AN ABSTRACT OF THE DISSERTATION OF

Carole Abourached for the degree of Doctor of Philosophy in Water Resources Engineering and Biological and Ecological Engineering presented on March 20, 2014.

Title: Microbial Fuel Cell for Wastewater Treatment: Heavy Metal Removal, Sewage Sludge Treatment, and its Potential Application in Wastewater Reuse in Irrigation.

Abstract approved:

Hong Liu Marshall J. English

While water scarcity and energy demand are continuously increasing in the world, alternative sources are needed to meet the requirement of a growing population. Microbial Fuel Cell (MFC) is a sustainable technology that converts organic matter in wastewater into electricity, thus it can be a potential alternative source for water and energy. Although significant advances in MFC research have been accomplished in the last few years, improvement in power generation and decrease in material cost are still necessary to bring MFC into practical application. The main goal of this work is to contribute in making MFC more applicable in industrial and municipal facilities, and to evaluate its scaling up for real world application.

First, heavy metal removal by MFC was studied. Simultaneous high power generation (3.6 W/m^2) and high Cd (90%) and Zn (97%) removal efficiencies were achieved in a single chamber air-cathode microbial fuel cell (MFC). The maximum tolerable concentrations (MTCs) that did not affect power output were 200 µM for Cd and 400 µM for Zn. Gradual increase of metals concentrations lead to much slower reduction in voltage output. Biosorption and sulfides precipitation are the major mechanisms for the heavy metal removal in the MFCs. This study expanded MFC application for the treatment of industrial waste streams containing both organic matter and heavy metals.

Then, enhancement of sewage treatment by MFC was investigated. Although energy costs required for wastewater treatment are offset by methane production from sewage sludge treatment, not all the energy is extracted from sludge and effluents need additional treatment, such as aeration, to meet environmental regulations. MFC has been used to convert organic matter in sludge into electricity. However, improvement of power production is still needed. We studied the effect of fermentation pre-treatment and a novel design cloth-electrode assembly microbial fuel cell (CEA-MFC) on electricity production from sewage sludge. Fermentation pretreatment of sludge effectively increased the soluble organic matter and improved the reactor performance. The optimum fermentation time was 96 hours and resulted in maximum power density of 1200 mW/m^2, which is 275% higher than those previously reached in MFC systems. Thus, MFCs could be added successfully to existing wastewater treatment infrastructure for more efficient energy conversion.

Last, we examined the feasibility of using MFC technology for field application before irrigation. Although wastewater use in irrigation resolves the problem of water shortage, it also presents a threat to the environment. Thus, wastewater treatment before irrigation is needed. MFC has potential to treat wastewater and generate electricity simultaneously while leaving low residual concentrations of nutrients in the effluent. In order to investigate the economic returns from using MFC to treat wastewater before agricultural application, a case study involving food wastewater in a semi-arid region was considered. The various profits from treated water, produced electricity and nutrients in effluent were evaluated. The effluent water quality was compared to environmental regulations. The analysis showed that MFC is a promising technology that can resolve issues of water and energy shortage and thus can ensure food security.

Microbial Fuel Cell for Wastewater Treatment: Heavy Metal Removal, Sewage Sludge Treatment, and its Potential Application in Wastewater Reuse in Irrigation

by
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I understand that my dissertation will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my dissertation to any reader upon request.

Carole Abourached, Author

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CONTRIBUTION OF AUTHORS

Hong Liu provided invaluable expertise, experimental oversight and manuscripts revisions.

Marshall English provided very constructive guidance and revisions for the third manuscript.

Tunc Catal contributed in the first manuscript.

Keaton Lesnik contributed in the second manuscript.

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1. General Introduction

While the world population is growing, energy and water resources are becoming limited. These issues are causing concerns about global food security for the first time since the Green Revolution of the 1960's (Baulcombe, 2010). An additional challenge associated with population growth is the increase in wastewater generation and environmental pollution. To address those serious problems, advances in research have been made to improve water management and to make wastewater treatment more effective and efficient. Also, alternative renewable energy sources (bioenergy, geothermal, solar, wind etc.) have been investigated and applied.

Microbial fuel cell (MFC) is a sustainable technology that has potential to treat wastewater while producing electricity and thus providing a solution for water and energy shortages. Unlike some renewable energy sources competing with food production for land and water, MFC can use organics in waste streams as energy source and enhance food security by providing treated water that could be applied in irrigation. Figure 1.1 illustrates how an MFC system works. The bacteria on the MFC anode decompose organic matter in wastewater, liberating electrons that flow to the cathode through an external circuit and generate electricity. At the cathode, electrons, protons and oxygen form water (Oliveira et al., 2013). The reactions occurring at the anode and cathode are the following:

Anode: $C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^-$

Cathode: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

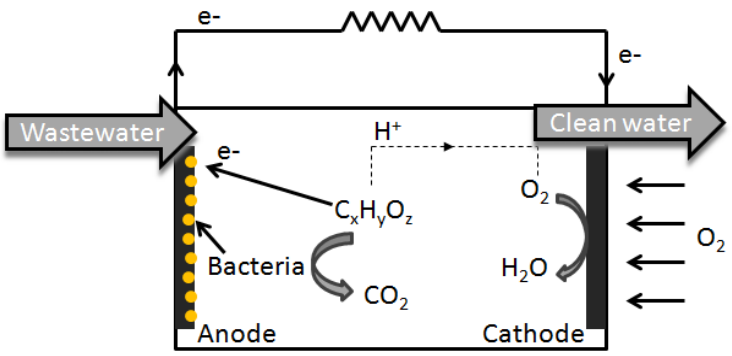

Figure 1.1: Microbial Fuel Cell diagram

Though it has been known that bacteria can produce electrical current (Potter, 1911), only in the last decade that research on MFCs for potential application in wastewater treatment and energy production has been conducted extensively (Liu et al., 2004), which resulted in large enhancements in MFC performance (Logan and Regan, 2006). The factors contributing to the improvements include the discovery of new electrochemically active bacterial species, the development of electrodes, and the modification of reactor design.

Electrochemically active bacteria have been also known as exoelectrogens, electricigens, and anode-respiring bacteria (Torres et al., 2007). The isolated electrochemically active bacteria belong to diverse genetic groups, including Firmicutes (Park et al., 2001), α-Proteobacteria (Zuo et al., 2008; Xing et al., 2008), β-Proteobacteria (Chaudhuri and Lovley, 2003), γ-Proteobacteria (Kim et al., 1999; Rabaey et al., 2004), δ-Proteobacteria (Bond et al., 2002; Pham et al., 2003; Holmes et al., 2004a; Holmes et al., 2004b), Acidobacteria (Bond and Lovley, 2005), and Actinobacteria (Wang et al., 2008). When grown as pure cultures, most of the microbes generate lower power than when grown as mixed cultures. This could be explained by the fact that mixed cultures

are more tolerant to oxygen and can use a variety of substrates compared to pure cultures. Such properties of mixed cultures allow them to use wastewater as fuel source (Rittman et al., 2008).

Electrodes is an additional factor affecting MFC performance. Electrodes include anode and cathode. Anode is usually formed of carbon-based materials because of their high conductivity, chemical stability, biocompatibility, and large surface area. Various carbon materials have been considered as anode electrodes for MFCs. So far, the highest power densities have been achieved with using carbon cloth anodes (Fan et al., 2008). The cathode is typically formed of a carbon base layer, a catalyst coating on the side facing the solution, and polytetrafluoroethylene (PTFE) diffusion layers on the air-facing side (Liu and Logan, 2004). Platinum was widely used previously as a cathode catalyst due to its high catalytic activity for oxygen reduction reaction. Since platinum is very expensive, extensive research efforts have tried to reduce the cathode material cost and to find alternative catalyst. Activated carbon proved to be effective catalyst resulting in comparable performance as Platinum at more affordable cost (Zhang et al., 2009).

MFC configurations that are most commonly used are formed either of one or two chamber MFCs. In two-chamber MFCs, anode and cathode chambers are separated by a membrane or salt bridge. The oxidant at the cathode could be ferricyanide or permanganate or others. Oxygen could be used as well but it is less efficient and requires energy for air sparging (You et al., 2006). Two-chamber MFCs are not sustainable due to the need of oxidant refilling in the cathode chamber (Pham et al., 2004).

In single chamber MFC, anode and cathode are in the same chamber but on opposite sides. A higher power density is obtained with single chamber MFC compared

to two chamber system due to a decrease in internal resistance. Single –chamber MFCs have also the advantage of being less expensive and simpler than double-chamber MFCs (Liu and Logan, 2004). Cloth Electrode Assembly (CEA) MFC is a single-chamber MFC where anode and cathode are separated by cloth layer (Figure 1.2). The minimum distance between the two electrodes reduces internal resistance and consequently, increases power production (Fan et al., 2007).

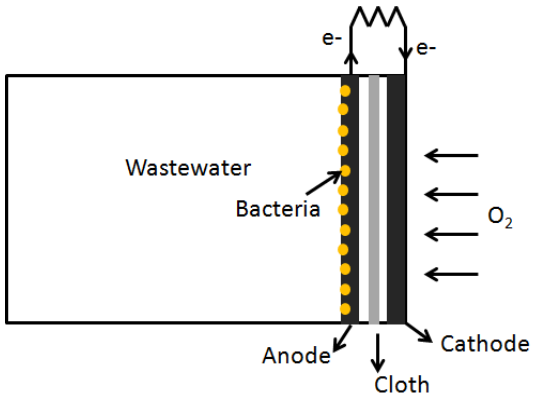

Figure 1.2: Schematic of CEA-MFC design

In spite of the significant research progress made on enhancing the power output, lowering the materials costs, and scaling up the MFC systems, many challenges are still to be faced for practical applications of MFC technology, especially for wastewater treatment. The objectives of this dissertation are to address the following important, but unanswered questions: (1) Can simultaneous heavy metal and organic matter removal be accomplished using MFC for treating waste streams containing both organics and heavy metals? (2) Does MFC have potential to be added to existing wastewater treatment infrastructure for sewage sludge treatment? (3) Is it economically feasible to use MFC for wastewater treatment before irrigation?

Heavy metal pollution is one of the most important environmental problems threatening public health. Physical, chemical and biological methods have been used for heavy metals removal from wastewater. Biological methods have demonstrated good performance while physical and chemical methods can be expensive or ineffective in removing low concentrations of metals. Chromium, copper, vanadium and mercury were effectively removed by MFCs but without consideration of removing organic matter simultaneously. However, numerous waste streams such as those from animal farms, petrochemical factory and rayon industry contain both organic matter and heavy metals. So, in order to be able to treat such wastewater sources, removal of both elements is necessary. The objective of our first study was to make MFC more applicable for treating industrial wastewater by removing both organic matter and metals. Cadmium and Zinc were studied as examples due to their different toxicity levels and redox potentials. The heavy metals removal efficacies and mechanisms as well as the effect of metals on power output were discussed in Chapter 2.

To further broaden MFC application, we also studied the use of the MFC technology in municipal facilities for sewage sludge treatment. While anaerobic digestion has been used effectively for treating sewage sludge and for energy extraction, large amounts of energy stay unrecovered in effluents and enhancement of energy conversion is required to offset treatment costs. In order to achieve this purpose, we investigated the feasibility of coupling MFC with anaerobic digestion through enhancing the power and energy output of MFC fed with sewage sludge. We employed fermentation pre-treatment of sludge because it increases soluble organic matter while being less energy intensive than other pre-treatment procedures. We used CEA-MFC configuration in this study

because of its low internal resistance and high power production potential. . The findings of the research are detailed in Chapter 3.

For further exploring real world application of MFC, we evaluated the possibility of coupling this technology with irrigation. Wastewater use in irrigation provides farmers with an alternative water source when water supplies are limited. In fact in some areas wastewater is the only remaining potential source of irrigation water. But, at the same time, wastewater could have a negative impact on the soil and plants because it could deteriorate the physical and chemical properties of the soil and consequently affect crop yield and quality. Adding high amounts of organic matter to the soil could result in biofilm formation, porosity reduction and aeration problems. High content of inorganic elements could cause chemical imbalance in the soil and nutrients deficiencies for the plants. Having heavy metals or organic pollutants in the wastewater would also present a threat to animal and human health. Thus, treatment of wastewater before its application on agricultural lands is necessary. Various reclamation methods have been applied for that purpose, for instance lagoon ponds, constructed wetlands, membrane filtration and others, but those methods are expensive or require large land areas. MFC presents an advantage over them by not only providing clean water to farmers but also generating electricity that can offset much of the treatment system cost. In addition, unlike other biofuel sources competing with food production for land areas and resources, MFC does not use agricultural lands. Another advantage of this application is helping industries with wastewater disposal. Also, because MFC does not remove organic matter and inorganic nutrients completely from wastewater, the residual nutrients could play the role of

fertilizers when applied to soil. In order to evaluate MFC use for wastewater treatment before irrigation, we conducted a partial economic analysis of a case study involving food wastewater in a dry region in the Colombia Basin of Oregon. The results of this study are presented in Chapter 4.

2. **Efficacy of Single-Chamber Microbial Fuel Cells for Removal of Cadmium and Zinc with Simultaneous Electricity Production**

Carole Abourached, Tunc Catal, Hong Liu

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2.1. Abstract

Simultaneous high power generation (3.6 W/m^2) and high Cd (90%) and Zn (97%) removal efficiencies were demonstrated in a single chamber air-cathode microbial fuel cell (MFC). The maximum tolerable concentrations (MTCs) were estimated as 200 μM for Cd and 400 μM for Zn. Increasing the concentrations of Cd to 300 μM and Zn to 500 μM resulted in voltage drops by 71 and 74%, respectively. Feeding the MFCs with incrementally increased Cd and Zn concentrations resulted in much slower reduction in voltage output. Biosorption and sulfides precipitation are the major mechanisms for the heavy metal removal in the MFCs.

2.2. Introduction

Heavy metal pollution is one of the most important environmental issues nowadays. Heavy metals present a serious danger to the environment and public health because of their toxicity, non-biodegradability and bio-accumulation (Guo et al., 2010). Physical, chemical and biological technologies are available for removing metals from wastewaters (Wang and Chen, 2009). The physical and chemical methods, such as chemical precipitation ion exchange, electrochemical treatment, reverse osmosis and evaporation recovery can be ineffective or very expensive especially if the metals concentrations are as low as 1-100 mg/L (Ahluwalia and Goyal, 2007). Biological materials including bacteria, algae, yeasts and fungi are available in large quantities and have demonstrated good performance in removing heavy metals (Volesky and Holan, 1995).

Microbial fuel cell (MFC) is a novel technology that can convert organic matter in wastewater into electricity (Liu and Logan, 2004, Cheng et al., 2006, Logan et al., 2006). Removal of metals, such as chromium, copper, vanadium and mercury has been studied using two-chamber MFCs, in which, heavy metals were removed in the anaerobic cathode chamber through cathode metal reduction while organics in the anodic chamber were used as carbon sources and electron donors (Wang et al., 2008; Li et al., 2008, Tandukar et al., 2009; Li et al., 2009, Huang et al., 2010, Heijne et al., 2010, Tao et al., 2011, Wang et al., 2011, Zhang et al., 2012a, Zhang et al., 2012b, Lefebvre et al., 2013). The cathodic medium solutions in these studies contained only heavy metals without organic compounds. Many waste streams, however, contain both heavy metals and organic substances such as those from animal farms, petrochemical factory and rayon industry (Price et al., 2001, Pathak et al., 2009, Malakahmad et al.,

2011, Ghosh et al., 2011). While it is well-known that electricity can be generated from various organic substances in wastewater using MFCs, it is still not clear how the presence of heavy metals affects power output and whether and how the heavy metals can be removed in the anodic chamber.

In this study, two heavy metals (Cd and Zn) were selected as representatives of hazardous heavy metals to investigate their impacts on power generation of single chamber membrane-less air-cathode MFC, an MFC type that has great potential to be scaled–up for practical wastewater treatment. These two heavy metals were selected due to their different toxicity levels and redox potentials. Cd is one of the most toxic heavy metals while Zn is one of the least toxic ones. The World Health Organization (WHO) and the US EPA limits for Cd and Zn in drinking water are 0.005 and 5 mg/L, respectively (Cazón et al., 2012). The heavy metals removal efficacies and mechanisms in the MFCs were also examined and discussed.

2.3. Material and methods

2.3.1. MFC Construction

Single chamber air cathode MFCs were constructed as described previously (Catal et al. 2008). The MFC consisted of a plastic (Plexiglas) cylindrical chamber (12 mL). The anode and cathode were placed in parallel on the opposite sides of the chamber with a spacing of 1.7 cm. The anode (1.8 cm^2) was made from type A carbon cloth (no wet proofing: E-Tek, USA) while the cathode (7cm^2) was made from type B carbon cloth (30% wet proofing; E-Tek, USA). The smaller anode surface area was selected in order to reduce the cathode limitation (Fan et al., 2008). The cathode was prepared by coating

1mg/cm^2 Pt catalyst on carbon cloth following the method previously reported (Cheng et al. 2006).

2.3.2. MFC Inoculation and Operation

The MFCs were inoculated with a mixed bacterial culture originally enriched from sewage sludge obtained from Corvallis Wastewater Treatment Plant (Corvallis, OR) and were operated in a batch fed mode using the medium with the following composition: 60 mM sodium acetate, 200 mM PIPES (piperazine-N,N′-bis(2-ethanesulfonic acid) buffer, and nutrients as described previously (Liu and Logan, 2004).

A series of tests were conducted to investigate the effects of Cd and Zn on the MFC performance and the removal of the heavy metals. Cadmium chloride and zinc sulfate were dissolved in the medium solution described above to obtain final concentrations of 200 μM, 300 μM, 400 μM and 500 μM of Zn and Cd. In the first set of experiments, the medium solutions containing different metal concentrations were added to individual MFCs and each MFC was operated for 10 batches to investigate the effects of the heavy metals (at a fixed concentration) on electricity generation and to determine the maximum tolerable concentrations (MTCs), the highest metal concentrations that do not inhibit the microbial culture for electricity generation. In the second set of experiments, heavy metal concentrations were increased gradually in an increment of 100 μM for the same MFC. The addition of heavy metal solutions continued until the maximum voltage output was reduced to 0.1V. Subsequently, the initial medium was added without heavy metals to investigate the possibility for voltage recovery. Some MFCs with mature biofilms on the anodes were autoclaved to investigate the heavy metal removal by

biosorption. Control experiments were also conducted by feeding MFCs with solutions only without adding the inoculum. All experiments were conducted in a temperature controlled chamber (32±1 °C).

2.3.3. Analyses

Cell voltages were recorded every 5 minutes using a multimeter with a data acquisition system (2700, Keithly, Cleveland, OH, USA). MFC voltages were assumed to be constant between readings. The power density was calculated according to P=I*V/A, where I is the current, V voltage, and A the projected area of the anode. Coulombic efficiency (CE) was determined by the ratio of total recovered coulombs to the theoretical amount of coulombs from acetate (Liu and Logan, 2004). Cd and Zn concentrations were analyzed using Inductively Coupled Plasma (ICP) Spectroscopy (Prodigy spec, Leeman Labs Inc., Hudson, NH, USA). Removal efficiencies of the heavy metals were calculated according to *(Ci – Ce)*100/ Ci*, where *Ci* and *Ce* are the metal concentrations in MFC influent and effluent, respectively.

2.4. Results and Discussion

2.4.1. Determination of external resistance for heavy metal experiments

To evaluate the anode at its optimal performance, the performance of the single chamber MFC was first evaluated at various external resistances. A maximum power density of 3.7 W/m^2 (based on anode surface area) was achieved at a current density of 11.7 A / m^2 when the external resistance was 150 Ω (Figure 2.1). Since the power output did not change significantly while varying the external resistance from 200 Ω to 100 Ω and to

avoid overshoot at high current density when heavy metals were added, 200 Ohms was selected for the subsequent experiments.

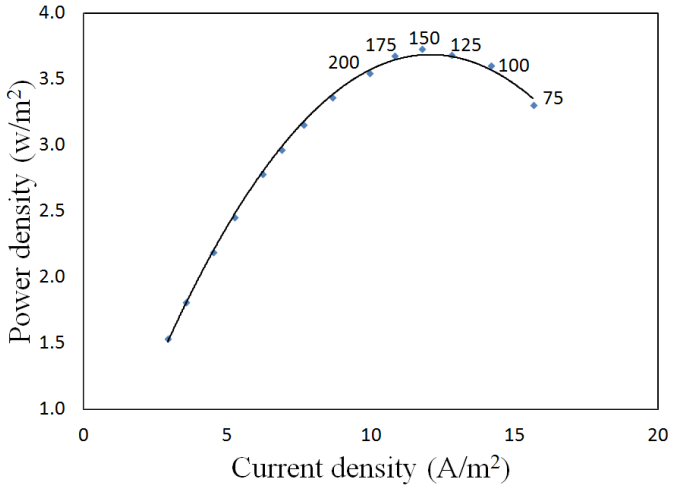


Figure 2.1: Polarization curve of the single-chamber MFC

2.4.2. Effects of Cd and Zn concentrations on MFC voltage output

The MTCs of Cd and Zn for the mixed culture at 200 Ω were estimated as 200 µM and 400 µM, respectively (Figures 2.2 and 2.3). The slight decrease in voltage output for the multiple batches operated under the same condition (Figures 2.2a, 2.3a, 2.3b and 2.3c) was possibly due to the formation of cathodic biofilm that reduces the cathode performance overtime, which was observed in our control experiment (data not shown) as well as reported by others (Yang et al. 2009). The maximum voltage (0.38 V corresponding to 4.0 W/m^2) dropped by 71% on the third batch when the MFC was fed with the medium solution containing 300 µM Cd (Figure 2.2b) and dropped by 74% on the second batch when fed with the solution containing 500 µM Zn (Figure 2.3d). The lower MTC of Cd than Zn in this experiment was consistent with some studies, in which Cd demonstrated higher toxicity to microbial species than Zn (Vullo et al., 2008; Cazón

et al., 2012; Norberg and Molin, 1983µM Cd and 382 µM Zn). However, some environmental bacterial strain, such as *Bacillus thuringiensis* S2 and *Proteus mirabilis* S19 showed more tolerance to Cd than Zn (Hassen et al., 1998).

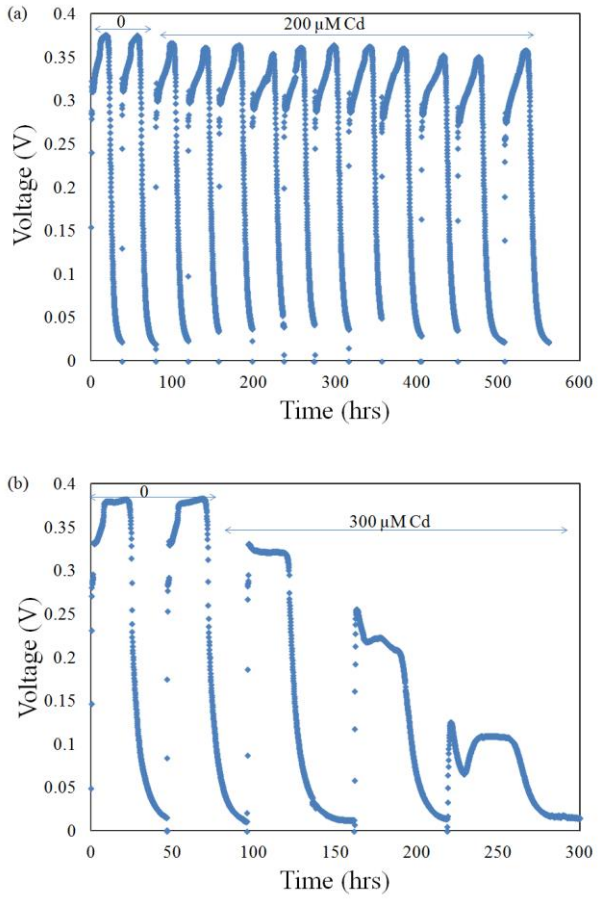
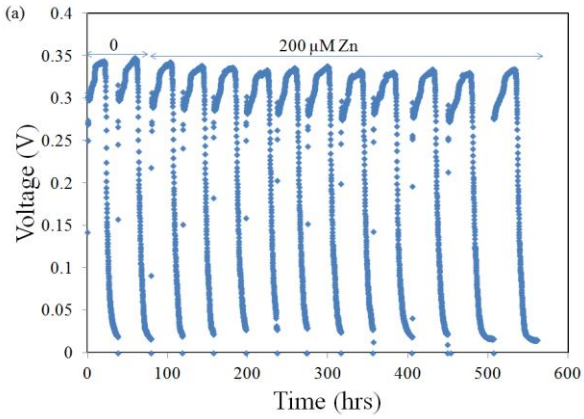
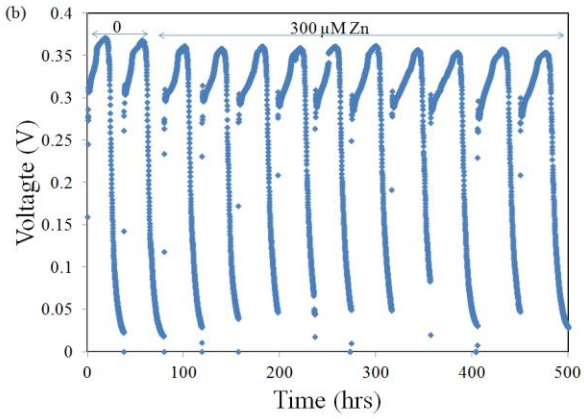


Figure 2.2: Voltage output with the addition of 200 and 300 µM Cd (200 Ω of external resistance).

The microbial community in this study is more tolerant to Cd and Zn than many bacterial strains enriched or isolated from wastewater or aerobic/anaerobic sludge. For example, a sulfate-reducing bacterial community enriched from anaerobic sludge has MICs of 180 µM for Cd and 300 µM for Zn (Hao et al., 1994) and several *Pseudomonas*

strains have MICs of 200 µM for both Cd and Zn (Hassen et al., 1998). It was also reported that 115 µM Zn can cause 50% inhibition of methane production by anaerobic granular sludge (Altas, 2009). However, a much higher tolerance to Cd and Zn was observed for some environmental bacterial strains such as *Pseudomonas aeruginosa* S6 (MIC of 1500 µM for Cd and Zn) and *Proteus mirabilis* S20 (MIC of 1200 µM for Cd and Zn) (Hassen et al., 1998). Bacterial strains isolated from industrial wastewater treatment plants also often have higher MICs of heavy metals (Muñoz et al., 2012).





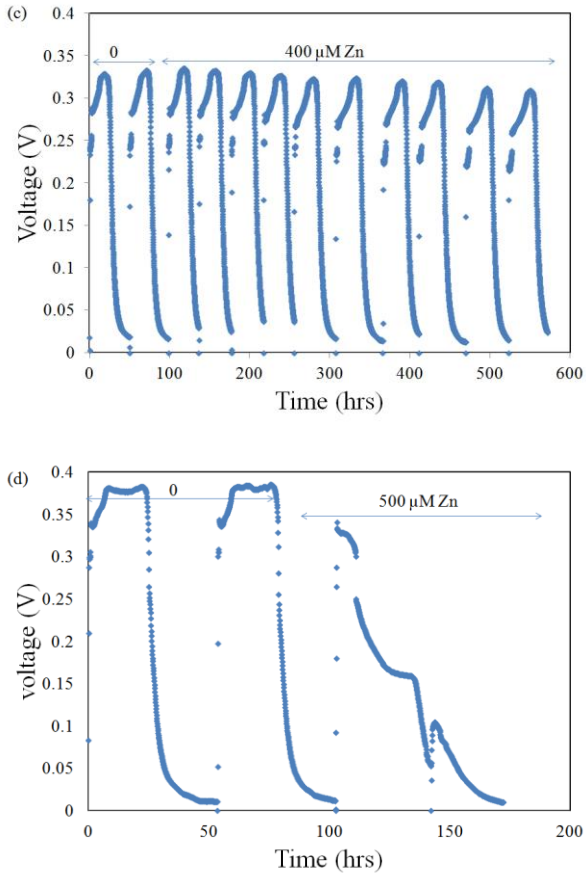


Figure 2.3: Voltage output with the addition of 200, 300, 400 and 500 µM Zn (200 Ω of external resistance).

2.4.3. Effects of incremental increase in Cd and Zn concentrations on MFC voltage output

Microbes may acclimate to medium solutions containing heavy metals and become more resistant to the toxicity of heavy metals if they were exposed to them at lower concentrations (Norberg and Molin, 1983). Gradual increase in Cd or Zn concentrations (with an increment of 100 µM) resulted in a much slower decrease in voltage output at concentrations higher than MTCs (Figures 2.4 and 2.5). The MFC voltage dropped to 0.1

V on the third batch when fed with a medium solution containing 300 µM Cd directly (Figure 2.2b). However, the same level of voltage drop occurred after 9 batches when the Cd concentration gradually increased. Similar results were obtained for the MFCs fed with Zn medium solutions.

After feeding the MFCs with the solutions containing Cd (300 µM) and Zn (500 µM) for 8-9 batches, the medium solutions were replaced with the original medium without Cd and Zn. The MFC voltages gradually increased and stabilized at 64% and 76% of the initial voltage, respectively (Figures 2.4 and 2.5). The less than 100% voltage recovery could be attributed to the acute toxicity of metals which inhibits the growth and reproduction of microorganisms resulting in a decrease in cell density and species richness (Kamika and Momba, 2011). Also, irreversible damage to microbial DNA could have been caused by heavy metals. Concentrations as low as 18µM Cd and 153 µM Zn caused 68% and 91% microbial DNA damage, respectively (Sheng et al., 2008).

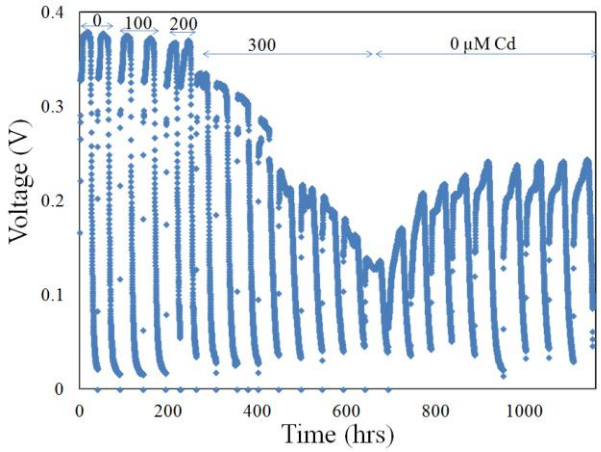


Figure 2.4: Effect of the gradual increase in Cd concentration on voltage output (200 Ω of external resistance).

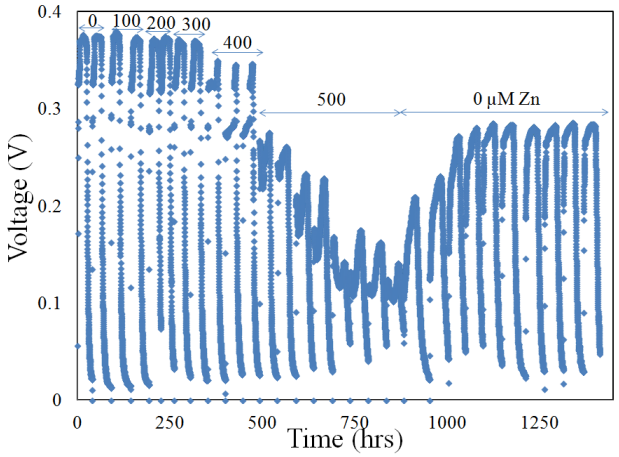


Figure 2.5: Effect of the gradual increase in Zn concentration on voltage output (200 Ω of external resistance).

2.4.4. Effects of Cd and Zn on MFC Coulombic efficiency

No drop in CE% was observed for MFCs with addition of both heavy metals at concentration lower than MTCs (200 µM Cd and 400 µM Zn). However, the addition of 300 µM Cd led to the reduction of CE from 34% to 18% after 3 batches (Figure 6).

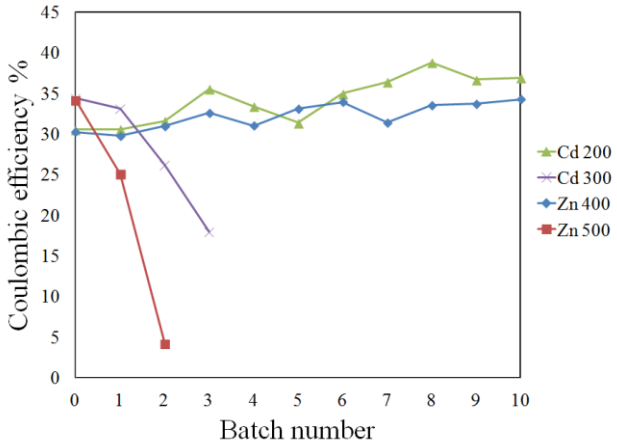


Figure 2.6: Coulombic efficiency variation with the successive batches of Cd and Zn

A similar result was obtained with Zn. The addition of 500 mM Zn toxic level resulted in a reduction of CE from 34% to 4% after 2 batches. The slight changes of CEs and voltage output at the concentration lower than MTCs and the significant drops at concentrations over the MTCs suggest that the heavy metals mainly affected the MFC anode performance through their toxic inhibition to anodic microbes rather than competing with the MFC anode for electron acceptance.

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2.4.5. Cd and Zn removal

Although the power density and CE were much lower for the MFCs fed with 300 µM Cd than those fed with 200 µM Cd, the average Cd removal efficiencies at the end of the batch were over 89% at both initial concentrations for all batches. Similarly, the average Zn removal efficiencies were over 94% for all batches for the MFCs fed with 400 µM and 500 µM medium solutions (Table 2.1). The high Cd and Zn removal efficiencies in this study are comparable to those using many other heavy metal wastewater treatment techniques at similar initial concentrations (Fu and Wang, 2011). The metals removal efficiencies by the autoclaved MFCs started at 80-91% for the first batch then decreased to 43-72% for the third batch.

There are several mechanisms that might contribute to heavy metal removal in the MFCs. The high metal removal in the autoclaved MFC with non-living microbial cells suggests that biosorption is an important mechanism for the heavy metal removal in the tested system, at least for the first few batches. The term biosorption here is used as a general term and may include several passive i.e. non-metabolic mechanisms involving biomass, such as complexation, chelation, coordination, ion exchange, and

microprecipitation. Both living and non-living cells can remove metals by biosorption mainly due to the functional groups (carboxylate, hydroxyl, phosphate, amine and sulfate) of polysaccharides, proteins and lipids on the bacterial cell walls (Vullo et al., 2008). Phospholipids and lipopolysaccharides are considered as the main molecules contributing in biosorption in gram-negative bacteria (Masoudzadeh et al., 2011). Bacterial metallothioneins, cysteine-rich proteins also have unparalleled capacity to bind metal ions (Valls and Lorenzo, 2002). Extracellular polymeric substances (EPS), mostly composed of polysaccharides and proteins, can also remove metal ions through complexation (Katsou et al., 2011).

Table 2.1 Cd and Zn removal (%) in MFCs.

Treatment	Batch number	Cd 200 µM	Cd 300 µM	Zn 400 µM	Zn 500 µM
MFC	1	91	92	97	99
	2	90	89	98	98
	3	90	90	97	100
	4	89	-	98	-
	5	89	-	98	-
	6	90	-	97	-
	7	90	-	98	-
	8	90	-	97	-
	9	89	-	94	-
	10	90	-	96	-
Autoclaved MFC	1	82	80	91	81
	2	82	71	82	73
	3	75	65	72	43

Note: Batches 4-10 for Cd 300µM and Zn 500µM were not conducted due to the low power output in batches 1-3.

Metal precipitation due to the presence of some inorganic anions in the solution may also contribute to the metal removal in this study. Yellow and white precipitates were also observed in the effluents of the MFCs fed with Cd and Zn, respectively. These precipitates are probably CdS (solubility constant $8x10^{-28}$) and ZnS (solubility constant $2x10^{-25}$), which were formed by combining metal ions with sulfide, generated from sulfate (354 μM in the medium solution) reduction under anaerobic condition (Valls and Lorenzo, 2002). Due to a slight change in solution pH (influent pH 6.8; effluent pH 7.1), the metals precipitation in the form of hydroxides should not contribute to the heavy removal significantly, although it is possible that small amount of metal hydroxides may be formed near/on the cathode inner surface due to the increased local pH. While metal ions with high standard potentials may compete with the anode to accept electrons directly from bacteria, the low standard potentials of Cd^{2+}/Cd and Zn^{2+}/Zn (equations 1, 2) make their reduction into elemental metals difficult. It is also difficult for them to compete with oxygen on the cathode due to the high cathode potential set by oxygen (equation 3).

$$Cd^{2+}_{(aq)} + 2e^{-} \Rightarrow Cd_{(s)} \quad E^0 = -0.4V \quad (1)$$

$$Zn^{2+}_{(aq)} + 2e^{-} \Rightarrow Zn_{(s)} \quad E^0 = -0.764V \quad (2)$$

$$O_{2\,(g)} + 4H^{+}_{(aq)} + 4e^{-} \Rightarrow 2H_2O_{(l)} \; E^0 = +0.8\ V \quad (3)$$

2.5. Conclusions

- Simultaneous high power generation (3.6 W/m^2) and high Cd (90%) and Zn (97%) removal efficiencies can be achieved in single chamber air-cathode microbial fuel cells.

- The estimated MTCs of Cd and Zn for the electrochemically active microorganisms in the single chamber MFCs were 200 μM and 400 μM, respectively.
- Incremental increase in Cd and Zn concentrations can result in slower reduction in voltage output.
- Heavy metals affected the MFC anode performance mainly through their toxic inhibition to anodic microbes rather than competing with the MFC anode for electron acceptance.
- The high heavy metal removal efficiencies were accomplished mainly through biosorption and sulfides precipitation.

2.6. Acknowledgments

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2.7. References

Ahluwalia, S.S., Goyal, D., 2007. Microbial and plant derived biomass for removal of heavy metals from wastewater. Bioresource Technology 98, 2243–2257.

Altaş, L., 2009. Inhibitory effect of heavy metals on methane-producing anaerobic granular sludge. Journal of Hazardous Materials 162, 1551–1556.

Catal, T., Xu, S., Li, K., Bermek, H., Liu, H., 2008. Electricity generation from polyalcohols in single-chamber microbial fuel cells. Biosensors and Bioelectronics 24, 849–854.

Cazón, J. P., Bernardelli, C., Viera, M., Donati, E., Guibal, E., 2012. Zinc and cadmium biosorption by untreated and calcium-treated Macrocystis pyrifera in a batch system. Bioresource Technology 116, 195–203.

Cheng, S., Liu, H., Logan, B.E., 2006. Increased performance of single-chamber microbial fuel cell using an improved cathode structure. Electrochemistry Communications 8, 489–494.

Fan, Y., Sharbrough, E., Liu, H., 2008. Quantification of the internal resistance distribution of microbial fuel cells. Environmental Science and Technology 42(21), 8101–8107.

Fu, F., Wang, Q., 2011.Removal of heavy metal ions from wastewaters: A review. Journal of Environmental Management, 92, 407–418.

Ghosh, P., Samanta, A.N., Ray, S., 2011. Reduction of COD and removal of Zn2+ from rayon industry wastewater by combined electro-Fenton treatment and chemical precipitation. Desalination, 266, 213–217.

Guo, H., Luo, S., Chen, L., Xiao, X., Xi, Q., Wei, W., 2010. Bioremediation of heavy metals by growing hyperaccumulaor endophytic bacterium *Bacillus sp.* L14. Bioresource Technology, 101, 8599–8605.

Hao, O.J., Huang, L., Chen, J.M., Buglass, R.L., 1994. Effects of metal additions on sulphate reduction activity in wastewaters. Toxicological and Environmental Chemistry, 46, 197–212.

Hassen, A., Saidi, N. Cherif, M. Boudabous, A., 1998. Resistance of environmental bacteria to heavy metals. Bioresource Technology 64, 7–15.

Heijne**,** A., Liu**,** F., Weijden**,** R., Weijma**,** J., Buisman**,** C.J.N., Hamelers**,** H. V.M.**,** 2010. Copper recovery combined with electricity production in a microbial fuel cell. Environmental Science and Technology 44, 4376–4381.

Huang, L., Chen, J., Quan, X., Yang, F., 2010. Enhancement of hexavalent chromium reduction and electricity production from a biocathode microbial fuel cell. Bioprocess and Biosystems Engineering 33, 937–945.

Kamika, I., Momba, M.N.B., 2011. Comparing the tolerance limits of selected bacterial and protozoan species to nickel in wastewater systems. Science of the Total Environment 410–411, 172–181.

Katsou, E., Malamis, S., Loizidou, M., 2011. Performance of a membrane bioreactor used for the treatment of wastewater contaminated with heavy metals. Bioresource Technology 102, 4325–4332.

Lefebvre, O., Tan, Z., Shen, Y., Ng, H.Y., 2013. Optimization of a microbial fuel cell for wastewater treatment using recycled scrap metals as a cost-effective cathode material. Bioresource Technology 127, 158–164.

Li, Y., Lu, A., Ding, H., Jin, S., Yan, Y., Wang, C., Zen, C., Wang, X., 2009. Cr (VI) reduction at rutile-catalyzed cathode in microbial fuel cells. Electrochemistry Communications 11, 1496–1499.

Li, Z., Zhang, X., Lei, L., 2008. Electricity production during the treatment of real electroplating wastewater containing Cr6+ using microbial fuel cell. Process Biochemistry 43, 1352–1358.

Liu, H., Logan, B.E., 2004. Electricity generation using an air-cathode single chamber microbial fuel cell in the presence and absence of a proton exchange membrane. Environmental Science and Technology 38, 4040–4046.

Logan, B. E., Hamelers, B., Rozendal, R., Schroder, U., Keller, J., Freguia, S., Aelterman, P., Verstraete, W., Rabaey, K., 2006. Microbial fuel cells: Methodology and technology, Environmental Science and Technology 17, 5181–5192.

Malakahmad, A., Hasani, A., Eisakhani., Isa, M.H., 2011. Sequencing Batch Reactor (SBR) for the removal of Hg^{2+} and Cd^{2+} from synthetic petrochemical factory wastewater. Journal of Hazardous Materials 191, 118–125.

Masoudzadeh, N., Zakeri, F., Lotfabad, T.B., Sharafi, H., Masoomi, F., Zahiri, H. S., Ahmadian, G., Noghabi K.A., 2011. Biosorption of cadmium by Brevundimonas sp. ZF12 strain, a novel biosorbent isolated from hot-spring waters in high background radiation areas. Journal of Hazardous Materials 197, 190–198.

Muñoz, A.J. Ruiz, E. Abriouel, H. Gálvez, A. Ezzouhri, L. Lairini, K. Espínola, F., 2012. Heavy metal tolerance of microorganisms isolated from wastewaters: Identification and evaluation of its potential for biosorption. Chemical Engineering Journal 210, 325–332.

Norberg, A.B., Molin, N., 1983. Toxicity of cadmium, cobalt, uranium and zinc to Zoogloea ramigera. Water Research 17, 1333–1336.

Pathak, A., Dastidar, M.G., Sreekrishnan, T.R., 2009. Bioleaching of heavy metals from sewage sludge: A review. Journal of Environmental Management 90, 2343–2353.

Price, M. S., Classen, J. J., Payne, G. A., 2001. *Aspergillus niger* absorbs copper and zinc from swine wastewater. Bioresource Technology 77, 41–49.

Sheng, Z., Wei, C., Liao, C., Wu, H., 2008. Damage to DNA of effective microorganisms by heavy metals: Impact on wastewater treatment. Journal of Environmental Sciences 20, 1514–1518.

Tandukar, M., Huber, S.J., Onodera, T., Pavlostathis, S., 2009. Biological chromium (VI) reduction in the cathode of a microbial fuel cell. Environmental Science and Technology 43, 8159–8165.

Tao, H. C., Liang, W., Li, W., Zhang, L.J., Ni, J.R., Wu, W.M., 2011. Removal of copper from aqueous solution by electrodeposition in cathode chamber of microbial fuel cell. Journal of Hazardous Materials 189, 186–192.

Valls, M., Lorenzo, V., 2002. Exploiting the genetic and biochemical capacities of bacteria for the remediation of heavy metal pollution. FEMS Microbiology Reviews 26, 327–338.

Volesky, B., Holan, Z.R., 1995. Biosorption of heavy metals. Biotechnology Progress 11, 235–250.

Vullo, D.L., Ceretti, H.M., Daniel, M.A., Ramírez, S.A.M., Zalts, A., 2008. Cadmium, zinc and copper biosorption mediated by *Pseudomonas veronii* 2E. Bioresource Technology 99, 5574–5581.

Wang, G., Huang, L., Zhang, Y., 2008. Cathodic reduction of hexavalent chromium [Cr(VI)] coupled with electricity generation in microbial fuel cells. Biotechnology Letters 30, 1959–1966.

Wang, J., Chen, C., 2009. Biosorbents for heavy metals removal and their future. Biotechnology Advances 27, 195–226.

Wang, Z., Lim, B., Choi, C., 2011. Removal of Hg^{2+} as an electron acceptor coupled with power generation using a microbial fuel cell. Bioresource Technology 102, 6304–6307.

Yang, S., Jia, B., Liu, H., 2009. Effects of the Pt loading side and cathode-biofilm on the performance of a membrane-less and single-chamber microbial fuel cell. Bioresource Technology 100, 1197–1202.

Zhang, B., Feng, C., Ni, J., Zhang, J., Huang, W., 2012a. Simultaneous reduction of vanadium (V) and chromium (VI) with enhanced energy recovery based on microbial fuel cell technology. Journal of Power Sources 204, 34–39.

Zhang, L.J., Tao, H.C., Wei, X.Y., Lei, T., Li, J.B., Wang, A.J., Wu, W.M., 2012b. Bioelectrochemical recovery of ammonia–copper (II) complexes from wastewater using a dual chamber microbial fuel cell. Chemosphere 89, 1177–1182.

3. Enhanced Power Generation and Energy Conversion of Sewage Sludge by CEA-Microbial Fuel Cells

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3.1. Abstract

The production of methane from sewage sludge through the use of anaerobic digestion has been able to effectively offset energy costs for wastewater treatment. However, significant energy reserves are left unrecovered and effluent standards are not met necessitating secondary processes such as aeration. In the current study a novel cloth-electrode assembly microbial fuel cell (CEA-MFC) was used to generate electricity from sewage sludge. Fermentation pretreatment of the sludge effectively increased the COD of the supernatant and improved reactor performance. Using the CEA-MFC design, a maximum power density of 1200 mW m^{-2} was reached after a fermentation pre-treatment time of 96 hours. This power density represents a 275% increase over those previously observed in MFC systems. Results indicate continued improvements are possible and MFCs may be a viable modification to existing wastewater treatment infrastructure.

3.2. Introduction

Accounting for 3-5% of the total electrical load in developed countries, conventional wastewater treatment is both an energy intensive and expensive process (Global Water Research Coalition, 2008). However, wastewater itself is intrinsically rich in energy, estimated to have an energy content 9.3 fold greater than the energy necessary to treat it (Shizas and Bagley, 2004). Approximately 66% of this energy is stored in sludge following treatment and further developing technologies capable of extracting energy from the organic material in sludge is key to decreasing external energy demands and overall treatment costs of wastewater treatment (Ting and Lee, 2007).

Energy usage of wastewater treatment plants (WWTP) can range from 0.4 to 1.4 kWh m^{-3}. While there are many technologies capable of extracting energy from sludge to offset this energy demand, anaerobic digestion has seen the most widespread application (Curtis, 2010; Tyagi and Lo, 2013). Anaerobic digesters are able to convert about 28% of the energy potential of the biodegradable organics in wastewater to electricity through generation and subsequent combustion of CH_4 biogas, meeting roughly a quarter to almost half the energy needs of an average WWTP (0.6 kWh m^{-3}) (McCarty et al., 2011). Though anaerobic digestion is a proven technology, significant energy reserves are left unrecovered, and effluent standards are not met necessitating secondary processes such as aeration. Further developing nascent wastewater technologies with the potential for increased energy efficiency can greatly decrease wastewater treatment costs.

Microbial fuel cells (MFCs) are able to the convert the potential energy of a wide range of organics directly into electricity (Pant et al., 2010). Various sludge types were tested directly in MFCs, including raw sludge (Jiang et al., 2009; Mohd Yusoff et al.,

2013; Xiao et al., 2011), primary sludge (Ge et al., 2013; Zhang et al., 2012), digested sludge from anaerobic digesters (Ge et al., 2013; Hu, 2008; Xiao et al., 2011) and membrane bioreactors (Su et al., 2013; Wang et al., 2013), as well as a mixture of primary sludge with primary effluent (Yang et al., 2013). However, coulumbic efficiencies were low (2.6 to 7.2%) and volumetric power densities observed (3.2 to 6.4 W m^{-3}) were a small fraction of what is achievable in MFC systems (2700 W m^{-3}) (Fan et al., 2012; Ge et al., 2013). Poor performance can be partly attributed to low concentrations of dissolved organics and well as inefficient reactor design.

In order to improve MFC power generation from sludge treatment, various sludge pretreatment procedures have been explored to increase dissolved organic concentrations, including sonication (Jiang et al., 2009), sterilization (Xiao et al., 2011), basification (Xiao et al., 2011), ozonation (Mohd Yusoff et al., 2013), the use of microwaves (Mohd Yusoff et al., 2013), and fermentation (Yang et al., 2013). Fermentation was not only highly effective at solubilizing organics, but less energy intensive than other pretreatment processes (Mohd Yusoff et al., 2013). The power density (340 mW m^{-2}) of a fermented sludge supernatant/primary effluent solution is much higher than that without the fermented sludge pretreatment. However adding phosphate buffer to fermented sludge solutions doubled or tripled power densities (870 – 1030 mW m^{-2}), indicating that lowering the internal resistance of MFC would be key for further increasing the power generation from pre-treated sludge (Yang et al., 2013).

A novel cloth electrode assembly (CEA) MFC has recently demonstrated high power while operated in both batch (1800 mW m^{-2}) and continuous flow modes (4300 mW m^{-2}) (Fan et al., 2012, 2007). Therefore this design and it's associated community

has the potential to generate high power using waste streams without high conductivity (Fan et al., 2007). However, this reactor setup has not been evaluated using a real waste stream.

In the present study, CEA-MFCs were used to investigate the possibility of generating high power outputs from fermented primary sludge. Optimization of fermentation time was also conducted to increase the concentrations of easily degradable compounds. The feasibility and efficiency of integrating MFC and anaerobic digestion treatment processes was also evaluated.

3.3. Materials and Methods

3.3.1. Sludge Collection and Fermentation

Sewage sludge was collected from the secondary sedimentation tank of the Corvallis

Wastewater Treatment Plant (Corvallis, OR, USA). The sludge was fermented in the dark at 32 ± 2 ºC after purging with nitrogen gas for 10 minutes. Samples were collected at 0, 48, 192, and 288 hours, centrifuged at 4000 rpm for 20 minutes, filtered, and adjusted to pH 7.0 using NaOH for MFC experiments.

3.3.2. MFC Design and Operation

A cloth-electrode assembly (CEA) MFC design was used to investigate power generation from fermented sludge (Fan et al., 2008). Anodes were carbon cloth with no wet proofing (type B, E-TEK, USA) with a projected surface area of 7 cm^2. Cathodes were made from the same type of carbon cloth but had a layer of 1.0 mg Pt cm^{-2} on the

solution-facing side and four polytetrafluoroethylene (PTFE) diffusion layers on the air-facing side. Projected surface area of the cathode was also 7 cm^2. Two layers of non-woven fabric (Armo Style #6000) were used to separate the anode and cathode.

MFCs were inoculated with a mixed bacterial culture previously characterized (Lesnik and Liu, 2014). MFCs were subsequently operated in batch using media with the following composition: $NaH_2PO_4 \cdot 7H_2O$ (15.47 g/L), $Na_2HPO_4 \cdot H_2O$ (5.84 g/L), NH_4Cl (0.31 g/L), KCl (0.13 g/L), $NaCH_3COO$ (60 mM), Wolfe's vitamin (12.5 mL) and mineral solutions (12.5 mL). Once consistent maximum power densities were obtained MFCs were fed with sludge supernatant. Experiments were performed in duplicate.

3.3.3. Analyses

MFC voltage across an external resistor was measured using a multimeter with a data acquisition system (Model 2700, Keithley Instruments, Inc., Cleveland, OH, USA). The power density was calculated according to P = IV/A, with I = V/R, where I (A) is the current, V (V) is voltage, R (Ω) is the external resistance, and A (m^2) the projected area of the cathode. During a batch, when the voltage reached a maximum and stable value, polarization curves were obtained by gradually changing the externally resistance from 400 to 20 Ω. Coulumbic efficiencies (CE) were determined by the following equation:

$$CE = \frac{\sum I\,(A)\; t\,(s)}{96485\ \left(\frac{C}{mol\ e^-}\right) \times\ sCOD_{removed}\ (mol) x\ \left(\frac{mol\ e^-}{mol\ O_2}\right)}$$

Energy recovery was determined by multiplying CE by voltage efficiency (operating voltage divided by theoretical potential difference). Treatment efficiencies were calculated by dividing COD removed by initial COD for each batch.

Soluble chemical oxygen demand (SCOD) was measured using COD dichromate reactor digestion kits (Chemetrics, Midland, VA, USA) following standard APHA methods (Eaton et al., 1995). Volatile fatty acid (VFAs) concentrations were analyzed using high-performance liquid chromatography (HPLC) (1200 series refractive index detector (RID)), Agilent, Santa Clara, CA, USA) using an Aminex 87H column (Bio Rad, Hercules, CA, USA). The mobile phase used was 0.01N H_2SO_4 at a flow rate of 0.6 mL min^{-1}. All samples were filtered through 0.20 μm pore diameter syringe filters before analysis. Total organic carbon (TOC) of the VFAs was calculated by multiplying carbon % of each compound by the concentration of each compound. pH was measured using a standard benchtop meter with a Ag/AgCl pH probe (VWR, Radnor, PA, USA).

3.4. Results and Discussion

3.4.1. Characterization of fermentation pretreatment

The initial SCOD of the sewage sludge was 607 mg L^{-1} and increased to 6900 mg L^{-1} over 288 hours of fermentation (Table 3.2). VFAs composed 33.4% of total SCOD at time 0, peaking at 93.6% of total SCOD after 96 hours then gradually decreasing to 87.0% at 288 hours. Initially, acetic acid was the dominant VFA comprising 42.8% of VFA SCOD with a concentration of 80.9 mg L^{-1}. After 288 hours of fermentation, acetic acid, propanoic acid and butyric acid concentrations increased to 2080, 1820, and 567 mg L^{-1}, respectively. While total SCOD continued to increase over the 288 hours, VFA concentrations stabilized after 96 hours and were responsible for 95.6% of the SCOD. Propanoic acid became the dominant VFA responsible for 46.1 ± 0.4% of VFA SCOD

from 96-288 hours. Over the same time acetate and butyric acid comprised 36.3 ± 1.0 % and 17.6 ± 0.6%, respectively.

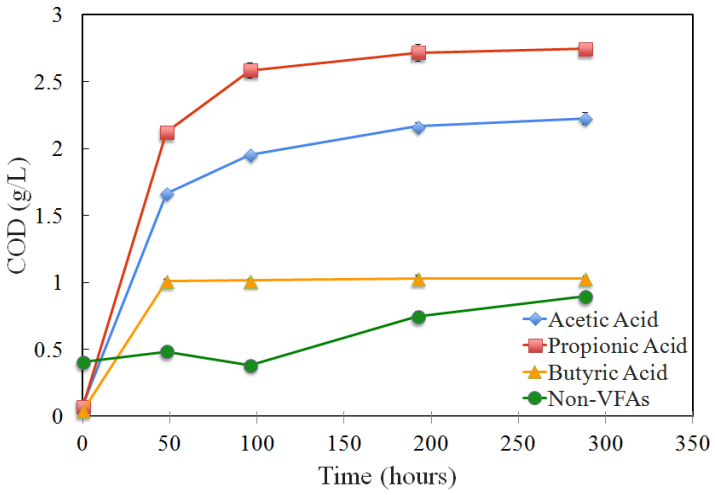

Figure 3.1: Characterization of VFA profiles during sludge fermentation

3.4.2. Power generation

Maximum power outputs of CEA-MFC reactors fed sewage sludge fermented for 0, 96, 192, and 288 hours are shown in Figure 3.2. Maximum power densities of the unfermented sludge were 0.28 ± 0.10 W m^{-2}. The highest maximum power densities were reached using supernatant from sludge fermented for 96 hours; at this time point MFCs reached a maximum power density of 1.22 ± 0.08 W m^{-2} (corresponding to a current density of 3.75 A m^{-2}). MFC designs fed supernatant from sludge fermented longer than 96 hours exhibited a 20-27% reduction in maximum power, possibly due to product inhibition associated with other types of fermentation (Zeng et al., 1994).

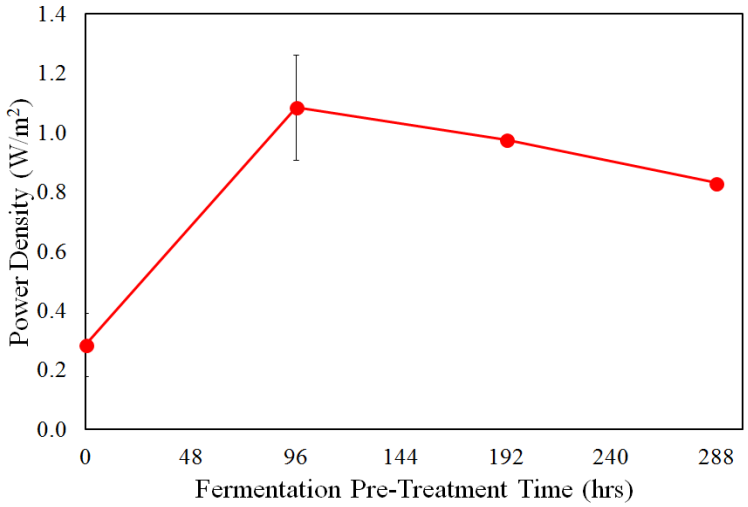

Figure 3.2: Maximum power density of MFCs fed sludge fermented for varying length of time.

Table 3.1 Power comparison from sludge of varying MFC designs/pretreatments

Configuration	Pretreatment	Power (mW m^{-2})	Power (W m^{-3})	References
CEA	Fermented	1,120	68.92	This study
Single-chamber	Fermented, diluted	320	–	Yang et al., 2013
Single-chamber	Fermented, buffered	1,030	–	Yang et al., 2013
Stacked	None	51	–	Su et al., 2013
Two-chamber	2-hour ozonation	21	–	Yusoff et al., 2013
Two-chamber	Microwave	42	–	Yusoff et al., 2013
Two-chamber	None	–	38.10	Wang et al., 2013
Two-chamber	Alkaline treated	46.8–55.9	–	Xiao et al., 2013

[1]Calculated based on MFC dimensions

The maximum power density achieved in the present study (1.2 Wm^{-2}) was more than 3 times than any previous MFC experiments treating sludge (Table 3.1).

The increased power densities of CEA-MFCs compared to previous fermented sludge studies can be attributed in part to reductions in internal resistances that are a result of the decreased electrode spacing in CEA-MFCs, as well as increased power generation observed from the previously characterized microbial community utilized in the current study (Lesnik and Liu, 2014).

3.4.3. SCOD and VFA Removal

All VFAs analyzed (acetic, propanoic, and butyric acid) were effectively removed by MFCs over 1 batch (72 hours) (Figure 3.3). VFA-associated TOC removal was 98-100% for all fermentation times for both CEA-MFCs (Table 3.2). Acetate was the preferred substrate in CEA-MFCs, being reduced from 1950 to 73.8mg COD L^{-1} (96.2 % removal) within the first 23 hours. Over the same time period initial propanoate (2590 mg COD L^{-1}) and butyrate (1020 mg COD L^{-1}) concentrations were reduced by 50.9% and 61.4% respectively. This preference is likely due to the enrichment of acetate-utilizing bacteria as acetate was used as the substrate during biofilm growth. Over a 48-hour batch VFAs were effectively removed by CEA-MFCs (99.2 ± 0.8% reduction in VFA SCOD L^{-1}), though a significant difference was observed in non-VFA SCOD removal (29.6 ± 23.2%).

Table 3.2 Treatment effectiveness of sewage sludge by CEA-MFC reactors

Fermentation time (hours)	Influent SCOD (mg/L)	SCOD removal (%)	Influent VFA TOC (mg/L)	VFA TOC removal (%)	CE (%)
0	607	55	68	100	93
96	5940	92	1870	99	35
192	6660	92	1990	100	33
288	6900	93	2020	98	32

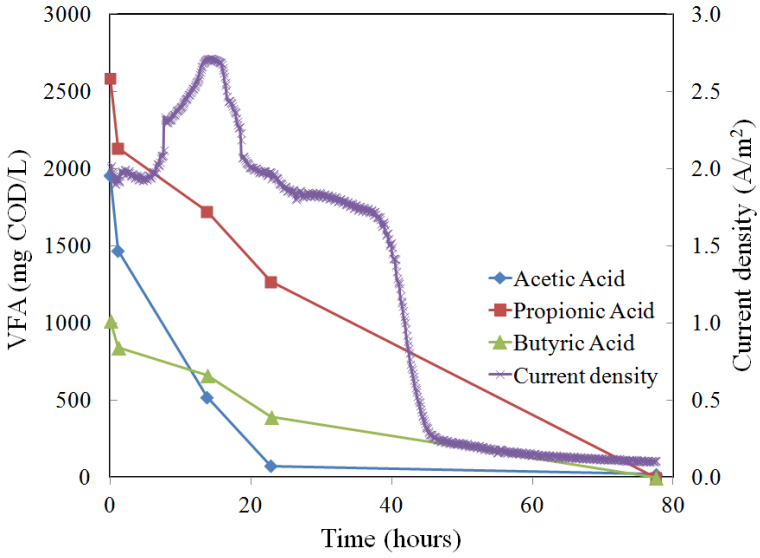

Figure 3.3: VFA profiles and current density from fermented sludge for 96 hours.

3.4.4. Coulombic and Energy Efficiencies

The couloumbic efficiencies of CEA-MFCs were 33.3 ± 1.5%. While differences previously observed in biofilm communities between SC-MFCs and CEA-MFCs were minimal (Lesnik and Liu, 2014), differing designs can have an affect on bacteria outside the biofilm. Differences in internal resistances and microbial communities not only affect power outputs but also the energy efficiency of MFC systems. In CEA-MFCs decreasing ohmic losses and increasing the abundance of bacteria actively participating in extracellular electron transfer (by limiting the growth of aerobic bacteria) can have a positive effect on CE and overall energy efficiency. Cloth separators present in CEA-MFCs not only prevent short circuits allowing the electrodes to be placed in closer proximity to each other but also serve as a barrier to oxygen diffusion, limiting growth of non-electrogenic aerobic bacteria.

CEA-MFC reactors with increased size and specific surface area operated in continuous flow mode have presented increased performance (up to 4.3 W m^{-2}) (Fan et al., 2012). While fermented sludge experiments with larger continuous flow CEA-MFCs were not conducted in the present, it is highly probable they too would see considerable increases in performance. Projected improvements to fermented sludge-fed MFCs related to the reactor design can be quantified by comparing the difference in performance of batch mode CEA-MFCs to the larger continuous flow CEA-MFCs when both are fed acetate, though verification through expanded experimentation is required and is a current research focus. A CE of around 35% was observed for both acetate-fed and fermented sludge-fed the smaller batch mode CEA-MFCs, though a CE in the range of 83% previously reported is expected in for larger continuous flow CEA-MFCs (Fan et al., 2012). Similarly, energy recovery is expected to increase from the 11.5% observed to 27.3% of total biodegradable energy content when larger continuous flow CEA-MFCs are utilized. This value is comparable to the 28% energy efficiency reported for anaerobic digestion systems (McCarty et al., 2011).

3.4.5. MFCs as part of WWTP infrastructure

A typical wastewater with a COD of 500 mg l^{-1} is estimated to have an energy content of 1.93 kWh m^{-3}, approximately 63.7% of which is biodegradable (1.23 kWh m^{-3}) (McCarty et al., 2011). The suspended fraction that develops into sludge after primary treatment contains 0.98 kWh m^{-3} of energy, of which 68% is biodegradable (0.67 kWh m^{-3}). While MFCs are more efficient at treating and generating electricity from dissolved organics, current designs are less efficient at handling the solids associated with sludge treatment, making a combined anaerobic digestion/MFC a practical option. The energy

recovery of an anaerobic digestion system versus a combined anaerobic digestion/MFC system with fermentation pretreatment is shown in Figure 3.4. Though complete hydrolysis of the organic compounds in sludge would be ideal for MFC treatment, methods such as sonication and the use of microwaves are energy intensive compared to fermentation which is still able to solubilize a large fraction of the organic content. Significant organic content remains in suspended form following the use of fermentation pre-treatment and anaerobic digestion would likely still be required.

In the current study energy recovery of sludge for MFC systems is 11.5% meaning overall efficiency of the combined fermentation/MFC/AD system would be 17.5%, currently less than anaerobic digestion by itself (28%). In order for MFCs to be considered as a viable modification to existing wastewater treatment infrastructure it must offer considerable advantages over current treatment processes. Most notably these advantages must be energetic in nature to offset the significant costs associated with wastewater treatment and bring wastewater treatment closer to a net energy producer. Potential increases in energy recovery using MFCs merit further development for sludge treatment as MFCs have potential for even greater efficiencies due to the direct conversion of organic compounds to electricity with an energy recovery of up to 44% theoretically attainable (Logan et al., 2006). More practically speaking, an energy efficiency of 35% could be obtained if an MFC were operated of 440 mV with a CE of 88%. In the present study an operating voltage of 440 mV corresponded to a power density 0.92 W m^{-2} for CEA-MFCs fed supernatant from sludge fermented for 4 days, equaling 75% of the maximum power. If the proposed MFC efficiency of 35% can be reached the fermentation/MFC modification to an anaerobic digestion system would

result in an estimated 33% energy efficiency and a power production of 0.22 kWh per cubic meter of wastewater treated (Fig. 4B). This represents 18% increase of the usable energy recovered compared to a conventional anaerobic digestion system operating at an energy efficiency of 28% (Fig. 4A). Fermentation pre-treatment was assumed to be capable of solubilizing 35% of the organic content, consistent with data from previous studies (Yang et al., 2013). The SCOD removal was 92% in CEA-MFCs in the current study, suggesting the remaining 8% was part of the refractory component. This value would mean 71% of the refractory organic content was not solubilized following fermentation. In Figure 3.4B, 64% of the total biodegradable organic content in the suspended portion of the wastewater was converted directly into electricity by the more efficient MFC while the remaining 36% contributed to methane generation in the anaerobic digester. Further increasing the percentage of organic material solubilized after fermentation would increase the biodegradable content available to the MFC and subsequently increase overall energy recovery.

While 0.22 kWh m^{-3} is only a fraction of the 0.44 – 1.4 kWh m^{-3} of energy required for wastewater treatment, recent studies have suggested the energy content in wastewater can be up to 20% greater than previously estimated, meaning energy capture over 0.25 kWh m^{-3} may be possible (Heidrich et al., 2011) Additionally, if MFCs were also operated in conjunction with secondary treatment systems currently being developed to capture additional energy, such as anaerobic fluidized bed and anaerobic fluidized bed membrane reactors, additional energy recovery would likely be possible. If a similar 35% recovery of the total energy associated with organics subjected to secondary treatment (0.56 kWh m^{-3}) could be reached, the combined energy recovery of wastewater treatment

plants could potentially reach 0.41 kWh m^{-3} or greater. Reaching these values would lead to wastewater treatment being near energy-neutral for some wastewater treatment plants and greatly reduce energy requirements for others.

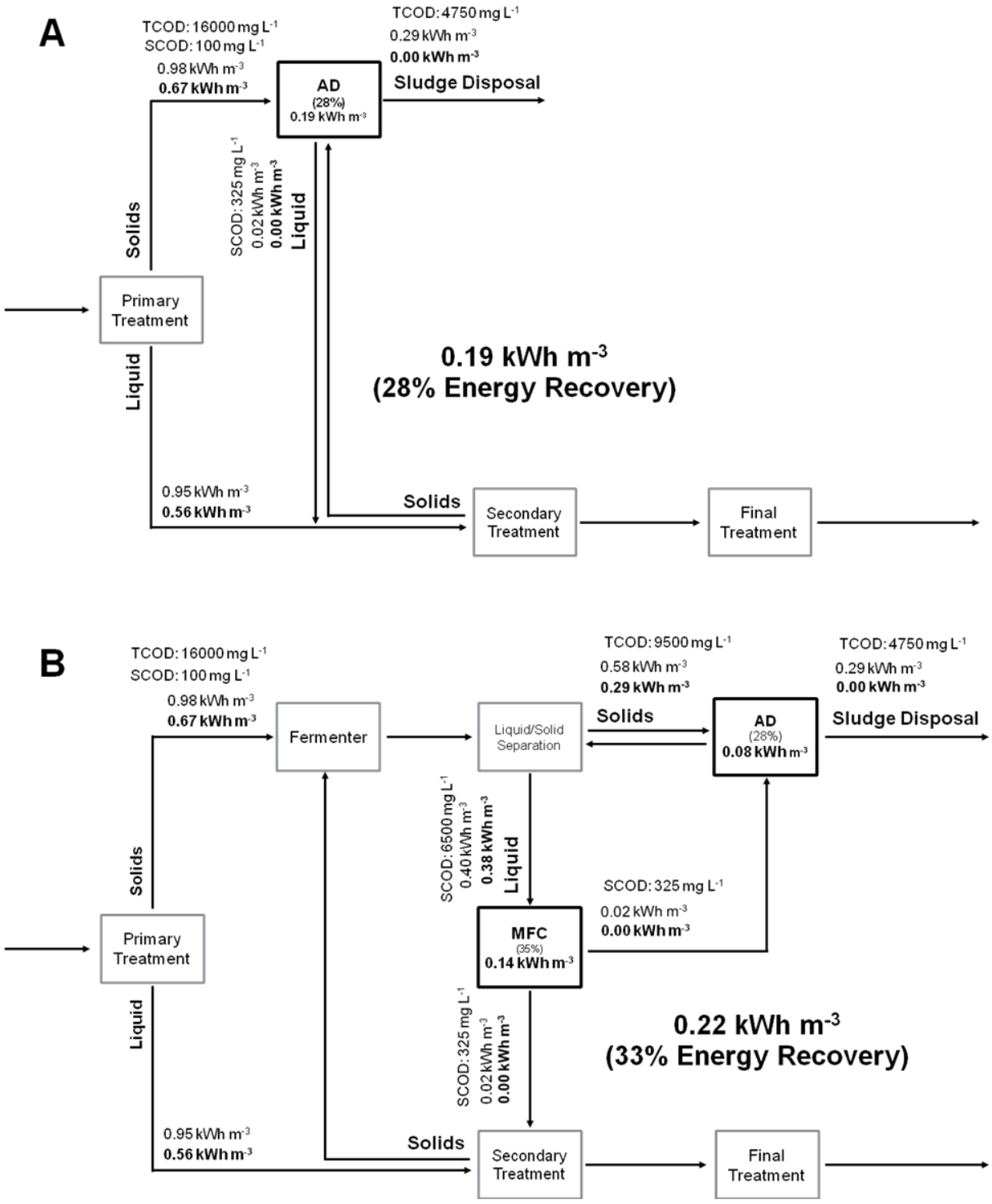

Figure 3.4. Energy content and recovery for varying wastewater treatment plant designs. Energy content and recovery using current anaerobic digestion (AD) technology (**A**) and projected performance in larger continuous flow systems (**B**). Total energy content (refractory fraction) (**biodegradable fraction**) and COD of influent/effluents, energy recovery (%) and total energy recovered from treatment processes are shown.

3.5. Conclusions

Though it has not yet been definitively determined if MFCs can significantly contribute to the field of domestic wastewater treatment, progress is being made towards this goal with the current study providing benchmarks to these ends. Current energy efficiency of MFCs treating sludge is 11.5% though significant improvements can be foreseen. MFCs were highly effective at treating sludge supernatant following fermentation pre-treatment and represent a promising modification to existing wastewater treatment infrastructure.

3.6. Acknowledgements

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3.7. References

Curtis, T.P., 2010. Low-Energy Wastewater Treatment: Strategies and Technologies, in: Mitchell, R., Gu, J.-D. (Eds.), Environmental Microbiology. John Wiley & Sons, Inc., pp. 301–318.

Eaton, A., Clesceri, L., Franson, M., 1995. Standard methods for the examination of water and wastewater, 19th ed. American Public Health Association (APHA), Washington, D.C.

Fan, Y., Han, S.-K., Liu, H., 2012. Improved performance of CEA microbial fuel cells with increased reactor size. Energy Environ. Sci. 5, 8273.

Fan, Y., Hu, H., Liu, H., 2007. Enhanced Coulombic efficiency and power density of air-cathode microbial fuel cells with an improved cell configuration. J. Power Sources 171, 348–354.

Fan, Y., Sharbrough, E., Liu, H., 2008. Quantification of the Internal Resistance Distribution of Microbial Fuel Cells. Environ. Sci. Technol. 42, 8101–8107.

Ge, Z., Zhang, F., Grimaud, J., Hurst, J., He, Z., 2013. Long-term investigation of microbial fuel cells treating primary sludge or digested sludge. Bioresour. Technol. 136, 509–514.

Global Water Research Coalition, 2008. Water and Energy: Report of the GWRC Research Strategy Group.

Heidrich, E.S., Curtis, T.P., Dolfing, J., 2011. Determination of the Internal Chemical Energy of Wastewater. Environ. Sci. Technol. 45, 827–832.

Hu, Z., 2008. Electricity generation by a baffle-chamber membraneless microbial fuel cell. J. Power Sources 179, 27–33.

Jiang, J., Zhao, Q., Zhang, J., Zhang, G., Lee, D.-J., 2009. Electricity generation from bio-treatment of sewage sludge with microbial fuel cell. Bioresour. Technol. 100, 5808–5812.

Lesnik, K.L., Liu, H., 2014. Establishing a core microbiome in acetate-fed microbial fuel cells. Appl. Microbiol. Biotechnol.

Liu, H., Logan, B.E., 2004. Electricity Generation Using an Air-Cathode Single Chamber Microbial Fuel Cell in the Presence and Absence of a Proton Exchange Membrane. Environ. Sci. Technol. 38, 4040–4046.

Logan, B.E., Hamelers, B., Rozendal, R., Schröder, U., Keller, J., Freguia, S., Aelterman, P., Verstraete, W., Rabaey, K., 2006. Microbial Fuel Cells: Methodology and Technology. Environ. Sci. Technol. 40, 5181–5192.

McCarty, P.L., Bae, J., Kim, J., 2011. Domestic Wastewater Treatment as a Net Energy Producer–Can This be Achieved? Environ. Sci. Technol. 45, 7100–7106.

Mohd Yusoff, M.Z., Hu, A., Feng, C., Maeda, T., Shirai, Y., Hassan, M.A., Yu, C.-P., 2013. Influence of pretreated activated sludge for electricity generation in microbial fuel cell application. Bioresour. Technol. 145, 90–96.

Pant, D., Van Bogaert, G., Diels, L., Vanbroekhoven, K., 2010. A review of the substrates used in microbial fuel cells (MFCs) for sustainable energy production. Bioresour. Technol. 101, 1533–1543.

Shizas, I., Bagley, D., 2004. Experimental Determination of Energy Content of Unknown Organics in Municipal Wastewater Streams. J. Energy Eng. 130, 45–53.

Su, X., Tian, Y., Sun, Z., Lu, Y., Li, Z., 2013. Performance of a combined system of microbial fuel cell and membrane bioreactor: Wastewater treatment, sludge reduction, energy recovery and membrane fouling. Biosens. Bioelectron. 49, 92–98.

Ting, C.H., Lee, D.J., 2007. Production of hydrogen and methane from wastewater sludge using anaerobic fermentation. Int. J. Hydrog. Energy 32, 677–682.

Tyagi, V.K., Lo, S.-L., 2013. Sludge: A waste or renewable source for energy and resources recovery? Renew. Sustain. Energy Rev. 25, 708–728.

Wang, Z., Ma, J., Xu, Y., Yu, H., Wu, Z., 2013. Power production from different types of sewage sludge using microbial fuel cells: A comparative study with energetic and microbiological perspectives. J. Power Sources 235, 280–288.

Xiao, B., Yang, F., Liu, J., 2011. Enhancing simultaneous electricity production and reduction of sewage sludge in two-chamber MFC by aerobic sludge digestion and sludge pretreatments. J. Hazard. Mater. 189, 444–449.

Yang, F., Ren, L., Pu, Y., Logan, B.E., 2013. Electricity generation from fermented primary sludge using single-chamber air-cathode microbial fuel cells. Bioresour. Technol. 128, 784–787.

Zeng, A.-P., Ross, A., Biebl, H., Tag, C., Günzel, B., Deckwer, W.-D., 1994. Multiple product inhibition and growth modeling of clostridium butyricum and klebsiella pneumoniae in glycerol fermentation. Biotechnol. Bioeng. 44, 902–911.

Zhang, G., Zhao, Q., Jiao, Y., Wang, K., Lee, D.-J., Ren, N., 2012. Efficient electricity generation from sewage sludge usingbiocathode microbial fuel cell. Water Res. 46, 43–52.

4. Challenges for Large Scale Application of Microbial Fuel Cell for Wastewater Treatment Prior Irrigation Water Reuse

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To be submitted

4.1. Abstract

Although wastewater use in irrigation provides one solution to water scarcity, it also presents a threat to the environment. Thus, wastewater treatment prior to irrigation is necessary. Microbial Fuel Cell (MFC) is a sustainable technology that treats wastewater and generates electricity simultaneously while leaving low concentrations of nutrients in the effluent. In order to explore the economic returns of using MFC as a pre-irrigation treatment method for wastewater, a case study involving food wastewater in a semi-arid region was conducted. The potential profit from treated water, produced electricity and nutrients in effluent was estimated. The effluent water quality was evaluated and compared to environmental regulations. CEA-MFC was compared to conventional wastewater treatment system. The analysis showed that MFC is a promising technology that appears to be economically feasible and that can reduce water and energy shortages which simultaneously increase food security.

4.2. Introduction

Fresh water applied in agriculture represents more than 70% of the total water use in the world (UNESCO-WWAP, 2003). In some regions, water consumption for agricultural purposes can reach up to 90% (Pereira et al., 2011). On the other hand, water scarcity is a growing issue in the world (Norton- Brandão et al., 2013) occurring most severely in the Middle East (El Kharraz et al., 2012). Thus, in order to ensure food security for an increasing world population, it is essential to meet water agricultural demand (Nikouei and Ward, 2013). In regions with limited freshwater resources, sewage and industrial wastewater can be used as alternative water sources for crop production (Khan et al., 2008). This reuse of wastewater in irrigation is essential for food security in some areas (Aliewi and Assaf, 2003).

Irrigating with wastewater may lead to an increase in soil organic matter and nitrogen as well as other nutrients (Adrover et al., 2012), and it presents a threat to crops and human health (Mukherjee et al., 2013). Application of untreated wastewater over the long-term can deteriorate soil quality and result in heavy metal accumulation (Adrover et al., 2012). Therefore, treatment is required before wastewater use in agricultural production. Irrigation with reclaimed wastewater has many benefits including conserving freshwater and fertilizer, as well as eliminating pollutant and nutrients discharge to surface and groundwater (Chen et al., 2013b). Nutrients in wastewater can result in higher yields than adding chemical fertilizers to freshwater (Murray and Ray, 2010).

Various reclamation technologies can be applied to wastewater treatment prior to irrigation, such as lagoon ponds, constructed wetlands, conventional wastewater treatment plants, membrane bioreactor, membrane filtration and others. However, the

need for large land areas or high investment cost is associated with these methods (Norton-Brandão et al., 2013). Microbial fuel cell (MFC) technology is a novel approach for treating wastewater (Zhuang et al., 2012). MFC converts the chemical energy of organic matter in wastewater into electricity (Liu and Logan, 2004, Logan et al., 2006). Unlike other wastewater treatment methods, MFC technology has the potential to not only help farmers in overcoming the problem of water shortage and in saving on fertilizers due to the nutrients remaining in the treated water, but also provides additional income from the generated electricity during the process of wastewater treatment.

The objective of this study is to gain perspectives on the potential application of MFC technology for partial wastewater treatment before irrigation. This paper begins with a review of the risks of using untreated wastewater in irrigation and a discussion of reported MFC wastewater treatment efficiencies. A case study is then conducted that involves using food processing wastewater for irrigation in a semi-arid region (the Columbia Basin of Oregon). The design and the economical feasibility of a projected MFC system are presented and discussed.

4.3. Effect of wastewater used in irrigation on soil, plants and the environment

While using wastewater in irrigation can alleviate the problem of water scarcity and wastewater disposal, it may result in crop yield and quality reduction and in harmful effect on the environment (Wang et al., 2007). Problems associated with organic matter, heavy metals and inorganic nutrients are presented below.

4.3.1. Organic matter

The type of organic matter, the organic loading rate and the soil environmental conditions are important factors to consider while applying wastewater to the soil (Crites et al., 2000). Organic matter overloading limits oxygen availability in the soil due to oxygen consumption by microbial aerobic degradation; the most effective way of organic matter mineralization (Ajwa and Tabatabai, 1994). Therefore, some state regulatory agencies limited the average weekly Biological Oxygen Demand (BOD) application rate to 112 kg ha/d/ (John and Bauder, 2007). This level was also recommended by the US EPA (1977) to avoid odors nuisance. The organic loading rate can be adjusted according to the organic matter degradation rate that is dependent on the organic matter type. For instance, carbon in fruit cannery wastewater was mostly degraded (≥ 88%) in the top layer of the soil within 8 weeks (John and Bauder, 2007). On the other hand, organic matter in olive mill wastewater was detected in the soil four months after its application (Mekki et al., 2007). Such organic matter is composed of large amounts of phenolic compounds that are toxic to plants and not easily mineralized (Mahmoud et al., 2012). In addition to the limitation of oxygen availability, organic carbon overloading can block soil pores and harm soil health (Mosse et al., 2012). Reduced soil porosity is caused by biofilm growth (Zhao et al., 2009).

4.3.2. Heavy metals

Using wastewater in irrigation can result in heavy metal build-up in the soil. Liu et al. (2005) reported accumulation of Cd, Zn, Cu, Cr and Pb in agricultural soils after irrigation with sewage sludge for 40 years in Beijing, China. Heavy metals in soil negatively impact crop yield and quality, as well as the atmosphere and water resources, because they are toxic and persistent in the environment (Elbana et al., 2013). After

accumulation in plants, heavy metals present a potential contaminant source for humans and animals (Madyiwa et al., 2004). In fact, heavy metals cause various disorders such as neurotoxicity, genomic instability, endocrine disruption and other serious health issues (Khan et al., 2013).

4.3.3. Nitrate and phosphorus

When used in irrigation, the high nutrient content in wastewater may have a negative impact on crops and the environment (Chávez et al., 2012). Nitrogen and phosphorus discharged in surface and groundwater result in eutrophication (Dimitriou and Aronsson, 2004). In addition, when those elements and other inorganic nutrients are not properly managed, nutrient imbalance in the soil may occur (Candela et al., 2007). For instance, excessive nitrogen concentration may lead to phosphorus and potassium deficiencies if the ratios of the three elements are not appropriate. Oversupply of nutrients may also result in adverse effects on crop quality and yield. For example, excessive nitrogen loading increases vegetative growth but delays maturation and reduces fruit quality (Chen et al., 2013a). Nitrogen concentration higher than 30 mg/L may have a negative impact on many crops (Shahalam et al., 1998).

4.4. Standards for irrigation water quality

There are no federal laws regarding reclaimed water quality used in irrigation, but the US EPA has recommended guidelines to protect human health and the environment and to encourage the different US states to establish their own regulations (Haering and Evanylo, 2009). The US EPA suggested guidelines for various crop types are presented in Table 4.1.

On the US state level, the parameters used in the evaluation of reclaimed water applied on non-food crops include UV disinfection dose, chlorine disinfection concentration, BOD, TSS, turbidity, bacterial indicators, and nitrogen concentration. The standards for those parameters vary between states. As for food crops, the use of reclaimed water is not allowed in some states while in others such as Florida, Nevada ,Virginia and others, it is permitted if the crop is processed and not consumed raw. However, other states such as California, allow the application of reclaimed water on food crops but with stringent water quality standards (near potable). In the states where reclaimed water is permitted on food crops, the standards are stricter than for non-food crops and include regulations for two additional parameters: viral indicators and pathogens. The treatment requirement of reclaimed water for food crops irrigation (filtration, oxidation, coagulation etc.) is determined in each state based on the crop type and irrigation method (US EPA, 2012).

Table 4.1: Suggested water quality guidelines for reclaimed water used in irrigation[1]

Irrigated crops	Water quality
Food crops not commercially processed Food crops eaten raw	• pH 6-9 • ≤ 10 mg/L BOD • ≤ 2 NTU[2] • No detection for fecal coliforms/100mL • 1 mg/L residual chloride[3]
Food crops commercially processed Non-food crops and pastures	• pH 6-9 • ≤ 30 mg/L BOD • ≤ 30 mg/L TSS • ≤ 200 fecal coliforms/100mL • 1 mg/L residual chloride[3]

[1] Adapted from US EPA, 2012
[2]NTU: Nephelometric Turbidity Units (unit for total suspended solids or TSS)
[3]When chloride is used for disinfection, the residual concentration should be 1 mg/L with a contact time of at least 90 minutes.

Table 4.2: Guidelines for evaluation of water quality for irrigation purpose[1]

		Parameter	Unit		All crops	Tolerant crops
Salinity		EC	dS/m		< 0.7	0.7 – 3
		TDS	mg/L		< 450	450 – 2000
Infiltration	Sodium (SAR)	0 – 3	meq/L	And EC	> 0.7	0.7 – 0.2
		3 – 6			> 1.2	1.2 – 0.3
		6 – 12			> 1.9	1.9 – 0.5
		12 – 20			> 2.9	2.9 – 1.3
		20 – 40			> 5.0	5.0 – 2.9
Ion toxicity	Surface irrigation	Sodium (SAR)[2]	meq/L		< 3	3 – 9
	Sprinkler irrigation	Sodium (SAR)	meq/L		< 3	> 3
	Surface irrigation	Chloride	meq/L		< 4	4 – 10
	Sprinkler irrigation	Chloride	meq/L		< 3	> 3
		Boron	mg/L		< 0.7	0.7 – 3.0
		Nitrate	mg/L		< 5	5 – 30
		Bicarbonate	meq/L		< 1.5	1.5 – 8.5
		Aluminum, iron, lead	mg/L		≤ 5	-
		Lithium	mg/L		≤ 2.5	-
		Zinc	mg/L		≤ 2	-
		Fluoride	mg/L		≤ 1	-
		Boron	mg/L		≤ 0.75	-
		Copper, Manganese, Nickel	mg/L		≤ 0.2	-
		Arsenic, Beryllium, Chromium Vanadium,	mg/L		≤ 0.1	-
		Cobalt	mg/L		≤ 0.05	-
		Selenium	mg/L		≤ 0.02	-
		Cadmium, Molybdenum	mg/L		≤ 0.01	-

[1]Adapted from FAO (1985)

[2] SAR is the sodium adsorption ratio = ratio of sodium concentration to the concentration of calcium and magnesium.

In many US States, Department of Environmental Quality (DEQ) or equivalent agency that regulates the quality of state's environment has established laws in each state

regarding quality of reclaimed water for irrigation. For instance, in the state of Oregon, two regulations have to be followed:

1- Irrigation water should not percolate below 5 feet of soil depth.

2- The nitrogen load should not exceed the yearly crop requirement (for example for alfalfa and wheat, 400 and 310 lb/acre/year are respectively the maximum allowable addition while for peas and beans, it is 150 lb/acre/year) (Oregon DEQ, 2013).

In addition to the US EPA suggestions and the DEQ-state specific laws, there are recommendations by the Food and Agriculture Organization (FAO) regarding irrigation water quality for avoiding any negative impact on crop yield (Table 4.2).

4.5. Water quality improvement by MFC

A typical MFC contains two electrodes (anode and cathode). Exoelectrogens (electrogens) on the anode decompose organic matter in wastewater producing electrons and protons (Figure 4.1). The electrons flow to the cathode through an external circuit, generating electricity, and protons diffuse from the anode to the cathode. Once at the cathode, the electrons and protons react with an electron acceptor, such as oxygen, and form water (Oliveira et al., 2013).

MFC has demonstrated its potential for treating wastewater containing organic matter, nitrogen, phosphorus and heavy metals. However, removal efficiencies of these contaminants are dependent on the system design, hydraulic retention time and initial concentrations.

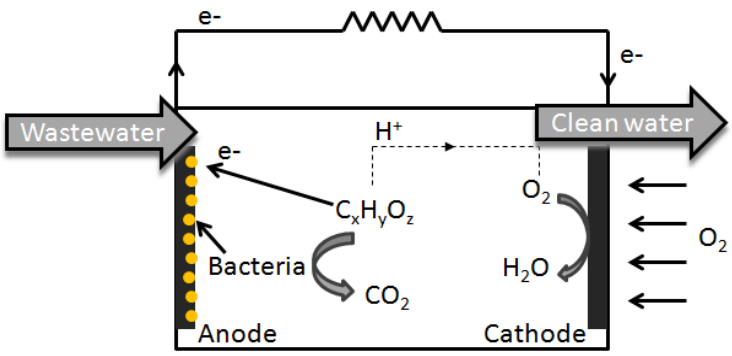

Figure 4.1: Microbial Fuel Cell diagram

4.5.1. Organic matter

Variable percentage removals of organic matter by MFC have been reported in the literature. A relatively low removal efficiency was observed when most of the organic matter is slowly biodegradable or non-biodegradable. Only 37 % COD removal efficiency was achieved by MFC while treating raw leachate of initial COD concentration of 3480 mg/L (Puig et al., 2011). On the other hand, a higher COD removal efficiency of 85% was obtained by treating mustard tuber wastewater at initial concentration of 2,968 mg/L (Guo et al., 2013). Therefore most organic matter can be removed by MFC when the organic matter is easily biodegradable.

4.5.2. Nitrate and ammonia

Nitrate and ammonia can also be removed at high percentages by MFC. A single chamber MFC with a rotating biocathode showed 91% ammonia removal efficiency with 53.3 mg/L as initial nitrogen concentration. Ammonia was removed by oxidation into nitrite by ammonia-oxidizing bacteria. The reaction was followed by nitrite oxidation into nitrate by nitrite-oxidizing bacteria. Then, nitrate was denitrified into nitrogen gas by denitrifiers (Zhang et al., 2013). As for nitrate, more than 90% of the initial concentration

(30.6 mg/L nitrogen) was removed in the anodic chamber of two chamber MFCs (Cai et al., 2013). Similarly, over 85% of nitrate (112 mg/L nitrogen in influent) was removed in one hour by single chamber MFC with a rate of 98 mg/L/h (Sukkasem et al., 2008). Table 4.3 presents examples of COD and nitrogen removal percentages from different wastewater sources.

Table 4.3: MFC treatment efficiency for various wastewater sources

Wastewater source	COD removal % (Ci[1])	Nitrogen removal % (Ci[1])	References
Protein food industry	86% (1,900)	73% ammonia (120)	Mansoorian et al., 2013
Olive mill + domestic	60% (4,000)	93% ammonia (47)	Sciarra et al., 2013
Dairy	95.5 (3,700)	78% protein (95.5)	Mohan et al., 2010
Starch processing	98% (4,852)	90.6% ammonia (337)	Lu et al., 2009
Swine (diluted 1:10)	86% (1,240)	83% ammonia (198)	Min et al., 2005
Swine	83.8% (5,845)	90.8% ammonia (623.3)	Zhuang et al., 2012
Domestic	79% (333)	71% total nitrogen (48)	Feng et al., 2014
Agricultural	91% (397)		Nimje et al., 2012
Paper	80% (1250)		Nimje et al., 2012

[1]Ci: Concentrations in wastewater (mg/L)

4.5.3. Phosphorus

Removal of phosphorus from wastewater by MFCs has also been reported. Phosphorus in swine wastewater can be precipitated as struvite (magnesium ammonium phosphate) in a single chamber MFC reducing the phosphorus concentration by 70–82% (Ichihashi and Hirooka, 2012). The presence of ammonium and magnesium is required for phosphorus precipitation as struvite. In the absence of ammonium, phosphorus can still precipitate

with magnesium in the form of cattiite (Hirooka and Ichihashi, 2013). So, the addition of magnesium to MFC influent can help in phosphorus removal.

4.5.4. Heavy metal

High heavy metal removal percentages by MFC occurred by different mechanisms depending on the MFC design (single or double chamber). Heavy metals such as copper, chromium, mercury and vanadium were precipitated in two-chamber MFCs by metal reduction (Wang et al., 2008, Li et al., 2008, Tandukar et al., 2009, Heijne et al., 2010, Tao et al., 2011, Wang et al., 2011, Zhang et al., 2012a, Zhang et al., 2012b). In all of those studies the removal efficiency exceeded 95% except for vanadium where it was 68%. On the other hand, biosorption and sulfide precipitation were the main mechanisms of heavy metal removal in single-chamber MFC. The achieved removal percentages in that case were 90% for Cadmium and 97% for Zinc (Abourached et al., 2013).

4.6. MFC scaling up for irrigation use

This section presents a preliminary assessment of the feasibility of using MFC technology for the treatment of wastewater from a food processing facility and reuse of the treated water for irrigation. The analysis begins with a conceptual scaling-up design based on an existing bench top MFC system in our lab. The economics and performance characteristics of this MFC system are then assessed in the context of a real-world case study.

4.6.1 MFC design

Various MFCs designs have been developed in the past two decades, including single chamber, double chamber and many others (Cheng et al., 2014). Among the various MFC configurations, the single chamber air-cathode Cloth Electrode Assembly (CEA) MFC design has the greatest potential for practical wastewater treatment because of the structural simplicity, low cost, and high power production (Fan et al., 2007, 2012). The anode and cathode are separated by a non-woven fabric layer in a CEA-MFC. With this configuration, the distance between anode and cathode is minimized to reduce the internal resistance and increase power production (Fan et al., 2007). Figure 4.2 shows the configuration of typical CEA-MFC design

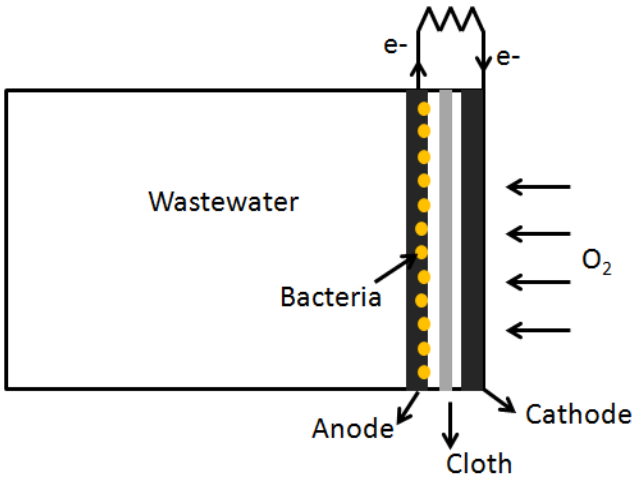

Figure 4.2: Schematic of configuration: A) MFC B) CEA-MFC

4.6.2 Case study

We consider a case study involving using food wastewater (such as potato, onion, and cheese processing wastewater) for irrigation in a semi-arid region (the Colombia Basin of Oregon). After being collected in a lagoon storage pond, the wastewater is pumped to irrigate agricultural fields. Wastewater reuse in irrigation helps with water shortage in this region. One local farm has been receiving 1400 gal/min (or 5300 l/min, 318 m^3/hr) of the food waste water. The volume of water used in irrigation on that farm has been limited by the high organic and nitrogen content in that wastewater which has been overloading the soil with nutrients, leading to the violation of state standards. The nitrogen loading limit was violated in several agricultural fields by adding nitrogen in an amount exceeding the crop requirement. The farm has also had problems with biofilm sealing of soil pores from BOD loading. Thus, wastewater treatment to reduce both nitrogen and BOD loading is needed so water can be used for land application without environmental restriction and soil. Though the current study benefits both the farmer and the industry producing the wastewater, the analysis is conducted for the industry that has to find a solution for the disposal of the wastewater. We consider using CEA-MFC to treat wastewater before its application to the agricultural fields. Figure 4.3 illustrates the proposed system.

The economic analysis focused on economic parameters that would distinguish the CEA-MFC system from a conventional waste treatment plant. Five economic parameters considered: (i) the capital costs of the 'core' elements of an MFC system, including the material costs and an estimate of the costs of assembly, and the capital cost of aeration system for the conventional plant; (ii) the value of energy produced by the

MFC system; (iii) the deferred pumping energy costs that would normally be incurred for a conventional treatment plant; (iv) the value of residual nutrients recaptured as fertilizer on receiving fields, and (v) the value of the recovered water when used for irrigation.

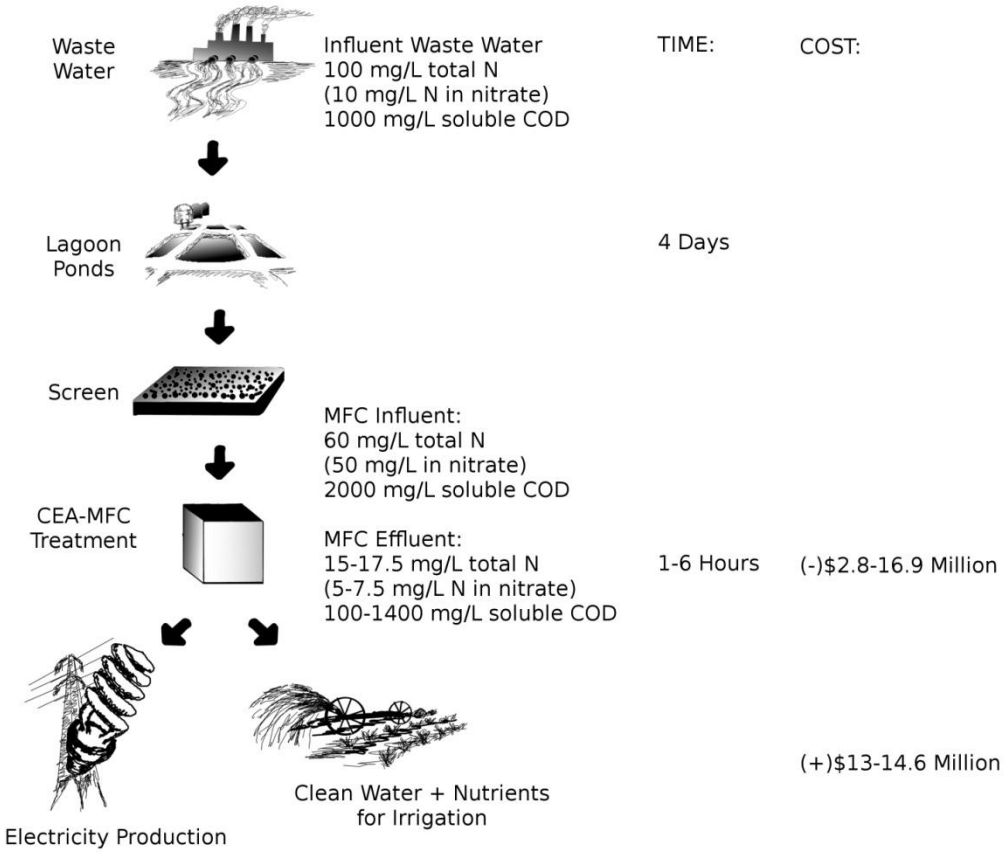

Figure 4.3: The proposed wastewater treatment system (CEA-MFC) prior irrigation

We consider that the wastewater (of 100 mg/L total nitrogen, 10 mg/L N as nitrate and 1000 mg/L soluble COD) is collected in a lagoon for 4 days in order to decompose complex compounds (Lovin, 2014). Solids are separated by sedimentation in the lagoon pond and by an additional screen, which reduces the total nitrogen and carbon content in

wastewater. However, the concentrations of soluble COD and N in the form of nitrate increase due to degradation of complex molecules and nitrification reaction. The CEA-MFC system then follows the lagoon storage and screen. The purpose of the study is to evaluate the use of CEA-MFC for wastewater treatment assuming that the lagoon and screen were already used to clean the water, but were not sufficient to meet environmental regulations.

4.6.2.1. Design specifications:

The MFC influent has the following characteristics:

a- Flow rate: 1400 gal/min (5300 l/min), or 318 m^3/hr

b- Influent concentrations of pollutants of concern (Lovin, 2014):

- Total nitrogen concentration: 60 mg/L (of which 50 mg/L is in form of nitrate).
- COD concentration: 2000 mg/L

Specified effluent concentrations:

a- Total nitrogen concentration in effluent needs to meet Oregon regulations for water reuse in irrigation; the nitrogen amount added per year should not exceed the yearly crop uptake. For instance for alfalfa, it is 400 lb/acre/year (44.9 g/m^2/year). Having alfalfa the crop to be irrigated, we consider the following assumptions:

- Irrigation water requirement per year for alfalfa: 43.8 inches (1.113 m) (Agrimet; The Pacific Northwest Cooperative Agricultural Weather Network)
- Irrigation efficiency for center pivot: 80%

With those assumptions and the yearly applied water volume after CEA-MFC treatment ($2.67x10^6$ m^3 corresponding to 23 hours of operation of CEA-MFC per

day), 474.3 acres of alfalfa can be irrigated. So the nitrogen application should be limited to 189,720 lb per year. This amount corresponds to 32.3 mg/L total nitrogen in effluent, so the required nitrate removal would be 55.4 % of the influent concentration.

b- Though Oregon regulations do not set a limit for BOD concentration in treated wastewater for irrigation use, BOD removal is important to avoid oxygen depletion and biofilm formation in the soil. The US EPA recommends that the average weekly BOD application rate should not exceed 112 kg/ha/d. For alfalfa grown in the considered region, the maximum daily water requirement is 0.4 inches/day which is equivalent to 101.6 m^3 for 1 ha of alfalfa (Agrimet). So, the maximum BOD concentration would be 1,102 mg/L. Assuming a BOD/COD ratio of 70%, the maximum COD concentration is 1,575 mg/L, which corresponds to 21.3% COD removal.

4.6.2.2. Design parameters

a- Hydraulic Retention Time (HRT):

Figure 4.4 illustrates COD removal percentages for different HRT based on results previously reported by Fan et al., (2012) using a small, lab scale MFC. The generated energy values are based on lab experiments and they are conservative to account for the uncertainty associated with scaling up. As for nitrate removal percentages for various HRT, our assumptions are made according to the findings of Sukkasem et al., (2008) using a small cubic MFC without a separator at a nitrogen concentration (in form of nitrate) of 112 mg/L. The rates used in the present analysis are therefore also conservative, since we expect to have even higher nitrate removal percentages under the

current conditions because the CEA-MFC design allows lower oxygen entrance to the solution, which would favor more denitrification. The electrode area to reactor volume in the proposed CEA-MFC design is larger than the MFCs reported in Sukkasem et al., (2008). With higher electrode area to reactor volume and lower nitrate concentration, a higher nitrate removal percentage is expected to occur. Again, the estimated levels of performance in this study are conservative. Ammonia removal is not considered in this analysis because the CEA-MFC design does not allow significant amount of oxygen to enter to the reactor for nitrification reactions to take place.

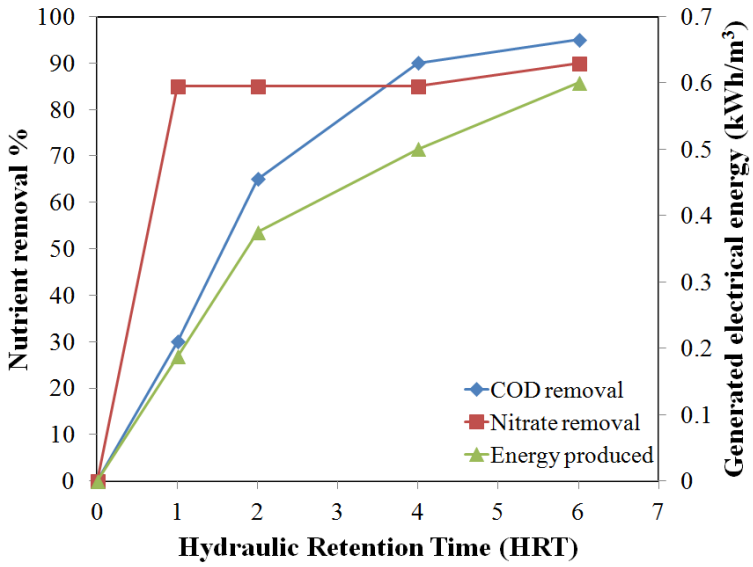

Figure 4.4: Variation of nutrient removal and energy generation with HRT

According to the previously described design specifications, nitrate and COD removals by CEA-MFC should be 55.4% nitrate rand 21.3% respectively. Those percentages correspond to HRT of 39 and 43 minutes for nitrate and COD respectively

(by interpolation from Figure 4.4). So, 1 hour HRT would be a conservative estimate of the HRT needed to ensure necessary nitrogen and organic matter removal percentages.

HRT affects MFC power generation and effluent quality (Akman et al., 2013). A longer HRT results in effluent containing less organic matter and nitrate (Figure 4.4), but larger reactor size and higher cost. A range of HRT (1, 2, 4 and 6 hours) was studied in order to compare the water quality and the economic returns at different HRT values.

b- Reactor liquid volume:

The reactor liquid volume is calculated according to:

$$V = Q * HRT \qquad (1)$$

Where:

V = reactor liquid volume (m^3)

Q = wastewater flow (m^3/h) = 318.

HRT figures used in this analysis were 1, 2, 4 or 6 hours.

c- Number of electrodes, number of units and total electrode area:

The reactor is assumed to be composed of multiple units and each unit contains 200 electrodes (100 anodes and 100 cathodes of 1 m^2 area each in one m^3 of reactor). A fabric layer (separator) is used to separate the anode and the cathode (Figure 4.2). Figure 4.5 depicts the schematics for CEA-MFC reactor unit. The number of anodes, cathodes and separator for each HRT is therefore determined by:

$$nc = na = ns = \frac{V}{v} \qquad (2)$$

Where:

N_c = number of cathodes

N_a = number of anodes

N_s = number of separators

V = reactor volume (m^3); described in equation (1)

v = liquid volume corresponding to one cathode and one anode; assumed to be 0.008 m^3 (0.8 cm spacing between anode and cathode).

The number of units is determined by equation (3):

$$Nu = \frac{na}{100} \qquad (3)$$

Where:

N_u = number of unit

The reactor specifications are summarized in Table 4.4.

Table 4.4: Reactor specifications at different HRT

HRT (hours)	**1**	**2**	**4**	**6**
Reactor liquid volume (m^3)	318	636	1,272	1,908
Number of anodes or cathodes	39,747	79,494	158,988	238,481
Number of units	398	795	1,590	2,385
Total electrode area (m^2)	79,494	158,988	317,976	476,962

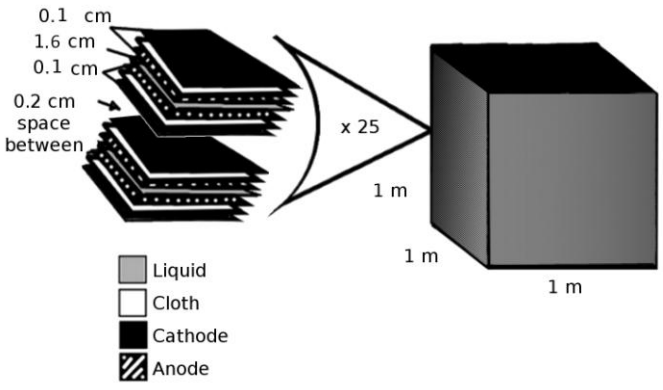

Figure 4.5: Schematic of CEA-MFC reactor unit

4.6.2.3. Economic analysis

4.6.2.3.1. CEA-MFC capital and operational costs

Based on the numbers of cathodes, anodes, separators and units, the cost of the reactor corresponding to various HRT can be determined by using the material cost in Table 4.5.

The lagoon and screen costs as well as the operational cost associated with solid removal were not considered in this study assuming that the lagoon and screen were already installed and used before starting this project. Both of them were helping in removing part of the nutrients from the wastewater, but the additional treatment by CEA-MFC was still needed to meet the environmental regulations (Oregon DEQ) and to avoid nutrient overloading in the soil.

CEA-MFC operational cost is assumed to be 4% of the capital cost. The design life time of 20 years is arbitrarily assumed for the CEA-MFC system for purposes of discussion only. The present worth of operational cost is discounted to present worth according to the following general equation for present worth of a continuous cost:

$$P0 = \frac{Pt}{i}(1 - e^{-iT}) \qquad (4)$$

Where:

P_0 = present worth ($)

P_t = yearly payment ($)

i = discount rate; assumed to be 5% (based on corporate bond rates at the time of this writing)

T = MFC lifetime; assumed to be 20 years

The operational and total CEA-MFC costs are also presented in Table 4.5.

Table 4.5: Cost of CEA-MFC for different HRT

Material	**Cost ($/m^2)**	**Cost ($/m^3 reactor)**	**Cost ($/CEA-MFC)**			
HRT (hours)			1	2	4	6
Anode	10	1,000	397,470	794,940	1,589,880	2,384,810
Cathode	50	5,000	1,987,350	3,974,700	7,949,400	11,924,050
Separator	1	100	39,747	79,494	158,988	238,481
Others		1,000	398,000	795,000	1,590,000	2,385,000
Total capital cost (million $)		7,100	2.8	5.6	11.3	16.9
P_0 operational cost (million $)			1.4	2.9	5.7	8.6
Total cost (million $)			**4.2**	**8.5**	**17.0**	**25.5**

*Capital costs are based on material development and pilot scale ongoing lab study

4.6.2.3.2. Revenue from generated electricity

The income from generated electricity per year was calculated as:

$$Pt\ electricity = Wy * E * Ev \quad (5)$$

Where:

P_t electricity = value of yearly produced electricity ($/year)

W_y = volume of yearly treated water (m^3/year) = 2,669,395

E = energy produced (kWh/m^3); different values are assumed for each HRT (Figure 4.4)

E_v = electricity value ($/kWh); assumed to be 0.12

The present worth of yearly income from generated electricity for 20 years is evaluated based on equation (4) with an assumed discount rate of 5%. Note that the estimated present worth of electricity used in this analysis is conservative and it could be higher in

other regions and with significant energy inflation; the US energy inflation rate forecast is estimated to be 15% in 2015 (forecast-chart.com/inflation-usa-energy.html, 2014).

4.6.2.3.3. Revenue from nitrogen in treated wastewater (fertilizer value)

In addition to the profit from electricity and water, residual nitrogen in treated wastewater plays the role of a fertilizer when applied to crops therefore, it results in fertilizer cost saving. In this study, we did not consider the value of other nutrients (phosphorus, potassium, etc.). The nitrate removal is assumed to be 85 – 90% of 50 mg/L of nitrate in influent. The nitrogen in CEA-MFC effluent is present as nitrate (5 – 7.5 mg/L) and other forms not readily available to crops (10 mg/L), but they become available after degradation and nitrification in the soil. To calculate the nitrogen value, both forms are considered. Leaching of nitrate from the soil during winter is negligible since the rainfall is not high in the region.

The revenue from fertilizer is estimated as:

$$Pt\ fertilizer = Cn * Wy * Nv \qquad (6)$$

Where:

P_t (fertilizer) = value of nitrogen fertilizer in yearly treated water ($/year)

C_n = effluent nitrogen concentration (mg/L)

(between 15 and 17.5 (the sum of 5 to 7.5 mg/L N in nitrate and 10 mg/L N in other forms))

W_y = volume of treated water per year (L/year) = 2,669,395,424

N_v = nitrogen monetary value ($/mg)

= $\$726*10^{-9}$/mg N based on a market value of $0.33/lb N

The present worth of yearly income from nitrogen for 20 years is evaluated based on equation (4) with an assumed discount rate of 5%.

4.6.2.3.4. The value of treated water

The water value in this case study is estimated as the value of water to the farm. There is no established water market from which to estimate that value, but a conservative assumption based on recent sale of farm water rights in the San Joaquin Valley of California for about $5500 per ac-ft implies a value on the order of $440/ac-ft[1] per year ($0.36/m^3) (English M., 2014). The water value could be higher in regions with serious drought and/or where valuable crops can be grown, for example spot market sales in central California in the recent drought have exceeded $1,300 per ac-ft. For the purposes of the present analysis we will use $440.

The value of yearly treated water by CEA-MFC is determined by:

$$Pt\ water = Wy * Wv \qquad (7)$$

Where:

P_t water = value of yearly treated water ($/year)

W_y = volume of yearly treated water (ac-ft/year) = 2164; assuming that the MFC operates 23 hours per day leaving one hour for maintenance.

W_v = water value ($/ac-ft) = 440

Pt water is calculated as $952,210, which present worth (P_0water) is determined based on equation (4) as $12 million. Note that the estimate is conservative. Inflation due to drought and climate change would result in a much higher present worth.

[1] The yearly payment for one acre-ft corresponding to present worth of $5500, assumed discount rate of 8% and infinite time as obtained from equation (5).

4.6.2.3.5. Net Income from using CEA-MFC

The net income from using CEA-MFC is presented in equation (8) and Table 4.6.

$$Net\ income = P0\ water + P0\ fertilizer + P0\ electricity - CEA\ capital\ cost \quad (8)$$

4.6.2.3.6. Advantage of using CEA-MFC

Replacement of the aeration system at a conventional treatment plant by CEA-MFC is evaluated; however this analysis is very conservative because CEA-MFC has the potential to substitute the whole conventional treatment plant.

The capital and the yearly operational costs of a conventional plant treating wastewater of 1,400 gal/min flow were estimated to be $14/gal/day and $1.57/gal/day respectively based on a study of treatment plant costs for a wide range of treatment systems in Massachusetts (Barnstable county wastewater cost task force, 2010). So, the estimated capital and yearly operational costs of the plant would be $28.2 million and $3.2 million respectively. Consequently, the total present worth of the operational cost for 20 years would be $40 million, which results in a total cost of $68.2 million. Since the capital cost of the aeration system is typically 20% of the conventional plant cost (Mueller et al., 2002), the capital cost of the aeration system component of the plant is $5.6 million.

Knowing that the energy usage by wastewater treatment plants is on average 0.9 kWh/m^3 (Curtis, 2010) and assuming that 60% of that energy is needed for aeration (Liu et al., 2011), the yearly required aeration energy in this case study would cost $172,977 and its present worth for 20 years of operation would be $2.2 million. Thus, the total cost of the aeration system in a conventional treatment plant is estimated to be the sum of capital cost ($5.6 million) and energy cost ($2.2 million), or $7.8 million.

The advantage of replacing the aeration system at a conventional plant by CEA-MFC (or the difference in net costs) is evaluated by equation (9) and the result is presented in Table 4.6. P_0 water is not considered in the calculations as it is common to both systems.

Difference in net costs by using CEA-MFC

= P_0 electricity + P_0 fertilizer – CEA-MFC total cost + aeration total cost (9)

Table 4.6: Net income and advantage of using CEA-MFC for different HRT

HRT (Hours)	**1**	**2**	**4**	**6**
MFC total cost ($million)	4.2	8.5	17.0	25.5
Generated energy (kwh/m^3)	0.19	0.38	0.50	0.60
Energy revenue ($million/year)	0.06	0.12	0.16	0.19
Total energy revenue (P_0) ($million)	0.76	1.52	2.03	2.43
Fertilizer revenue ($million/year)	0.03	0.03	0.03	0.03
Total fertilizer revenue (P_0) ($million)	0.27	0.27	0.27	0.23
Conventional treatment capital cost ($million)	28.2	28.2	28.2	28.2
Total conventional treatment cost ($million)	68.2	68.2	68.2	68.2
Total aeration cost ($million)	7.8	7.8	7.8	7.8
Net income from using CEA-MFC ($million)	**8.8**	**5.3**	**-2.7**	**-10.8**
Difference in net costs by using CEA-MFC ($ millions)	**4.6**	**1.1**	**-6.9**	**-15.0**

Comparing the results obtained with the different HRT, the use of CEA-MFC for 1 hour meets DEQ regulations and results in the highest net income of $8.8 million (Table 4.6). In that case, the total CEA-MFC cost ($ 4.2 million) is only 6% of the total conventional treatment cost ($68.2 million). If only the aeration system of the conventional plant is replaced by CEA-MFC and all other treatment costs are assumed to be common to both CEA-MFC and conventional treatment plant, $3.6 million in capital and aeration energy costs would be saved. When the additional revenues from energy production and fertilizer recovery are included, the use of CEA-MFC would result in saving of at least

$4.6 million. Note that CEA-MFC has potential of replacing the whole conventional plant and it could result in larger savings.

Optimizing HRT according to return on investment, while meeting regulations, is case specific. For instance, HRT depends on the wastewater composition, local environmental regulations, crop nutrient uptake, soil composition and environmental conditions.

4.7. Conclusion and future perspectives

This paper presents a novel approach for MFC scaling up for real world application. The study demonstrates that MFC has the potential of producing reclaimed water for irrigation with simultaneous electricity generation; both of large economic benefit to farmers in regions with water scarcity issues. Another advantage of the application is providing an affordable method for wastewater discharge. The costs for treating food processing and beverage wastewater have been increased significantly the past few years, ranging from $300,000 to $1,000,000 annually for medium to large food and beverage industries. By integrating results from the literature it can be concluded that MFC can produce effluent of water quality within the environmental regulations for irrigation application. Incomplete removal of organic and inorganic matter by MFC is an advantage as MFC effluents may help in saving fertilizers and in improving soil health while avoiding oversupplying the soil with nutrients (Table 4.3). Removal percentage of nutrients increases with HRT. Optimizing HRT consists of obtaining effluent of acceptable water quality with simultaneous feasible reactor size and cost. Although the analysis in the current case study is conservative, CEA-MFC is promising and it could be more feasible than conventional systems for wastewater treatment prior irrigation.

MFC can remove organic matter and nitrate, but it is not capable of removing all elements of concern such as sodium, chloride and carbonate. Decomposition of slowly degradable organic pollutants is an additional concern with using MFC prior irrigation. Other challenges consist of the need of wastewater pH adjustment before MFC treatment if the pH is not close to neutrality. Pathogens removal after MFC treatment is necessary especially if the MFC effluent is used for food crops. Developing and testing the system on a pilot scale is needed before the application of a full scale system due to the lack of developed models in the literature and due to additional challenges such as unstable bacterial biofilm and low power density when COD and buffer concentrations are low in wastewater.

This paper suggests significant potential for using MFC in enhancing water, energy and food security.

4.8. Acknowledgements

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4.9. References

Abourached, C., Catal, T., Liu, H., 2013. Efficacy of single-chamber microbial fuel cells for removal of cadmium and zinc with simultaneous electricity production. Water Research, In Press.

Adrover, M., Farrús, E., Moyà, G., Vadell, J. 2012. Chemical properties and biological activity in soils of Mallorca following twenty years of treated wastewater irrigation. Journal of Environmental Management 95: S188-S192

Ajwa, H.A., and M.A. Tabatabai. 1994. Decomposition of different organic materials in soils. Biology and Fertility of soils 18:175–182.

Akman, D., Cirik, K., Ozdemir, S., Ozkaya, B., Cina, O. 2013. Bioelectricity generation in continuously-fed microbial fuel cell: Effects of anode electrode material and hydraulic retention time. Bioresource Technology 149: 459-464.

Aliewi A.S., Assaf K.K. 2003. Assessment of water demand management in Palestine. Identifying the gaps and the constraints, envisioning challenges and opportunies. Second regional conference on water demand management and pollution control. Sharm Al-Sheikh, Egypt.

Barnstable county wastewater cost task force. 2010. Comparison of costs for wastewater management systems applicable to Cape Cod: Guidance to Cape Cod towns undertaking comprehensive wastewater management planning.

Cai, J., Zheng, P., Zhang, J., Xie, Z., Li, W., Sun, P. 2013. Simultaneous anaerobic sulfide and nitrate removal coupled with electricity generation in Microbial Fuel Cell. Bioresource Technology 129: 224-228.

Candela, L., Fabregat, S., Josa, A., Suriol, J., Vigués, N., Mas, J., 2007. Assessment of soil and groundwater impacts by treated urban wastewater reuse. A case study: Application in a golf course (Girona, Spain). Science of The Total Environment 374(1): 26-35.

Chávez, A., Rodas, K., Prado, B., Thompson, R. Jiménez, B., 2012. An evaluation of the effects of changing wastewater irrigation regime for the production of alfalfa (Medicago sativa). Agricultural Water Management 113: 76-84.

Chen, W., Lu, S., Jiao, W., Wang, M., Chang, A.C., 2013a. Reclaimed water: A safe irrigation water source? Environmental Development 8: 74-83.

Chen, W., Lu, S., Peng, C., Jiao, W., Wang, M. 2013b. Accumulation of Cd in agricultural soil under long-term reclaimed water irrigation. Environmental Pollution 178: 294-299.

Cheng, S., Ye, Y., Ding, W., Pan, B. 2014. Enhancing power generation of scale-up microbial fuel cells by optimizing the leading-out terminal of anode. Journal of Power Sources 248: 931-938.

Crites, R.W., S.C. Reed, and R.K. Bastian. 2000. Land treatment systems for municipal and industrial wastes. McGraw-Hill, New York.

Curtis, T.P. 2010. Low-Energy Wastewater Treatment: Strategies and Technologies, in: Mitchell, R., Gu, J.-D. (Eds.), Environmental Microbiology. John Wiley & Sons, Inc., pp. 301–318.

Dimitriou, I., Aronsson, P. 2004. Nitrogen leaching from short-rotation willow coppice after intensive irrigation with wastewater. Biomass and Bioenergy 26(5): 433-441.

Elbana, T.A., Ramadan, M.A., Gaber, H.M., Bahnassy, M.H., Kishk, F.M., Selim, H.M. 2013. Heavy metals accumulation and spatial distribution in long term wastewater irrigated soils Journal of Environmental Chemical Engineering 1(4): 925-933.

El Kharraz, J., El-Sadek, A., Ghaffour, N., Mino, E. 2012. Water scarcity and drought in WANA countries. Procedia Engineering 33: 14-29.

English, M. 2014. Personal communication.

Fan, Y, Hu, H., Liu, H., 2007. Enhanced columbic efficiency and power density of air-cathode microbial fuel cells with an improved cell configuration. Journal of Power Sources 171: 348-354.

Fan, Y., Han, S-K., Liu H. Improved performance of CEA microbial fuel cells with increased reactor size. Energy and Environmental Science 5: 8273-8280.

Feng, Y., He, W., Liu, J., Wang, X., Qu, Y., Ren, N. 2014. A horizontal plug flow and stackable pilot microbial fuel cell for municipal wastewater treatment. Bioresource Technology 156: 132-138.

Food and Agricultural Organization (FAO). 1985. Water quality for agriculture. Rome, Italy.

Forecast-chart.com/inflation-usa-energy.html. 2014.

Guo, F., Fu, G., Zhang, Z., Zhang, C., 2013. Mustard tuber wastewater treatment and simultaneous electricity generation using microbial fuel cells. Bioresource Technology 136:425-430.

Haering, K.C., Evanylo, G.K. 2009. Water reuse: using reclaimed water for irrigation. Virginia Cooperative Extension. Publication 452-014.

Heijne, A., Liu, F., Weijden, R., Weijma, J., Buisman, C.J.N., Hamelers, H. V.M., 2010. Copper recovery combined with electricity production in a microbial fuel cell. Environmental Science and Technology 44, 4376–4381.

Hirooka, K., Ichihashi, O., 2013 Phosphorus recovery from artificial wastewater by microbial fuel cell and its effect on power generation, Bioresource Technology 137: 368-375.

Ichihashi, O., Hirooka, K., 2012. Removal and recovery of phosphorus as struvite from swine wastewater using microbial fuel cell. Bioresource Technology 114: 303-307.

John M.M., Bauder J.W., 2007. Root zone leachate from high chemical oxygen demand cannery water irrigation. Soil Science Society of America Journal 71:1893–1901.

Khan, S., Aijun, L., Zhang, S., Hu, Q., Zhu, Y.Z., 2008. Accumulation of polycyclic aromatic hydrocarbons and heavy metals in lettuce grown in the soils contaminated with long-term wastewater irrigation. Journal of Hazardous Materials 152(2): 506-515.

Khan, M.U., Malik, R.N., Muhammad, S. 2013. Human health risk from Heavy metal via food crops consumption with wastewater irrigation practices in Pakistan. Chemosphere 93(10): 2230-2238.

Li, Z., Zhang, X., Lei, L., 2008. Electricity production during the treatment of real electroplating wastewater containing Cr^{6+} using microbial fuel cell. Process Biochemistry 43, 1352–1358.

Liu, C., Li, S., Zhang, F. 2011. The oxygen transfer efficiency and economic cost analysis of aeration system in municipal wastewater treatment plant. Energy Procedia 5: 2437-2443.

Liu, H., Logan, B.E., 2004. Electricity generation using an air-cathode single chamber microbial fuel cell in the presence and absence of a proton exchange membrane. Environmental Science and Technology 38: 4040 - 4046.

Liu, W.H., Zhao, J.Z., Ouyang, Z.Y., Söderlund, L., Liu, G.H., 2005. Impacts of sewage irrigation on heavy metal distribution and contamination in Beijing, China, Environment International 31(6): 805-812.

Logan, B. E., Hamelers, B., Rozendal, R., Schroder, U., Keller, J., Freguia, S., Aelterman, P., Verstraete, W., Rabaey, K., 2006. Microbial fuel cells: Methodology and technology, Environmental Science and Technology 17, 5181–5192.

Lovin, D. 2014. Personal communication.

Lu, N., Zhou, S., Zhuang, L., Zhang, J., Ni, J. 2009. Electricity generation from starch processing wastewater using microbial fuel cell technology. Biochemical Engineering Journal 43 3: 246-251.

Madyiwa, S. Chimbari, M.J. Schutte, F. 2004. Lead and cadmium interactions in *Cynodon nlemfuensis* and sandy soil subjected to treated wastewater application under greenhouse conditions, Physics and Chemistry of the Earth 29: 1043–1048.

Mahmoud, M., Janssen, M., Peth, S., Horn, R., Lennartz B., 2012. Long-term impact of irrigation with olive mill wastewater on aggregate properties in the top soil. Soil and Tillage Research 124: 24-31.

Mansoorian, H.J., Mahvi, A.H., Jafari, A.J., Amin, M.M., Rajabizadeh, A., Khanjani N. 2013. Bioelectricity generation using two chamber microbial fuel cell treating wastewater from food processing. Enzyme and Microbial Technology 52(6–7): 352-357.

Mekki, A., Dhouib, A., Sayadi, S. 2007. Polyphenols dynamics and phytotoxicity in a soil amended by olive mill wastewaters. Journal of Environmental Management 84: 134-140.

Min, B., Kim, J.R., Oh, S.E., Regan, J.M., Logan, B.E., 2005. Electricity generation from swine wastewater using microbial fuel cells. Water Research 39: 4961–4968.

Mohan, S.V., Mohanakrishna, G. Velvizhi, G., Lalit Babu, V. , Sarma P.N. , 2010. Bio-catalyzed electrochemical treatment of real field dairy wastewater with simultaneous power generation. Biochemical Engineering Journal 51(1–2): 32-39.

Mosse, K.P.M., Patti, A.F., Smernik, R.J., Christen, E.W., Cavagnaro T.R. 2012. Physicochemical and microbiological effects of long- and short-term winery wastewater application to soils. Journal of Hazardous Materials 201–202: 219-228.

Mueller J. A., Boyle W.C., Popel H.J. 2002. Aeration: principles and practice. CRC press LLC.

Mukherjee, V., Das, A., Akhand, A., Gupta, G. 2013. Toxicity and profitability of rice cultivation under wastewater irrigation: the case of the East Calcutta Wetlands. Ecological Economics 93: 292-300.

Murray, A., Ray, I. 2010. Wastewater for agriculture: A reuse-oriented planning model and its application in peri-urban China. Water Research 44(5): 1667-1679.

Nikouei, A., Ward, F.A., 2013. Pricing irrigation water for drought adaptation in Iran. Journal of Hydrology 503: 29-46.

Nimje, V. R., Chen, C., Chen, H., Chen, C., Huang, Y.M., Tseng, M., Cheng, K., Chang, Y. 2012. Comparative bioelectricity production from various wastewaters in microbial fuel cells using mixed cultures and a pure strain of Shewanella oneidensis. Bioresource Technology 104:315-323.

Norton-Brandão, D., Scherrenberg, S.M., van Lier, J.B., 2013. Reclamation of used urban waters for irrigation purposes – A review of treatment technologies. Journal of Environmental Management 122: 85-98.

Oliveira, V.B., Simões, M., Melo, L.F., Pinto, A.M.F.R. 2013. Overview on the developments of microbial fuel cells. Biochemical Engineering Journal 73:53-64.

Oregon State Department of Environmental Quality (DEQ). 2013. Personal communication.

Pereira, B.F.F., He, Z.L., Silva, M.S., Herpin, U., Nogueira, S.F., Montes, C.R., Melfi, A.J. 2011. Reclaimed wastewater: Impact on soil–plant system under tropical conditions. Journal of Hazardous Materials 192(1): 54-61.

Puig. S., Serra, M., Coma, M., Cabré, M., Balaguer, M. D. Colprim, J. 2011. Microbial fuel cell application in landfill leachate treatment. Journal of Hazardous Materials 185(2–3): 763-767.

Sciarria, T.P., Tenca, A., D'Epifanio, A., Mecheri, B., Merlino, G., Barbato, M., Borin, S., Licoccia, S., Garavaglia, V., Adani, F., . 2013. Using olive mill wastewater to improve performance in producing electricity from domestic wastewater by using single-chamber microbial fuel cell. Bioresource Technology 147: 246-253.

Shahalam, A., Zahra, B.M.A., Jaradat, A. 1998. Wastewater Irrigation Effect on Soil, Crop and Environment: a Pilot Scale Study at Irbid, Jordan. Water, Air, and Soil Pollution 106(3-4): 425-445.

Sukkasem, C., Xu, S., Park, S., Boonsawang, P., Liu H., 2008. Effect of nitrate on the performance of single chamber air cathode microbial fuel cells. Water Research 42(19): 4743-4750.

Tandukar, M., Huber, S.J., Onodera, T., Pavlostathis, S., 2009. Biological chromium (VI) reduction in the cathode of a microbial fuel cell. Environmental Science and Technology 43, 8159–8165.

Tao, H. C., Liang, W., Li, W., Zhang, L.J., Ni, J.R., Wu, W.M., 2011. Removal of copper from aqueous solution by electrodeposition in cathode chamber of microbial fuel cell. Journal of Hazardous Materials 189, 186–192.

UNESCO-WWAP, 2003. Water for People Water for Life: The United Nations World Water. Development Report. UNESCO and Berghahn Books, New York.

US EPA, 2012. Guidelines for water reuse. Washington, DC.

US EPA. 1977. Pollution abatement in the fruit and vegetable industry. Washington, DC.

Wang, G., Huang, L., Zhang, Y., 2008. Cathodic reduction of hexavalent chromium [Cr(VI)] coupled with electricity generation in microbial fuel cells. Biotechnology Letters 30, 1959–1966.

Wang, J.F., Wang, G.X. Wanyan, H., 2007. Treated wastewater irrigation effect on soil, crop and environment: Wastewater recycling in the loess area of China. Journal of Environmental Sciences 19(9): 1093-1099.

Wang, Z., Lim, B., Choi, C., 2011. Removal of Hg^{2+} as an electron acceptor coupled with power generation using a microbial fuel cell. Bioresource Technology 102, 6304–6307.

Zhang, G., Zhang, H., Zhang, C., Zhang, G., Yang, F., Yuan, G., Gao, F. 2013. Simultaneous nitrogen and carbon removal in a single chamber microbial fuel cell with a rotating biocathode Process Biochemistry 48(5–6): 893-900.

Zhang, B., Feng, C., Ni, J., Zhang, J., Huang, W., 2012a. Simultaneous reduction of vanadium (V) and chromium (VI) with enhanced energy recovery based on microbial fuel cell technology. Journal of Power Sources 204, 34–39.

Zhang, L.J., Tao, H.C., Wei, X.Y., Lei, T., Li, J.B., Wang, A.J., Wu, W.M., 2012b. Bioelectrochemical recovery of ammonia–copper (II) complexes from wastewater using a dual chamber microbial fuel cell. Chemosphere 89, 1177–1182.

Zhao, L. Zhu, W., Tong, W. 2009. Clogging processes caused by biofilm growth and organic particle accumulation in lab-scale vertical flow constructed wetlands. Journal of Environmental Sciences 21(6): 750-757.

Zhuang, L., Zheng, Y., Zhou, S., Yuan, Y., Yuan, H., Chen, Y., 2012. Scalable microbial fuel cell (MFC) stack for continuous real wastewater treatment. Bioresource Technology 106: 82-88.

5. General Conclusions and Future Perspectives

5.1. General Conclusions

The objectives of this research were to expand MFC application in industrial and municipal industries and to bring it to real world application. The obtained results were presented in three chapters.

First, chapter 2 demonstrated that single-chamber MFC, of great potential for scaling-up, can be used simultaneously for heavy metal and organic matter removal as well as power generation. The study was conducted on Cadmium (Cd) and Zinc (Zn). The key findings of this research were the following:

- Simultaneous high Cd (90%) and Zn (97%) removal efficiencies and high power generation (3.6 W/m^2) can be obtained in single chamber air-cathode MFC.
- Cd and Zn start having a negative impact on the electrochemically active microorganisms and power generation at concentrations of 200 and 400 µM respectively.
- Gradual increase in metal concentrations led to a slower reduction in voltage output.
- Biosorption and sulfides precipitation are the major mechanisms for heavy metal removal in single-chamber MFC.

Second, chapter 3 showed that an enhancement in power generation and energy conversion from sewage sludge can be accomplished by a novel design of cloth-electrode assembly (CEA) MFC cell and after sludge fermentation. The results can be summarized as follows:

- Fermentation pretreatment of sewage sludge increased soluble organic carbon in the supernatant and increased power production.
- Fermentation was conducted for 96, 192 and 288 hours. Optimum fermentation time was 96 hours resulting in maximum power density by CEA-MFC of 1.2 W/m^2, (275% increase in power production compared to previous research findings).
- Energy efficiency from fermented sludge treatment by CEA-MFC is 11.5% and CEA-MFC system can be a promising modification to existing wastewater treatment infrastructure.

Third, in chapter 4, perspectives on scaling up MFC for wastewater treatment before irrigation were presented. A case study was presented involving food processing wastewater in a semi-arid region (the Columbia Basin of Oregon). A conceptual design was developed and the feasibility was evaluated in terms of water quality and economics. The analysis focused on economic performance parameters that would distinguish a conventional mid-scale treatment plant from an MFC system in an agricultural setting. It was found that MFC could be a feasible solution to wastewater disposal in the region by bringing the following advantages: (i) the value of electrical power generated; (ii) the fertilizer costs deferred by nutrient recovery; and (iii) the elimination of power costs needed for aeration during conventional treatment. Additionally, the value of recovered water, though presumably much lower in a rural setting than an urban center, would be a significant source of income. The obtained results are summarized as follows:

- MFC could be the solution to wastewater disposal in the region.

- Treated wastewater provides the farmers with clean water resolving the problem of water shortage.
- Residual nutrients in the treated wastewater reduce fertilizers cost.
- Generated electricity is an additional profit resulting in possible return on investment.
- Compared to conventional treatment, energy consumption is significantly reduced with the use of MFC due to the elimination of aeration in the process.

5.2. Future Perspectives

Though substantial progress has been achieved on MFC research in the last decade, many challenges still need to be faced to make MFC a commercially viable technology. For instance, improvement of reactor performance and reduction of the system capital cost (especially cathode) are required to make MFC competitive with other technologies converting waste to energy. Although MFC removes high percentages of organic matter, nitrogen and heavy metals from wastewater, the system is still not capable of removing some elements of concern such as sodium, chloride, carbonate and slowly degradable organic pollutants. Also MFC is sensitive to acidic and basic pH and high suspended solids in influent. Developing and testing the system on a pilot scale is needed before application on full scale due to the lack of developed models in the literature.

MFC technology could either replace traditional treatment technologies or could be used in conjunction with current treatment methods such as anaerobic digestion and aeration. The most promising application of MFC is in decentralized industrial treatment of fruit processing or brewery wastewater because those wastewater contain higher organic

content and simpler compounds compared to municipal wastewater and other waste streams. To date, the highest maximum power obtained with small scale MFC configuration is 2kW/m^3 while converting more than 90 g COD/L/d of synthetic wastewater. If similar power density could be obtained while taking this technology to pilot scale or beyond, MFC technology would become competitive with anaerobic digestion (generating 1 kW/m^3) on treatment efficacy and energy production. Though there are still many obstacles to overcome, MFC can indeed increase not only energy security but also water and food securities. Also, it can result in energy diplomacy between countries.

Additional references

Baulcombe, D. 2010. Reaping Benefits of Crop Research. Science 327: 271.

Bond, D. R., Lovley, D.R. 2005. Evidence for involvement of an electron shuttle in electricity generation by Geothrix fermentans. Appl. Environ. Microbiol. 71:2186–2189.

Bond, D. R., D. E. Holmes, L. M. Tender, Lovley, D. R. 2002. Electrodereducing microorganisms that harvest energy from marine sediments. Science 295:483–485.

Chaudhuri, S. K., Lovley, D. R. 2003. Electricity generation by direct oxidation of glucose in mediatorless microbial fuel cells. Nat. Biotechnol. 21: 1229–1232.

Fan, Y., Sharbrough, E., Liu, H. 2008. Quantification of the internal resistance distribution of microbial fuel cells. Environ. Sci. Technol. 42 (21): 8101–8107.

Holmes, D. E., D. R. Bond, Lovley, D. R. 2004. Electron transfer by Desulfobulbus propionicus to Fe(III) and graphite electrodes. Appl. Environ. Microbiol. 70:1234–1237.

Holmes, D. E., J. S. Nicoll, D. R. Bond, Lovley, D. R. 2004. Potential role of a novel psychrotolerant member of the family Geobacteraceae, Geopsychrobacter electrodiphilus gen. nov., sp. nov., in electricity production by a marine sediment fuel cell. Appl. Environ. Microbiol. 70:6023–6030.

Kim, H. J., M. S. Hyun and I. S. Chang, Kim, B. H. 1999. A fuel cell type lactate biosensor using a metal reducing bacterium, Shewanella putrefaciens, J. Microbiol. Biotechnol. 9: 365-367.

Liu, H., Logan, B. E. 2004. Electricity generation using an air-cathode single chamber microbial fuel cell in the presence and absence of a proton exchange membrane. Environ. Sci. Technol. 38: 4040-4046.

Liu, H.; Ramnarayanan, R.; Logan, B. E. 2004. Production of electricity during wastewater treatment using a single chamber microbial fuel cell. Environmental Science & Technology 38(7): 2281-2285.

Logan, B. E. and Regan, J. M. 2006. Electricity-producing bacterial communities in microbial fuel cells. Trends Microbiol., 14: 512–518.

Park, H. S., Kim, B. H., Kim, H. S., Kim, H. J., Kim, G. T., Kim, M., Chang, I. S., Park, Y. K., Chang, H. I. 2001. A novel electrochemically active and Fe(III)-reducing bacterium phylogenetically related to Clostridium butyricum isolated from a microbial fuel cell. Anaerobe 7: 297-306.

Pham, C. A., Jung, S. J., Phung, N. T., Lee, J., Chang, I. S., Kim, B. H., Yi, H., Chun, J. 2003. A novel electrochemically active and Fe(III)-reducing bacterium phylogenetically related to Aeromonas hydrophila, isolated from a microbial fuel cell. FEMS Microbiol. Lett. 223: 129–134.

Pham, T.H., Jang, J.K., Chang, I.S., Kim, B.H. 2004. Improvement of cathode reaction of a mediatorless microbial fuel cell Journal of Microbiology and Biotechnology 14 (2): 324-329.

Potter, M. C. 1911. Electrical effects accompanying the decomposition of organic compounds. Proceedings of the Royal Society of London. Series B, Containing Papers of a biological Character 84: 260-276.

Rabaey, K., N. Boon, S. D. Siciliano, M. Verhaege, Verstraete, W. 2004. Biofuel cells select for microbial consortia that self-mediate electron transfer. Applied and Environmental Microbiology 70: 5373-5382.

Rittmann, B.E., Krajmalnik-Brown, R., Halden, R.U. 2008. Pre-genomic, genomic and post-genomic study of microbial communities involved in bioenergy, Nature Reviews Microbiology 6: 604-612.

Torres, C.I., A. K. Marcus, Rittmann, B.E.. 2007. Kinetics of Consumption of Fermentation Products by Anode-Respiring Bacteria. Appl. Microbiol. Biotechnol. 77: 689-697.

Wang, Y.F., M. Masuda, S. Tsujimura, Kano, K.. 2008. Electrochemical regulation of the end-product profile in Propionibacterium freudenreichii ET-3 with an endogenous mediator. Biotechnol. Bioeng., 2008. 101(3): 579-586.

Xing, D., Zuo, Y., Cheng, S., Regan, J. M., Logan, B. E. 2008. Electricity generation by Rhodopseudomonas palustris DX-1. Environ. Sci. Technol. 42: 4146–4151.

You S., Q. Zhao, J. Zhang, J. Jiang, Zhao, S. 2006. A microbial fuel cell using permanganate as the cathodic electron acceptor. Journal of Power Sources 162: 1409–1415.

Zhang, F., Cheng, S., Pant, D., Van Bogaert, G., Logan, B.E. 2009. Power generation using an activated carbon and metal mesh cathode in a microbial fuel cell. Electrochemistry Communications 11(11): 2177-2179.

Zuo, Y., Xing, D., Regan, J. M., Logan, B. E. 2008. An exoelectrogenic bacterium Ochrobactrum anthropi YZ-1 isolated using a U-tube microbial fuel cell Appl. Environ. Microbiol. 74(10):3130-3137.