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SELF-SUSTAINED DESALINATION IN COMBINATION WITH WASTEWATER TREATMENT – HYBRID MICROBIAL DESALINATION SYSTEM

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Abstract

Current desalination technologies are energy intensive and may hinder their practical applications to produce fresh water to communities. In our study, we evaluated the microbial desalination cell (MDC) as a new self-sustained desalination system. The principle of MDC is to use electricity-generating bacteria to consume organic matters in water and create an electrical field that separates salts in saline water. Most current MDC studies use easily degradable substrates such as glucose and sodium acetate. There have been limited studies conducted using wastewater as a substrate for real-world applications, especially for triple purposes of generating electricity, desalination, and wastewater reclamation as designed in our studies. Our experiments were conducted with three-cell MDCs and two-cell microbial fuel cells (MFC) as batch operation systems. Glucose and diluted wastewater were used as substrates to assess the system efficiency of using wastewater. The anion and cation exchange membranes were used to separate the anode, desalination, and cathode chambers. MFCs were used as control to investigate the impact of salt transport from desalination chamber to anode chamber on electricity generating performance and organic matters removal.

Evaluation of the experimental results demonstrates that MDC is a promising technology for self-sustained wastewater treatment and desalination. Desalination efficiency is closely related to the removal rate of organic matter and energy output. Less electricity was generated with wastewater compared to glucose, which may be caused by the large molecular size, complexity and refractoriness of the organic matters in wastewater. Transport of salt from desalination chamber to wastewater of lower conductivity in anode chamber enhanced the energy output of the MDC due to the increase of electrical conductance of the overall reactor. Future experiments should be conducted to improve MDC performance by evaluating the impact of competition of other bacteria in wastewater on electricity generation and COD removal. Preoxidation process should be tested to modify the biodegradability of wastewater for MDC

treatment. Chloride concentration may have complex impact on promoting or inhibiting the microbial activities in anode chamber depending on its concentration; thus there is a need of more studies to identify its impact on MDC performance.

1. Introduction

Water and energy are two of the greatest challenges facing humanity. Due to continued population growth, economic development, frequently occurring droughts, and other factors, the demand for freshwater and energy has increased significantly. However, freshwater resources are very limited, and these limited sources are further declining due to salinity buildup, contamination, and overdraft (USBOR and SNL, 2003). Desalination of impaired waters such as seawater, brackish water, and wastewater has been used to help provide a reliable water supply to address the global water crisis. Even though the desalination processes employing thermal and membrane technologies have been improved significantly in recent years, they are still considered energy and cost intensive (NRC, 2008). The need to provide fresh water, reduce energy demand, and address climate change associated with greenhouse gas emissions is putting pressure on the society.

A potential method of desalinating water without using external electricity is microbial desalination. This innovative technology can utilize microbes that feed on organic matter in water to generate electricity for desalination (Cao et al., 2009). In a bioelectrochemical system (such as microbial fuel cell (MFC)), bacteria capture and oxidize organic matter, releasing some of the electrons produced from cell respiration to the anode, where they flow through an external circuit to the counter-electrode (cathode) and create electrical current (Logan et al., 2006, Luo et al., 2011, Dewan et al., 2008). By inserting a pair of cation exchange membrane (CEM) and anion exchange membrane (AEM) in the microbial fuel cell reactor, with the AEM next to the anode and the CEM by the cathode, the middle chamber is able to desalinate salty water, such as sea water or brackish water (Figure 1). At the same time, the water in anode chamber is treated by removal of organic matter and other reducing substances from water. Microbial desalination cell (MDC) is similar to conventional desalination technology – electrodialysis in the fact that there is an electrical potential applied to drive salt ions out of desalination chamber, but instead of using an external source of electricity, energy for MDC desalination is achieved with the current and potential generated by the bacteria within the system. Therefore, the hybrid MDC

may provide a self-sustainable option to municipal and industrial wastewater treatment by recovering the energy stored in organic matter of wastewater while simultaneously achieving desalination goals.

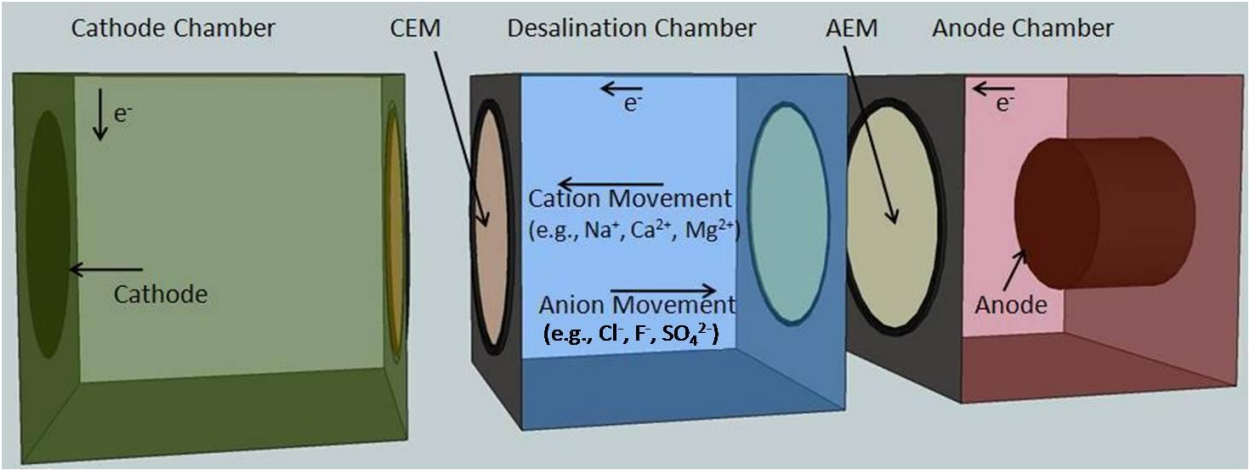

Figure 1. Schematic diagram of microbial desalination cell (MDC)

We believe that hybrid MDC can concurrently:

- Generate renewable electrical energy from wastewater
- Treat wastewater
- Desalinate brackish water without an external energy source and without additional carbon emission

However, MDC is a very new concept. Based on our extensive literature review, currently there is no reported study to power desalination system using the energy generated directly from MDC using municipal wastewater. Previous MDC studies used easily degradable substrates such as glucose and sodium acetate (Cao et al., 2009, Chen et al., 2011, Luo et al., 2011, Mehanna et al., 2010). Besides the simple and easily biodegradable organic substances, other waste materials, such as primary clarifier effluent (Liu et al., 2004) and cellulosic waste (Ren et al., 2007) have been used in MFCs for direct power and H_2 production.

The objective of the study is to demonstrate the feasibility of MDC as a self-sustained system for desalination and wastewater treatment. Primary wastewater was used as a substrate in both the MFC and MDC experiments in comparison with glucose substrate. MFC was used as a control to investigate the impact of salt passage to anode chamber on microbial activities.

2. Experimental Methods

2.1 MDC and MFC Construction

All experiments were conducted using 3-cell MDC reactors at a batch operation as shown in Figure 1. The MDC reactors were constructed from polycarbonate blocks. The chambers were produced by drilling a 3-cm diameter hole in each block (as shown in Figure 2). The three chambers were clamped together and divided by placing an AEM (AMI 7001, Membranes international, NJ) between the anode and middle desalination chambers and a CEM (CMI 7000, Membranes international, NJ) between the middle and cathode chambers. After inserting the electrodes, the volumes of the anode, middle, and cathode chamber were 140, 60, and 140 mL, respectively. Heat treated graphite brushes were used as the anode, and carbon cloth was selected as the cathode material. MFCs were constructed in an identical manner as MDC, but they had no desalination chamber and CEM was used to separate the anode and cathode chambers (as shown in Figure 3).

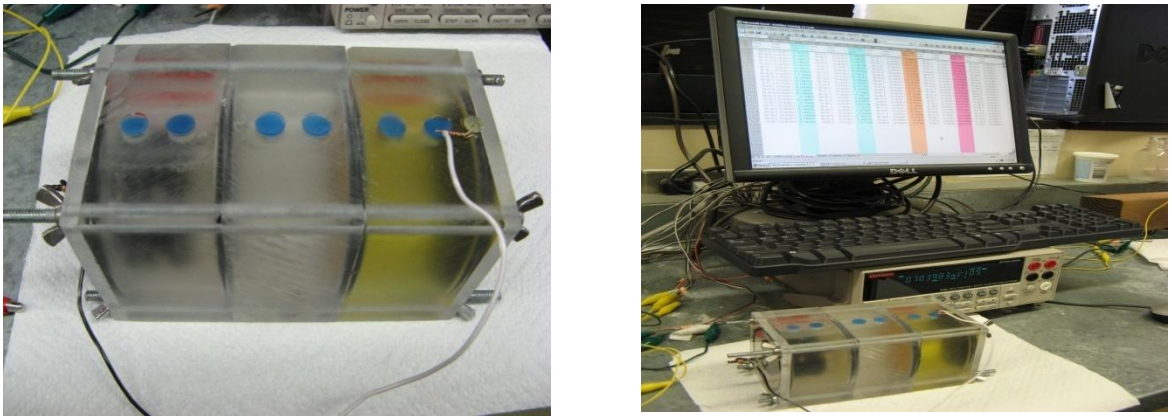

Figure 2. Pictures of experimental setup of microbial desalination cell (MDC)

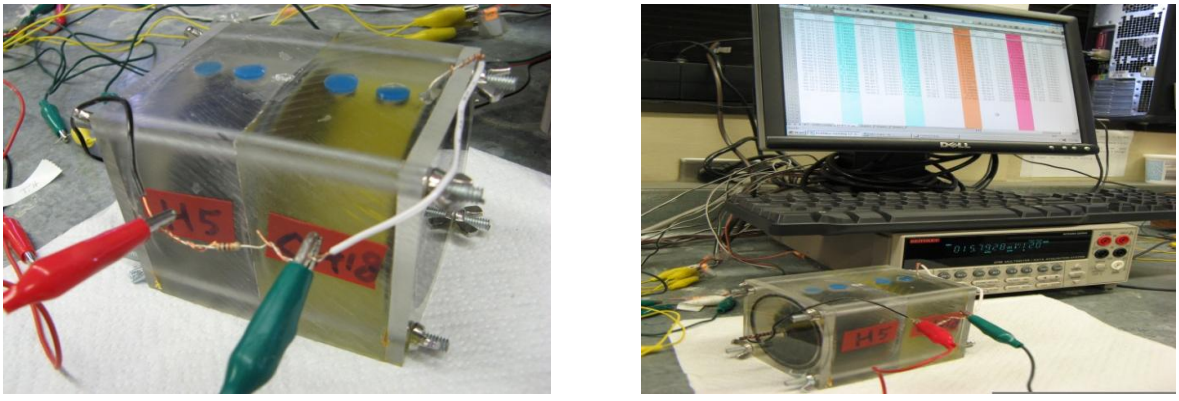

Figure 3. Pictures of experimental setup of microbial fuel cell (MFC)

2.2 MDC Operation

The reactors were inoculated from a mixed culture by transferring the anodes of the stable wastewater-fed MFCs to the MDC reactors. The artificial wastewater contained (per liter): $C_6H_{12}O_6$ 1 g, Na_2HPO_4 4.58 g, $NaH_2PO_4 \cdot H_2O$ 2.45 g, NH_4Cl 0.31 g, KCl 0.13 g, trace mineral solution 12.5 mL, and vitamin solution 12.5 mL. Domestic wastewater was collected from the Englewood City Government Wastewater Treatment Plant in Colorado. The wastewater was diluted with deionized (DI) water and then used as the anode medium. The cathode chamber was filled with 50 mM ferricyanide and 50 mM phosphate buffer solution (Na_2HPO_4 4.58 g/L, $NaH_2PO_4 \cdot H_2O$ 2.45 g/L, pH=7.0). The buffer solution was used to control the pH variations in the cells. The middle chamber was filled with artificial salt water contained NaCl solution (10 g/L). The MDCs were kept at room temperature (20^{o}C) throughout the entire experiment.

2.3 Data Collection

Desalination efficiency was measured by monitoring the conductivity in different chambers. Salt concentrations were evaluated by conductivity measurements using a conductivity meter (Sension 156, HACH Co., Loveland, CO). Organic matter in wastewater was measured using chemical oxygen demand (COD) using a COD analyzer. The voltage across an external resistor (1000 ohm) was recorded using a data acquisition system (model 2700, Keithley Instruments, Inc. OH).

2.4 Calculations

The removal efficiency of organics in terms of COD (R_{COD} in %) was calculated using the following equation:

$$R_{COD} = \frac{Ci - Ce}{Ci} \times 100 \qquad \text{(equation 1)}$$

where *Ci* is the influent COD concentration (mg/L) and *Ce* is the effluent COD concentration (mg/L).

The COD removal was further normalized by the time (T in day) of an operating cycle because the operating time of a cycle (voltage decreases to close to zero signifying the end of one experiment – one cycle) varied when treating different types of water. The rate of COD removal (R_{RCOD} in % removal per day) was calculated using the following equation:

$$R_{RCOD} = \frac{RCOD}{T}$$ (equation 2)

where R_{COD} is the COD removal (%) and T is the time of a MDC or MFC cycle (day).

The desalination efficiency (R_{del} in %) can be calculated using the following equation:

$$R_{del} = \frac{ECi - ECe}{ECi} \times 100$$ (equation 3)

where *ECi* is the influent electrical conductance (mS/cm) and *ECe* is the effluent electrical conductance (mS/cm).

Same as the COD removal rate, the salt removal was further normalized by the time (T in day) of an operating cycle. The rate of salt removal (R_{Rdel} in % removal per day) was calculated using the following equation:

$$R_{Rdel} = \frac{Rdel}{T}$$ (equation 4)

Voltage across the anode and the cathode was continuously monitored using a data acquisition system. Power output (P in walt) can be calculated using the following equation:

$$P = \frac{V^2}{R_{res}}$$ (equation 5)

where V is voltage of the cell (volt), and R_{res} is the external resistance (Ω). Power density (P_{den} in W/m^2/day) is the power output (P in walt) normalized by operating time T (day) and cathode surface area (A in m^2), which is calculated as

$$P_{den} = \frac{P}{A\,T}$$ (equation 6)

To calculate the power generation efficiency taking into account the organic carbon degradation, the power density was further normalized to the carbon removed in terms of grams of COD removed (P_{norm} in W/m^2/day/g) using the following equation:

$$Pnorm = \frac{Pden}{(Ci - Ce) \times L}$$ (equation 7)

where L is the volume of wastewater in the anode chamber.

2.5 Procedures

The experiments were designed to change only one variable at a time to identify the total electrical output of the MDC and the effectiveness of purifying different types of wastewaters (easily degradable simple organic substances such as glucose *versus* more refractory effluent organic matter in wastewater) and desalinating water.

Test 1: Test the performance of the MFC using diluted influent wastewater (initial COD 950 mg/L and conductivity 300 μS/cm). Fill the wastewater in the anode chamber of MFC, and cathode chambers with ferricyanide and buffer solution. Monitor the cell voltage, and COD concentration of the solution in the anode chamber.

Test 2: Test the performance of the MFC using diluted influent wastewater modified with NaCl solution (initial COD 950 mg/L and conductivity 900 μS/cm). Fill the wastewater solution in the anode chamber of MFC, and cathode chambers with ferricyanide and buffer solution. Monitor the cell voltage, and COD concentration of the solution in anode chamber.

Test 3: Test the performance of the microbial desalination cell (MDC) using synthetic wastewater (1g/L glucose, or ~1g/L COD). Fill the wastewater in the anode chamber of MDC, fill desalination chamber with NaCl concentration of 10 g/L (~ conductivity 20 mS/cm), fill cathode chamber with ferricyanide and buffer solution. Monitor the cell voltage, electrical conductance of the solution in desalination chamber, and COD concentration in anode chamber.

Test 4: Test the electrical output of the microbial desalination cell (MDC) using diluted influent wastewater (1g/L as COD) in the MDC. Fill the wastewater in the anode chamber of MDC, fill desalination chamber with NaCl concentration of 10 g/L, fill cathode chamber with ferricyanide and buffer solution. Monitor the cell voltage, electrical conductance of the solution in desalination chamber, and COD concentration of the solution in anode chamber.

3. Results and Discussion

The focus of the study is to demonstrate a new concept, the results generated in the experiments are used to prove that the MDC is an efficient method for desalinating saline water, generating electricity, and removing organic matter from wastewater. Also, these results can be used as a base for future research on MDC with wastewater as a substrate for University of Colorado at Denver, where this research project was conducted.

3.1 Electricity Generation

Figure 4 shows the energy output, in terms of voltage, of MFC and MDC using wastewater as substrate. The MDC generated more electricity than the MFC. This is likely attributed to the addition of the desalination function in the MDC. Since there was 10 g/L salt solution in the desalination chamber, the transport of chloride ions to anode chamber under the influence of generated electrical field increased the electrical conductance of wastewater in anode chamber as well as the MDC, which in turn, increased voltage generation. We achieved a maximum voltage of 0.41 V in the MDC using wastewater as substrate, which is comparable to the experiments by Liu et al. (2004), where the maximum voltage generation was 0.45 V using primary clarifier effluent as substrate in MFC.

Figure 5 compares the energy output, in terms of voltage, of MDC between wastewater and glucose substrates. The glucose substrate generated much more electricity than the wastewater substrate, but both were still able to desalinate brackish water in MDC. This difference in electricity generated is because glucose is a smaller molecule than the complex organic matters present in wastewater which makes it easier for the bacteria to consume. When the wastewater was used as substrate for MFC experiments, for the first two cycles (0-222 hours, and 222-430 hours), the two MFCs with wastewater or wastewater adjusted with NaCl exhibited very similar energy generation performance. For the third cycle (430-550 hours), the MFC with the addition of NaCl in wastewater generated much more energy than the one without addition of NaCl. It seems that energy generating bacteria needs two cycles to be acclimated to the presence of NaCl in water, and small amount of NaCl in anode solution can enhance the performance of MFC. This finding of MFC operation may imply that the MDC performance of treating wastewater and 10 g/L of NaCl might also be improved after the electricity generating bacteria are acclimated to the salt solution. The microbes in anode for MDC experiments were inoculated using glucose solution prior to the desalination experiments. Due to the time limit of the study, we were only able to run one cycle of the MDC experiment using wastewater, which was 573 hours. The longer operating time of a cycle is due to the refractoriness of the organic matter in wastewater as opposed to easily degradable glucose. Future experiments will be needed to investigate the long-term impact of salt transport from desalination chamber to anode and cathode chambers on microbiological activities and overall MDC performance.

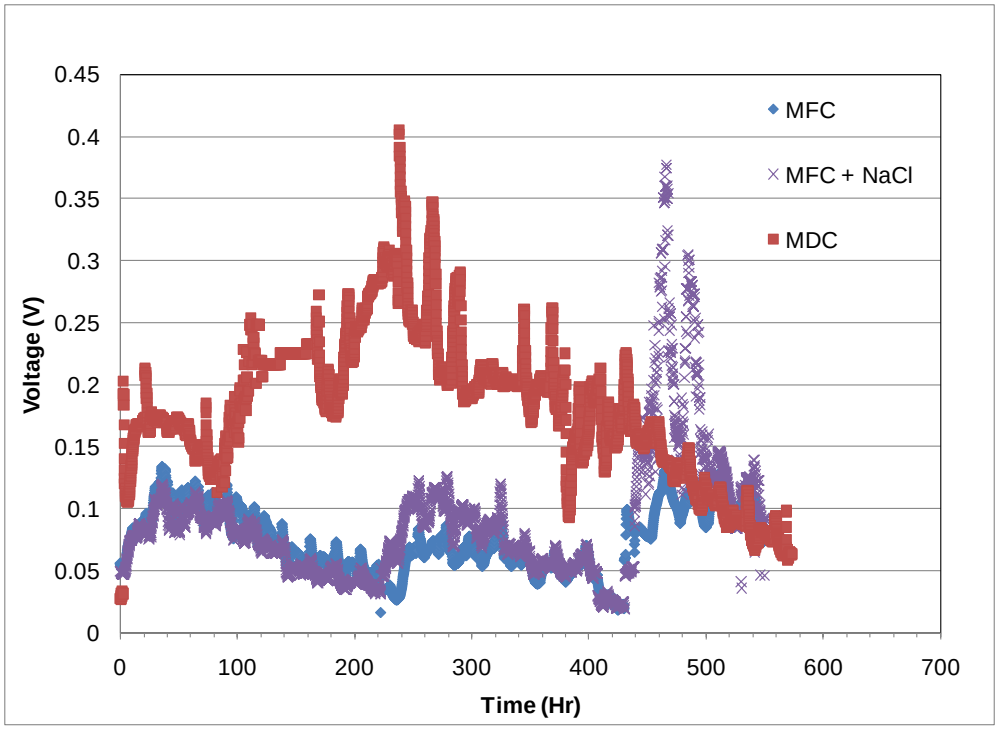

Figure 4. Energy generation of MFC versus MDC with diluted wastewater

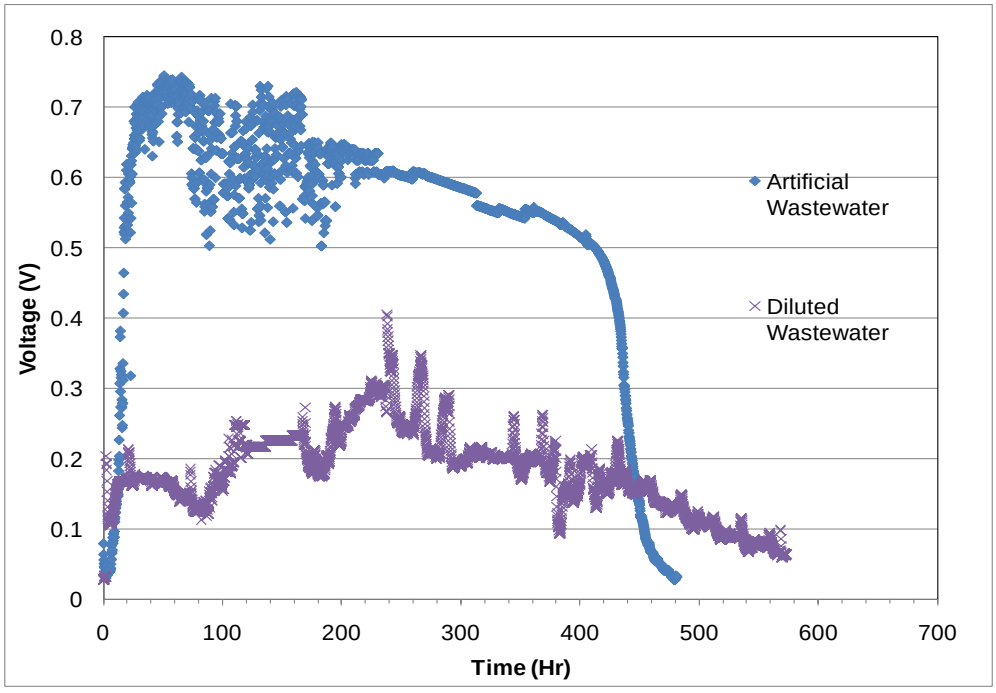

Figure 5. Comparison of energy generation of MDC with synthetic (glucose solution) and diluted wastewater

Table 1 summarizes the results of normalized energy production of MDC and MFC using glucose and wastewater as substrates. It is observed that the MDC with glucose generates the most voltage and power, followed by the MDC with wastewater, the MFC with wastewater and NaCl, and the least power-generating is the MFC with wastewater.

Table 1. Summary of normalized energy generation of MDC and MFC

	Microbial Fuel Cells		Microbial Desalination Cells	
	Diluted Wastewater	Diluted Wastewater and NaCl	Diluted Wastewater	Glucose solution
Average Voltage (V)	0.079	0.154	0.184	0.537
Power (mW/day)	1.788	4.227	5.765	40.305
Power Density (W/m^2/day)	2.531	5.982	8.160	57.049
Normalized Power Density to COD Removed (W/m^2/day/gram)	41.180	61.395	68.827	553.660

3.2 Wastewater Treatment

Totals of 85% and 74% of organic matter (in terms of COD) were degraded in MDC using wastewater and glucose as substrates, respectively. Figure 6 shows that the rate of COD removal is slightly faster for diluted wastewater as the substrate in the MDC (0.155 % per hr) as opposed to that of using glucose as substrate (0.144 % per hour). Reasons for this may be that there was a wide variety of microorganisms in wastewater substrate than in the synthetic wastewater that was prepared using deionized water and glucose of analytical grade. The bacteria in the diluted wastewater, which were more in quantity and species than in glucose solution, provided additional degradation of organic matter in wastewater. However, those non electricity generating bacteria might also compete with the electricity generating bacteria on the food

sources, thus resulting in lower energy output than using glucose as substrate in anode chamber (Table 1).

Figure 6 also revealed a higher rate of COD removal for diluted wastewater in the MFC (0.261 % per hour) and diluted wastewater with NaCl in MFC (0.441 % per hour) as opposed to diluted wastewater in the MDC (0.155 % per hour). It seems that the transport of large amount of chloride from the desalination chamber to the anode chamber (approximately 1.5 g/L chloride at the end of the MDC experiments using wastewater as anode substrate and initial 10 g/L NaCl solution in desalination chamber) might inhibit electricity generating bacterial activity, in turn inhibiting COD removal. In contrast, Figure 6 shows that the rate of COD removal was highest when diluted wastewater with addition of sodium chloride was used as substrate in the MFC. It seems lower concentration of chloride ions (about 0.23 g/L) promotes the activity of microorganisms including energy-producing bacteria. The higher rate of COD removal for diluted wastewater with sodium chloride (conductivity 0.9 mS/cm) in MFC in comparison with the rate of COD removal for diluted wastewater (conductivity 0.3 mS/cm) in MFC may be due to the higher concentration of sodium chloride in the anode chamber for the former. Although there is no study to investigate the impact of chloride concentration on electricity generating bacteria, it has been reported an increased concentration of sodium chloride, up to 0.30M, promotes bacterial growth (Sherman and Holm, 1922) while a higher concentration of chloride ions inhibits the activity of microorganisms (Kuwabe, 2000). Further studies are needed to prove our hypothesis and investigate the impact of chloride concentration on electricity generating bacteria.

3.3 Desalination

Using a diluted wastewater anode solution and a ferricyanide cathode solution, the MDC removed approximately 45% and 55% of the salt in the 10g/L NaCl solution over the period of thirteen days and three weeks, respectively. However, it is important to note that the rate of desalination decreases dramatically after 300 hours. This is due to the fact that the system desalinates water via an electric current. Furthermore, the rate of desalination was shown to be positively correlated to the voltage output of the system (Figure 7). Thus, after 300 hours of operation, the energy output started to decrease (Figure 5), resulting in the decrease of the driving force for desalination.

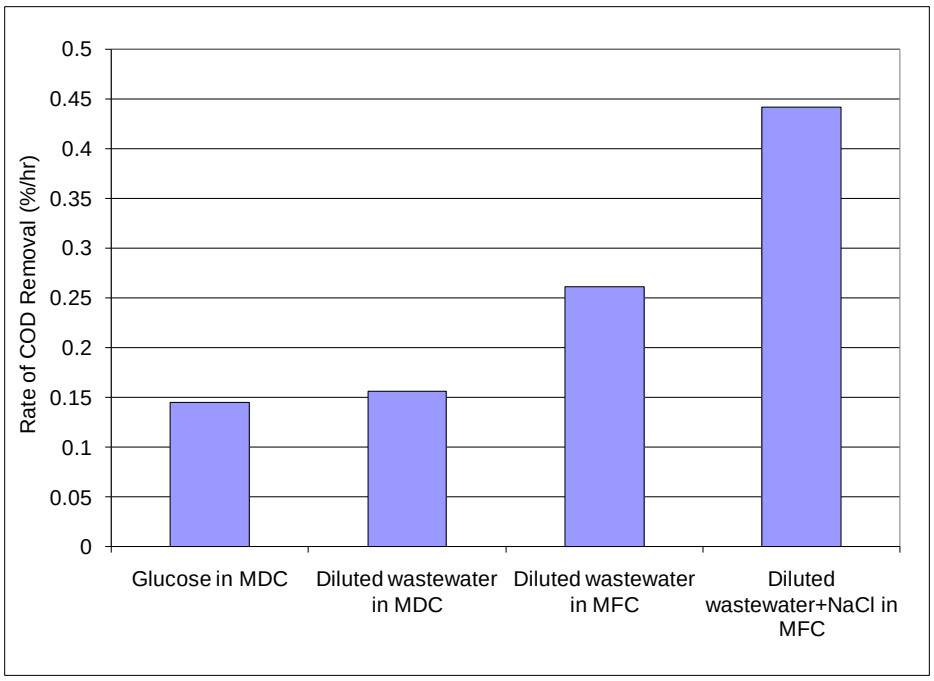

Figure 6. Removal rate of organic matter in MDC and MFC

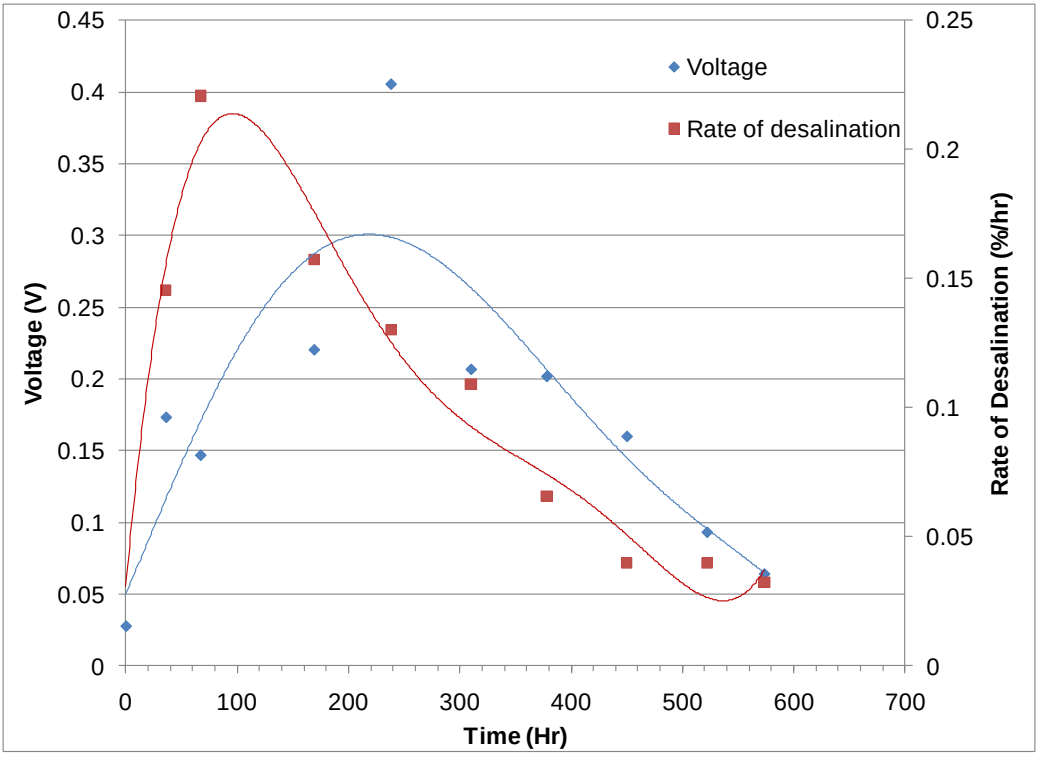

Figure 7. Rate of desalination compared to voltage output of MDC using diluted wastewater substrate

4. Conclusion

MDC is a promising technology for self-sustained wastewater treatment and desalination. Salt in brackish water and organic matter in wastewater were removed efficiently within MDC. This experiment concludes that, when using wastewater as substrate, MDC could generate more electricity, in terms of power density, than MFC as a result of increase of overall electrical conductance in the MDC reactor. Also, it shows that glucose substrate generated more electricity than a wastewater substrate because glucose is more easily biodegradable than the organic matters in wastewater which are more complex and refractory. But MDC using wastewater still generates electricity effectively to power the desalination of brackish water. The MDC system was able to remove 55% of the salt and 85% of organic matter over the course of a cycle using diluted wastewater.

Further experiments are needed to demonstrate our hypothesis that lower concentration of chloride can promote the growth of electricity generating bacteria while higher concentration of chloride inhibits the microbial activities in MFC and MDC. It is also recommended to evaluate the impact of preoxidation process on biodegradability of wastewater on the generation of electricity. Less electricity was generated with wastewater compared to glucose, which is caused by the large molecular size and complexity of organic matter in wastewater. Using pre-oxidation of wastewater might reduce the molecular complexity of wastewater organic matter and increase the biodegradability for electricity generation. Also, the reactor design of MDC needs to be improved and optimized, such as increase the contact and diffusion of organics matter with anode, and enhance the surface area of electrodes.

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