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FINAL REPORT

Electricity Generation from Anaerobic Wastewater Treatment in Microbial Fuel Cells

OWSO8C09

ELECTRICITY GENERATION FROM ANAEROBIC WASTEWATER TREATMENT IN MICROBIAL FUEL CELLS

NYSERDA Agreement 11095

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2011

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Library of Congress Catalog Card Number: 2011928797

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The research on which this report is based was funded by the New York State Energy Research and Development Authority in partnership with the Water Environment Research Foundation (WERF).

ACKNOWLEDGMENTS

The authors wish to acknowledge the funding support provided by the New York State Energy Research and Development Authority (NYSERDA) and the Water Environment Research Foundation (WERF), and the helpful guidance of Kathleen O'Connor, P.E. and Lauren Fillmore, Project Officers for NYSERDA and WERF, respectively. The project participation provided by Joy M. McGrath (HydroQual, Inc.), Elizabeth Troop, P.E. (Fuss & O'Neill), and Daqian Jiang (University of Connecticut) was important and appreciated.

The authors also wish to express their appreciation to the project advisory committee for its guidance in the design and conduct of the project.

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ABSTRACT AND BENEFITS

Abstract:

This project tested anaerobic microbial fuel cell (MFC) treatment of domestic wastewater and produced sustainable electricity at the pilot scale. The collaborative team of HydroQual, Inc., Fuss &O'Neill, and the University of Connecticut developed a novel MFC system in a multiple anode/cathode granular activated carbon configuration (MAC-GACMFC); effectively integrating multiple MFCs into a single unit. The unique advantage of this novel configuration is increased power generation in a small footprint, which is beneficial when considering wastewater treatment plant applications. Four pilot-scale, 16-liter (L) MAC-GACMFCs were operated over a six-month period, with the primary focus on organic loading rate and hydraulic retention time (HRT). The MAC-GACMFCs achieved COD removal exceeding 80%, and effective power densities on the order of 300 mW/m^3. In addition, a new, cost-effective catalyst, manganese dioxide (MnO_2) was developed and tested at pilot-scale. The results show that the MnO_2 catalyst is capable of achieving similar power generation compared to the more costly platinum catalyst that has been used to date in other MFCs.

Benefits:

- Demonstrates that the MAC-GACMFC configuration can generate electricity at levels significantly higher than that produced by conventional single anode/cathode MFC configurations. The MAC-GACMFC was highly efficient in the removal of COD from a dilute wastewater stream under anaerobic conditions. With less costly cathode materials and improved power generation efficiencies, scale-up of the MAC-GACMFC configuration may prove a cost-effective, sustainable alternative to conventional wastewater treatment processes.
- Demonstrates that MAC-GACMFCs are capable of achieving stable power generation from domestic wastewater.
- Provides insights into the design, operation, and optimization of the next generation MFCs.

Keywords: Microbial fuel cell (MFC), wastewater, COD, HRT, catalyst, pilot-scale.

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LIST OF ACRONYMS

Ac	Acetate
BOD	Biochemical oxygen demand
CE	Coulombic efficiency
Co	Cobalt
COD	Chemical oxygen demand
Cu-MnO2	Copper Manganese Dioxide
DO	Dissolved oxygen
GAC	Granular activated carbon
HRT	Hydraulic residence time
L	liter
m	meter
MAC	Multi anode cathode
MAC-GACMFC	Multi Anode Cathode Granular Activated Carbon Microbial Fuel Cell
MFC	Microbial fuel cell
mW	milli-watts
NaAc	Sodium Acetate
ORR	Oxidation-reduction reaction
PGCR	Power Generation per COD Removed
Pt	Platinum
R	Resistance
Rext	External Resistance
Rin	Internal Resistance
SEM	Scanning Electron Microscope
TDS	Total Dissolved Solids
TSS	Total Suspended Solids
UConn	University of Connecticut
V	Volt
W	Watt

EXECUTIVE SUMMARY

This project is believed to be one of the first demonstrations of pilot-scale microbial fuel cell (MFC) systems capable of treating dilute municipal wastewater. The operation of MFC systems involves the fundamental mechanisms of microbiology (e.g. biofilm growth on granular activated carbon (GAC) particles), biochemistry (e.g. COD removal inside biofilms), and electrochemistry (e.g. electron generation and transfer on anodes and cathodes), which make it truly challenging to achieve desirable power generation simultaneously with effective wastewater treatment. Although these mechanisms have been extensively investigated in laboratory-scale MFC systems fed with pure organic substances, this is one of the first demonstrations of MFC systems using municipal wastewater. The results of this project have been successful, with highly effective COD removal and simultaneous power generation.

Beyond the fundamental challenges, it is critical to develop MFC configurations that can be adapted for use in existing wastewater treatment plants and are cost effective, if the feasibility of using MFC technology for wastewater treatment is to be established. The multidisciplinary research team investigated MFC operations in terms of wastewater treatment (i.e., organic removal), electricity generation, operations and maintenance, electrode materials, and biochemical and electrochemical characteristics. The successful operation of a pilot-scale multi-anode/cathode granular activated carbon microbial fuel cell (MAC-GACMFC) suggests the potential for future technology commercialization and wide-spread deployment.

This research has shown that MAC-GACMFCs can successfully treat municipal wastewater while generating electrical power. It is particularly interesting to note that the MFCs were capable of achieving secondary wastewater treatment standards via an anaerobic process. The municipal wastewater treatment sector is one of the more energy-intensive operations in the nation, with the majority of this energy used to transfer oxygen from the atmosphere to biological reactors, whereby the carbohydrate and other constituents in the wastewater are oxidized. Development of a technology that uses this embedded energy as a resource, as opposed to a waste, that minimizes microbial growth and produces renewable energy, has an obvious potential to be a game changing technology for the sector.

ES.1 Purpose of the Research

The purpose of this research was to develop and test an anaerobic microbial fuel cell (MFC) at pilot-scale. In laboratory-scale research, MFCs have been shown to simultaneously treat organic wastewater and generate electricity. However, most MFC studies have been limited to small (typically <250 mL) batch reactors using a single compound or simulated wastewater. This project operated 16 liter (L) reactor at a continuous flow using filtered municipal primary effluent as the feedstock.

ES.2 Brief Description of the Research Carried Out

Four (4) MAC-GACMFCs, each with a working volume of 16 L and with12 anode-cathode circuits, were constructed and operated at the Gloversville-Johnstown Joint Wastewater Treatment Facility in Johnstown, NY in 2009. Two generations of reactors were tested. Start-up

and acclimation of the GAC beds was initiated first with sodium acetate (NaAc) as the reactor feedstock, and then using a mixture of primary effluent supplemented with NaAc. The reactors were ultimately operated using only filtered primary effluent as the feedstock.

ES.3 Research Findings and/or Results

The results of this study show that at the COD loading, HRT, and temperature conditions tested, low-strength domestic wastewater can be effectively treated in a MAC-GACMFC, producing an effluent that consistently meets secondary treatment standards (BOD and TSS less than 30 mg/L, on average). This is an important result, in that anaerobic treatment is often not considered feasible for low-strength dilute wastewater due to the low cell yield of anaerobic microorganisms. Another important result is that for the duration of the study, the reactors generated electricity. However, since the amounts of electricity generated was less than the maximum rates seen at laboratory scale, new mechanisms for improving electrical efficiency require further investigation. This would include developing low-cost alternative catalyst materials and alternate MAC-GACMFC reactor configurations that enhance power generation.

ES.4 Potential Applications of the Research

Anaerobic MFCs use substantially less energy to treat wastewater than conventional aeration technologies. It is estimated that wastewater treatment uses approximately 3% of the electrical power consumed nationwide (Logan, 2005). By generating renewable electricity on-site, MFCs could help enable municipal wastewater treatment plants to become self-sustaining. Additionally, the extension of MAC-GACMFC technology to higher strength wastewaters, such as those generated in the food, beverage and dairy industries, have obvious application as sustainable, renewable energy production alternatives.

CHAPTER 1.0

PROJECT BACKGROUND AND OBJECTIVES

1.1 Project Background

This project, titled *Electricity Generation from Anaerobic Wastewater Treatment in Microbial Fuel Cells,* was conducted with support from the New York State Energy Research and Development Authority (NYSERDA) and the Water Environment Research Foundation (WERF), with funds leveraged from a grant under the EPA SBIR program (EP-D-09-022). The project was conducted as a collaborative effort of HydroQual, Inc., Fuss & O'Neill, and the University of Connecticut. This report details the project.

Conventional wastewater treatment processes consume large amounts of energy; and the demand for energy by these systems is expected to increase as much as 20% over the next 15 years (Logan, 2005). Currently, the primary technologies for treating municipal, agricultural, and industrial wastewater are based on energy intensive aerobic biological processes that were developed more than a century ago. And in fact, aeration accounts for as much as 70% of the energy used in wastewater treatment plants.

Microbial fuel cells (MFCs) are a promising technology for sustainable wastewater treatment. In an MFC, biochemical reactions are carried out by electrogenic bacteria in an anaerobic anode chamber, generating electrons and protons through the degradation of the organic substrates embedded in wastewater; concurrently, electrochemical reactions occur in the aerobic cathode chamber, whereby electrons and protons are accepted through an oxygen reduction reaction (ORR). Anaerobic treatment of wastewaters is substantially less energy intensive than aerobic treatment, however it takes longer to accomplish due to the inherently slow growth process of anaerobic microorganisms. Because of this, there has been little interest in applying anaerobic processes to dilute wastewaters (e.g., domestic wastewater).

To help offset the large power demand from aerobic treatment, it is important that cost-effective processes be developed that can convert the contaminant loads in domestic wastewater to useable forms of energy. MFCs may just be this technology. Over the past several years, a great amount of effort has been invested in testing MFCs at bench-scale, successfully converting the organic substrates inherent in the wastewater treatment to power.

1.2 Objectives

Though MFCs are a very promising technology, considerable development is still needed to make them a commercially-viable alternative. This research addressed five important issues with respect to MFC technology development:

- MFCs had previously been studied only at laboratory-scale (typically <250 mL). Practical scale-up was necessary to determine whether the laboratory-scale results could be translated to large-scale systems.
- Most MFC studies have used only pure bacterial cultures. The reactor beds in this study were seeded with municipal wastewater; as such, a wide variety of bacteria inherent in domestic

wastewater were used.

- Most MFC studies have used synthetic wastewater, such as that derived from sodium acetate or other readily degraded materials. This study used municipal wastewater.
- MFC development has been limited by costly materials (e.g. carbon cloth, silicon wafers, proton exchange membranes, platinum-based catalysts) and configurations that would make retrofitting existing wastewater treatment plants impractical. This study focused on developing new electrode materials and MFC configurations that would be feasible for wastewater treatment plant retrofit applications.
- Previous MFC studies have not comprehensively considered the goals of simultaneous power generation and wastewater treatment. As such, there was very limited information available regarding the operational conditions and MFC configurations that could achieve these goals. This study focused on demonstrating that MFCs could simultaneously achieve power generation and wastewater treatment efficiency.

Based on prior work, a novel MFC configuration with multi-anodes/cathodes and granular activated carbon (termed MAC-GACMFC) was developed. Pilot-scale MAC-GACMFCs were operated in continuous-flow mode at a wastewater treatment plant using municipal wastewater as the substrate. The systems were monitored for COD removal and power generation across a range of COD loadings and hydraulic retention times.

CHAPTER 2.0

PROJECT APPROACH

Considerable MFC research is on-going world-wide. As a result, the "state of the art" is constantly progressing, and the WERF/NYSERDA project evolved to take advantage of recent technological breakthroughs. The most important of these was the project team's development of a multi anode/cathode granular activated carbon microbial fuel cell (MAC-GACMFC), which improves upon the conventional single-electrode system by employing a multi-electrode system that provides higher power generation than a single electrode system.

The project involved five major research activities:

1) The design and construction of the MAC-GACMFC systems;
2) Start-up and acclimation of the systems;
3) Flow mode testing of the systems;
4) COD removal and HRT testing of the systems; and
5) The development of a new cathode catalyst to replace conventional platinum catalysts used in most MFC systems.

The overall timeline of the project is shown in Table 2-1.

Table 2-1. Timeline of the WERF/NYSERDA Project (1/2009-11/2009).

Research Activities	Time
Design and construction	1/2009-6/2009
Start-up and acclimation	6/2009-7/2009
Flow mode testing	7/2009-8/2009
COD removal and HRT testing	8/2009-9/2009
Development of the new cathode catalysts (MnO2)	2/2009-9/2009
Demonstration of new cathode catalyst tests in the MAC-GACMFC systems	9/2009-11/2009

2.1 Description of the MAC-GACMFC Reactors

The project team developed and tested a laboratory-scale MFC with multiple anodes and cathodes (termed multi-anode/cathode-GACMFC or MAC-GACMFC). It consists of multiple graphite rods inserted in a GAC bed (anode) and multiple discs of carbon cloth (cathode). [GAC was selected as the anode material due to its high surface area for biofilm growth, excellent electron conductivity, and relatively low cost.] Compared with the conventional single-electrode MFC, the MAC-GACMFC provides concurrent power generation and contaminant removal at a lower capital cost and in a relatively small footprint; attributes that make the MAC-GACMFC appealing for retrofitting wastewater treatment plants with the technology in the future.

The initial MAC-GACMFC design had five graphite rods placed in a horizontal orientation and five carbon cloth cathodes (Figure 2-1). However, the team was concerned that the electron transfer resistance would substantially increase along the depth of the GAC bed, especially in the bottom sections, since there would be a long distance between graphite rods (anode) and carbon cloth (cathode) at the top of the reactor.

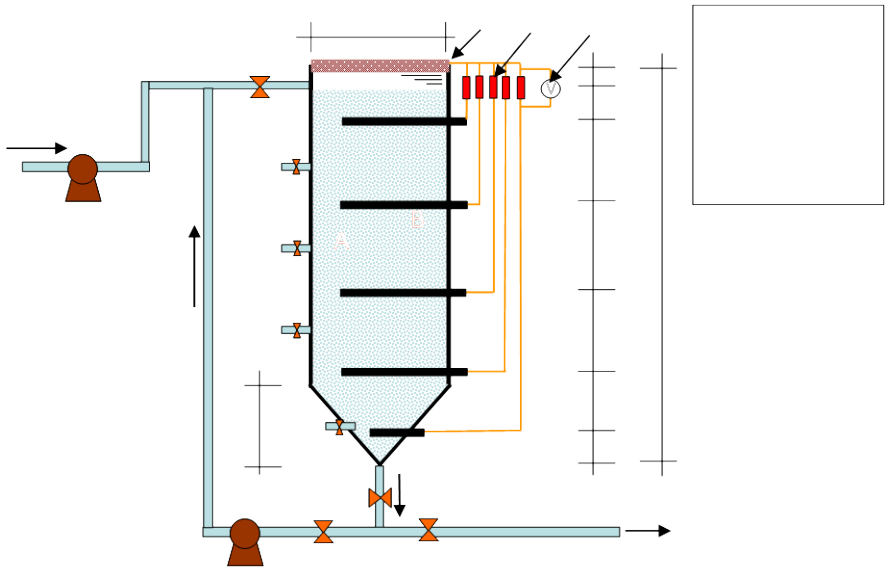


Figure 2-1. Schematic Diagram of the Originally Proposed Pilot-Scale GAC-MFC System.
(Shown in down-flow mode with horizontally oriented Graphite Rods.)

In the second MAC-GACMFC design, the graphite rods were reoriented vertically and the carbon cloth cathodes installed on top of the reactor (Figure 2-2). The cathodes were designed to use diffused oxygen as the electron acceptor. It was thought that this orientation would produce more efficient electron transfer from the bottom section of the reactor to the top. Additionally, it was thought that this orientation would alleviate the accumulation of protons (H+) within the GAC bed.

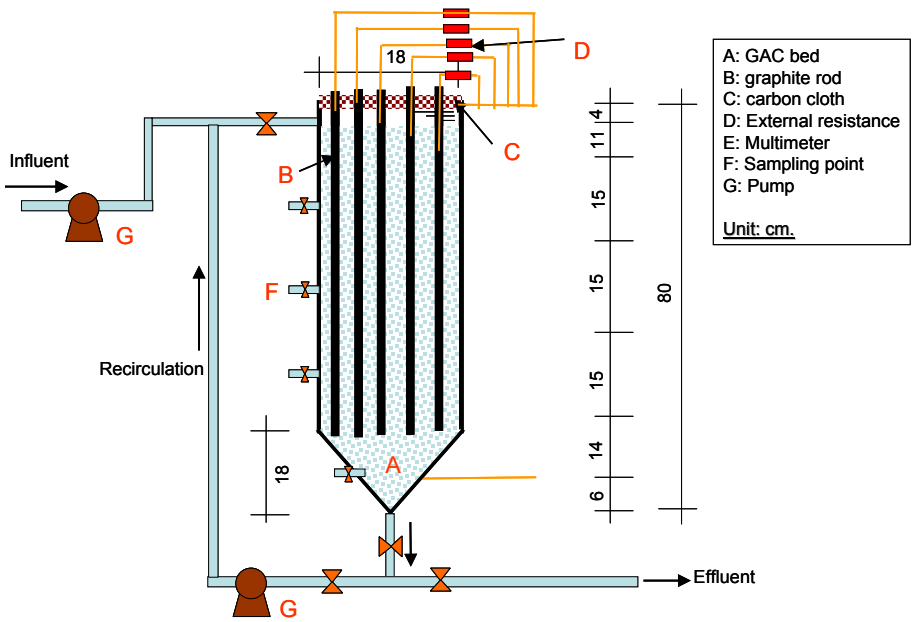


Figure 2-2. Schematic Diagram of the First 16-L Pilot-Scale GAC-MFC System Unit Installed at the Johnstown Facility with Cathode Horizontally Oriented on the Top Plate.
(Shown with vertically oriented graphite rods and in down-flow mode.)

Pilot-scale testing took place at the Gloversville Johnstown (New York) Joint Wastewater Treatment Facility (GJJWWTF) in 2009. Each reactor had a total working volume of approximately 16 liters, and was constructed with a bottom chamber, a bed (or reactor) chamber, and a top collection zone. A multi-anode "nest" was installed in the reactor, which was comprised of 12 graphite rods on a frame; GAC was then poured into the reactor chamber, surrounding the anode nest. [Prior to adding the GAC to the reactor chamber, it was seeded with wastewater treatment plant effluent and placed in a sealed container for approximately two month to encourage proliferation of anaerobic bacteria.] Twelve (12) platinum-coated carbon cloth discs (cathodes) were placed in cut-outs located on the top of the MFC system. Copper wiring was installed from the graphite rods through 100-ohm resisters, to the cathodes; thus yielding 12 circuits. Additionally, the system included influent feeding tanks, effluent collection tanks, recirculation pumps, flow meters, water level pipelines, an external resistance panel, and a potentiostat.

The system was brought on-line in early June 2009. It was immediately obvious that there were problems with the placement of the cathodes. With its flat surface orientation, the cathode fabric could not be kept fully sealed and there was a tendency for gas bubbles to collect at the slightly concave cathode surface.

In the third design, the cathodes were placed on the sides of a top-mounted "box", immediately above the GAC bed. The square cathode chamber had three carbon cloth cathodes on each side and in total held 12 cathodes in a vertical orientation (Figure 2-3). This design solved the problem of gas bubble accumulation. In all, four such MFC systems were constructed (Figure 2-4).

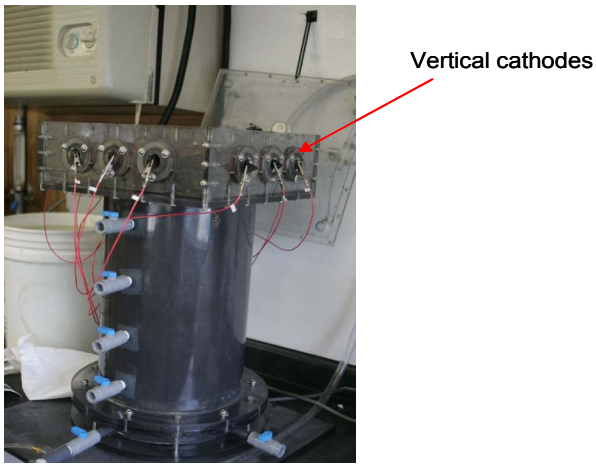


Figure 2-3. Current Version with Vertically Oriented Carbon Cloth Cathodes on the Top Chamber of the MFC System.

Figure 2-4. Four Pilot-Scale MAC-GACMFC Systems in the Test Trailer at the Gloversville-Johnstown Wastewater Treatment Plant.

2.2 Feed Sources for the MAC-GACMFC Systems

In total, three (3) feedstocks were used: sodium acetate (NaAc); a mixture of filtered primary effluent and NaAc; and filtered primary effluent. The characteristics of the filtered effluent were as follows: COD concentration of approximately 300 mg/L, pH at 7.2, and dissolved oxygen (DO) concentration of 3.0 mg/L. When supplemental NaAc was added to the primary effluent it was added in concentrations sufficient to boost the COD of the mixture to the 1000 to 2000 mg/L range.

2.2.1 MAC-GACMFC Start-Up and Acclimation

Start-up and acclimation was designed to establish the electrogenic microorganisms in the MAC-GACMFC systems and to achieve stable voltage generation and contaminant removal. Initially, sodium acetate was used as the reactor feedstock due to its rapid biodegradability. Next, a mixture of sodium acetate and filtered primary effluent was used. Once power generation and organic removal stabilized, unadulterated primary effluent was continuously pumped to the MFC system. Start-up and acclimation took approximately six to eight weeks, until steady-state conditions were achieved.

2.3 Operational Conditions

COD removal and HRT were evaluated to assess MFC performance, within a narrow temperature range of 25-30°C. Various HRT regimes were achieved by adjusting the feed-forward flow rates to the MFCs. Under each condition, power generation and COD removal efficiency were measured. The units were operated continuously, with recycles rates between 3 and 10 times the feed-forward rate.

2.3.1 MAC-GACMFC Flow Mode Testing

After start-up and acclimation, the MFC systems were operated in two distinct flow modes – up-flow and down-flow. It was anticipated that the up-flow configuration would cause

expansion of the GAC bed, thereby minimizing clogging potential and possibly enhancing organic removal as a result of increased available GAC surface area and reduced accumulation of protons (H+) in the lower section of the GAC bed. However, the up-flow configuration also had the potential to cause electrical disconnection between the GAC particles, which could prevent electron transfer inside the GAC bed. In the down-flow configuration, there was a potential benefit from better contact with the graphite rods, which were inserted into the reactor bed to maintain electron transfer among GAC particles; but, down-flow operation also had the potential for accumulation of protons in the lower section of the GAC bed and clogging.

2.3.2 MAC-GACMFC HRT Tests

The reactors were tested at HRTs of 5, 10, and 20 hours. The HRT was 20 hours during the flow mode testing described above. Then, one of the 20-hr units (MFC1) was maintained in an up-flow mode, and MFC3 and MFC4 were operated at 10 and 5 hours, respectively, each in an up-flow mode.

2.3.3 New Cathode Catalyst (MnO_2) Tests

Three Cu-MnO_2 cathodes and three Co-MnO_2 cathodes were installed on the MFC with the 5-hr HRT, once the MFC had achieved stable power production and COD removal. The three (3) platinum (Pt) cathodes on the right side of the top box were replaced with the Cu-MnO_2 cathodes and the three (3) Pt cathodes on the left side of the top box were replaced with the Co-MnO_2 cathodes; the remaining cathodes were Pt cathodes.

After the MnO_2 cathodes were installed, the MFC was fed primary influent (COD: 100 to 500 mg/L) for three weeks. The HRT and working temperature for the MFC remained at 5 hours and 25°C, respectively. COD removal, as well as the power density and the internal resistance of the cathodes were monitored on a regular basis.

2.4 Sampling Location, Frequency, and Analysis

The sampling and analysis plan for the project is briefly summarized in Table 2-2, which includes the analytes tested, the approximate frequency of testing, and the methods used. The pilot-scale MAC-GACMFC systems were operated in a trailer located on the GJJWWTF grounds. Both electrochemical and biochemical measurements were taken during testing. Electrochemical measurements were taken using a potentiostat with voltage, electrode potential, internal resistance, and polarization curve. Biochemical measurements included influent and effluent COD and suspended solids, dissolved oxygen (to ensure that none was present), pH, alkalinity, redox potential, temperature, and feed-forward and recycle flow rates.

Table 2-2. Sampling and Analysis of GAC-MFCs in the Pilot-Scale Tests.

	Sampling points	Sampling & measurement frequency	Method
Electrochemical measurement			
Voltage	GAC-MFCs	Real-time	Multi-meter
Internal resistance	GAC-MFCs	3/week	Potentiostat
Electrode potential	GAC-MFCs	3/week	Potentiostat
Polarization curve	GAC-MFCs	3/week	Potentiostat
Biochemical measurement			
COD	Influent/effluent	3/week	Ampulometric (Hach)
Dissolved oxygen	GAC-MFC	1/day	YSI DO meter/probe
pH	Influent and GAC-MFC	1/day	meter/pH probe
Alkalinity	Influent/Effluent	3/week	Std Methods
Redox potential (ORP)	GAC-MFCs	1/day	ORP meter/probe
Suspended solids	Influent/Effluent GAC-MFCs	3/week	Std Methods
Temperature	Influent GAC-MFCs	1/day	In-line temperature probe
Flow rate	Influent/Recycle	Real-time	Volume/Time; In-line monitor

2.5 Analytical Methods

2.5.1 Chemical Analytical Methods

2.5.1.1 pH and Conductivity

An Orion Three Star pH meter and conductivity meter (Thermo Scientific, Beverly MA) were used, following standard procedures. The pH meter was calibrated with pH 4 and 10 standard buffers and checked with a pH 7.0 standard before field measurements. The conductivity meter was checked with 12.9 and 1.314 mS/cm standards before field measurements.

2.5.1.2 Total Suspended Solids (TSS) and Total Dissolved Solids (TDS)

TSS and TDS measurements were conducted following Standard Methods, using Whatman GF/C 47-mm diameter glass fiber filters and aluminum pans, respectively. Twenty-five (25) mL samples were typically used for filtration and for TDS aliquots. Drying was at 105°C for both TSS and TDS. Weighing was conducted with the GJJWWTP laboratory analytical balance.

2.5.1.3 COD

The influent/effluent COD was measured with the HACH digestion/absorbance procedure. Filtered samples were generated through 0.22um fiber glass syringe filters. Two-mL filtered and unfiltered samples were transferred to HACH high range COD vials and digested at 150°C for 2 hours. After cooling to room temperature, the COD reading was taken on a HACH

DR2000 spectrophotometer at 625nm. A standard sample with a COD of 300 mg/L was measured every 20 samples to check the accuracy of the measurement.

2.5.1.4 Nitrogen, Phosphorus, and BOD Measurements

The ammonia-N, TKN, total phosphorus and BOD measurements were conducted by Columbia Analytical Services (CAS, Rochester, NY) on a weekly basis. The samples for ammonia-N, TKN and total phosphorus were stored at 4°C and pH<2 and samples for BOD were stored at 4°C. All were shipped overnight to CAS in coolers.

2.5.2 Electrochemcial Analytical Methods

2.5.2.1 Voltage and Internal Resistance

The voltage over R_{ext} was recorded by a Keithley 2701 data logging system at 2-hour intervals; all measurements were saved as an Excel file.

The polarization curve was plotted to determine the R_{in} and the power generation at different external resistors (R_{ext}). The R_{ext} was changed from 15 to 380 Ω during the measurement. The voltage over each R_{ext} was recorded by a multimeter. The power output (P) generated was calculated according to $P=V^2/R$ (V is the voltage, R is the R_{ext}) and plotted with respect to R_{ext}. R_{in} was calculated at the maximum power point on the plot where R_{in} was equaled to R_{ext} [3].

2.5.2.2 Power Generation

Power (W) equals the square of voltage (V) generated divided by external resistance (ohm). Power density (W/m^3) was calculated using the total power produced in the MFCs divided by the total volume of MFCs.

2.5.2.3 Electrical Efficiency Measurement

Based on voltage generation and COD removal data, two parameters were calculated to evaluate the power generation efficiency of MFC systems. The first was coulombic efficiency (CE), which is the ratio of the actual coulombs generated in the MFC to the theoretical coulombs in the COD that is removed, described by Eq [1]:

$$CE = \frac{M\int_0^{t_b} Idt}{Fbv_{An}\Delta COD} \qquad [1]$$

Where:

M = oxygen molecular weight, 32g/mol

$\int_0^{t_b} Idt$ = actual coulombs generated over the time period (t)

F = Faraday constant (96485C/mol electrons)

B = number of electrons exchanged per mole of oxygen, (b = 4)

v_{An} = volume of the MFC (L), and

ΔCOD =amount of COD removed (g/L) over time period (t).

The second was power generation per gram COD removed (PGCR, W-h/g-COD_R). The calculation to develop this is:

$$PGCR = \frac{\frac{V^2}{R}}{COD \times Q} \qquad [2]$$

Where:

PGCR =power generation per COD removed (W-h/$gCOD_{removed}$)
V =voltage generation of MFCs (V)
R =the external resistance of MFCs (ohm)
COD_R =COD removed (g/L), and
Q = Flow through system (L/hr)

CHAPTER 3.0

RESULTS

This chapter presents the results for the four experimental phases: Phase I-Start-up and Acclimation; Phase II-Flow Mode Testing; Phase III-COD Removal and HRT Testing; and Phase IV-New Catalyst Development and Testing. For operation and data reporting purposes, June 1, 2009 is designated as the first day of the first week of operations. Appendix A contains weekly summaries of COD and nitrogen removal data. Appendix B contains weekly summaries of voltage generation and internal resistance data.

3.1 Phase I: Start-Up and Acclimation

During preliminary laboratory-scale GACMFC testing power generation was greatest when the COD concentration in the reactor was between 1000-1500 mg/L. Therefore during the initial start-up and acclimation period the COD concentration of the feedstock (sodium acetate) was kept in this range. The voltage produced by each MFC system was recorded by a data-logger every two hours; voltage generation steadily increased during the first two weeks of this phase until the voltage stabilized in the range of 100-120 mV (Table 3-1).

Table 3-1. Voltage Generation and COD Removal during Start-up and Acclimation with Acetate as the Substrate in Batch Mode.

Days	Date	MFC 1		MFC 2	
		Voltage (V)	Reactor COD (mg/L)	Voltage (V)	Reactor COD (mg/L)
1	2009/6/23	0.020	1473	0.041	888
2	2009/6/24	0.020		0.096	
3	2009/6/25	0.046		0.095	
4	2009/6/26	0.077		0.086	
5	2009/6/27	0.082		0.083	
6	2009/6/28	0.084		0.081	
7	2009/6/29	0.082	674	0.079	731

Along with the voltage generation increase, COD removal efficiencies of 47.5% and 17.6% were observed in MFC1 and MFC2, respectively (Table 3-2); as the biofilm grew on the GAC particles, the degradation of acetate and generation of electrons began, leading to steady COD removal and power generation.

After the voltage stabilized, the feedstock was changed; the COD concentration of the new feedstock was in the 600-1000 mg/L range, with acetate added to primary settled effluent at a rate of 0.5 g/L. The reactors were operated in a continuous flow mode at a retention time (HRT) of 20 hours; MFC1 was operated in an up-flow mode and MFC2 was operated in a down-

flow mode. During this period COD removal gradually increased, but voltage generation did not increase (Table 3-2). This may possibly be due to an increase in the electron transfer resistance.

Table 3-2. Voltage Generation and COD Removal Efficiency during Start-Up with a Mixture of Acetate and Wastewater in Continuous Flow Mode.

		MFC 1 (Upflow)			MFC 2 (Downflow)		
Day	Date	Voltage (V)	COD Removal	Influent COD (mg/L)	Voltage (V)	COD Removal	Influent COD (mg/L)
1	2009/6/30	0.081	3.1%	646	0.076	5.4%	698
2	2009/7/1	0.086	42.4%	990	0.077	6.6%	681
3	2009/7/2	0.088	39.0%	935	0.092	35.9%	1053
4	2009/7/3	0.090	36.9%	940	0.083	32.6%	996
5	2009/7/4	0.093	40.2%	1034	0.086	30.8%	1070
6	2009/7/5	0.096	0.5%	640	0.089	3.8%	759
7	2009/7/6	0.094	29.8%	955	0.086	36.3%	837
8	2009/7/7	0.096	48.4%	770	0.089	33.0%	770
9	2009/7/8	0.103	60.1%	1495	0.094	24.9%	762
10	2009/7/9	0.112	10.1%	988	0.099	39.9%	907
11	2009/7/10	0.112	14.2%	845	0.101	38.1%	888
12	2009/7/11	0.105	12.7%	670	0.097	61.5%	680
13	2009/7/12	0.096	27.5%	738	0.090	35.1%	730
14	2009/7/13	0.093	54.1%	850	0.091	66.0%	1000
15	2009/7/14	0.101	51.9%	900	0.102	65.3%	980
16	2009/7/15		57.3%	960		61.0%	1000
17	2009/7/16	0.105			0.109		
18	2009/7/17	0.101	51.5%	1010	0.108	72.4%	1140
19	2009/7/18	0.094			0.093		
20	2009/7/19	0.100	51.4%	658	0.107	77.9%	712
21	2009/7/20	0.101			0.108		
22	2009/7/21	0.094	59.1%	1040	0.093	82.2%	1105

Table 3-2. (Continued)							
		MFC 1			MFC 2		
Day	Date	Voltage (V)	COD Removal	Influent COD (mg/L)	Voltage (V)	COD Removal	Influent COD (mg/L)
23	2009/7/22	0.091			0.090		
24	2009/7/23	0.094			0.093		
25	2009/7/24	0.094	79.9%	1160	0.088	88.1%	1128
26	2009/7/25	0.079			0.086		
27	2009/7/26	0.073			0.081		
28	2009/7/27	0.073	91.2%	885	0.077	90.3%	804
29	2009/7/28	0.020					
30	2009/7/29	0.046	87.6%	885	0.059	91.0%	804
31	2009/7/30	0.056					
32	2009/7/31						
33	2009/8/1		86.4%	640		91.2%	681
34	2009/8/2						
35	2009/8/3		88.2%	645			
36	2009/8/4						
37	2009/8/5		94.0%	785			
38	2009/8/6						
39	2009/8/7		91.2%	605			
40	2009/8/8						
41	2009/8/9						
42	2009/8/10		90.8%	590			
43	2009/8/11						
44	2009/8/12		96.0%	719			
45	2009/8/13	0.098					
46	2009/8/14	0.094					
47	2009/8/15	0.093					
48	2009/8/17	0.085	83.9%	708			
49	2009/8/18	0.077					
50	2009/8/19	0.082	97.2%	792			
51	2009/8/20	0.081					

Note: operation of MFC 2 (down-flow mode) was discontinued in August due to stress fractures in the reactor. MFC 3 and MFC 4 were then brought into service, with MFC 2 operated in standby mode to maintain the viability of the GAC bed in the unit, in case it was needed in the future.

3.2 Phase II: Flow Mode

MFC1 and MFC 2 were operated with an HRT of 20 hours, in up-flow mode and down-flow mode, respectively, for a total of 51 days, during which a mixture of acetate and wastewater was used as the feedstock. Biochemical parameters (COD, pH) and electrochemical parameters (voltage, power generation, internal resistance, polarization curve, and conductivity) were measured periodically to evaluate MFC performance. The results were similar for both flow configurations (Table 3-3).

Table 3-3. Measured Biochemical and Electrochemical Parameters for MFC1 and MFC2 in Continuous Flow Mode (HRT: 20 hrs)

	Voltage (V)	COD Removal (%)	Power Density (mW/m^2 cathode)	Internal Resistance (Ohm)	Coulombic Efficiency (%)	PGCR (W-hr/g COD_R)
Upflow (MFC1)	0.084±0.021	60%±31%	150±60	123±8	3±5	0.006±0.010
Downflow (MFC2)	0.091±0.011	51%±29%	170±40	128±5	3±4	0.007±0.010

The calculated results for coulombic efficiency (CE) and power generation per gram COD removed (PGCR) were similar for both systems (Table 3-3). However, the CE values calculated based on flow mode testing data were 1-5%, which were much lower than the values calculated based on the batch-mode data (10-30%). The lower CE values may have resulted due to less efficient electron transfer between the biofilm and GAC particles during flow mode testing. The laboratory-scale flow mode testing also demonstrated that shorter HRTs (5 hours compared to 50 hours) resulted in substantially reduced CE values.

The PGCR values calculated based on flow mode testing data were also lower (about 0.006 kW-h/$kgCOD_{removed}$ after counting all twelve circuits) than the values calculated based on the laboratory-scale data (0.32 kW-h/$kgCOD_{removed}$), due mainly to shorter HRTs, larger MFC volumes, and high COD removal rates (refer to Equation [2]). The pilot-scale MAC-GACMFC systems were 25 times larger than the laboratory-scale systems, but had half the HRT and a similar COD removal efficiency, which led to much lower PGCR values. In other words, increasing COD removal efficiency will reduce PGCR unless there is a simultaneous increase in power output.

A polarization curve measurement was conducted for MFC1 and MFC2 to determine the highest power density (W/m^2cathode area) achievable by changing the external resistance (R_{ext}) in the reactors (from 50 to 700 ohm). The results showed that the highest power density achievable in both systems was 750 mW/m^2 (Figure 3-1); a value over 20 times higher than results produced in pilot-scale MFC system testing conducted in Australia, which used a membrane configuration to increase the electron transfer between anode and cathode. This shows that the multi anode/cathode (MAC) configuration can effectively enhance power generation by essentially incorporating multiple MFC units in a single system. It also reveals the need for continued research if MFCs are to be commercialized: optimization of electrode numbers in

GACMFC systems for higher power generation and better COD removal.

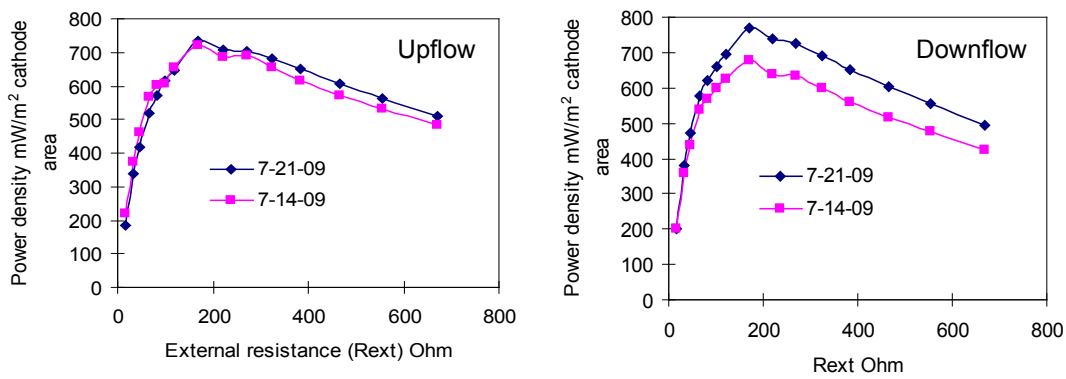
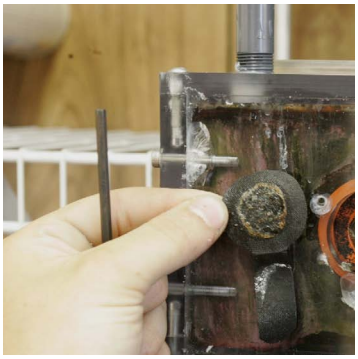


Figure 3-1. The Change of the Power Density with External Resistance in the Polarization Curve Measurement of the Upflow and Downflow MAC-GACMFCs.

Since there was no substantial difference in biochemical and electrochemical performance between MFC1 and MFC2 during this period, additional parameters were evaluated in an attempt to determine the best flow mode; these included power generation, contaminant removal, and operational observations (e.g., clogging). Ultimately, it was decided that operation in the down-flow mode had a greater tendency to clog, which would require more frequent backwashing of the GAC bed, and subsequently higher operational costs. Therefore, subsequent testing was continued solely in the up-flow mode.

Another important finding during this phase was that deposition of organic and inorganic substances on the carbon cloth (cathodes) increased with over a period of several days. In the first unit, a relatively thick layer of a brownish deposit was observed (Figure 3-2) and the voltage gradually decreased from 100 mV to 50 mV. The deposition (fouling) lead to higher resistances for electron transfer and acceptance; the internal resistance (R_{in}) increased from 100 to 180 ohm. Once the deposit was removed, the voltage quickly returned to 100 mV. This provides valuable guidance for optimizing the operation of MFCs; prior to commercialization, either anti-fouling electrode materials or physical cleaning devices should be developed to prolong the operational duration of MFC cathodes and maintain high power generation.

Figure 3-2. The Fouling of the Cathodes in MAC-GACMFCs.



3.3 Phase III: COD Removal and HRT

As mentioned previously, the remaining testing was performed with the MRC systems operating only in the up-flow mode. For HRT testing, MFC1 was operated at an HRT of 20 hours, MFC3 was operated at an HRT of 10 hours and MFC4 was operated at an HRT of 5 hours by varying the forward flow rate to the reactor. Influent and effluent conductivity and COD were monitored during the testing period. Previous studies had shown that for MFCs operated in batch mode, substrate COD and conductivity were closely related with power production [Logan and Regan 2006, Rozendal et al., 2008; Jiang and Li, 2009]. The pilot-scale results verified this correlation.

In the MFC1, power production increased significantly with increasing influent COD and conductivity. Greater than 600 mW/m^2 was achieved when influent COD and conductivity were high (COD = 700 mg/L, conductivity = 1.8 mS/cm), while only 100 mW/m^2 was achieved when influent and conductivity was low (COD = 150mg/L, conductivity = 1.1 mS/cm). However, fouling of the cathodes had a negative impact on power production. On the few days when the cathodes were heavily fouled, even operation at high COD and conductivity did not result in high power production (Figure 3-3). MFC3 and MFC4 produced similar correlations between COD, conductivity and power density.

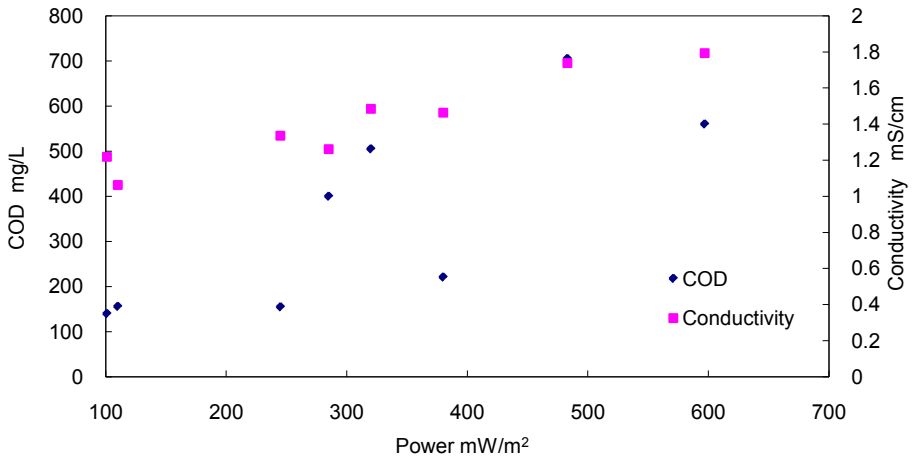


Figure 3-3. The Effects of COD Concentrations on Power Density (HRT: 5 hours).

The results of HRT testing are presented in Tables 3-4, 3-5, and 3-6 and Figure 3-4, and show each unit reaching steady-state COD removal. It is important to note that based on typical ratios of COD to BOD in treated effluent, the BOD levels achieved by these systems are consistent with secondary treatment requirements. Additionally, limited nitrogen and phosphorus data were collected, which also demonstrated expected conversions of organic nitrogen to ammonia.

Table 3-4. The Voltage Generation and COD Removal Efficiency of the MAC-GACMFC Systems Fed with the Primary Settled Wastewater as the Sole Feedstock in a Continuous Flow Mode (HRT: 20 hr).

Days	Date	MFC1 HRT: 20hrs				
		Voltage (V)	COD Removal	Influent COD (mg/L)	Effluent COD (mg/L)	PGCR (W-h/g COD_R)
1	21.08.2009	0.082	81%	226	42	0.006
2	22.08.2009	0.073				
3	23.08.2009	0.068				
4	24.08.2009	0.054	92%	218	18	0.002
5	25.08.2009					
6	26.08.2009	0.043	95%	409	20	0.001
7	27.08.2009	0.044				
8	28.08.2009	0.044	94%	390	25	0.001
9	29.08.2009					
10	30.08.2009					
11	31.08.2009					
12	01.09.2009					
13	02.09.2009	0.032				
14	03.09.2009	0.021				
15	04.09.2009					
16	05.09.2009					
17	06.09.2009					
18	07.09.2009					
19	08.09.2009	0.005				
20	09.09.2009	0.032	85%	250	38	0.001
21	10.09.2009					
22	11.09.2009					
23	12.09.2009					
24	13.09.2009		73%	280	75	

Table 3-4. (Continued)						
		MFC1 HRT: 20hrs				
Days	Date	Voltage (V)	COD Removal	Influent COD (mg/L)	Effluent COD (mg/L)	PGCR (W-h/g COD_R)
25	14.09.2009					
26	15.09.2009					
27	16.09.2009		86%	132	18	
28	17.09.2009					
29	18.09.2009					
30	19.09.2009		90%	512	52	
31	20.09.2009					
32	21.09.2009					
33	22.09.2009					
34	23.09.2009		73%	183	50	
35	24.09.2009					
36	26.09.2009					
37	27.09.2009		76%	245	60	
38	28.09.2009					
39	29.09.2009		76%	163	39	
40	30.09.2009					
41	01.10.2009	0.042				
42	02.10.2009	0.042				
43	03.10.2009	0.044				
44	04.10.2009	0.049	78%	295	66	
45	05.10.2009	0.049				
46	06.10.2009					
47	07.10.2009		82%	138	25	
48	08.10.2009	0.037				
49	09.10.2009	0.036				
50	10.10.2009	0.035				
51	11.10.2009	0.034	78%	338	75	0.001
52	12.10.2009	0.029				
53	13.10.2009	0.027				
54	14.10.2009	0.027	74%	151	40	0.001
55	15.10.2009	0.027				
56	16.10.2009	0.027				
57	17.10.2009	0.026				
58	18.10.2009	0.026	59%	242	100	0.001
59	19.10.2009	0.024				
60	20.10.2009	0.024				

Table 3-4. (Continued)						
		MFC1 HRT: 20hrs				
Days	Date	Voltage (V)	COD Removal	Influent COD (mg/L)	Effluent COD (mg/L)	PGCR (W-h/g COD_R)
61	21.10.2009	0.024	92%	900	75	0.000
62	22.10.2009	0.025				
63	23.10.2009	0.027				
64	24.10.2009	0.026				
65	25.10.2009	0.026	78%	385	85	0.000
66	26.10.2009	0.026				
67	27.10.2009	0.027				
68	28.10.2009	0.023	61%	173	68	0.001
69	29.10.2009	0.022				
70	30.10.2009	0.021				
71	31.10.2009	0.020				
72	01.11.2009	0.021	67%	210	70	0.000
73	02.11.2009	0.020				
74	03.11.2009	0.020				
75	04.11.2009	0.020	56%	142	63	0.001
76	05.11.2009	0.020				
77	06.11.2009	0.020				
78	07.11.2009	0.019				
79	08.11.2009	0.019				
80	09.11.2009	0.019				
81	10.11.2009	0.019				
82	11.11.2009	0.018	47%	86	46	0.001

Table 3-5. The Voltage Generation and COD Removal Efficiency of the MAC-GACMFC Systems Fed with the Primary Settled Wastewater as the Sole Feedstock in a Continuous Flow Mode (HRT: 10 hr).

Days	Date	MFC HRT: 10hrs				
		Voltage(V)	COD Removal	Influent COD (mg/L)	Effluent COD (mg/L)	PGCR (W-h/g COD)
1	01.10.2009					
2	02.10.2009					
3	03.10.2009		72%	353	99	
4	04.10.2009					
5	05.10.2009					
6	06.10.2009		90%	195	20	
7	07.10.2009					
8	08.10.2009	0.019				
9	09.10.2009	0.018				
10	10.10.2009	0.018	71%	292	85	0.000
11	11.10.2009	0.017				
12	12.10.2009	0.016				
13	13.10.2009	0.015	78%	172	37	0.000
14	14.10.2009	0.014				
15	15.10.2009	0.018				
16	16.10.2009	0.030				
17	17.10.2009	0.019	43%	225	129	0.001
18	18.10.2009	0.036				
19	19.10.2009	0.019				
20	20.10.2009	0.028	67%	225	75	0.001
21	21.10.2009	0.029				
22	22.10.2009	0.020				
23	23.10.2009	0.018				
24	24.10.2009	0.018	69%	390	120	0.000
25	25.10.2009	0.021				
26	26.10.2009	0.047	Cathodes	Replaced		
27	27.10.2009	0.038	88%	570	68	0.000
28	28.10.2009	0.040				
29	29.10.2009	0.037				
30	30.10.2009	0.034				
31	31.10.2009	0.031	57%	230	99	0.001
32	01.11.2009	0.032				
33	02.11.2009	0.034				

Table 3-5. (Continued)						
		MFC HRT: 10hrs				
Days	Date	Voltage(V)	COD Removal	Influent COD (mg/L)	Effluent COD (mg/L)	PGCR (W-h/g COD)
35	04.11.2009	0.034				
34	03.11.2009	0.034	80%	150	30	0.001
36	05.11.2009	0.033				
37	06.11.2009	0.032				
38	07.11.2009	0.029				
39	08.11.2009	0.032				
40	09.11.2009	0.032				
41	10.11.2009	0.033	43%	68	39	0.005
42	11.11.2009	0.032				

Table 3-6. The Voltage Generation and COD Removal Efficiency of the MAC-GACMFC Systems Fed with the Primary Settled Wastewater as the Sole Feedstock in a Continuous Flow Mode (HRT: 5 hr).

Days	Date	MFC HRT: 5hrs				
		Voltage(V)	COD Removal	Influent COD (mg/L)	Effluent COD (mg/L)	PGCR (W-h/g COD)
1	01.10.2009	0.041				
2	02.10.2009	0.054				
3	03.10.2009	0.050	72%	353	99	0.001
4	04.10.2009	0.046				
5	05.10.2009	0.047				
6	06.10.2009		90%	195	20	
7	07.10.2009					
8	08.10.2009	0.029				
9	09.10.2009	0.028				
10	10.10.2009	0.028	71%	292	85	0.001
11	11.10.2009	0.027				
12	12.10.2009	0.026				
13	13.10.2009	0.025	78%	172	37	0.001
14	14.10.2009	0.024				
15	15.10.2009	0.028				
16	16.10.2009	0.040				
17	17.10.2009	0.029	43%	225	129	0.001
18	18.10.2009	0.036				
19	19.10.2009	0.019				
20	20.10.2009	0.028	67%	225	75	0.001
21	21.10.2009	0.029				
22	22.10.2009	0.020				
23	23.10.2009	0.028				
24	24.10.2009	0.031	69%	390	120	0.001
25	25.10.2009	0.036				
26	26.10.2009	0.029				
27	27.10.2009	0.028	88%	570	68	0.000
28	28.10.2009	0.022				
29	29.10.2009	0.021				
30	30.10.2009	0.021				
31	31.10.2009	0.020	57%	230	99	0.000
32	01.11.2009	0.021				
33	02.11.2009	0.021				

Table 3-6. (Continued)						
		MFC HRT: 5hrs				
Days	Date	Voltage(V)	COD Removal	Influent COD (mg/L)	Effluent COD (mg/L)	PGCR (W-h/g COD)
34	03.11.2009	0.021	80%	150	30	0.001
35	04.11.2009	0.020				
36	05.11.2009	0.019				
37	06.11.2009	0.018				
38	07.11.2009	0.016				
39	08.11.2009	0.016				
40	09.11.2009	0.016				
41	10.11.2009	0.015	43%	68	39	0.001
42	11.11.2009	0.015				

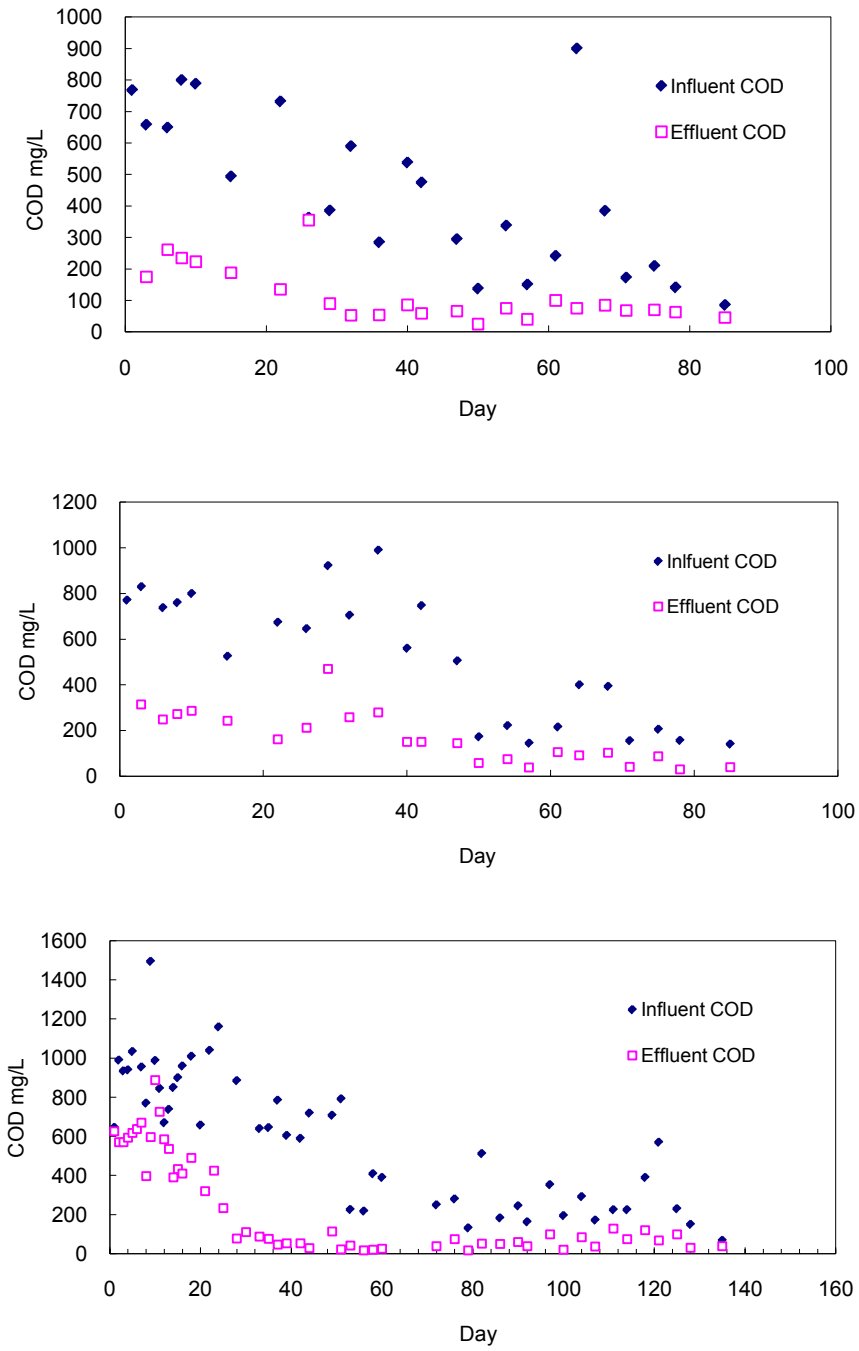


Figure 3-4. COD Removal of Continuous, Multi-Electrode MFCs at Different HRTs (5, 10, and 20 hours)

3.4 Phase IV: New Catalyst Development and Testing

The high cost of platinum is a significant obstacle if widespread application of MFCs in wastewater treatment plants is to occur in the future. Although the development of an alternative cathode catalyst was not part of this project, the project team has been working with the University of Connecticut Chemistry Department to develop alternative cathode catalysts for laboratory-scale GACMFCs.

A cathode catalyst based on MnO_2 was developed. Cathode catalysts based on MnO_2 need to be doped with metals to enhance conductivity (Suib et al., 2008). The morphology and composition of cathode catalysts was analyzed by SEM. The analysis showed that the structures produced by the application of MnO_2 were nanowire-like (Figure 3-5A), while the Pt-coated cathodes had flat surfaces (Figure 3-5D). The nanowire structure of the OMS-2 (MnO_2-based) catalyst has a high surface area, which results in easier adsorption of organic substrates on the cathodes; it should enhance oxygen absorption and electron acceptance on the catalyst surface.

Several metal ions were doped into the OMS-2 structure, and the carbon cloth cathodes were coated with the material and placed in the laboratory-scale MFC system. After 400 hours of operation, biofilms were clearly observed on the cathodes (Figures 3-5B and 3-5C). The doped MnO_2-coated cathodes had twice the reaction rate and similar power generation to platinum-coated cathodes (Table 3-7), with similar voltage generation and internal resistance. Of all the metal-doped MnO_2 catalysts tested in the laboratory, Cu-doped and Co-doped MnO_2 demonstrated the highest power production (Li et al., 2009). Since the laboratory-scale tests showed encouraging results, and the cost of MnO_2 is less than 5% the cost of platinum, it was decided to test Cu-doped and Co-doped MnO_2 cathodes at pilot-scale (Table 3-8).

Table 3-7. Performance Comparison of MnO_2-Coated Cathodes and Pt-Coated Cathodes in the Lab-Scale Batch-Mode GACMFCs.

	Voltage (mV)	Duration time needed for COD removal (hr)	COD Removal (%)	Power density (mW/m^2)	Internal resistance (R_{in}, ohm)
MnO_2 coated cathode	190±20	91	80%±5%	180±30	22±6
Pt coated cathode	180±15	187	82%±5%	198±4	18±2

Table 3-8. The Performance Comparison of MnO_2-Coated Cathodes and Pt-Coated Cathodes in the Lab-Scale Batch-Mode GACMFCs.

Cathodes	Internal resistance (ohm)	OCP vs. Ag/AgCl (mV)	COD removal efficiency (%)	Maximum Power density (mW m^{-2})	Coulombic Efficiency (%)
Pt	18±1	149	86.7	198	9.6
Co-OMS-2	18±1	147	99.6	180	8.7
Cu-OMS-2	18±1	116	96.3	165	8.9
Ce-OMS-2	55±2	31	80.0	35	6.6
ud-OMS-2	18±1	82	66.7	86	11.3

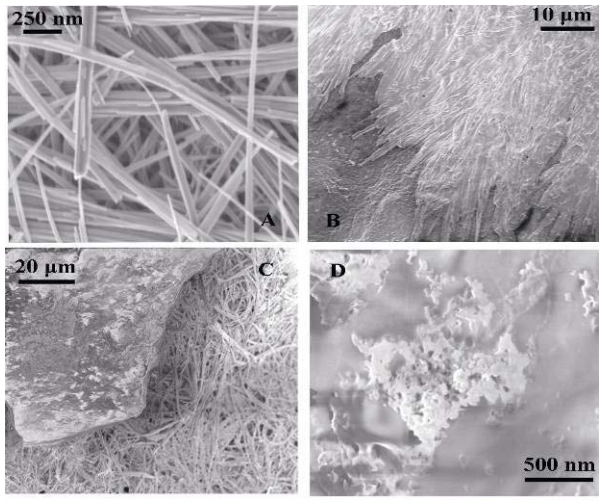


Figure 3-5. SEM Pictures of MnO2-Coated Cathode and Pt-Coated Cathode.

Three Co-doped MnO_2 and three Cu-doped MnO_2 cathodes were installed in MFC1; the remaining cathodes were platinum. The MnO_2 cathodes exhibited higher power production than the conventional Pt cathodes in the first three weeks of operation (Table 3-9). The average power density of Cu-MnO_2, Co-MnO_2 and Pt in the first three weeks was 275, 250 and 160 mW/m^2, respectively. However, fouling developed faster on the MnO_2 cathodes, resulting in a lower power generation than Pt cathodes in the fourth week.

The Cu-doped MnO_2 cathodes were found to be better than the Co-MnO_2 cathodes in terms of power density. The power density of Cu-MnO_2 cathodes was on average 50mW/m^2 higher than Co-MnO_2 cathodes, except in the initial week when Cu-MnO_2 cathodes were 35mW/m^2 lower than Co-MnO_2 cathodes. Additionally, MnO_2 cathodes exhibited equivalent R_{in} to Pt cathodes. The difference in R_{in} between Pt, Cu-MnO_2 and Co-MnO_2 cathodes was less than 20 Ohm.

Fouling of the cathodes lead to a significant reduction in power density and increased R_{in}. The power density of the MnO_2 cathodes dropped by 300 mW/m^2 and the R_{in} of both Pt and MnO_2 cathodes increased from 220 to 270 Ohm. But the high R_{in} in the second week was more

likely due to a low influent conductivity than the fouling of cathodes (Table 3-10). Subsequently, six of the 12 Pt cathodes were replace with MnO_2 cathodes, which had no affect on the COD removal of the MFC. The effluent COD remained at 50 mg/L after the MnO_2 cathodes were installed.

Table 3-9. Power Density of MnO_2 Cathodes in Comparison with Pt Cathodes.

Power (mW/m^2)	Cu-MnO_2 Cathodes	Co-MnO_2 Cathode	Pt Cathodes
10.24.2009	465±3	500±50	213±50
10.31.2009	219±100	130±70	177±100
11.06.2009	145±115	112±70	84±60
11.11.2009	133±20	96±40	163±40

Table 3-10. R_{in} of MnO_2 Cathodes in Comparison with Pt Cathodes.

R_{in} (Ohm)	Pt Cathodes	Cu-MnO_2 Cathodes	Co-MnO_2 Cathodes
10.24.2009	218±12	233±20	227±15
10.31.2009	334±20	317±20	383±20
11.07.2009	273±30	280±20	287±15
11.11.2009	270±10	260±30	280±20

CHAPTER 4.0

DISCUSSION

4.1 Correlation of Power Generation and Wastewater Treatment

MFCs hold great potential to simultaneously treat wastewater and generate electricity. MFCs are a biofilm technology, in which biofilm growing on particles, in this case GAC, degrade the wastewater organics and transfer the electrons generated by this biochemical reaction to the surface of the particles. [Note: since anaerobic electrogenic bacteria grow slowly, the GAC particles tend not to clog. During the six-month of pilot-scale testing using filtered primary effluent, no clogging was observed.] The growth and activity of the biofilm greatly affects overall MFC performance.

In this project, two parameters critical for biofilm growth, COD removal and HRT, were the subject of extensive testing. Bacterial cells require organic substrates (i.e., COD) to grow; but too much substrate will lead to an overly-thick biofilm, which increases the resistance to electron and mass transfer within the biofilm. Both laboratory-scale and pilot-scale testing have shown that low concentrations of COD results in low power generation, that power generation steadily increases with increasing COD concentration, and finally that it levels off at high COD concentrations.

In terms of HRT, biofilm requires sufficient contact time with organic substrates in order to both absorb and degrade the substrates. A start-up/acclimation period of two to four weeks was found necessary for sufficient biofilm growth. After the start-up/acclimation period, effective wastewater treatment efficiency was observed when the HRT was 10 or more hours.

4.2 Power Generation Efficiency

In addition to the growth and activity of biofilm, the cathode/anode configuration also greatly affects overall MFC performance. The electrons generated from the anaerobic degradation of the organic substrates should quickly collect on the anode; otherwise they will accumulate within the GAC bed and inhibit microbial activity. Similarly, the electrons should be quickly accepted on the cathode, where they can react with protons and oxygen; otherwise an accumulation of protons will occur in the MFC. The multi-anode/cathode configuration effectively promotes the collection and transfer of electrons from within in the GAC bed (anode) to the carbon cloth (cathode).

To justify real-world application of MFCs in wastewater treatment plants, sufficient power generation is required. Normally, two parameters are used to evaluate power generation efficiency: coulombic efficiency (CE, %), which is the ratio of the actual coulombs generated in the MFC to the theoretical coulombs in the COD removed; and power generation per gram of COD removed (PGCR, kW-h/kg-$COD_{removed}$). In the smaller, laboratory-scale MFC systems (less than 0.1-0.2 L) treating pure organic substrates (e.g. acetate), CE values reached 60-70%, and PGCR 0.32-0.6 kW-h/kg$COD_{removed}$. However, in the pilot-scale systems treating only domestic wastewater, the CE only reached 3-5% and the PGCR was much less than that produced in the laboratory. There are a number of possible reasons for this:

- The internal resistance (R_{in}) in the pilot system was higher than in the batch units. Observations have shown that internal resistance has a significant impact on power production, with an almost exponential correlation (not linear as might be intuitively imagined). In the laboratory, when the internal resistance was reduced from 80 ohm to 30-40 ohm, power production was nearly 10 times higher rather than expected. The internal resistance of the pilot-scale system was on the order of 120-180 ohm.
- The distance between the anode and cathode in the pilot-scale MFC systems (about 12 cm) was much longer than in the laboratory-scale MFC systems (typically 2.7 cm), since the pilot-scale systems were more than 10-20 times as large as the laboratory-scale units. This longer distance lead to increased mass and electron transfer resistance, whereby lowering power generation efficiency.
- This was the first pilot-scale test of a GACMFC. There are inherent challenges in scaling up any technology, and the system has not yet been optimized for power production. In subsequent efforts, it will be important to improve the MAC-GACMFC configuration and electrode materials for higher power generation.
- Power recovery in MFCs is a voltage-limited process. With the cathode material currently used in the pilot-scale MFC systems, 0.6 V is the absolute maximum an MFC circuit can produce. Research into alternative cathode materials may change this limitation. The newly-develped cathode catalyst described previously should be included in future pilot-scale MAC-GACMFC systems.

4.3 Identification of Limiting Reaction Steps in MFCs

MFCs are still in the early stage of development, and the fundamental mechanisms of electron generation and transfer are yet under investigation. Electron generation in the anode chamber must be balanced with electron acceptance in the cathode chamber to avoid the accumulation of electrons and protons within MFCs and enhance power generation.

Previously, it had been assumed that electron generation carried out by the anaerobic bacteria in the anode chamber was the limiting factor. As such, much effort has been invested in determining the impacts of substrate concentration, temperature, pH, flow rate, and conductivity on anode performance; various MFC configurations have been developed to reduce internal resistance and enhance electron generation and transfer.

However, it has recently been determined that electron acceptance on the cathode is actually the limiting factor. Unlike the biochemical reactions carried out by bacteria in the anode, the cathode requires a chemical catalyst (e.g. platinum) to accelerate the reaction rate of electron acceptance and oxygen reduction. [Note: the voltage loss on the anode is about 0.1-0.3 V, while the voltage loss on the cathode could be as much as 0.6-0.7 V.] If the reaction rate is low on the cathode, the electrons and protons will accumulate inside MFCs and rates of reaction of organic substrate degradation and microbial activity will be lower. Therefore, the cathode reactions must be accelerated if MFCs are to be a viable process for dilute wastewater.

Prior work has found that multi-cathode MFCs can generate more power than single-cathode MFCs. For instance, the power generation of a two (2)-anode/cathode MFC was twice as that of single-anode/cathode MFC, and the power generation of a four (4)-anode/cathode MFC was 3.5 times as that of single-anode-cathode MFC. In addition, the four (4)-anode/cathode MFC was capable of generating a desirable amount of power at a high COD (>3000 mg/L), while the

single-anode/cathode MFCs leveled off at CODs higher than 1000 mg/L. Clearly multi-anode/cathode MFCs are more effective in generating power and COD removal.

4.4 New Cathode Development for Power Generation and Contaminant Removal

Unlike the biochemical reactions carried out by anaerobic bacteria in the anode chamber, the reactions carried out in cathode chamber are solely electrochemical. Due to the slow oxygen reduction rate (ORR), cathodes are coated with a catalyst to accelerate this rate. Platinum has been widely used as the cathode catalyst; but its high cost impedes real-world applications of MFCs. The project team developed a low-cost MnO_2 catalyst as a substitute for Pt. Laboratory-scale and pilot-scale tests have demonstrated that metal-doped MnO_2 catalysts have similar power generation to, and faster organic contaminant removal efficiency than, platinum. Additionally, different metal dopants produce different levels of power generation. The development of MnO_2 as cathode catalyst is one of the breakthroughs of this project; however, the optimal metal dopant and dosage requires future research.

Another issue is that the water formed in the electrochemical reactions could cause cathode flooding and inhibit the direct contact between the catalyst and the wastewater, which would reduce the catalyst efficiency. It has been reported that more than 90% of the catalyst placed on the cathode is not efficiently used due to flooding and lack of contact. Therefore, mechanisms to inhibit flooding require future research. One approach may be to develop a hydrophobic layer on the cathode (see below). Another may be to use tubular cathodes that would increase the surface area so that water formed can be quickly removed from the cathode surface.

4.5 Long-Term Stable MFC Operation

As previously reported, pilot-scale tests using primary effluent as the feedstock fouled after three to four weeks of operation, after which the internal resistance increased and the voltage generation decreased. After washing the cathode with clean water, MFC performance returned to normal. But frequent cleaning may be required to prevent excessive cathode fouling, and the cathode will eventually have to be replaced. For the long-term stable operation of MFCs treating wastewater, an alternative approach should be developed to prevent fouling.

The research team is developing a cathode with an anti-fouling layer to inhibit deposition from occurring. A relatively low-cost silicon-based hydrophobic (water repelling) layer will be applied to the MnO_2. The hydrophobic nature of the layer will prevent water, and subsequently deposits, from collecting on the surface. Different thicknesses will be tested to determine the most effective coating thickness, and adhesion will be tested to ensure a durable coating. Since antifouling coatings have not previously been used in MFC systems, this work represents a significant step towards reducing the costs associated with frequent cathode replacement and should justify any additional cost associated with the coating.

4.6 Development of Next Generation GAC-MFCs to Further Enhance Power Generation

Based on the COD removal efficiencies observed during pilot-scale testing using domestic wastewater as a feedstock, future research should be undertaken to enhance power generation in conjunction with COD removal efficiency. Two modifications initially anticipated to improve MFC performance are reducing electrode distance and increasing the number of electrodes.

The existing GAC-MFC has multiple graphite rods inserted within the GAC bed (anode) and connected to the carbon cloth (cathode) on the top of the reactor. Although this design solves the problem of electrons collecting within the GAC bed, the distance between the anode and cathode is lengthy, which leads to high resistance of electron and proton transfer. Furthermore, the protons generated within the GAC bed may accumulate at the upper portion of the reactor; this will lower the pH in the reactor, inhibiting bacterial growth and metabolic activity, which can in turn reduce power generation potential and wastewater treatment efficiency.

The research team found that by increasing the number of anodes/cathodes in an MFC, the internal resistance (R_{in}) is reduced and power generation increases. As shown in Table 4-1, the internal resistance in multi-anode/cathode GAC-MFCs (2-anode/cathode GAC-MFC and 4-anode/cathode GAC-MFC) is reduced by 40-70% and the total power density (mW/m^3) increased by 2-2.7 times when compared with single-electrode GAC-MFCs. Clearly, by adding more electrodes in MFCs, the resistances of mass and electron transfer can be reduced substantially, thereby leading to higher power output per MFC unit. However, it is also noted that the power density is not linearly proportional to the number of anode/cathode pairs. In fact, the specific power density per anode/cathode pair decreases with the increasing number of anode/cathode pairs (Table 4-1). The exact mechanism for this undesired phenomenon is currently under investigation. At present, the hypothesis is that the decreased power density per anode/cathode pair is partially due to the low substrate oxidation efficiencies of the anodes at the upper proportion of the MAC-MFC; their low efficiencies are due to the accumulation of protons at the upper proportion of the reactor.

Table 4-1. The Internal Resistance (R_{in}) and Power Density (mW/m^2) of Single-Electrode GAC-MFCs and Multi-Anode/Cathode GAC-MFCs.

	Single-electrode GAC-MFC	**2-anode/cathode GAC-MFC**	**4-anode/cathode GAC-MFC**
Internal resistance (R_{in}, ohm)	140 ± 15	103 ± 15	**63 ± 10**
Power density (mW/m^3)	350 ± 20	550 ± 30	**920 ± 35**
Power density per anode/ cathode pair (mW/m^3)	**350 ± 20**	**275 ± 30**	**306 ± 35**

A new MFC configuration should be developed with the anode and cathode placed side by side. For example, a shorter, wider reactor with tubular steel mesh cathodes inserted into the GAC, which replace the flat-sheet carbon cloth. With this side by side placement, the electrons and protons generated within the GAC bed could be quickly transferred to the cathode, whereby solving the problem of accumulation within GAC bed. An increasing number of anodes/cathodes pairs should be tested within the new configuration to determine whether power generation steadily increases with an increasing number of electrodes, or levels off at some point. This information would be valuable for optimizing power generation and capital costs, which is key for real-world application of MFCs in wastewater treatment plant settings.

CHAPTER 5.0

CONCLUSIONS

MFC systems operate on the fundamental mechanisms of microbiology (e.g. biofilm growth on GAC particles), biochemistry (e.g. COD removal inside biofilms), and electro-chemistry (e.g. electron generation and transfer on anodes and cathodes), which make it truly challenging to achieve effective power generation simultaneously with effective wastewater treatment. The major conclusions of this project are summarized below:

1. The MAC-GACMFC is a promising configuration that integrates multiple MFCs into a single unit. The system achieves excellent wastewater treatment efficiency and produces power when treating domestic wastewater.
2. Greater power generation is produced in MAC-GACMFCs (compared to conventional MFCs) as a result of the biofilm that grows on the GAC particles.
3. Influent COD concentration and reactor HRT affect MFC performance. To achieve optimal COD removal, sufficient contact time is need between the biofilm and substrate.
4. Oxygen reduction at the cathode limits power generation. To achieve optimal power generation, greater numbers of electrodes are required, as opposed to greater surface area.
5. Compared to single-anode/cathode MFCs, MAC-GACMFC produce substantially more power.
6. A metal-doped MnO_2 catalyst demonstrated good power generation and efficient wastewater treatment; and has great potential for providing a low-cost alternative to Pt catalysts.
7. MAC-GACMFCs have the potential to play a significant role in achieving self-sustaining wastewater treatment systems in the future.
8. Further improvements are required, including alternative MFC configurations and electrode materials, to enhance power conversion efficiency and provide steady-state operations that consistently achieve secondary treatment objectives.

APPENDIX A

WEEKLY SUMMARY OF WASTEWATER TREATMENT EFFICIENCY

	MFC with 20-hour HRT										
	Influent					Reactor	Effluent				
Date	COD Total (mg/L)	pH	Alkalinity (mg/L)	TSS (mg/L)	TDS (mg/L)	pH	COD Total (mg/L)	pH	Alkalinity (mg/L)	TSS (mg/L)	TDS (mg/L)
30.06.2009	646	8.17	400	144	1150		626	7.39	320	40	2210
01.07.2009	990	8.02	280				570	7.16	340		
02.07.2009	935	7.61	380				570	7.17	420		
03.07.2009	940	7.53	700				593	7.13	600		
04.07.2009	1034	7.61	800				618	7.21	560		
05.07.2009	640	7.47	500				637	7.62	700		
06.07.2009	955	8.03				6.53	670	6.92			
07.07.2009	770	7.48	640	64	1430	6.84	397	7.42	620	80	1580
13.07.2009	850	7.43	680	88	1920	7.13	390	7.94	620	32	1490
20.07.2009		7.67	660	96	1650	7.38	320	8.17	680	60	1740
27.07.2009	885	8.05	680	184	2080		78	7.94	560	48	1350
03.08.2009	645	7.6	620	52	1560	7.17	76	7.6	580	20	1180
10.08.2009	590	7.62		60	1930	7.4	54	8.05		28	1410
17.08.2009	708	7.34		44	990	7.39	114	7.92		16	890
24.08.2009	218	7.87	400	48	950	7.41	18	8.38	540	24	1080
13.09.2009	280	7.45	380	36	890	8.17	75	8.4	360	0	860
19.09.2009	512	7.39	440	148	1000	6.95	52	7.48	460	40	1080
27.09.2009	245		360	44	810		60		320	16	670
04.10.2009	353	7.43	380	44	1020	6.89	99	7.26	280	24	770
11.10.2009	292	7.7	360	36	690	7	85	7.3	360	4	580
18.10.2009	225	7.7	300	32	670	7.1	129	7.3	320	0	710
25.10.2009	390	7.39	320	36	760	7.03	120	7.28	340	20	690
01.11.2009	230	7.42	300	60	670	6.93	99	7.11	280	8	560
07.11.2009	150	7.72				7.15	30	7.29			

	Influent				Effluent				
Date	Ammonia as Nitrogen (mg/L)	BOD (mg/L)	Nitrogen, Total Kjeldahl (TKN) (mg/L)	Phosphorus, Total (mg/L)	Ammonia as Nitrogen (mg/L)	BOD (mg/L)	Nitrate+ Nitrite as nitrogen (mg/L)	Nitrogen, Total Kjeldahl (TKN) (mg/L)	Phosphorus, Total (mg/L)
28.07.2009	25.1		11.3	4.81	31.6		0.05	8.4	3.03
06.08.2009	32.6		41.1	3.97	27.4		0.05	26	2.57
12.08.2009	14.6		22.5	2.79	25.4		0.05	23.6	2.78
17.08.2009	26.6		34	4.69	21.1		0.05	20.3	3.15
13.09.2009	17.5	70.5	25.1	3.78	17.7	96.3	0.05	21.7	3.36
20.09.2009	32.2	245	44.9	7.31	26.5	15.8	0.05	26.5	4.89
27.09.2009	22	247	28.5	4.68	35.7	4.5	0.05	27.4	4.67
04.10.2009	27.4	55.3	31.2	4.95	22.9	6.8	0.072	20.6	3.95
17.10.2009	17	45.7	22.1	4.08	23.6	36.2	0.963	24.2	3.12
25.10.2009	20.7	109	28.1	4.4	27.9	38.3	0.706	25.9	3.56

MFC with 10-hour HRT

		Influent					Reactor	Effluent				
Date	Operation Days	COD Total (mg/L)	pH	Alkalinity (mg/L)	TSS (mg/L)	TDS (mg/L)	pH	COD Total (mg/L)	pH	Alkalinity (mg/L)	TSS (mg/L)	TDS (mg/L)
13.09.2009	26	363	7.59	400	44	1190	7.17	355	7.89	740	88	1630
19.09.2009	32	590	7.31	620	184	1780	7.33	53	8.13	740	32	1530
27.09.2009	40	538	7.38	540	52	1410	7.4	86	8.09	480	12	1160
04.10.2009	47	295	7.74	380	24	880	7.5	66	8.03	420	24	770
11.10.2009	54	338	7.8	380	60	700	7.5	75	7.9	400	12	630
18.10.2009	61	242	7.8	280	64	700	7.6	100	7.8	320	24	720
25.10.2009	68	385	7.44	340	40	750	7.48	85	7.94	340	4	780
01.11.2009	75	210	7.51	280	36	690	7.3	70	7.7	260	0	530
07.11.2009	82	86	7.64				7.32	46	7.77			

	Influent				Effluent				
Date	Ammonia as Nitrogen (mg/L)	BOD (mg/L)	Nitrogen, Total Kjeldahl (TKN) (mg/L)	Phosphorus, Total (mg/L)	Ammonia as Nitrogen (mg/L)	BOD (mg/L)	Nitrate+ Nitrite as nitrogen (mg/L)	Nitrogen, Total Kjeldahl (TKN) (mg/L)	Phosphorus, Total (mg/L)
13.09.2009	19.2	36.7	27.5	3.79	20.3	2.8	1.55	21.3	0.814
20.09.2009	21.5	71.1	29.2	4.58	28.5	14.2	0.862	27.3	2.47
27.09.2009	21.8	57.3	29.4	5.13	24.2	4.5	0.878	25.4	2.81

04.10.2009	28.4	93.9	34.6	5.06	24.3	6	1.01	23.4	2.22
17.10.2009	13.1	15.7	19.4	3.44	18.3	4.5	1.43	20.8	3.02
25.10.2009	20.8	101	27	4.69	24.7	13.2	0.05	25.2	9.3

MFC with 5-hour HRT

		Influent					Reactor	Effluent				
Date	Operation Days	COD Total (mg/L)	pH	Alkalinity (mg/L)	TSS (mg/L)	TDS (mg/L)	pH	COD Total (mg/L)	pH	Alkalinity (mg/L)	TSS (mg/L)	TDS (mg/L)
13.09.2009	26	646	7.69	380	244	1590	7.23	212	7.5	540	60	1210
19.09.2009	32	705	7.4	520	152	1430	7.31	258	7.82	720	132	1570
27.09.2009	40	560	7.38	540	76	2520	7.56	150	7.74			
04.10.2009	47	505	7.63	360	128	940	7.47	145	7.64			
11.10.2009	54	221	7.8	380	36	760	7.6	75	7.8	380	28	610
18.10.2009	61	215	7.7	300	28	660	7.5	106	7.8	340	20	760
25.10.2009	68	393	7.42	340	24	800	7.43	103	7.45	320	16	770
01.11.2009	75	205	7.51	260	32	710	7.15	88	7.32	280	12	570
07.11.2009	82	140	7.54				7.19	40	7.39			

	Influent				Effluent				
Date	Ammonia as Nitrogen (mg/L)	BOD (mg/L)	Nitrogen, Total Kjeldahl (TKN) (mg/L)	Phosphorus, Total (mg/L)	Ammonia as Nitrogen (mg/L)	BOD (mg/L)	Nitrate+ Nitrite as nitrogen (mg/L)	Nitrogen, Total Kjeldahl (TKN) (mg/L)	Phosphorus, Total (mg/L)
13.09.2009	22.8	253	34.7	5.35	19.1	78.9	0.05	19.7	2.86
20.09.2009	28	320	39.9	6.57	31.7	122	0.05	32.8	6.94
27.09.2009	20.4	215	25.1	4.87	25.7	31.8	0.05	24.1	4.4
04.10.2009	25.1	5.3	22.7	4.3	27.1	139		48.9	7.3
17.10.2009	15.8	36.1	24.7	4.05	19	4.2	0.05	18.2	2.82
25.10.2009	20.2	107	27.7	4.59	27.7	11.8	0.05	29.1	4.5

APPENDIX B

WEEKLY SUMMARY OF VOLTAGE GENERATION AND INTERNAL RESISTANCE

The change of Rin during the MFC operation (unspiked influents are italicized) Unit: Ohm

MFC with 5-hour HRT

	Power mW/m2	**R_{in} Ohm**
09.19.2009	483±95	182±8
09.26.2009	597±90	180±11
10.03.2009	*320±40*	*216±15*
10.10.2009	*380±46*	*217±14*
10.17.2009	*285±58*	*213±14*
10.24.2009	*245±107*	*224±16*
10.31.2009	*110±82*	*342±33*
11.07.2009	*101±85*	*278±20*

MFC with 10-hour HRT

	Power mW/m^2	**R_{in} Ohm**
10.03.2009		*227±19*
10.10.2009		*190±14*
10.17.2009		*214±18*
10.24.2009	*467±30*	*238±24*
10.31.2009	*278±177*	*320±36*
11.07.2009	*264±135*	*285±28*

MFC with 20-hour HRT

	Power mW/m2	R_{in} Ohm
07.02.2009	216±74	128±8
07.14.2009	724±217	123±5
07.21.2009	738±214	119±8
07.29.2009	574±178	151±16
08.11.2009 (cathode cleaning)	1268±629	189±15
08.18.2009	637±130	153±6
09.19.2009	*425±128*	*211±13*
09.26.2009	*302±97*	*257±18*
10.03.2009	*307±150*	*193±6*
10.10.2009	*218±113*	*193±10*
10.17.2009	*145±105*	*232±61*
10.24.2009	*148±105*	*208±15*
10.31.2009	*110±82*	*272±11*
11.07.2009	*101±78*	*267±25*

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