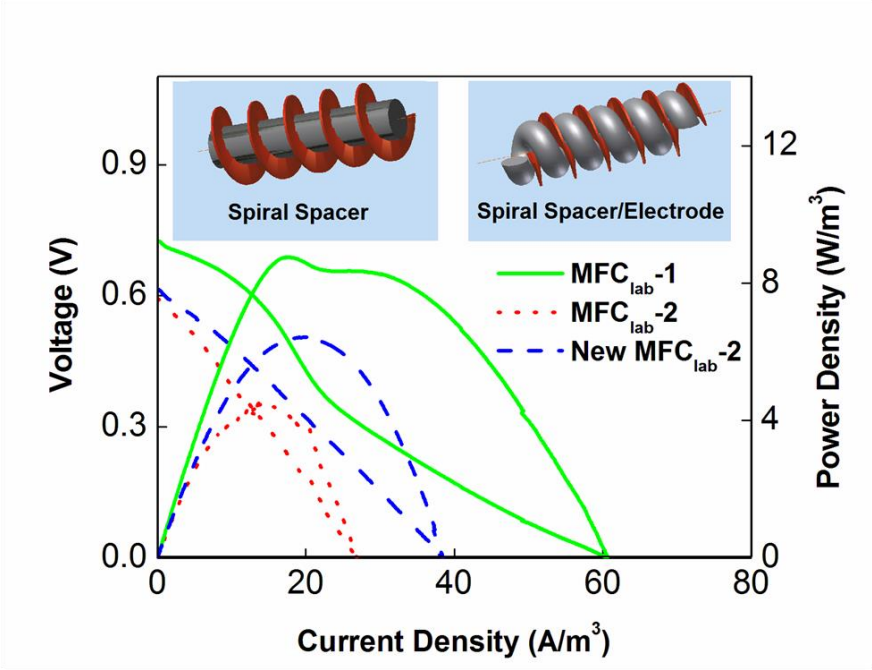

Figure 2.4 *The voltage and power curves of the MFC_{lab}-1 (green solid line) and the MFC_{lab}-2 (red dotted line) in the horizontal installation. The new MFC_{lab}-2 (blue dash line) contained a spiral anode electrode, as shown in the inset figures.*

Because the previous study showed the improved electricity production with spiral anode electrodes [13], it could be of interest to investigate whether having a carbon brush in a spiral arrangement along the spiral spacers would further improve the MFC performance. To do this, we twisted a carbon brush that was similar to the anode electrode of the MFC_{lab}-1 and modified the MFC_{lab}-2 with this spiral anode electrode (and the spiral spacers) (the inset pictures of Figure 2.4). The new MFC_{lab}-2 produced more electricity than the previous one (Figure 2.4), indicating that the spiral arrangement inside an anode compartment indeed helped to improve electricity production. However, the spiral anode electrode did not exhibit superior performance to that of the spiral spacers only. The maximum power density of the new MFC_{lab}-2 was 6.4 W/m^3, lower than that of the MFC_{lab}-1. Likewise, the energy production in the new MFC_{lab}-2 was 0.043 kWh/kg COD, also lower than that in the MFC_{lab}-1 (Table 2.1). The lower performance of the new MFC_{lab}-2, compared with the MFC_{lab}-1, was possibly due to several reasons. First, for a fair comparison between the new MFC_{lab}-2 and the MFC_{lab}-1, we used carbon brushes with the same dimension; the twisted carbon brush in the MFC_{lab}-2 became shorter than the CEM tube and thus a portion of the CEM in the MFC_{lab}-2 was not well used for electricity generation. Second, the twisted carbon brush increased the density of the carbon fiber between the spiral spacers and could hinder the water flow, thereby reducing the effect of the helical flow. The detailed reasons require further investigation; however, from the perspective of electrode fabrication and lab experiences, , it appears that adding spiral spacers to a straight carbon

brush will be easier and simpler than twisting a carbon brush with the spiral spacers. Therefore, the model of the MFC_{lab}-1 was chosen for the on-site test.

2.4.3 Onsite test

To further demonstrate the technical viability and the advantages of the spiral spacers, we conducted an on-site test by installing two MFCs in an aeration tank of a municipal wastewater reclamation facility. Both MFCs were used to treat the primary effluent and took advantage of aeration for the oxygen supply to their cathode. Such a concept has been studied in the lab but not in an actual wastewater treatment process [1, 28]. At an HRT of 11.1 hours and an average organic loading rate of 0.23 kg COD/m^3/day, the MFC_{onsite}-1 containing the spiral spacers produced more electricity than the MFC_{onsite}-2, although the current generation fluctuated strongly due to the varied organic concentration in the primary effluent and the strong motion of the MFCs disturbed by aeration. The average current of the MFC_{onsite}-1 in the 60-d operation was 15.5 mA, almost twice the current of the MFC_{onsite}-2 (8.2 mA) (Figure 2.5 A). The CEs were 36.3% and 20.0% for the MFC_{onsite}-1 and the MFC_{onsite}-2, respectively. On average, the operating power density of the MFC_{onsite}-1 was 1.20 W/m^3, which was 3.5 times that obtained from the MFC_{onsite}-2 (0.34 W/m^3). The MFC_{onsite}-1 achieved slightly higher COD removal efficiency than the MFC_{onsite}-2 (Figure 2.5B). At day 55, the MFC_{onsite}-2 had a negative TCOD removal efficiency, which was related to a very low COD concentration (< 20 mg/L) in the primary effluent after a major storm. Unlike the lab test, the spiral spacers led to a positive net energy in the MFC_{onsite}-1, while the MFC_{onsite}-2 still had a negative energy balance (Table 2.1). However, it should be noted that we did not include the aeration energy into our energy analysis because the estimate of aeration energy for the MFCs in an actual aeration tank would be very difficult. The MFC_{onsite}-1 generated higher energy intensity (0.205 kWh/kg COD) than those of the lab MFCs, mainly due to a lower organic loading rate in the wastewater treatment plant. Those results from the on-site tests further confirmed our findings from the lab tests that spiral spacers contributed to improved electricity production in MFCs.

2.5 Conclusions

This study has presented a simple approach to use spiral spacers to optimize the anolyte flow for improving electricity production in MFCs. This method is effective in both vertical and horizontal installations of MFC reactors. The advantage of the spiral spacers becomes greater at a higher recirculation rate or a higher organic loading rate. Although some issues, such as optimal spacer gaps, selection of spacer materials and better manufacturing method of spiral spacers, need to be further explored, the results from both lab tests and

on-site examination have clearly demonstrated that using spiral spacers benefits electricity generation in MFCs.

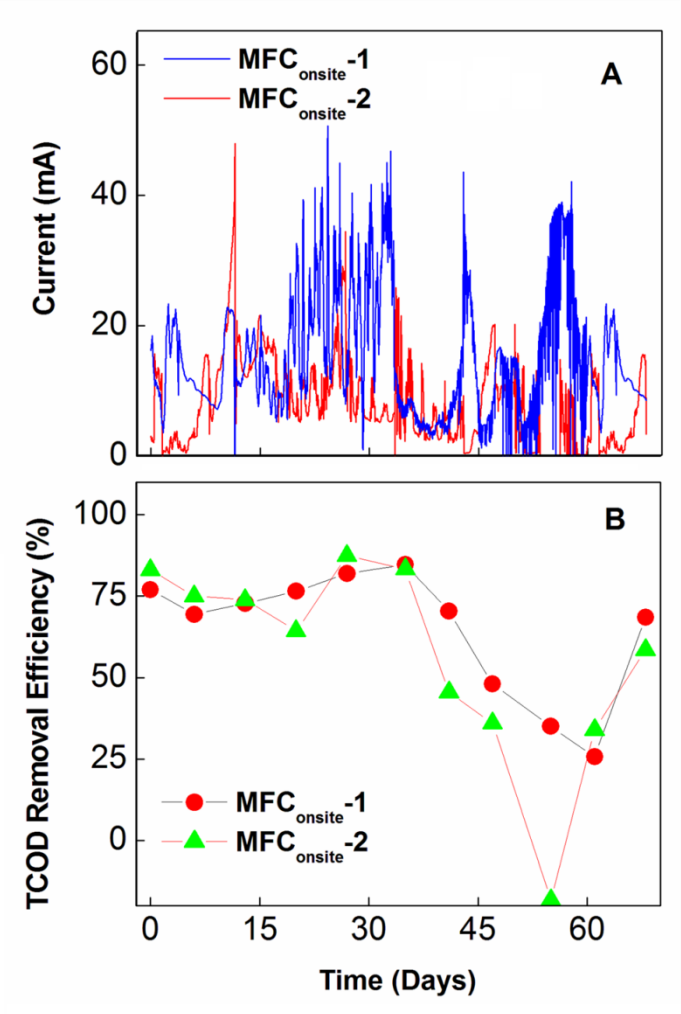

Figure 2.5 *Current generation (A) and the removal of total COD (B) in the MFCs installed in an aeration tank of a municipal wastewater reclamation facility.*

3. In Situ Investigation of Tubular Microbial Fuel Cells Deployed in an Aeration Tank at a Municipal Wastewater Treatment Plant

(This section has been published as: Zhang, F., Ge, Z., Grimaud, J., Hurst, J. and He, Z.* (2013) In situ investigation of tubular microbial fuel cell deployed in an aeration tank at a municipal wastewater treatment plant. Bioresource Technology. Vol 136, pp 316-321)

3.1 Abstract

To examine the feasibility of integrating microbial fuel cells (MFCs) into an activated sludge process, three MFCs with different ion exchange membranes and/or cathode catalysts were installed in an aeration tank to treat primary effluent. Both contaminant treatment and electricity generation were studied during the operation for more than 400 days. The effects of membrane/catalysts on MFC performance were not observed, likely due to the low removal of chemical oxygen demand (COD) (<53%) caused by low electricity generation. The MFCs did not achieve any obvious removal of nutrients. The produced energy was lower than the theoretic energy consumption. The performance was seriously affected by cathode biofouling, variation of wastewater quality, and other operating conditions. Unlike prior lab studies by others, the results of this study suggest that MFCs may not be suitable for deployment in an aeration tank, unless the key problems such as biofouling are solved.

3.2 Introduction

Microbial fuel cells (MFCs) are a promising technology for wastewater treatment with simultaneous bioenergy production [29-30]. Depending on the type of wastewater, MFCs may be applied as a main treatment process for some industrial wastewater or domestic wastewater from decentralized communities, or as a part of an existing treatment process for large-scale domestic wastewater treatment. The application of MFC technology may require new construction of infrastructure, especially for industrial or decentralized wastewater treatment, which requires significant capital investment [31]. A faster and more cost-effective way to apply MFCs is to integrate them into existing treatment facilities; for example, MFCs may be combined with activated sludge processes to treat primary effluent, or linked to anaerobic digesters to polish the digested liquid [32]. Primary effluent with low-concentration organics could be a more appropriate substrate for MFCs than high-strength wastes, because MFCs have not been proved more efficient than

anaerobic digesters in terms of bioenergy production from high-strength wastes [33-34]. Therefore, there is strong interest in examining the feasibility of MFC operation in the aeration tanks of activated sludge processes.

Integrating MFCs into an aeration tank will not require additional land space in a wastewater treatment plant. In addition, there are several other potential benefits by installing MFCs into an aeration tank. First, a portion of wastewater can be treated under an anaerobic condition in the anode of MFCs, and thus the requirement of aeration, as well as energy consumption, is greatly reduced. Second, the treated effluent from MFCs contains much lower concentrations of suspended solids, and thus the secondary sludge production will be lower than that of activated sludge treatment only. Third, MFCs can produce some electric energy (although low at this moment), which can be potentially applied to offset the energy consumption by the treatment process. Fourth, MFCs may physically act as solid media to form a hybrid attached/suspended growth system, with advantages demonstrated in previous integrated fixed-film-activated sludge processes [35]. These potential benefits can hardly be verified or examined at the current stage of research because of small scales of MFCs; however, it is beneficial to consider them in future studies.

The concept of linking an MFC to an activated sludge process has been proposed and examined in the laboratory in several previous studies. A research group suggested assembling air-filled hollow-fiber membrane MFCs in an aeration tank, but unfortunately they did not carry out the proposed design [36]. The first lab demonstration was conducted in single-chamber MFCs installed in a plastic aeration chamber that mimicked an aeration tank in an activated sludge process [1]. The authors of the study found that the MFCs produced more electricity in the presence of aeration, and graphite felt was an optimal electrode material that resulted in the best performance. They also observed a significant drop in MFC voltage when aerobic sludge was introduced into the aeration chamber. A later study investigated the installation of membrane-less MFCs in an aerated chamber operated as a sequencing batch reactor [28]. The results showed that the MFC produced a maximum power density of 2.34 W/m^3 and removed 18.7% of chemical oxygen demand. These prior studies provide a proof of concept that MFCs could be integrated into activated sludge process; however, they were conducted under laboratory conditions and for a short period of time. Furthermore, there is a significant difference between an artificial (lab) aeration tank and a real aeration tank of activated sludge process, for instance, in the concentrations of dissolved oxygen and biomass. Therefore, it is necessary to conduct an *in situ* study of MFC performance in an aeration tank to demonstrate the technical viability of MFC integration with activated sludge processes.

In this study, three tubular MFCs were installed in an aeration tank at a municipal wastewater treatment plant (Milwaukee Metropolitan Sewerage District–MMSD) ; the MFCs had different ion exchange membranes and/or cathode catalysts. We attempted to compare the MFC performance with cation or anion exchange membranes, and with the catalysts containing platinum or not. The long-term performance of MFCs in treating primary effluent and producing electricity was examined through more than 400 days' operation. The performance of contaminant treatment was studied by monitoring the variation of multiple parameters, including organics, suspended solids, nitrogen, phosphorus, turbidity, and coliform bacteria. The electricity generation was described with current, power, and electric energy. We also analyzed the energy production and consumption by those MFCs.

Figure 3.1 *MFCs installation in the aeration tank.*

3.3 Materials and Methods

3.3.1 MFC Setup and Operations

Three tubular MFCs were constructed similarly, except the difference in ion exchange membrane and/or cathode catalysts (Figure 3.1). Two MFCs, MFC-C-Pt and MFC-C-AC, were made of cation exchange membrane (CEM, Membranes International, Inc., Glen Rock, NJ, USA), and one (MFC-A-Pt) was made of anion exchange membrane (AEM, Membranes International, Inc.). Each membrane tube (which formed an anode compartment) had a diameter of 5 cm and length of 100 cm, resulting in an anode liquid volume of 2000 mL (excluding the anode electrode). Each MFC contained a 100-cm long carbon brush as its

anode electrode, and a carbon cloth that wrapped the membrane tube as its cathode electrode. Both MFC-C-Pt and MFC-A-Pt had 0.1 mg/cm^2 of Pt (10% Pt on carbon black) and 4 mg/cm^2 of activated carbon as cathode catalysts for oxygen reduction, while MFC-C-AC contained only activated carbon powder (5 mg/cm^2) as a cathode catalyst. The catalysts were applied to the cathode electrode by using 5% PTFE solution as binder. Each MFC was placed in a PVC-tube sleeve that had a diameter of 7.6 cm and a length of 100 cm; the PVC tube contained 2.2-cm holes throughout. The completed MFCs were installed in an aeration tank (submerged in water) at the MMSD's South Shore Water Reclamation Facility (Milwaukee, WI, USA). The anodes of the MFCs were inoculated with the primary effluent, which also acted as the anode feeding solution and was pumped from a sample site was fed into the MFCs at 3 mL/min, resulting in an anolyte HRT of 11.1 h. The anolytes were recirculated at 200 mL/min by a peristaltic pump.

3.3.2 Measurement and analysis

The MFC voltages were monitored by digital meters (2700, Keithley Instruments, Inc., Cleveland, OH, USA) every 5 min. The concentrations of chemical oxygen demand (COD) and nutrients, including phosphate, ammonium nitrate, and nitrite were measured using a colorimeter (DR/890, Hach Company, Loveland, CO, USA) according to the manufacturer's procedure. The temperature was recorded with an industrial multi-meter (EX-540, Extech, Nashua, NH, USA). The concentrations of total suspended solids (TSS) and volatile suspended solids (VSS) were measured according to the standard methods [37]. The coliform bacteria were determined by using the membrane filter technique for members of the coliform group approved by Standard Methods Committee [37]. Turbidity was measured with a turbidimeter (Scientific Inc., Fort Myers, FL, USA). Power density and COD loading and removal rates were calculated based on the liquid volume of the anode compartment. The theoretical power requirement for the pumping system was estimated as [16]:

$$P_{pumping} = \frac{Q\gamma E}{1000}$$

where P is the power requirement (kW), Q is the flow rate (m^3/s), γ is 9800 N/m^3, and E is the hydraulic pressure head (m). In this study, we assumed hydraulic pressure heads of 0.03 m and 0.05 m for the anolyte feeding and recirculation pumps.

3.4 Results and Discussion

3.4.1 Treatment performance

Contaminant treatment is a key evaluation factor in determining whether MFCs can be applied for wastewater treatment. In this study, the treatment performance of the three MFCs was described by COD, suspended solids, nutrients, and other parameters. During the operation period, we observed significant variation in organic concentration in the primary effluent that was fed into the MFCs, affected by season, rainfall, and tubing that linked the sampling site and the MFCs. The concentration of total COD (TCOD) ranged from 50 to 600 mg/L, resulting in an organic loading rate of 0.1 to 1.3 kg TCOD/m^3/d, while the concentration of soluble COD (SCOD) varied from 10 to 290 mg/L with a loading rate of 0.02 to 0.62 kg SCOD/m^3/d (Figure 3.2A and B). The extremely low organic concentrations usually occurred after a major storm. This variation of organic concentrations in the primary effluent (or the feeding to the MFCs) clearly affected the quality of the MFC effluents, and higher organic inputs were associated with higher organic concentrations in the MFC effluents. There was no obvious difference in organic removal between the MFCs. The concentrations of TCOD in the effluents of the three MFCs were 81.7±59.8 mg/L (MFC-C-Pt), 83.1±50.1 mg/L (MFC-A-Pt), and 81.1±53.8 mg/L (MFC-C-AC), respectively, resulting in TCOD removal rates of 0.19±0.14, 0.19±0.14, 0.19±0.13 kg COD/m^3/d for each MFC (Table 3.1). The concentrations of SCOD in the MFC effluents were 52.6±43.3 mg/L (MFC-C-Pt), 51.6±38.5 mg/L (MFC-A-Pt), 52.6±39.2 mg/L (MFC-C-AC), respectively; accordingly, the SCOD removal rates achieved by those MFCs were 0.17±0.13, 0.17±0.13, 0.17±0.12 kg COD/m^3/d (Table 3.1). This is different from our expectation that the MFCs with different ion exchange membranes or catholyte catalysts would perform differently. We attribute the results to the low performance of the MFCs in a real aeration tank. Unlike the previous work conducted under well-controlled laboratory conditions, the MFCs installed in an aeration tank had significant variation in their operating conditions such as organic loading, temperature, pH, and corrosion of the wires in the electric circuit; especially, the biofilm had seriously formed on the cathode electrode. These situations exhibited a larger influence on MFC performance than ion exchange membranes and catalysts. The organic concentrations in the effluent of the three MFCs were generally higher than that in the effluent of the secondary clarifier (e.g., 25±11 mg TCOD/L) in the wastewater treatment plant where the MFCs were deployed.

Although the COD removal in the MFCs was lower than that of the activated sludge process, the MFCs produced much less sludge. In general, the concentrations of suspended solids (both total suspended solids (TSS) and volatile suspended solids (VSS)) in the MFC effluents were similar to those in the primary effluent (Figure 3.3). The primary effluent contained 0.044±0.021 g TSS/L, and 0.032±0.021 g VSS/L. The TSS concentrations in the MFC effluents were 0.029±0.018 g/L (MFC-C-Pt), 0.031±0.016 g/L (MFC-A-Pt), and

0.040±0.036 g/L (MFC-C-AC); the VSS concentrations were 0.027±0.02, 0.025±0.016, and 0.031±0.028 g/L, respectively (Table 3.1). For comparison, the concentrations of suspended solids in the effluent of the aeration tank were 2.214±0.314 g TSS/L and 1.642±0.242 g VSS/L, significantly higher than those of the MFCs. The turbidities of the MFC effluents were slightly lower than that of the primary effluent. The low-suspended solids in the MFC effluents result in low sludge production, thereby reducing the requirement of sludge treatment and the use of a secondary clarifier, resulting in potential economical benefits.

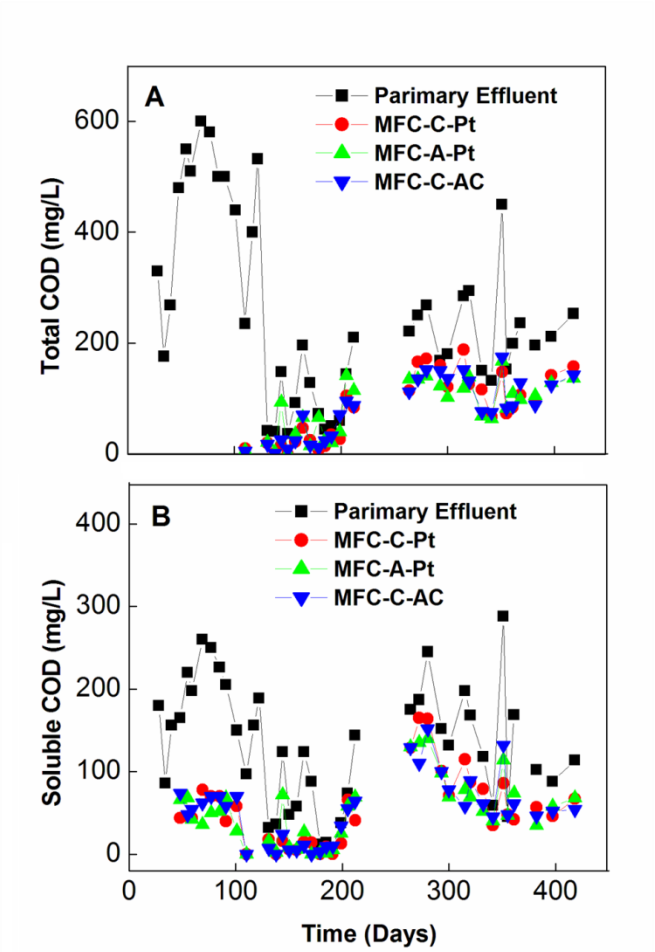

Figure 3.2 *The concentrations of total COD (A) and soluble COD (B) in the primary effluent and the MFC effluents during the operating period.*

The concentrations of nutrients were monitored, including inorganic nitrogen and phosphate; however, we did not expect any significant removal in the MFC anodes because of the anaerobic conditions. The results matched our expectation: the primary effluent had a phosphate concentration of 3.1±1.4 mg/L, while the three MFCs contained similar phosphate concentrations in their effluents. The ammonium concentration in the primary

effluent was 21.4±5.5 mg/L; there was no obvious reduction in the ammonium concentration with the MFC treatment. As concluded from the previous studies, additional processes/chemicals are required to remove nutrients in an MFC [38-39]. Concentration of coliform bacteria, which has not been reported before in MFCs were also monitored. Coliform bacteria concentrations are an important quality parameter of the treated wastewater; however it was concluded that MFCs could not reduce coliform bacteria level which are closely related to temperature.

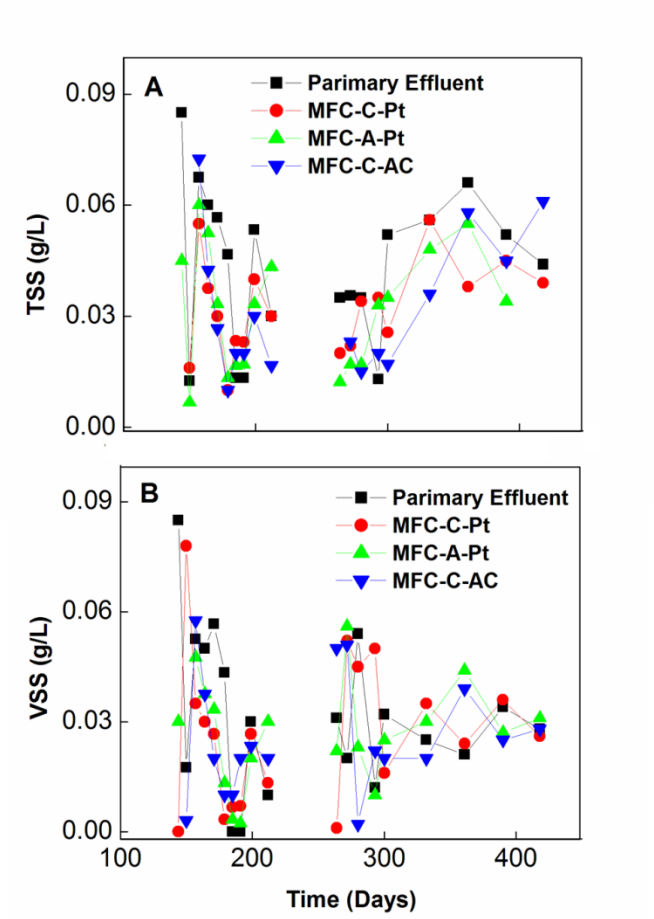

Figure 3.3 *The concentrations of total suspended solids (TSS) (A) and volatile suspended solids (VSS) (B) in the primary effluent and the MFC effluents during the operating period.*

3.4.2 Electricity generation

Current generation at external resistance of 10 Ω was monitored in the three MFCs for more than 400 days (Figure 3.4). It was observed that the MFCs produced highly unstable electric current, mostly varying between 0 and 30 mA. The operating power densities were

0.37±0.31 W/m^3 (MFC-C-Pt), 0.27±0.20 W/m^3 (MFC-A-Pt), and 0.18±0.20 W/m^3 (MFC-C-AC), much lower than those (2-60 W/m^3) obtained from laboratory tubular MFCs [8, 40]. We can roughly see that the use of Pt in the cathode catalysts might be beneficial to improving power output, but large variation in the data does not lead to a firm conclusion. Activated carbon power has been demonstrated as an effective cathode catalyst for MFCs [41-42], and its (lower) performance can be compensated by its much lower cost compared with Pt.

Table 3.1 *COD removal rates, COD concentrations, and SS concentrations in the primary effluent, the MFC effluents, and the effluent of the secondary clarifier (SCE).*

	Removal Rate (kg/m^3/d)		**COD Concentration (mg/L)**		**Suspended Solids (g/L)**	
	TCOD	**SCOD**	**TCOD**	**SCOD**	**TSS**	**VSS**
PE	N/A	N/A	256.1±166.3	132.8±73.8	0.044±0.021	0.032±0.021
MFC-C-Pt	0.19±0.14	0.17±0.13	81.7±59.8	52.6±43.3	0.029±0.018	0.027±0.02
MFC-A-Pt	0.19±0.14	0.17±0.13	83.1±50.1	51.6±38.5	0.032±0.016	0.025±0.016
MFC-C-AC	0.20±0.13	0.17±0.12	81.1±53.7	52.6±39.2	0.040±0.036	0.031±0.028
SCE	0.50±0.36	0.28±0.17	25.0±11.0	N/A	2.214±0.314	1.642±0.242

Table 3.2 *Energy production, consumption, and balance in the three MFCs. The values in the brackets are standard deviations.*

	Energy Production		**Energy Consumption**		**Energy Balance**	
	kWh/m^3	**kWh/kg TCOD**	**kWh/m^3**	**kWh/kg TCOD**	**kWh/m^3**	**kWh/kg TCOD**
MFC-C-Pt	0.009 (0.014)	0.082 (0.100)	0.009	0.088 (0.102)	0.000 (0.014)	-0.006 (0.202)
MFC-A-Pt	0.007 (0.010)	0.073 (0.107)	0.009	0.094 (0.131)	-0.002 (0.010)	-0.021 (0.239)
MFC-C-AC	0.005 (0.008)	0.043 (0.038)	0.009	0.075 (0.064)	-0.004 (0.008)	-0.031 (0.103)

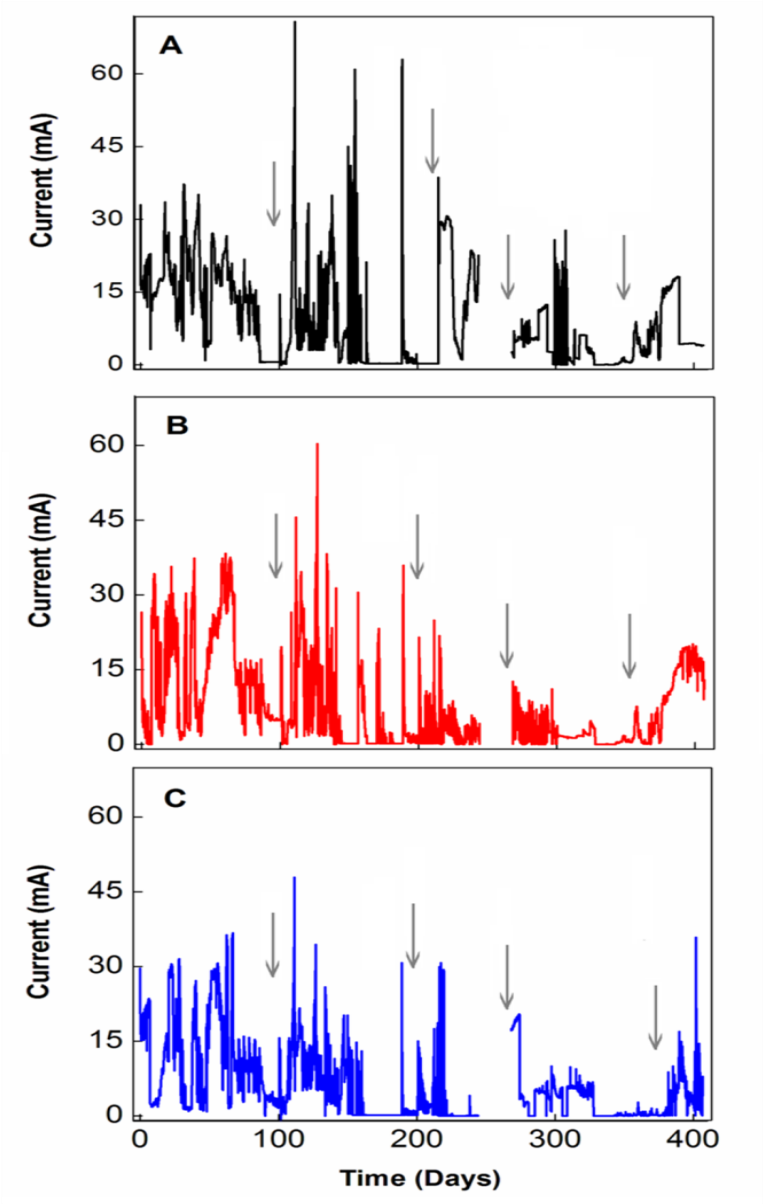

Figure 3.4 *Current generation in the MFCs during the operating period: (A) MFC-C-Pt; (B) MFC-A-Pt; and (C) MFC-C-AC. The arrows indicate the cathode cleaning to remove biofilm.*

The unstable current generation and low power output might be due to several reasons. First, the primary effluent that was fed as an anode substrate contained more complex compounds, including those recalcitrant compounds that cannot be well-degraded by microorganisms (while the laboratory tests usually use simple substrates such as acetate or glucose that result in much higher conversion efficiency). Second, biofilm formation on the cathode electrode negatively affected oxygen uptake by the cathode reaction, thereby limiting electron transfer to the cathode electrode. Serious biofouling on the cathode electrode was observed, however cleaning the biofilm by simply washing the cathode electrode with water (the MFCs were taken out of the aeration tank during the cleaning)

quickly restored current generation (arrows in Figure 3.4). However, biofilm quickly formed again once the MFCs were installed back into the aeration tank, which decreased the current. Third, the tubing for the anode feeding clogged frequently and the substrate supply to the anode often stopped due to the slow flow of the primary effluent in the tubing, which accumulated substances and stimulated the biofilm buildup. Fourth, the strong aeration in the aeration tank put the MFCs under a swaying condition, which negatively affected the connection of wires in the electric circuit for current collection. Some problems, like tubing clogging and swaying condition, can be overcome in large-scale system with faster feeding rates and better installation, but other problems, like biofilm formation on the cathode, are great challenges in future development.

Although electricity generation was not stable during MFC testing, attempts were made to obtain a rough picture of the MFC energy issue by analyzing energy production and consumption. The energy production from the three MFCs ranged from 0.005 to 0.009 kWh/m^3, or 0.043 to 0.082 kWh/kg TCOD with large standard deviations (Table 3.2). The energy consumption was mainly due to the pumps for feeding and recirculating the anode solutions. At the same rates of both feeding and recirculation, and the same HRTs, the three MFCs theoretically consumed the same energy of 0.009 kWh/m^3. When the energy consumption was expressed based on the organic removal, the three MFCs had different values (Table 3.2). The energy balance (i.e., the difference between energy production and consumption) was generally negative, likely resulting from low energy production during MFC testing; however, energy consumption in those MFCs was also low. Compared with the activated sludge process, which can require 0.1-0.2 kWh/m^3 [43] or up to 0.6 kWh/kg COD [44], the MFCs consumed much less energy, potentially generating economic benefits. It should be noted that the MFCs in this study took advantage of the existing aeration in the aeration tank and the energy consumption by that part of aeration was not included in our analysis.

3.4.3 Prospective of MFC integration with activated sludge process

This effort appears to be the first long-term study of MFCs installed in a real aeration tank at a municipal wastewater treatment plant. Although prior laboratory studies have demonstrated the feasibility of integrating MFCs into an aeration tank, the results of our onsite tests do not fully support it. The tested MFCs did not show any advantages or comparable performance in COD removal compared with activated sludge processes. The low COD removal was due to low electricity production, which was caused by multiple factors. Some of the problems encountered are expected to be resolved, such as tubing clogging and MFC installing positions during larger-scale deployment, but other issues, such as cathode biofouling, will present a difficult challenge.

Exposing the cathode to an environment (e.g., an aeration tank) containing high concentrations of both microorganisms and organic compounds does not favor the cathode reaction. To achieve high power output, the cathode electrode is usually designed to have a high-surface area, which also facilitates biofilm growth. The thick biofilm on the surface of a cathode electrode can slow down oxygen transfer through both physical obstruction and microbial consumption. The presence of a large amount of organic compounds in the aeration tank stimulates the growth of heterotrophic bacteria, which competes for oxygen with the electrochemical oxygen reduction on the cathode electrode. We do not expect any biological cathode activities in this case, because of the overwhelming growth of heterotrophic bacteria; in contrast, biocathode microbes are expected to be autotrophic organisms [45-46]. It is also possible that the strong aeration in the aeration tank promoted oxygen transfer into the anode compartment, thereby inhibiting electrochemically-active microbes, although further evidence is required.

Based on the results of this study, there are no obvious advantages of installing MFCs in an aeration tank at this moment; however, that does not exclude the possibility of applying this concept in the future if key problems such as cathode biofouling can be solved and energy production in MFCs can be further improved. It is also possible that MFCs function as pretreatment and their effluent can be polished by the activated sludge process for improved COD removal.

3.5 Conclusion

This study has demonstrated the great challenges and problems in applying MFC technology in an aeration tank through *in situ* examination. The study reveals significant differences between laboratory experiments and onsite tests. The long-term operation helps to disclose the details of problems that cannot be observed under laboratory conditions. Although the results suggest that MFCs may not be suitable for deployment in an aeration tank, this study is very important to identifying the potential application niche of MFCs for domestic wastewater treatment. There is an urgent need for more *in situ* experiments to examine the technical viability of MFC technology.

4. Long-term Investigation of Microbial Fuel Cells Treating Primary Sludge or Digested Sludge

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4.1 Abstract

The long-term performance of sludge treatment in microbial fuel cells (MFCs) was examined by operating two MFCs for almost 500 days. In Phase I, one MFC fed with primary sludge removed 69.8±24.1% of total chemical oxygen demand (TCOD) and 68.4±17.9% of volatile suspended solids (VSS); the other MFC with digested sludge reduced 36.2±24.4% of TCOD and 46.1±19.2% of VSS. In Phase II, both MFCs were operated as a two-stage system that removed 60% of TCOD and 70% of VSS from the primary sludge. An energy analysis revealed that, although the total energy in the MFC system was comparable with that of anaerobic digesters, the electric energy had a minor contribution and methane gas still dominated the total energy production. The results suggest that MFCs may not be suitable for treating primary sludge for energy recovery, but could potentially be used to polish the effluent from anaerobic digesters.

4.2 Introduction

Sewage sludge is a byproduct of municipal wastewater treatment and generated from primary and secondary sedimentation. In municipal wastewater treatment plants, the treatment and disposal of sewage sludge can comprise up to 50% of the operation costs [47]. There are several approaches for treating sludge to reduce solid contents and to stabilize biomass; however, anaerobic digestion (AD) is generally preferred because of its cost-effectiveness and bioenergy production. Digested sludge can be further composted for agriculture uses, and biogas can be converted into electricity and/or heat through combustion and thus compensate for some energy use in a wastewater treatment plant. Because of a large amount of organic contents, primary sludge contains about 66% of the energy content of wastewater [48], and about 81% of biodegradable organic energy may be converted to methane [44]. Despite the great energy potential with biogas production, several issues limit successful AD application; for instance, electric generators and their maintenance are costly, and biogas may need pre-treatment to remove contaminants such as hydrogen sulfide [47]. In addition, energy will be lost during methane conversation,

because the common efficiency of methane-to-electricity is about 33%. Therefore, it is of great interest to explore alternative technologies for sludge treatment and energy recovery.

The use of microbial fuel cells (MFCs) is a promising approach for direct production of electric energy or other energy carriers such as hydrogen gas from various organic substrates [29, 49]. Sewage sludge has also been studied in MFCs for electricity generation. A single-chamber MFC with a baffle inside its anode compartment generated low power from anaerobic sludge due to a large internal resistance caused by the baffle [50]. Because hydrolysis is considered to be a limiting step in AD [51], appropriate pretreatment is expected to improve the contents of soluble and small-particle organics that can be better used by microorganisms. The ultrasonic and alkaline pretreatment of sludge improved its degradability and resulted in a higher power output of 12.5 W/m^3, with 61.0% and 62.9% reduction of total chemical oxygen demand (TCOD) and volatile solids (VS), respectively [52-53]. Likewise, improved power output and solid production was observed in an MFC after pretreatment with sterilization and alkalization [54]. When an MFC was linked to an anaerobic digester to form an integrated recirculation loop, it was found that methane production was higher than the digester alone [55], because a high concentation of ammoninium/ammonia will inhibit methanogenic activity [56]. The improved biogas production, resulting from the use of a recirculation loop, was likely due to the migration of ammonium ions from the digester to the cathode compartment of the MFC driven by electricity generation in the MFC, which was also demonstrated previously [57]. A recent study reported the performance of MFCs in treating a fermentation solution from primary sludge, in which higher power production was obtained when treating a mixture of fermentation supernatent and primary effluent, because of elevated concentrations of soluble COD and volatile fatty acids after the fermentation process [58].

In general, previous research on using MFCs to treat sludge focused on the short-term performance of power production and COD removal, and few studies have examined biogas production and solid reduction in great detail. Furthermore, no studies have really shown the production of electric energy (in kWh) from sludge; power is not an energy parameter [22]. In this study, a long-term (almost 500 days) investigation of MFCs treating sewage sludge for energy production, organics removal, and solid reduction was concluded. The experiment consisted of two phases: in Phase I, two tubular MFCs were operated with primary sludge and digested sludge, respectively, for more than ten months; in Phase II, both MFCs were operated as a two-stage system to treat primary sludge for about six months. Biogas production in the MFCs and energy production between MFCs and anaerobic digesters were compared. The results helped to better understand the application niche of MFC technology in wastewater treatment.

4.3 Materials and Methods

4.3.1 MFCs setup

Two identical tubular MFCs were constructed based on a tube made of cation exchange membrane (Ultrex CMI7000, Membranes International, Inc., Glen Rock, NJ, USA) (Figure 4.1). The membrane tube had a diameter of 6 cm and a height of 70 cm. A carbon brush (Gordon Brush Mfg. Co., Inc., Commerce, CA, USA) was used as an anode electrode and installed inside the membrane tube, resulting in an anode liquid volume of 1.8 L. The cathode electrode was carbon cloth (PANEX® 30-PW03, Zoltek, Corporation, St Louis, MO, USA) coated with Pt/Carbon catalyst (0.2 mg Pt/cm^2). The cathode electrode wrapped the membrane tube and connected to the anode electrode by titanium wire and copper wire across a resistance decade box.

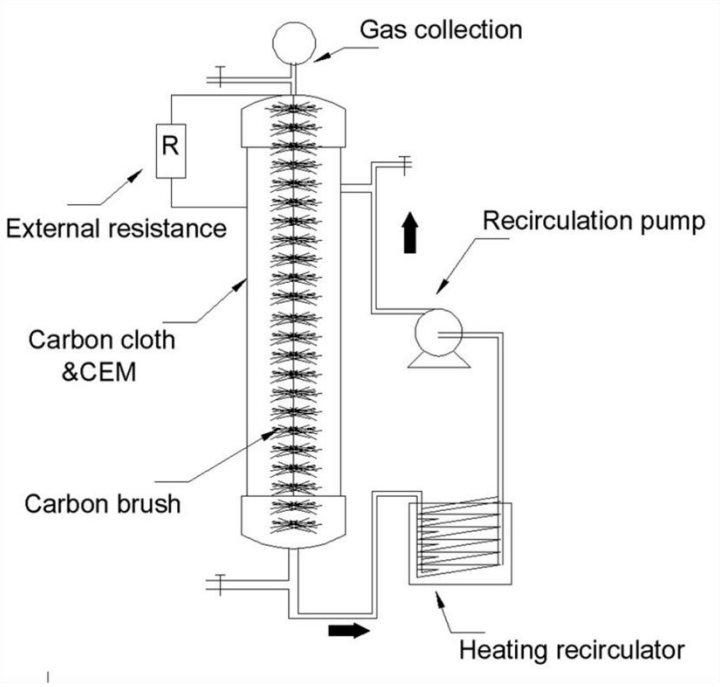

Figure 4.1 *Schematic of the tubular MFC used for sludge treatment.*

4.3.2 MFCs operation

Both MFCs (MFC-1 and MFC-2) were inoculated with raw sludge from a primary sedimentation tank at the Milwaukee Metropolitan Sewerage District's (MMSD)South Shore Water Reclamation Facility(Milwaukee, WI). In Phase I, two MFCs were operated at an HRT of 9 d in each reactor: MFC-1 used the primary sludge as an anode substrate, while MFC-2 was fed with the digested sludge from the anaerobic digesters at South Shore Water

Reclamation Facility. In Phase 1, the large particles in the sludge were removed using a 4-mm sieve before feeding. In Phase II, the two MFCs formed a two-stage MFC system, in which the primary sludge was first fed into MFC-1, and then the treated effluent of MFC-1 was transferred into MFC-2. Each MFC had an HRT of 7 d, resulting in a total HRT of 14 d in the two-stage MFC system. An electric blender was used to break the large particles in the primary sludge, and then the sludge was screened through a 3.3-mm sieve. To buffer the pH of the anolytes in the two MFCs, 20-40 mL of 1 M $NaHCO_3$ solution was added at the beginning of each feed cycle. The anolytes were recirculated at 150 and 100 mL/min in Phase I and II, respectively. The temperature of the anolytes was maintained around 35 °C by using a heating recirculator (Model 1104; VWR International, LLC, USA), which heated a water bath housing the recirculation of the anolyte. The acidified tap water (pH = 2, adjusted using sulfuric acid) was recirculated at ~ 45 mL/min as the catholyte for both MFCs.

4.3.3 Measurement and analysis

The MFC voltage across an external resistor was measured using a multimeter (Model 2700; Keithley Instruments, Inc.). Biogas was collected and measured by the water replacement method. The composition of biogas (mainly CO_2 and CH_4) was analyzed by using a gas chromatography (Focus GC, Thermo Fisher Scientific, Waltham, MA, USA). TCOD concentrations were measured using a COD digester and colorimeter according to the manufacturer's instructions (Hach Company, Loveland, CO, USA). Total suspended solids (TSS) and volatile suspended solids (VSS) were measured using standard methods [37]. The pH was measured using a Benchtop pH meter (UB-10, Denver Instrument, Denver, CO, USA). Polarization curves were constructed using a Gamry Reference 600 potentiostat (Gamry Instruments, Warminster, PA, USA). The power density and current density were calculated based on the anode liquid volume. Coulombic efficiency (CE) was calculated according to a previous study [25].

4.4 Results and Discussion

This study shows the long-term performance of MFCs in treating high-concentration/high-solids sewage sludge. The results exhibit relative stability and repeatability of both sludge treatment and electricity generation during operation for almost 500 days.

4.4.1 MFC treatments of primary sludge and digested sludge

Both MFCs were acclimated for about two months at an initial external resistor of 2000 Ω (which was changed to 40 Ω later) to reach a condition with stable electricity generation, and then polarization analysis was carried out to determine the internal resistance. Although the maximum power densities obtained from polarization curves were very different, 6.4 and 3.2 W/m^3 for MFC-1 and MFC-2, respectively, the two MFCs had a similar internal resistance of ~ 20 Ω. These power densities were in the typical range of 2.4 to 7.8 W/m^3 from the MFCs using sludge as substrates [59]. Subsequently, the external resistance of both MFCs was adjusted to 20 Ω for the maximum power output during the remaining period of Phase I. Figure 4.2 shows the current generation at an HRT of 9 d for more than 250 days. The fluctuation in current generation was due to the large variation in the sludge characteristics of TCOD and the solid contents in the feeding sludge (Table 4.1). The primary sludge contained more than 80% of volatile organics, whereas about only half of the solid content was volatile in the digested sludge because of the stabilization during anaerobic digestion. The pH of the primary sludge was partially acidified because of hydrolysis and fermentation in the sedimentation tank, but the digested sludge had a neutral pH, possibly due to the alkalinity addition during anaerobic digestion.

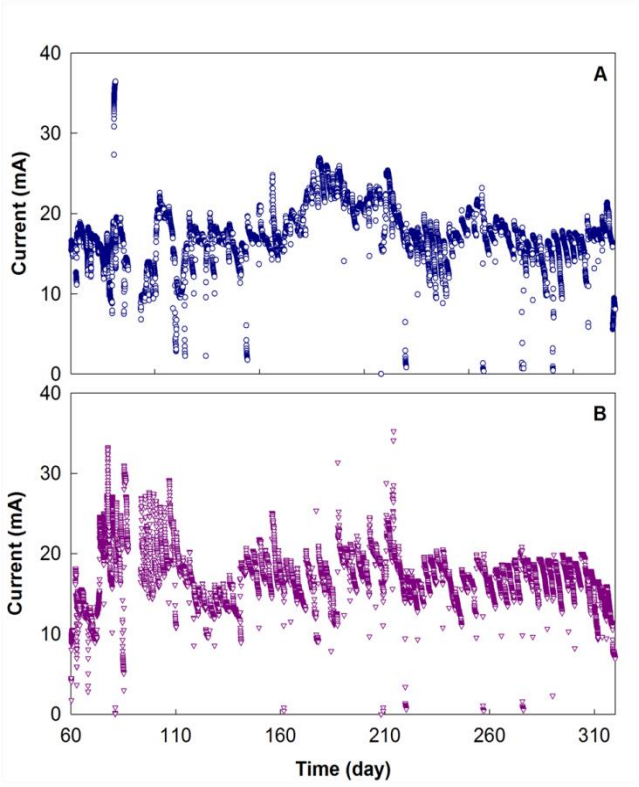

Figure 4.2 *Current generation of individual MFC in Phase I with an HRT of 9 d in each reactor: (A) MFC-1 fed with primary sludge and (B) MFC-2 fed with digested sludge.*

For sludge treatment, MFC-1 had a higher TCOD removal of 69.8±24.1% from the primary sludge compared with 36.2±24.4% from the digested sludge in MFC-2. Because of the high concentrations of organic matters in the sludge, both MFCs had relatively low CEs of 7.2±8.1% in MFC-1 and 2.6±1.4% in MFC-2; MFC-1 also had greater solid reduction than MFC-2. MFC-1 reduced 63.7 ±19.6% of TSS and 68.4±17.9% of VSS, while MFC-2 achieved 42.8±17.1% of TSS reduction and 46.1±19.2% VSS reduction.

Table 4.1 *Characteristics of the primary sludge (PS) and the digested sludge (DS) in Phase I.*

	PS	**DS**
TCOD (g/L)	14.2±11.2	16.7±11.4
TSS (g/L)	6.9±5.5	5.8±4.7
VSS (g/L)	6.1±5.0	3.0±2.9
pH	6.0±0.4	7.1±0.6

In Phase I, the main difference between the two MFCs fed with different sludge was in the reduction of organics/solids, not in electricity generation, although polarization curves did show some difference at the initial period. The primary sludge was better treated in the MFC, because it contained a high fraction of readily degradable compounds; on the other hand, the digested sludge had much less volatile solid and became more stable after anaerobic digestion. Biogas production observed in MFC-1 but not in MFC-2 during the Phase I also indicated the digested sludge had much fewer "useful" organic compounds; even its higher pH than the primary sludge should have favored the growth of methanogens. However, MFC-2 still extracted some electric energy from the digested sludge and further reduced TCOD and VSS, suggesting that MFCs may be used as a post-treatment process following anaerobic digesters [32]. However, the high-solid sludge could clog the MFC reactors that contain high surface-area materials as electrodes, and thus its treatment in MFCs may require more maintenance. The supernatant of digested sludge could be a more appropriate substrate for MFCs. In a wastewater treatment facility, digested liquid (supernatant) from anaerobic digesters is usually returned to primary treatment and will eventually be treated by aerobic processes (e.g., activated sludge). If this digested liquid can be further polished in an MFC, the amount of energy needed to remove organic materials will be reduced by eliminating or reducing aeration, and some organics can be directly converted into electric energy in MFCs, thereby decreasing operating expense.

The effects of recirculation rates (mixing intensity) and electrolyte pH on electricity generation in MFC-1 were examined. More current production was expected due to better

mixing by a higher recirculation rate; however, we did not observe any obvious improvement when adjusting the recirculation rates from 150 to 400 mL/min. Therefore, to minimize energy consumption by the recirculation, the recirculation rate was fixed at 150 mL/min for the remaining test period. The pH of the anolyte could significantly affect electricity generation by affecting the growth of electrochemically-active bacteria. The anolyte pH of MFC-1 decreased to 5.48±0.43 at the end of each feeding cycle in the absence of any buffering solutions, which was caused by concurrent reactions from acidification process and proton accumulation in the anode compartment. The current generation was not negatively affected by the pH until day 75. When phosphate buffer solution (PBS) was added on day 80 to adjust the pH, the current recovered to ~ 20 mA. When $NaHCO_3$ was dosed instead of PBS on day 100 to buffer the anolyte, the pH was 6.5±0.6 after each cycle while the electricity generation varied relatively stable between 10 and 20 mA. Unlike the primary sludge, the digested sludge (in MFC-2) had sufficient alkalinity to maintain a pH at 6.5±0.4 at the end of the operating cycle so that no buffer was added into MFC-2.

The limited effect of recirculation rates (mixing intensity) on electricity generation could be due to a sufficient supply of organic compounds with the high-concentration sludge. Previously, significant improvements in electricity generation were observed at higher recirculation rates with a low-strength anode feeding solution [8, 60]. In this study, a high concentration of TCOD was overly supplied to the anode compartment, in which there was no zone with deficiency of organic substrates. Therefore, improving the mixing did not obviously alter the substrate supply to the anode electrode.

4.4.2 Two-stage MFC system treating primary sludge

After operating for about 300 days, the two MFCs were changed to a two-stage mode, in which the primary sludge was fed into MFC-1, and then the MFC-1 effluent was transferred into MFC-2. The HRTs were same at seven days in both MFCs. It took about 50 days to reach a condition of stable current generation due to system clogging, availability of substrate, and other instrumental problems. Figure 4.3 shows current generation in the two MFCs for more than 120 days. During this phase, the primary sludge was blended and then screened, resulting in a much higher content of both solids and organics supplied to the MFCs than that of MFC-1 in Phase I (Table 4.2).

Initially, only MFC-1 was buffered by adding $NaHCO_3$; its effluent pH was maintained at around 6.5 and the current varied between 10 to 25 mA. On day 390, the current of the MFC-2 started to decrease below 10 mA. On day 415 we added $NaHCO_3$ to the MFC-2 feeding, which gradually improved the peak current to 30 mA. In addition, biogas was observed in MFC-2 following the addition of bicarbonate, which will be discussed in the following section. Because of the changes in current generation, we conducted another

polarization test and obtained different internal resistances for both MFCs. As a result, the external resistance was changed to 15 Ω for MFC-1 and 12 Ω for MFC-2 on day 467. We also found that the acidified catholyte resulted in maximum power densities of 8.5 and 10.7 W/m^3 for MFC-1 and MFC-2, respectively, almost twice the maximum power densities when the catholytes were neutralized. The acidified catholytes also resulted in a higher open-circuit voltage (0.2 V) than that with the neutralized catholytes.

Table 4.2 *Characteristics of the primary sludge (PS) and the treatment performance of the two MFCs in Phase II.*

		PS	MFC-1	MFC-2
Day 380-434	TCOD (g/L)	78.0±12.4	46.7±15.0	24.2±14.2
	TSS (g/L)	58.4±12.0	28.0±5.9	10.4±7.2
	VSS (g/L)	44.8±7.6	19.0±3.2	7.12±3.8
	TCOD Reduction (%)		37.3±23.0	67.0±17.3
	VSS Reduction (%)		54.4±10.5	82.1±9.0
Day 435-470	TCOD (g/L)	52.7±8.8	31.8±7.4	19.6±5.7
	TSS (g/L)	31.8±14.0	19.1±7.6	8.4±4.5
	VSS (g/L)	25.8±14.0	13.1±6.0	5.3±3.5
	TCOD Reduction (%)		41.8±12.6	63.9±10.5
	VSS Reduction (%)		57.4±12.9	79.6±16.3
Day 471-495	TCOD (g/L)	35.0±6.54	19.0±8.8	15.2±3.1
	TSS (g/L)	23.8±4.6	12.4±6.5	8.3±3.6
	VSS (g/L)	25.8±14.0	10.0±5.4	5.7±1.4
	TCOD Reduction (%)		51.1±22.8	60.8±14.2
	VSS Reduction (%)		51.1±27.8	71.7±9.1
pH		5.6±0.1	6.6±0.4	6.4±0.4

The treatment performance of the MFC system in Phase II was divided into three periods: day 380-434, day 435-470, and day 471-495, according to the difference in sludge characteristics from different samplings (Table 4.2). The corresponding removal efficiencies of TCOD in MFC-1 were 37.3±23.0%, 41.8±12.6%, and 51.1±22.8%, respectively; the total TCOD removal efficiencies after the MFC-2 treatment were 67.0±17.3%, 63.9±10.5%, and 60.8±14.2%, respectively, during the three periods. In Phase II, the columbic efficiency was generally low, as the CEs were only 2±1% and 4±1% for MFC-1 and MFC-2, respectively. For solid reduction, the MFC-1 reduced 51.1-54.4% of VSS; the use of MFC-2 as the second-stage treatment improved solid reduction by about 20% (Table 4.2). The two-stage MFC system had higher reduction efficiencies of both TCOD and VSS at higher initial concentrations.

MFCs may be competitive to anaerobic digesters in terms of primary sludge treatment, especially in reducing volatile solids (VS). A few examples of AD treatment reported in the previous studies include a 56% reduction in VS at an HRT of 15 days [61], 35% reduction in VS from primary sludge at an HRT 20 d [62], 61.7% reduction in VS from waste-activated sludge at an HRT 15 d [63], and 40-50% reduction in VS from sewage sludge [64]. In our study, MFC-1 could reduce 68% of VSS in nine days in Phase I, and about 50% of VSS in seven days in Phase II. If we include MFC-2 in the Phase II, the two-stage MFC system could reduce more than 70% of VSS in 14 days. Faster solid reduction in the MFCs was possibly due to oxygen intrusion into the anode compartment through the cation exchange membrane, and bioelectrochemical oxidation using oxygen as a terminal electron acceptor that is an "indirect" aerobic reaction. The carbon brush anode electrode with a high specific area provided sites for biofilm formation that could facilitate the growth of robust organisms for organic oxidation; the carbon fibers of the carbon brush might also help with solid-liquid separation that retained organic compounds for microbial use in a longer period of time.

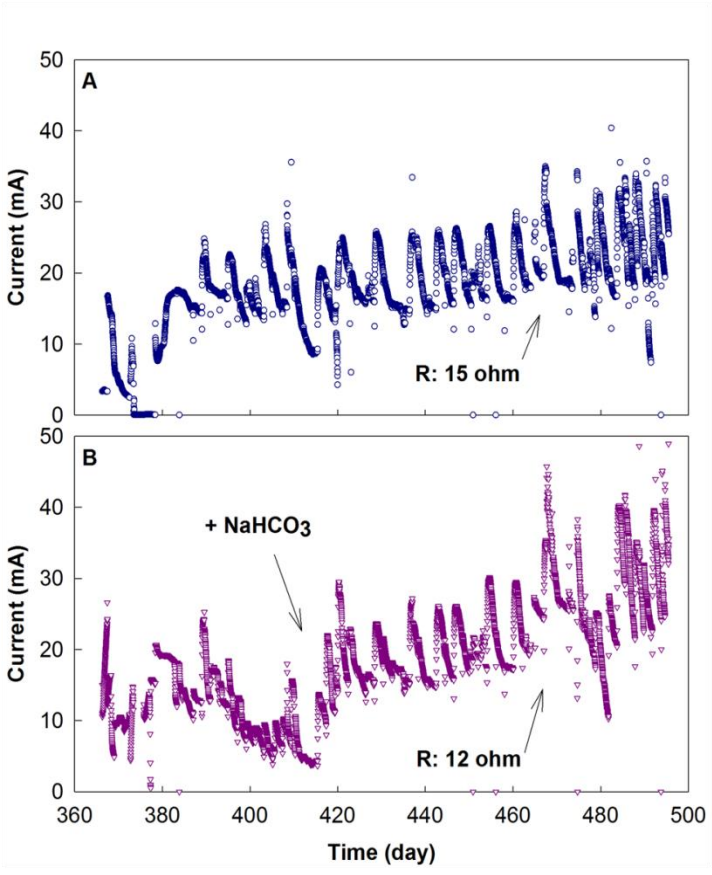

Figure 4.3 *Current generation in the two-stage MFC system fed on primary sludge in Phase II with an HRT of 7 d in each reactor: (A) MFC-1 and (B) MFC-2.*

4.4.3 Biogas and energy production

Biogas production in the MFCs was observed and analyzed. In Phase I, biogas production occurred only in MFC-1 with the primary sludge, ranging from 190 to 1467 mL/d. MFC-2 was used to treat the digested sludge and did not generate any obvious biogas. During Phase II, biogas was produced in both MFCs (Figure 4.4). MFC-1 had increasing biogas production that reached the highest rate of about 2200 mL/d during day 435-470. MFC-2, on the other hand, did not produce any biogas at the initial period; after the bicarbonate was added into MFC-2 to buffer the anolyte, biogas was produced subsequently, although not as much as MFC-1. The highest production rate in MFC-2 was about 1175 mL/d. The biogas contained 62.7±3.6% and 51.4±12.7% of methane from MFC-1 and MFC-2, respectively.

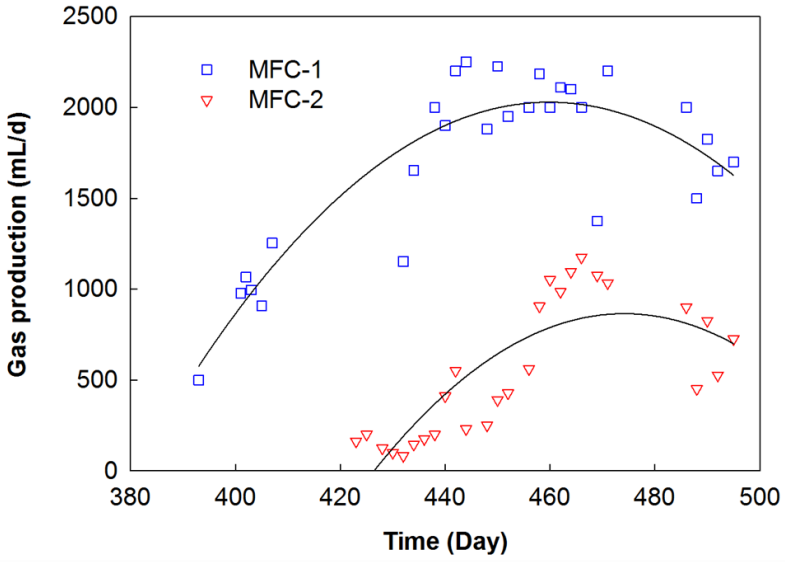

Figure 4.4 *Biogas production in the MFCs during Phase II.*

Energy production was analyzed in Phase II as a sum of electric energy from direct electricity generation in the MFCs, and electricity that could be generated from biogas conversion. The direct electric energy was calculated using power production from either a regular operation or the maximum power output from the polarization test. In a regular operation, electric power was produced at external resistance of 20 Ω for both MFCs; the average energy production in MFC-1 and MFC-2 was 0.78 and 0.95 kWh/m^3, respectively, resulting in a total electric energy production of 1.73 kWh/m^3 in the two-stage MFC system (Table 4.3). At the maximum power output obtained from the polarization curves, the energy production will be 1.43 and 1.80 kWh/m^3 from MFC-1 and MFC-2, respectively (Table 4.3); thus, the total electric energy will be 3.23 kWh/m^3.

The energy in biogas was calculated assuming that the methane percentage is 65%, the heating value of methane is 30 J/mL, and the conversion efficiency of methane-to-electricity is 34%. We used biogas production of 2000 mL/d from MFC-1 and 1000 mL/d from MFC-2 for the calculation, and obtained the energy production from biogas as 21.06 kWh/m^3 (sum of 13.90 kWh/m^3 from MFC-1 and 7.16 kWh/m^3 from MFC-2). The results show that the electric energy from direct generation was only 8-15% of the energy from biogas. The total energy production (sum of electric energy and biogas energy) in the two-stage MFC system was 22.79 or 24.29 kWh/m^3. The energy production in the anaerobic digesters at the MMSD's South Shore Water Reclamation Facility was estimated to be 10.73 - 38.06 kWh/m^3. Therefore, the total energy production in the MFC system was comparable with that of anaerobic digesters, but direct electricity generation had a minor contribution (8-15%) to the total energy production.

Table 4.3 *Energy production (kWh/m3) from the two-stage MFC system in Phase II and energy production from biogas at MMSD's South Shore Water Reclamation Facility.*

MFC Energy	**Two-stage MFC system**			**AD** [c]
	Electric energy		Methane	Methane
	(Operation) [a]	(Maximum) [b]		
MFC-1	0.78	1.43	13.90	10.73-38.06
MFC-2	0.95	1.80	7.16	
Total	1.73	3.23	21.06	
Total energy (kWh/m^3) [d]	22.79	24.29		10.73-38.06

[a] Electricity generation from regular operation of the MFC system with external resistance of 20 Ω for both MFCs.

[b] Electric energy from the maximum power output obtained from polarization tests.

[c] Methane production data were obtained from four anaerobic digesters at South Shore Water Reclamation Facility.

[d] The total energy is the sum of total electric energy (under one of the conditions) and total energy from methane gas.

Although the MFCs achieved good sludge reduction that is important to sludge treatment, energy production is a key parameter to evaluate whether MFC technology is suitable for treating primary sludge, because primary sludge is usually treated for energy recovery in anaerobic digesters. Energy production in MFCs, including those treating sludge, has not been properly presented before. Most prior studies only showed power production, which is not an energy parameter. In addition, methane production has not been well monitored in the sludge-fed MFCs. In this study, both electric energy and potential energy production from methane gas were analyzed to develop a better picture of energy production in the sludge-fed MFCs. Although the total energy production in the two-stage MFC system was

comparable to that of anaerobic digesters, we do not think MFCs are efficient energy producers from primary sludge at this moment. Our results show that direct production of electric energy has a minor contribution to the overall energy production, which is still dominated by methane gas. The low CEs also confirm that the majority of organic removal was not associated with direct electricity generation; therefore, the MFCs fed with the primary sludge acted mostly as the "modified" anaerobic digesters.

Diverting some organic compounds to direct electricity generation in an MFC could reduce biogas processing and conversion, resulting in some (potentially) economic benefits, but we also need to understand the challenges of MFC application. For example, MFCs generally have much more complex structures and higher capital cost than anaerobic digesters. The use of high surface-area electrodes and high-solid substrate like sludge can create problems such as reactor clogging. Unlike anaerobic digesters that can be constructed in a single reactor with a large volume, MFCs are expected to be built in small-scale modules to form an MFC assembly; a single MFC with a very large volume will have a larger distance between the anode and the cathode electrodes, thereby increasing the internal resistance and decreasing electricity generation. With multiple small-scale MFC modules, the heating and feeding of the anolytes will be very challenging.

Furthermore, there will be loss during harvesting the electricity from MFCs or other bioelectrochemical systems [65], and the "useful" electricity will be less than what was presented here. Therefore, without significant advantages in energy production, MFCs may not be suitable for treating primary sludge; however, as stated earlier, MFCs could function as a post-treatment process to polish the supernatant of digested sludge. In that way, energy production is not a key factor to performance; instead, with satisfactory treatment performance and reduced energy consumption via anaerobic treatment, energy recovery will be an additional benefit.

4.5 Conclusions

A long-term investigation was conducted on the technical performance of MFCs used to treat sewage sludge. The MFCs satisfactorily reduced of both organics and suspend solids. The total energy production from primary sludge in the two-stage MFC system was comparable to that of anaerobic digesters; however, direct electricity generation had a minor contribution while energy from biogas still dominated the overall energy production. It will be very challenging to apply MFC technology to treat primary sludge; but MFCs may be used to polish the digested effluent from anaerobic digesters, offering potential benefits in energy savings compared with aerobic treatment.

5. Long-term Performance of Liter-scale Microbial Fuel Cells Treating Primary Effluent Installed in a Municipal Wastewater Treatment Facility

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5.1 Abstract

Two 4-L tubular MFCs were installed in a municipal wastewater treatment facility and operated for more than 400 days on primary effluents. The performance of the MFCs was largely affected by organic input and temperature. Both MFCs removed 65-70% of chemical oxygen demand at a hydraulic retention time (HRT) of 11 h and reduced about 50% of suspended solids. They could handle fluctuation such as anode emptiness for 1-3 days or different HRTs. The preliminary analysis of energy production and consumption indicated the two MFCs could theoretically achieve a positive energy balance, and energy consumption could be reduced by using larger tubing connectors. By linking to a denitrifying MFC, the MFC system improved the removal of total nitrogen from 27.1% to 76.2%; however, the energy production substantially decreased because of organic consumption in the denitrifying MFC. Establishing a carbon (electron) balance revealed that sulfate reduction was a major electron scavenger and methane production played a very minor role in electron distribution. These results demonstrate the technical viability of MFC technology outside the laboratory and its potential advantages in low energy consumption, low sludge production, and energy recovery from wastes.

5.2 Introduction

Microbial fuel cells (MFCs) have been intensively studied in the past decade, and much of the fundamental knowledge in microbiology, electrochemistry, and reactor architecture has been obtained from laboratory investigation [6, 66]. The working theory and performance of MFCs (both organic treatment and power production) is well demonstrated, however, it is mostly in small-scale and batch-operated reactors. Among the studies reported in MFC-related literature, less than 2% reported a reactor larger than 1 L, less than 30% were operated continuously, and most studies were conducted with pure substrates under a controlled laboratory condition and for a short period of time,

indicating that engineering development of MFC technology lags behind fundamental research. To further demonstrate the technical viability of MFC technology, it is necessary to examine the long-term performance and stability of larger-size MFCs with actual wastewater.

There have been several studies reporting the long-term operation of MFCs. A cubic MFC with an anode working volume of 20 mL was operated for more than two years and achieved stable electricity generation from glucose [67]. By using electrochemical impedance spectroscopy, the researchers found that the anode impedance decreased in the first 50 days due to biofilm formation and then became stable in the next few months, resulting in a constant power output in an air-cathode MFC with a working volume of 16 mL [68]. However, the cathode electrode of the air-cathode MFC could clog over time, and it was observed that the maximum power density decreased by 20-40% after operating an MFC with a working volume of 28 mL for one-year [41]. Chemical and biological cathodes were evaluated and compared during a 400-d operation of the MFCs fed on glucose with an anode working volume of ~ 53 mL, and the results showed that the chemical cathodes had deteriorated performance while the biological cathode remained relatively stable [69]. An upflow tubular MFC with an anode working volume of 750 mL was used to treat animal carcass wastewater and continuously produced electricity during more than a 280-d operation [70]. An MFC system consisting of 40 individual tubular MFCs had a total liquid volume of 10 L and was operated for more than 180 d with a maximum power density of 4.1 W/m^3 generated from brewery wastewater [27]. The researchers also operated a 16-L MFC in a municipal wastewater treatment facility and obtained good treatment performance but low electricity production [71].

These prior long-term studies are healthy attempts to evaluate MFC performance; however, none of them analyzed energy production/consumption, which is the key parameter of MFC performance [22], and most of them were conducted in laboratories. Clearly, more work is needed to understand the long-term behavior of MFCs outside of the laboratory. In this study, we installed two tubular MFCs (4 L/each) in a municipal wastewater treatment facility and operated them for more than 400 d without temperature control. We evaluated the stability, treatment performance, and energy production/consumption of the MFCs treating primary effluent by monitoring various parameters, including organic contents, electricity, nutrient (nitrogen and phosphate), suspended solids, pH, turbidity, coliform bacteria, and temperature. The resulting information was expected to help to assess scalability and application niche of MFC technology.

5.3 Materials and Methods

5.3.1 MFC Setup

Two identical tubular MFCs (except different cathode catalysts) were made of cation exchange membrane (CEM, Ultrex CMI7000, Membranes International, Inc., Glen Rock, NJ) according to a previous study [8]. Each MFC consisted of two CEM tubes connected on the bottom to form a "U" shape. Each CEM tube had a diameter of 5 cm and a length of 100 cm containing a carbon brush as an anode electrode and carbon cloth as cathode electrode. The total anode liquid volume of a "U" shape MFC was about 4 L. One MFC used activated carbon powder (5 mg/cm^2) as cathode catalysts (designated as MFC-AC), and the other had both activated carbon powder (4 mg/cm^2) and 10% platinum in carbon black (0.1 mg Pt/m^2) as cathode catalysts (named "MFC-Pt"). The catalysts were coated to the carbon cloth (cathode electrode) by mixing with 5% polytetrafluoroethylene (PTFE), and then being applied to the surface of carbon cloth. The coated carbon cloth was heat-treated at 370 °C for 30 min. The anode and the cathode electrodes were connected to an external circuit containing a resistance decade box via titanium wire.

5.3.2 Operating Conditions

The MFCs were installed in a small room without any temperature control at the Milwaukee Metropolitan Sewerage District's (MMSD) South Shore Water Reclamation Facility (Milwaukee, WI). The MFCs were fed with the effluent from the primary settling tanks by pumps without any further pretreatment, and the anode effluent was used as a catholyte to rinse the cathodes of the MFCs. The final effluent was collected in a tank under the MFCs and then returned to the flow channel of the primary effluent that was about 3 m under the room. The hydraulic retention time (HRT) of the wastewater in the anodes was 11 h, or otherwise adjusted by the feeding pump. The anolyte was recirculated at ~ 165 mL/min, and the catholyte was recirculated at 21 mL/min. When the denitrifying MFC was linked to the MFC-AC, the primary effluent was first fed into the anode of the denitrifying MFC and then the anode of the MFC-AC; the anode effluent of the MFC-AC rinsed its cathode and flowed into the cathode of the denitrifying MFC for nitrate reduction (the inset of Figure 5.4 A). To study the effect of inhibiting sulfate reduction, 3.25 mM sodium molybdate was added to the anode feeding wastewater of the MFC-Pt for two weeks.

5.3.3 Measurement and Analysis

The cell voltage was recorded every 10 min by a by HOBO U12 Outdoor/industrial data logger. The concentrations of total COD (TCOD), soluble COD (SCOD), ammonium, nitrite,

nitrate, phosphate, and sulfate were measured using a colorimeter according to the manufacturer's instructions (Hach Company, Loveland, CO). The concentrations of total suspended solids (TSS) and volatile suspended solids (VSS) were measured according to the standard methods [37]. The coliform bacteria were determined by using the membrane filter technique for members of the coliform group approved by Standard Methods Committee [37]. The concentration of total Kjeldahl nitrogen (TKN) was measured by a Digesdahl® Digestion Apparatus (Hach Company) according to the manufacturer's instructions. Turbidity was measured with a turbidimeter (Scientific Inc., Fort Myers, FL). The pH, temperature, and dissolved oxygen (DO) were measured using a 556 MPS multi-parameter instrument (YSI Incorporated, Yellow Spring, OH). Biogas was analyzed using a gas chromatography (Thermo Fisher Scientific, Inc.), and the dissolved methane was determined according to a previous publication [72].

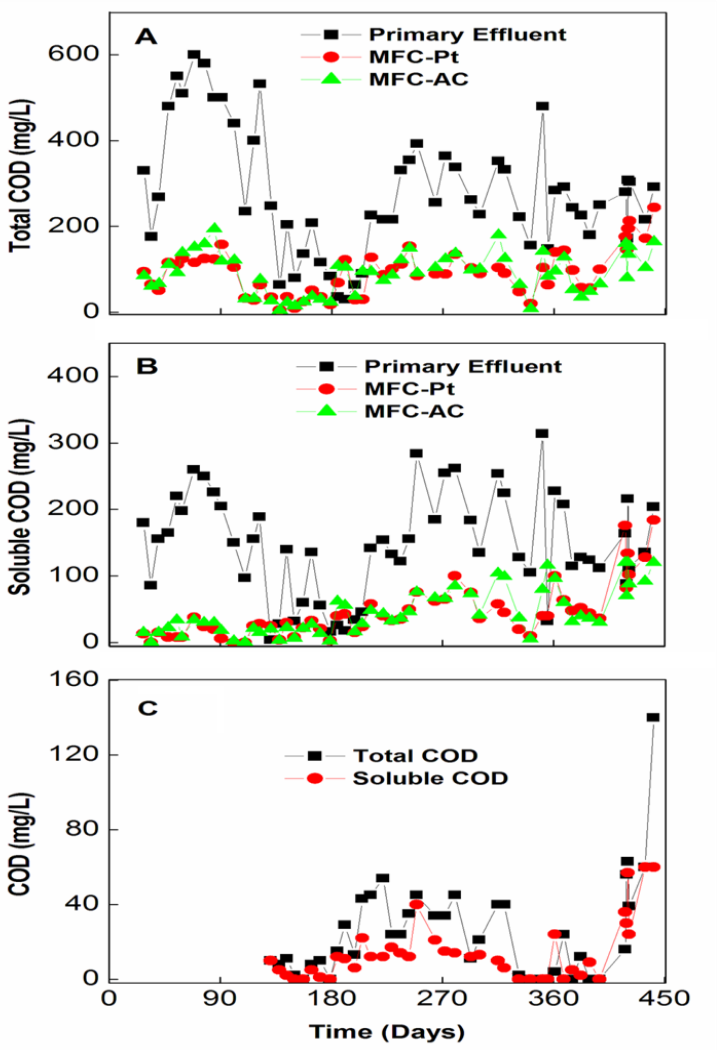

Figure 5.1. *The organic concentrations in the primary effluent and the MFC anode effluents: (A) TCOD; (B) SCOD; and (C) the organic concentrations in the catholyte.*

5.4 Results and Discussion

5.4.1 Treatment Performance

The organic concentration in the primary effluent (feeding solution) was highly variable (279.7±144.4 mg TCOD/L and 146.2±77.1 mg SCOD/L) and could reach a very low level after a major storm (Figure 5.1 A and B). In general, both MFCs achieved similar COD removal efficiency of 65-70%, or COD removal rate of ~ 0.40 kg TCOD/m^3/d or ~ 0.22 kg SCOD/m^3/d in their anodes at an HRT of 11 h. The anode effluent of the MFC-AC contained 90.3±48.3 mg TCOD/L and 45.0±35.0 mg SCOD/L, while the MFC-Pt produced 93.2±53.2 mg TCOD/L and 44.6±41.1 mg SCOD/L. The COD removal efficiencies of both MFCs started to decrease after day 400 (Figure 1A and B) because of significantly decreased temperature, and the experiments were stopped on day 450 because the MFCs were completely frozen at a room temperature of ~ -10 °C. We observed further reduction of organic concentration after the anode effluent flowed over the cathode surface: the water in the tank under the MFCs that collected the catholytes contained low concentrations of both TCOD and SCOD (Figure 5.1C), resulting in an overall organic removal > 90%. This improved organic removal was likely due to aerobic treatment (without active aeration), confirming that the quality of the effluent from anaerobic treatment (MFC anode) can be further improved through aerobic polishing [73]. This post-aerobic treatment was also important to the solution's pH, as we observed the anolyte pH varied between 4.0 and 6.5, and the pH of the catholyte was about 7.5-8.5.

Suspended solids (SS) in biological treatment are related to the production of secondary sludge. In this study, we monitored the concentrations of both TSS and VSS (Figure 5.2), and found that the anodes of the MFCs reduced about 50% of TSS and VSS. In the tank that collected the catholyte (which possibly acted as a sedimentation tank), the SS concentrations became even lower at 14±18 mg TSS/L and 4±10 mg VSS/L. Similarly, the MFC anodes decreased turbidity, another indicator of particle concentration in water, which was also further reduced in the catholyte. For comparison, the SS concentrations in the aeration tanks of the MMSD's South Shore Water Reclamation Facility were 2214±314 mg TSS/L and 1642±242 mg VSS/L. The low SS concentrations indicate that the MFCs did not accumulate much secondary sludge compared with that in an activated sludge process; as a result, the use of a secondary clarifier will be greatly reduced, thereby saving a tremendous amount of energy and effort for sludge disposal.

As expected, the anodes of the MFCs did not achieve any obvious removal of nitrogen and phosphorus. However, the catholyte showed a significantly lower concentration of ammonium and accumulation of nitrate, indicating the presence of nitrification. We have investigated nitrogen removal in greater detail by linking a denitrifying MFC to the MFC-AC, which is introduced in the following section. The MFC anodes did not achieve any

significant removal of coliform bacteria, which were mainly affected by season and temperature.

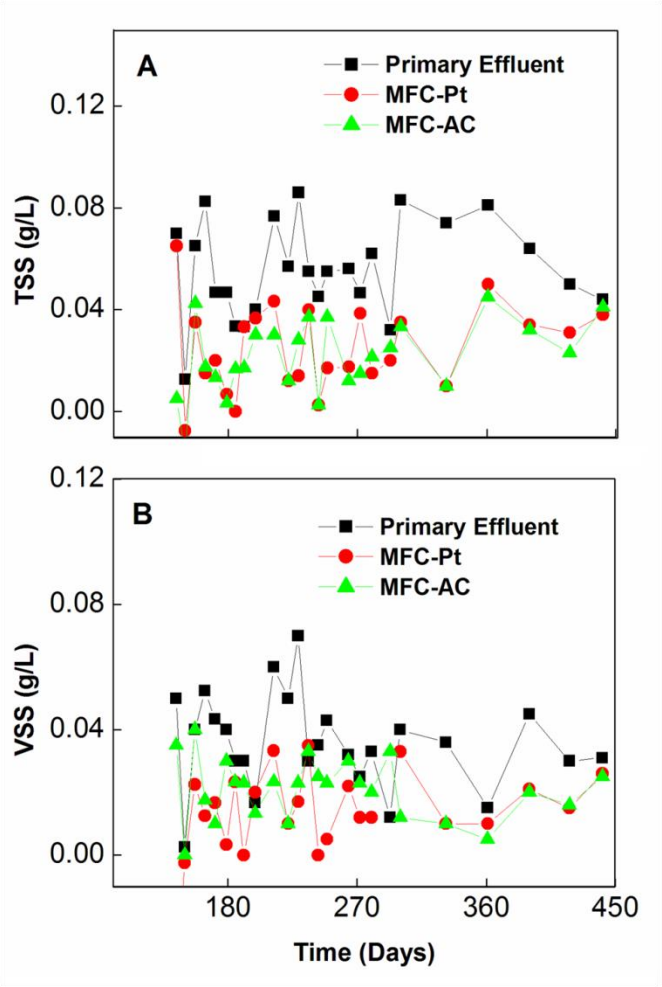

Figure 5.2 *The concentrations of suspended solids in the primary effluents and the MFC anode effluents: (A) TSS; and (B) VSS.*

5.4.2 Electricity Generation

Electric current was used as a parameter to monitor the long-term performance of electricity generation in the MFCs; power and energy were also analyzed. Both MFCs exhibited high current generation in the first 180 days (Figure 5.3), likely because of high organic concentrations in the primary effluent during that period (Figure 5.1A and B). For most of the time, two tubes of an MFC were connected by one electric circuit, in which two anode carbon brushes were connected together as one anode and two cathodes were linked as one cathode. Between day 57 and 104, the circuit was separated in to two in

order to examine whether power and energy production could be higher; that is, each tube functioned as an independent MFC. The results did not support this theory; therefore, the two individual circuits were combined back to one after day 104. The large variation in current generation was due to the varied organic concentrations in the primary effluent; the sharp decreasing lines, especially those that decreased to a level close to zero in a short period of time, were mostly because the tubing clogging stopped the supply of the primary effluent (or the anode emptiness test). We expect that the tube-clogging can be overcome in a larger-scale MFC system, which will have a much faster feeding flow rate. The gradual decrease in current after day 400 was due to the decreasing temperature. In general, there was not an obvious difference in current generation between the two MFCs, both of which achieved similar coulombic efficiencies and recoveries, suggesting that activated carbon (AC) powder can be an effective catalyst in an MFC [42]. However, we do not think that AC powder is good enough to replace platinum in any other oxygen-reduction processes like hydrogen fuel cells. The relatively comparable performance that AC powder achieved in an MFC is likely due to the low demand of oxygen reduction; that is, platinum is "overqualified" to be a catalyst for MFCs. The low Pt loading rate on the cathode electrode might also be one of the reasons why the MFC-Pt did not outperform the MFC-AC. Nevertheless, cathode catalyst is not the focus of this study and the results show that AC powder could be an alternative catalyst for further MFC development.

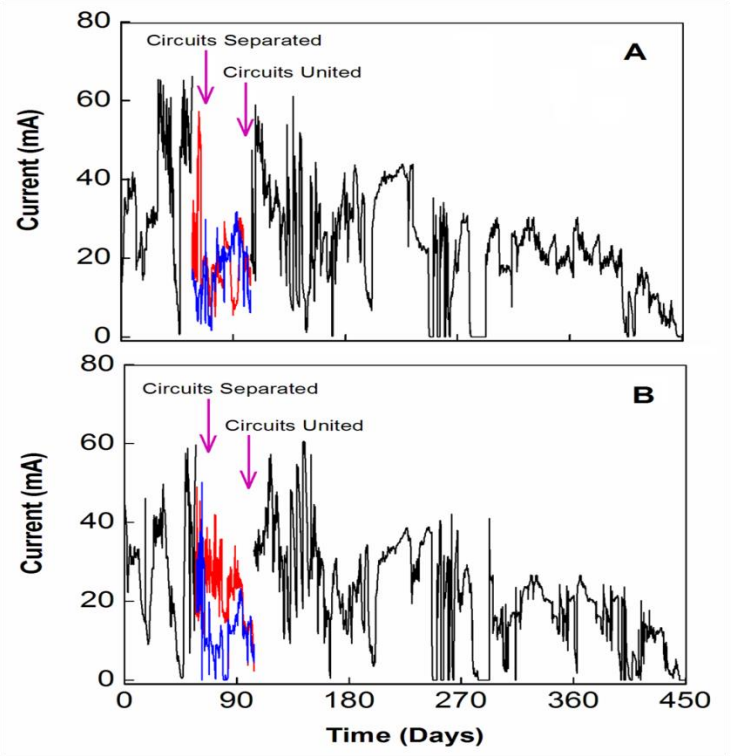

Figure 5.3 *The profiles of current generation during the operating period: (A) MFC-AC; and (B) MFC-Pt.*

Energy production is a key parameter to properly evaluate the benefits of MFC technology for wastewater treatment [22]. We analyzed energy production and consumption, and established a preliminary energy balance (Table 5.1). Energy production was expressed as kWh per cubic meter of treated wastewater, or kg removed COD (either TCOD or SCOD). Energy consumption included the consumption by pumps for feeding and recirculation; the feeding energy could be neglected compared with the recirculation energy. The two MFCs produced comparable electric energy but had different energy consumption, mainly due to the difference in hydraulic head loss, which is a key element in estimating energy consumption. The measured hydraulic head loss of the anode recirculation pump for the MFC-AC was 19.0±6.1 cm, significantly higher than 6.7±0.6 cm with the MFC-Pt. It was found that this difference was related to the size of tubing connectors; smaller-size were accidently used connectors in the MFC-AC, which resulted in a higher hydraulic head loss. This indicates that in designing future MFC systems, the size of connector/port should be large enough to reduce hydraulic head loss and thus energy consumption. Overall, both MFCs achieved positive energy balances with large standard deviations (Table 5.1); the MFC-Pt had a more positive balance because of less energy consumption.

Table 5.1 *Summary of energy production and consumption in the MFCs. The values in the bracket are standard deviations.*

	Energy Production			**Energy Consumption**			**Energy Balance**		
	kWh/ m^3	**kWh/kg TCOD**	**kWh/kg SCOD**	**kWh/ m^3**	**kWh/kg TCOD**	**kWh/kg SCOD**	**kWh/ m^3**	**kWh/kg TCOD**	**kWh/kg SCOD**
MFC-AC	0.0255 (0.0204)	0.0794 (0.1015)	0.1702 (0.2433)	0.0238 (0.0045)	0.0761 (0.0748)	0.1698 (0.1915)	0.0017 (0.0248)	0.0034 (0.1763)	0.0004 (0.4348)
MFC-Pt	0.0239 (0.0186)	0.0739 (0.0653)	0.1643 (0.1792)	0.0147 (0.0004)	0.0547 (0.0473)	0.1462 (0.2206)	0.0092 (0.0190)	0.0192 (0.1127)	0.0181 (0.3998)
N-MFC*	0.0078 (0.0059)	0.0236 (0.0195)	0.0391 (0.0287)	0.0238 (0.0045)	0.0769 (0.0293)	0.1746 (0.1442)	-0.0160 (0.0104)	-0.0532 (0.0488)	-0.1356 (0.1729)
* The MFC system for nitrogen removal consisting of the MFC-AC and a denitrifying MFC									

For practical application, it is important to have durable and stable treatment technology, which is related to maintenance and operating expense. A potential concern with using the anode effluent as a catholyte is the overgrowth of biofilm on the cathode electrode stimulated by the remaining organics/nitrogen in the anode effluent. During the operation, biofilm formed on the cathode electrode and possibly functioned as post-treatment of organics and nitrogen; however, we did not clean the cathode electrode during the entire experimental period. This suggests that biofilm formation was not as serious as expected and did not significantly affect electricity generation. The response of the MFCs to fluctuation under the two conditions were examined. The first condition was to mimic a situation in which the anode compartments were emptied for repair or other maintenance;

in this case, oxygen enters the anode compartment after the water was emptied. The emptiness was held for 3, 2, and 1 day, and we observed that the current generation in the two MFCs recovered from oxygen intrusion in a few days, depending on the length of the exposure (Figure 5.4A). This demonstrates that the MFCs could successfully handle oxygen flux for a short period of time, likely benefiting from facultative microorganisms in the anode community. The second condition was to simulate a larger water flux for a short period in the case of rain or storm. The large water flux alters the anolyte HRT, and thus we examined three HRTs, 12 h (regular condition), 6 h, and 3 h. The amount of the wastewater at HRT 3 h was four times greater that at 12 h, higher than common ratios of the treatment capacities between dry weather and wet weather. TCOD removal decreased with the decreasing HRTs in both MFCs, because of a higher organic loading rate at a smaller HRT (Figure 5.4B). The current generation in the MFC-AC slightly decreased, but the MFC-Pt had a more significant drop in its current at shorter HRTs (the insert of Figure 5.4B), which might be attributed to Pt catalyst contamination by serious biofouling from more organic input, but the exact reason is not clear at this moment. Both MFCs recovered to regular performance after the HRT was adjusted back to 12 h. We are more optimistic about the COD removal during shorter HRTs and expect much higher removal efficiencies than those shown in Figure 4B, because rainwater will greatly dilute the COD and the actual organic loading rate may not increase significantly.

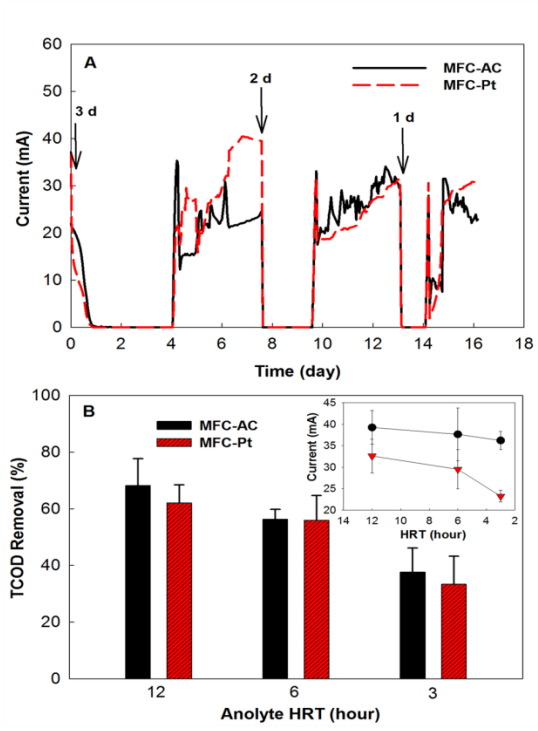

Figure 5.4 *The MFC performance in response to fluctuation: (A) emptying the anode for different periods; and (B) different HRTs.*

5.4.3 Nitrogen Removal

Nitrogen removal is of great interest in wastewater treatment because of the tightened regulations on nitrogen discharge. Ammonia cannot be effectively oxidized under the anaerobic condition of the anode of an MFC [74]; however, it was found that nitrate can be bioelectrochemically reduced on the cathode by accepting electrons from a cathode electrode [75]. In the cathode of the present MFCs, nitrate was produced and accumulated, and ammonium was reduced to a very low level, indicating the occurrence of nitrification. The concentration of total nitrogen in the final effluent (from the cathode) was dominated by the nitrate concentration; therefore, to improve the removal of total nitrogen, we connected a denitrifying MFC for nitrate reduction to the MFC-AC on day 301.

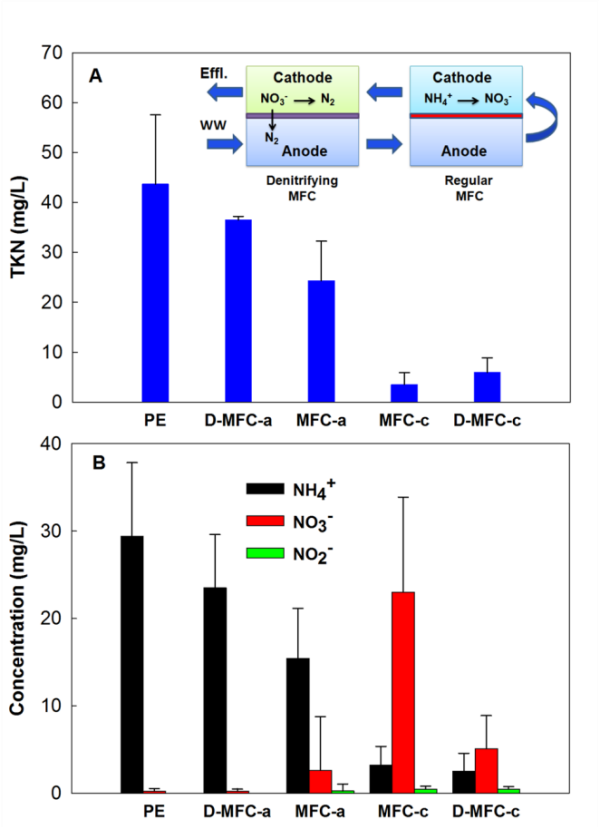

Figure 5.5 *The concentrations of nitrogen compounds in the MFCs designed for nitrogen removal: (A) TKN; and (B) ammonium, nitrate and nitrite. Insert: schematic of the MFC system consisting of a denitrifying MFC and the MFC-AC. PE: primary effluent; D-MFC-a: the anode of the denitrifying MFC; MFC-a: the anode of the MFC-AC; MFC-c: the cathode of the MFC-AC; and D-MFC-c: the cathode of the denitrifying MFC.*

Such a cooperative system between a denitrifying MFC and a regular MFC (as shown by the insert of Figure 5.5A) significantly improved the nitrogen removal. The concentration of nitrate was reduced from 21.4±10.2 mg/L in the cathode effluent of the MFC-AC to 4.9±3.8

mg/L in the cathode effluent of the denitrifying MFC (also the final effluent of the MFC treatment), about 77% reduction (Figure 5.5B). The average current of the denitrifying MFC was about 8.6 mA, resulting in a CE of 14.3% based on nitrate removal, which was lower than those obtained in our previous studies [39, 76]. The total nitrogen (sum of TKN, nitrate and nitrite) was reduced by 76.2%, much higher than 27.1% without the denitrifying MFC. As expected, the ammonium or TKN concentrations were not obviously affected by the denitrifying cathode (Figure 5.5A and B), and some loss of ammonium or TKN in the anodes of the MFCs was likely due to ammonium ion movement through CEM [77] and microbial synthesis. The denitrifying MFC also removed 31.8±23.2% of TCOD or 38.3±15.3% of SCOD. Excessive consumption of organic compounds in the anode of the denitrifying MFC was not desired, because it would reduce energy production in the MFC-AC and result in a negative energy balance (Table 5.1); the denitrifying MFC was operated under a high-current mode, and thus little electric power/energy was produced.

5.4.4 Carbon Balance

A mass balance of carbon compounds based on either TCOD or SCOD was established with the MFC-Pt by analyzing the contributions from different sources, including electricity, methane, oxygen, sulfate, and other unknown factors (Figure 5.6). Because carbon is an electron donor, this balance could also represent an electron balance. Derived from coulombic efficiency, the carbon distribution to electricity production was 13.2 % (based on TCOD) or 22.8% (based on SCOD). Surprisingly, sulfate consumed much more carbon than electricity production (37.2% of TCOD or 64.0 % of SCOD). The primary effluent contained a sulfate concentration of 119.6±69.7 mg SO_4^{2-}/L and the anode removed 81.2±17.2% of sulfate, indicating an active sulfate reduction in the MFC anode. The primary effluent contained dissolved oxygen of 3.3±1.3 mg/L, which could consume 2.2% of TCOD or 3.8% of SCOD. Methane production was observed in MFCs [78] and thus both methane gas and the dissolved methane in the anode effluent were examined. The average concentration of the dissolved methane was about 1 mg/L and methane gas production was ~ 0.5 mL/g SCOD, resulting in carbon consumption of 1.3% of TCOD (or 2.1% of SCOD) and 0.04% of TCOD (or 0.1% of SCOD), respectively. The contribution from methane gas might not be accurate (could be underestimated), because onsite collection of biogas from the continuously-operated MFCs was very challenging. A portion of the organic removal (46.1% of TCOD or 7.2% of SCOD) was due to unknown reasons; the possible measurement/analytic errors (e.g., collection of methane gas) might also lead to unknown carbon flow.

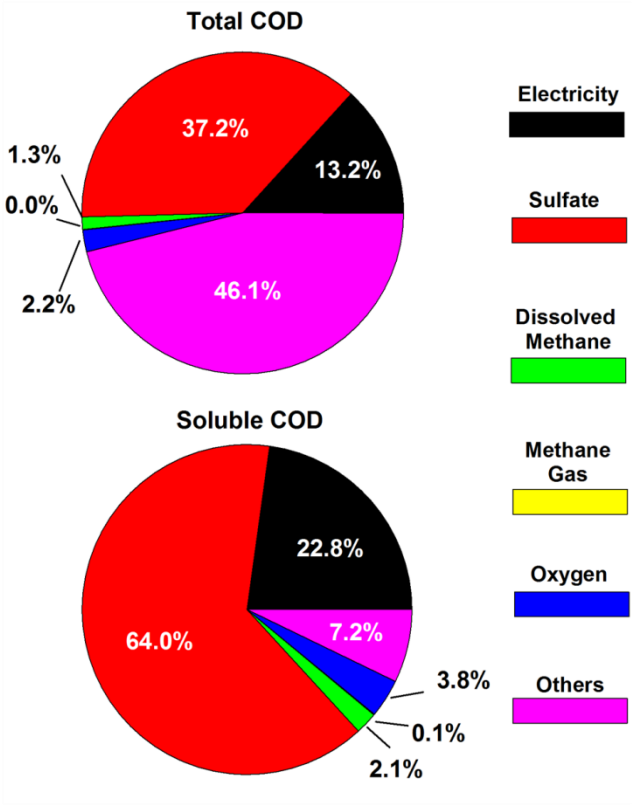

Figure 5.6. *Carbon balance based on either total COD or soluble COD obtained from the MFC-Pt.*

Because sulfate reduction was found to be a major contributor to COD removal, it would be interesting to know whether inhibiting sulfate reduction could improve electricity production. To study this, we added 3.25 mM sodium molybdate into the feeding stream of the MFC-Pt. Sodium molybdate was reported to effectively inhibit biological sulfate reduction [79]. A strong inhibition of sulfate reduction was observed after sodium molybdate was added: the anode effluent of the MFC-Pt contained 86.0±9.6 mg SO_4^{2-}/L, slightly lower than that in its influent (95.1±33.5 mg SO_4^{2-}/L), but much higher than 20.4±5.4 mg SO_4^{2-}/L from the MFC-AC (without sodium molybdate addition). During the period of this test, the MFC-Pt had a higher TCOD concentration of 184.7±34.7 mg/L in its anode effluent than that of the MFC-AC (122.7±38.0 mg/L); the SCOD in the MFC-Pt anode effluent was 106.0±26.2 mg/L, slightly higher than 92.7±25.3 mg/L from the MFC-AC. However, the recorded current generation did not obviously increase, and the average current was 14.2 mA, slightly lower than 15.1 mA obtained before sodium molybdate addition. Considering the temperature drop (the test was conducted during winter) of almost 5 °C during the inhibition test, the decreased current might be due to temperature decrease instead of sodium molybdate, which was expected to help with current generation by inhibiting sulfate reduction, resulting in more carbon contents available for electrochemically-active microorganisms. A definitive conclusion on the effect of sulfate reduction on electricity generation will need more laboratory tests, because the significant

variation of wastewater quality and testing conditions in the field could strongly disturb the experimental results.

5.5 Conclusions

Proper understanding of the application niche and the benefits of the MFC technology is very important to its development. It is critical to acknowledge that the primary function of MFCs is wastewater treatment instead of energy production (which is an added benefit). MFCs are advantageous in several aspects: (1) Low energy consumption: An MFC system avoids the use of aeration, which consumes about 50% of the electric energy of an aerobic wastewater treatment process. (2) Low sludge production: the anaerobic process in the anodes of an MFC system accumulates little secondary sludge. This result has two potential benefits: minimizing the use of a secondary clarifier to save both operation and infrastructure expense, and reducing the treatment of secondary sludge, which requires significant effort and energy. (3) Energy recovery from wastewater: the electric energy produced by an MFC system could be used to offset the energy requirement by the pumping system, thereby further reducing the energy consumption of the wastewater treatment process. Satisfactory energy production from high-strength/high-solid wastes in MFCs was not obsvered; therefore, it's believe that MFCs cannot compete with anaerobic digestion for the treatment of high-strength/high-solid wastes [32], and MFCs are more suitable for medium- and low-strength wastewater that is currently treated by aerobic processes.

Although energy production may not be the most important feature of MFC technology, it is still beneficial to further improve electricity production by optimizing MFC configuration, materials, and operation. For instance, recently spiral spacers were used to double energy production in tubular MFCs [60]. Nitrogen removal is certainly possible in the present MFC system, and carbon distribution should be carefully coordinated for the purpose of energy production.

6. Outlook

This project has demonstrated the long-term performance of MFCs under different conditions, which significantly contributes to the MFC field that lack of the similar studies. A more important outcome of this project is that it indicates what MFCs can or cannot do. These studies reveal significant challenges of applying MFCs into an aeration tank or to treat high-solid wastes. On the other hand, the results also show the promising application of MFCs for treating low-strength wastewater such as domestic wastewater, especially with improved energy production by using spiral spacers. Those findings have greatly shaped the future focus of MFC development. The next key step of MFC development is to demonstrate the technical viability of the technology at a transitional scale of 200-500 L, which will act as a bridge between fundamental research and future development.

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