Harvesting Energy from Wastewater in a 2-Chamber Microbial Fuel Cell

Sikandar

Present day wastewater treatment plants utilize high amounts of energy and are costly to operate. These conventional wastewater treatment plants utilize aerobic bacteria. Organic material in wastewater contains energy that can be harvested. I propose to biologically harvest this energy in the form of electricity from wastewater obtained at the Seneca Wastewater Treatment Plant in Germantown. Besides capturing energy in the form of electricity, one could use that electricity to power the wastewater treatment plant and clean the water.

To construct a microbial fuel cell (MFC), it takes a source of bacteria, food, no oxygen, and two electrodes. The microorganisms oxidize the organic food matter, and transfer the electrons to the anode. The electrons travel on an insulated copper wire to the cathode to generate a current. Many MFCs use a proton exchange membrane (PEM) to keep the electrons on the anode side from escaping to the cathode side, but allow the protons to pass through. At the cathode chamber, the protons combine with purged oxygen to form water. The cathode chamber contains a phosphate buffered saline solution.

I want to test whether it is essential to incorporate a PEM into the MFC design, or whether a cation exchange membrane can replace the PEM. A PEM is quite expensive and requires a platinum catalyst, which is also costly. Although I believe that a PEM is essential in the productivity of a MFC, it is crucial to reduce the cost of a MFC.

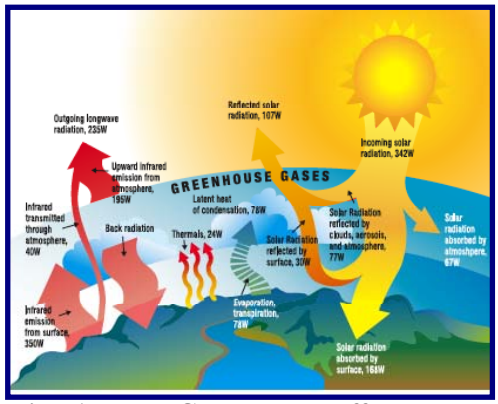

Fig. 1: The Greenhouse Effect-Due to combustion of fossil fuels, carbon dioxide is released into the atmosphere causing the atmosphere to trap solar radiation that then leads to global warming. **(Figure courtesy of National Oceanic and Atmospheric Administration)**

Introduction

It is important to find an alternative form of energy before the world's fossil fuels are depleted. It is predicted that oil and gas reserves will be depleted by 2032 and 2030.[1] Due to the combustion of fossil fuels, carbon dioxide is released into the atmosphere causing the atmosphere to trap solar radiation that then leads to global warming or the "green house effect."

The development of MFCs is important to the advancement of alternative fuels. Electricity can be produced using the degradation of organic matter by microorganisms in a MFC. A MFC is usually made up of two chambers; one anaerobic and one aerobic. In the anaerobic chamber the organic material is oxidized by the microbes and the lost electrons are transferred to the anode by either an added electron carrier or directly from the respiratory enzyme of the bacteria (mediatorless).[2] In a mediatorless MFC, certain bacteria have cytochromes (electrochemically-active redox enzymes) that transfer electrons to

an external material like the electrode. Recently it has been discovered that wastewater, as a source of substrate and microorganism, can be used to generate energy in a MFC. Mr. Sam Amad, Plant Superintendent at the Seneca Wastewater Treatment Plant in Germantown, MD., states that approximately $4 million is spent per year for direct cost of operation and maintaining the plant. 25% is for energy operation of the plant.[3] One of my goals was to find a way to reduce the cost of cleaning up wastewater by using the microbes found in the wastewater to produce the energy to operate the plant. This can be done by using a MFC to harvest that energy. In addition to reducing the cost of plant operation, I hoped to clean up the wastewater by utilizing the anaerobic bacteria naturally found in the sewage.

Materials and Methods

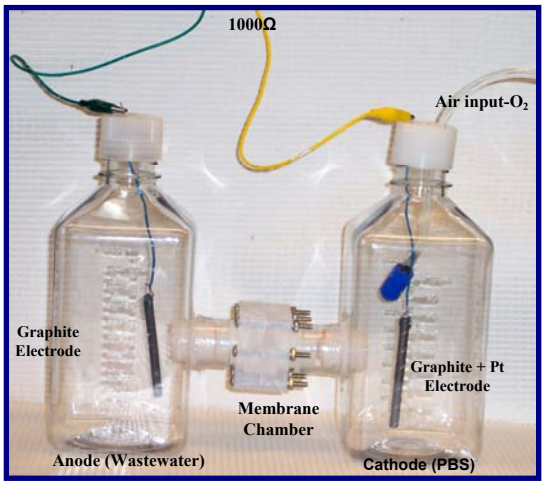

Fig. 2: 2-Chamber Microbial Fuel Cell design with membrane chamber.

MFCs were constructed by joining two recycled 1.0 liter plastic reagent bottles with 1.3 cm length x 2.0 cm ID plastic tubing and 2.5 cm x 2.0 cm ID connectors (PB222N Watts, North Andover, MA.) attached to each bottle and a membrane chamber in between, also connected with the same dimensions of connector and tubing. The membrane chamber that houses the PEM or cation exchange membrane was constructed using Polytex G plastic and the CAD (Computer Aided Design) program and mill. Each side of the chamber was 5 cm x 5 cm x 1.9 cm. The inner square was 3 cm. x 3 cm. x 1.9 cm. and a 2.7 cm forstner bit was used to drill a circle in the middle that would house the connector. Eight holes were drilled along the outer dimensions of the chamber to hold 0.8 cm x 5 cm stainless steel screws, bolts, and nuts. (Hillman) Liquid gasket (Permatex high-temp red RTV silicone) plus the membrane was placed between the two portions of the chamber and sealed together with the screws. All connections were made using silicone (GE silicone II sealant).

Nafion-117 (Dupont Co., Delaware), a PEM, I.C.E. 450 (PALL Corporation, East Hills, NY), a cation exchange membrane, and Hybond™-N (Amersham Life Science, Piscataway, NJ.) were the tested membranes. Nafion-117 was pretreated by boiling in each of the following solutions for 1 hour; distilled water, 3% hydrogen peroxide, 0.5 M sulfuric acid, distilled water three times and then stored in water until use.[4] Both I.C.E. 450 and Hybond™-N were pretreated in distilled water only.

Nafion-117 is composed of a perfluorosulfonic acid polymer film. When in contact with water, the hydrogen proton (H^+) detaches and hops from one sulfonic molecule (SO_3^-) to another and thus acts like an electrolyte in the presence of water. Therefore, Nafion-117 transfers H^+ across the PEM to the cathode, but does not allow electrons to cross. H^+ yielded in the degradation of organic material by

microorganisms in the wastewater (anode chamber) is then transported across the Nafion-117 to the cathode where the protons come in contact with oxygen to form water.[4]

I.C.E. 450 is a cationic membrane made up of polysulfone on a polyester support. The sulfonic acid looses H^+, which then gives the membrane a negative charge. This negative charge attracts H^+ from the wastewater that becomes bound on the membrane. Eventually all the negative sites will become neutralized. Hybond™-N was used as a control because of its neutral charge and a pore size of 0.45 microns (micrometers). This membrane was used to prevent microorganisms from crossing to the aerated PBS cathode chamber. The I.C.E. 450 has a pore size of 0.45 microns also. The Nafion-117 has a pore size of 50 Å (10^{-10} meters).

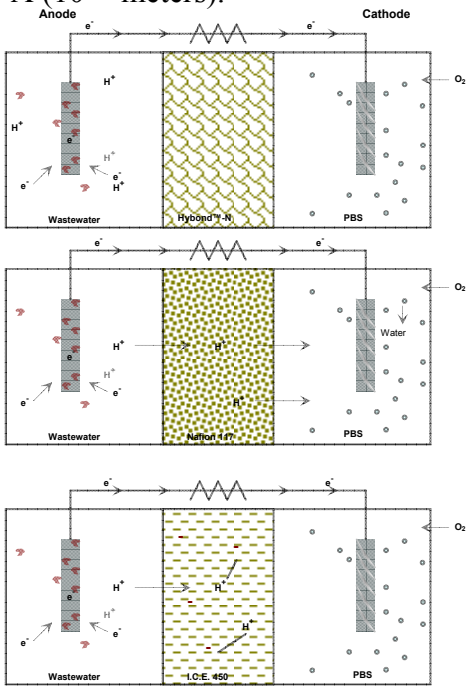

Fig. 3: Depicts 3 membranes tested; Hybond-N (control), Nafion-117, and I.C.E. 450. Nafion is a perfluorosulfonic acid polymer and when in contact with water, the H^+ detaches and hops from one SO_3^- to another; acting like an electrolyte. I.C.E.- 450 is a cationic membrane with a negative charge. Hybond-N was chosen as a control to prevent bacteria from crossing to the cathode chamber.

The anode used was 7.6 cm x 0.6 cm graphite rods (Graphite Store Buffalo Grove, IL) and the cathode was the same material and size as the anode except a 15.2 cm length of Platinum wire was twisted around the graphite rod. The electrodes were soaked in deionized water over-night before usage. Copper wire was inserted through a drilled 0.2 cm hole in each of the graphite rods and sealed with conductive sealant (Star brite liquid electrical tape™, Ft. Lauderdale, FL).

The copper wire was inserted through the lid of each chamber. The cathode lid had two extra 0.6 cm drilled holes in which air was pumped and released. The stripped wire exposed through the lid was clamped with electrode wires attached to a 1000-ohm resistor. Non-conductive sealant was used to plug the wire hole in the anode chamber lid. (PUG DUCT SEAL, GB Electrical, Milwaukee, WI.). The distance between the anode and cathode electrode was 17 cm.

The anode chamber was filled with 1.0 liter of wastewater and the cathode compartment was filled with 1.0 liter of phosphate buffered saline (PBS). The pH of each was 7.0. The cathode chamber was continuously sparged with air. Voltage readings were taken with a voltmeter once a day. All MFC were placed at room temperature within a large tub to contain any spillage.

After 7 days, 6.6 ml of 3M sodium acetate (pH=5.2) was added to 1.0 liter of present wastewater with a syringe through the anode wire hole. This was added as a nutrient for the microorganisms and a source of electrons due to oxidation of acetate by microorganisms.

Results

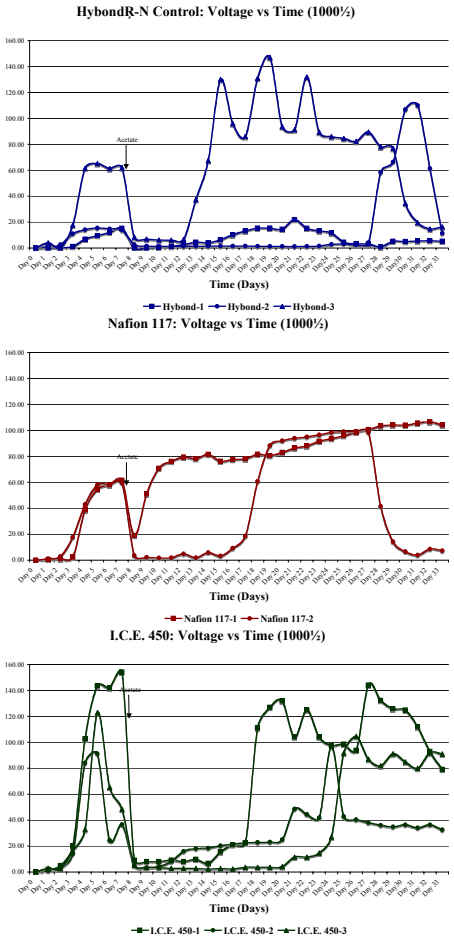

Fig. 4: Electricity generation by the I.C.E. 450 was 2.5 times that of Hybond-N and Nafion-117 during the first week. 7 out of 9 MFCs functioned well, although they progressed at different rates. It appears that all MFC membranes performed adequately. Nafion-117, the membrane of choice., generated a stable and constant voltage, unlike the erratic voltages of I.C.E.-450 and Hybond control.

Electricity generation was readily obtained using a MFC inoculated with wastewater from the Seneca Wastewater Treatment Plant. Although there were minor engineering difficulties, the I.C.E. 450 performed the best in the first week by a factor of 2.5 over the Nafion-117 PEM and Hybond™-N, which was the control membrane. Nafion-117 is the PEM of choice by most hydrogen fuel cell and MFC scientists. Dr. Logan feels that a PEM is not necessary for a MFC.[5] However; he used a single chamber microbial fuel cell design.

During experimental set-up, one of the Nafion-117 MFCs leaked excessively and had to be eliminated.

Out of the remaining eight MFCs, only one performed poorly probably due to some fault in the electrical circuit. However, a total of seven functioned well, although they progressed at different rates and times.

The voltage increased continuously during the first week for most of MFCs. During the second week, the voltage dropped after the addition of sodium acetate, but then gradually increased again. By the third week, most MFCs had surpassed their first voltage peaks.

Most fuel cell researchers express their data in Power Density, which is the power output of the fuel cell per surface area of the anode electrode. See figure 5 for a representation of the power density of the three types of membranes used in the two-chamber MFCs. You can see that that the power density of the I.C.E. 450 was five times higher than that of Hybond™-N and Nafion-117 at the end of the first week. However, by the end of the third week, I.C.E. 450 and Hybond™-N had power densities between 12-14 milliWatts/m^2. By comparison Nafion's highest power density was 7.63 milliWatts/m^2.

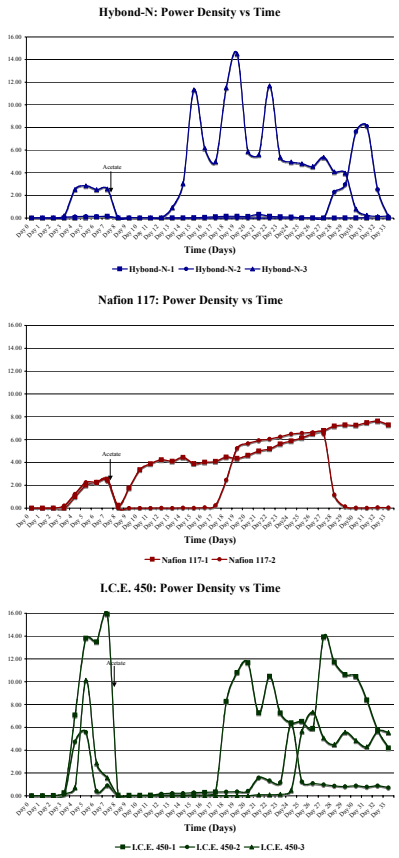

Fig. 5: These graphs show the power density of all 3 membranes in the MFCs. Hybond-N and I.C.E. 450, pore size of 45 microns, appear to perform better than Nafion-117, which has a pore size of 50 Å. However, Nafion-117 results are more consistent and smooth. The small pore size of Nafion 117 may block all waste impurities, whereas the I.C.E. 450 and Hybond actually trap impurities inside of the membranes. Thus, these membranes become clogged and interfere with the passage of protons to the cathode. This leaves the protons to recombine with the electrons in the anode chamber.

The Seneca Wastewater Treatment Plant performs chemical analysis on their raw influent wastewater before it is purified. I was able to obtain a pre and post analysis of the wastewater that I used in my MFC experiment. The table in figure 6 shows this analysis. The percent volatile solids decreased from 89.0 % to 47%. Note also that the suspended solids were reduced from 188 to 38 mg/L.

Comparison of Wastewater Analysis (Pre & Post)
(Analysis provided by Seneca WWTP)

Analysis Test	Pre-Test	Post-Test
Percent Volatitle Solids	89.00%	47.00%
Ammonia	27.17 mg/L	5.208 mg/L
Biochemical Oxygen	195.00 mg/L	ND
Nitrate + Nitrite	0.0058 mg/L	0.0192 mg/L
Suspended Solids	188.00 mg/L	38.00 mg/L
Kjeldahl Nitrogen	12.68 mg/L	7.769 mg/L
Phosphorus	5.33 mg/L	16.34 mg/L

Fig. 6: The % volatile solids and suspended solids were significantly reduced after 33 days of oxidation of organic materials in wastewater by microorganisms.

Discussion

Millions of dollars are spent each year to operate Wastewater Treatment Plants. I wished to utilize the bacteria found in wastewater to generate enough electricity to power a wastewater plant and successfully clean the water at the same time.

Although many people in the MFC area of research use different measures to increase the power output of their MFC, I felt it necessary not to add more expense to the wastewater MFC. Some of these expensive measures include the addition of metals to be utilized by specific bacteria.[6] Also, potassium ferricyanide is added to the cathode to accept electrons. It is very reactive with the graphite electrode. Ferricyanide has a fairly positive potential compared to the organic matter in the anode and helps to drive the flow of electrons. With the addition of ferricyanide ions, the power can be increased 50-80% over a MFC with dissolved oxygen.[4] L-cysteine-HCl added to the anode chamber is used to chemically scavenge the dissolved oxygen. Addition of cysteine increases power output by 7.8 mW/m^2.[7] Nitrogen

gas can be used to purge the anode chamber also. Efficiency in the MFC is increased by 47-55% compared to no gas sparging.[7] Addition of more wastewater, glucose or acetate feeding, and pure bacterial cultures inoculated into specific medium with growth factors, are other measures used to increase electrical output of MFCs.

MFCs powered by wastewater only in a two chamber MFC give approximately 26 milliWatts/m^2 power density.[8] The data reported from these MFCs were generated when the anode could be refilled repeatedly with wastewater until bacteria colonized on the electrode. I.C.E. 450 membrane MFC gave a power density of 15.92 milliWatts/m2 on day 7. Hybond™-N MFC peaked at 14.50 milliWatts/m^2 on day 19. Without the addition of chemicals, which increase the expense of a MFC, these two-chamber MFCs performed similarly to those noted in the literature.

It is important to look at each individual MFC setup and not the average of the setups because of the different progression rates of each system. During the first week, the I.C.E. 450 performed superior to the other setups. After the addition of sodium acetate, the readings decreased considerably. The addition of sodium acetate was to 'feed' the microorganisms. By doing this the bacteria would oxidize the acetate which would provide more electrons and increase the voltage of the setups. During the addition of the sodium acetate, oxygen was unfortunately let into the anode chamber. A decrease in voltage readings could be due to oxygen and the concentration and pH of the sodium acetate (5.2) on the anaerobic bacteria. Also, the addition of sodium acetate caused the cathode chamber to look cloudy as if the acetate crossed the membrane and precipitated out of solution in the PBS. However, not all of the acetate would have crossed the membrane and there would still be plenty of acetate for the microorganisms to oxidize. It was also noted that the cathode chambers of the Nafion-117 setups did not have a blurred look. I believe that the Nafion-117 membrane has a pore size that was too small for the sodium acetate to cross over.

After the addition of sodium acetate, the setups had some very significant results. Nafion-117 MFCs leveled off at 95-100 mVolts (6.6 milliWatts/m^2). One Hybond™-N (control) setup had erratic, but high voltage readings for several days and then leveled off at 85 mVolts (5-6 milliWatts/m2). The second control MFC finally showed voltage on day 27 which lasted about 5 days. The last Control did not perform well and had background readings only. The I.C.E. 450 membrane exceeded the Nafion-117 voltage with 95-110 mVolts (7 milliWatts/m^2). Two of the I.C.E. 450 setups eventually maximized at 100-145 mVolts (7.5-14 milliWatts/m^2).

My experiment has proven that Nafion-117, a proton exchange membrane, is not necessary in a microbial fuel cell. Voltage was measured in the MFCs with the cation-exchange membrane, I.C.E. 450, and a simple 0.45-micron filter membrane with no charge. The Nafion-117 membrane had a constant and stable production of voltage, while the other membranes had erratic voltage readings. The small pore size of Nafion 117 may block all waste impurities, whereas the I.C.E. 450 and Hybond actually trap impurities inside of the membranes. Thus, these membranes become clogged with impurities and interfere with the passage of protons to the cathode. This

leaves the protons to recombine with the electrons in the anode chamber.

Not having to use a PEM in a MFC will greatly reduce the cost of MFC engineering and make the possibility of taking MFCs from the lab setting and incorporating them into a onsite anaerobic wastewater treatment plant.

The second part of my question was whether I could clean the wastewater with the use of a MFC. Mr. Amad has told me that 50 million gallons of water are purified per day at his wastewater treatment plant. I am still a long way from being able to compete with such high scale water purification. Figure 6 shows a comparison of the amount of volatile and suspended solids in the wastewater that I obtained, pre and post-33 days in one of my MFCs. The reduction of volatile and suspended solids (89% to 47% and 188 to 38 mg/L) shows the MFCs reduced the amount of waste in the wastewater; thus cleaning it. Ammonia was oxidized to nitrate and the nitrate oxidized to nitrite by anaerobic nitrobacteria bacteria.

One very important observation on day eleven was the growth of fungi and algae on top of the wastewater, and I concluded that due to diffusion of oxygen into the system, artificial light, and wetness, that the conditions were optimal for their growth. According to researchers at the Ohio State University, it is possible that fungi can produce electricity in a MFC.[9] To test if this works, OSU scientists inhibited the growth and production of many species of bacteria by the addition of penicillin and streptomycin (broad-spectrum antibacterial) and found that electricity production was reduced, but not eliminated. To test this in my system, I picked one of the I.C.E. 450 MFC and added 100 mls of Penicillin-Streptomycin (P-S) (Gibco #1308; 10,000 units/ml Penicillin and 10,000 ug/ml Streptomycin) to give a final concentration of 1,000 units or mg per ml of P-S. There was a definite reduction in the voltage reading of that MFC in 24 hours, (108 to 24.4 mVolts); however, not as low as background readings. This could indicate that fungi and algae could also be used in a MFC design or that the P-S did not kill all the bacteria.

I predicted that the Nafion-117 would perform better than the other membranes in a 2-chamber MFC powered from wastewater. The Hybond™-N and I.C.E. 450 membranes performed adequately, but not as consistently as Nafion-117 over a period of 33 days. Not only was I able to obtain energy from the wastewater MFCs, I was able decrease the amount of solid waste in the wastewater.

Acknowledgements:

1. Amad, Sam, Plant Superintendent. Oamad@wsscwater.com.

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Citations:

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