Feasibility of using Waste Heat as a power source to operate Microbial Electrolysis Cells towards Resource Recovery

Akshay Jain

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Zhen (Jason) He, Chair
Andrea Dietrich
Zhiwu (Drew) Wang
Haibo Huang

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Akshay Jain

Abstract (Academic)

Wastewater treatment has developed as a mature technology over time. However, conventional wastewater treatment is a very energy-intensive process. Bioelectrochemical system (BES) is an emerging technology that can treat wastewater and also recover resources such as energy in the form of electricity/hydrogen gas and nutrients such as nitrogen and phosphorus compounds. Microbial electrolysis cell (MEC) is a type of BES that, in the presence of an additional voltage, can treat wastewater and generate hydrogen gas. This is a promising approach for wastewater treatment and value-added product generation, though it may not be sustainable in the long run, as it relies on fossil fuels to provide that additional energy. Thus, it is important to explore alternative renewable resources that can provide energy to power MEC. Waste heat is one such resource that has not been researched extensively, particularly at the low-temperature spectrum. This was utilized as a renewable resource by converting waste heat to electricity using a device called thermoelectric generator (TEG). TEG converted simulated waste heat from an anaerobic digester to power an MEC. The feasibility of TEG to act as a power source for an MEC was investigated and its performance compared to the external power source. Various cold sources were analyzed to characterize TEG performance. To explore this integrated TEG-MEC system further, a hydraulic connection was added between the two systems. Wastewater was used as a cold source for TEG and it was recirculated to the anode of the MEC. This system showed improved performance with both systems mutually benefitting each other. The operational parameters were analyzed for the optimization of the system. The integrated system could generate hydrogen at a rate of 0.36 ± 0.05 m³ m⁻³ d⁻¹ for synthetic domestic wastewater treatment. For the practical application, it is necessary to estimate the cost and narrow the focus on the functions of the system. Techno-economic analysis was performed for MEC with cost estimation and net present value model to understand the economic viability of the technology. The application niche of the BES was described and directions for addressing the challenges towards a full-scale operation were discussed. The present system provides a sustainable method for wastewater treatment and resource recovery which can play an important role in human health, social and economic development and a strong ecosystem.
Feasibility of using waste heat as a power source to operate Microbial Electrolysis Cell towards Resource Recovery

Akshay Jain

Abstract (General)

An average person produces about 50-75 gallons of wastewater every day. In addition to the households, wastewater is generated from industries and agricultural practices. As the population increases, the quantity of wastewater production will inevitably increase. To keep our rivers and oceans clean and safe, it is essential to treat the wastewater before it is discharged to the water bodies. However, the conventional wastewater treatment is a very energy (and thus cost) intensive process. For low-income and developing parts of the world, it is difficult to adapt the technology everywhere in its present form. Furthermore, as the energy is provided mostly by fossil fuels, their limited reserves and harmful environmental effects make it critical to find alternative methods that can treat the wastewater at a much lower energy input. For a circular and sustainable economy, it is important to realize wastewater as a resource which can provide us energy, nutrients, and water, rather than discard it as a waste. Bioelectrochemical systems (BES) is an emerging technology that can simultaneously treat wastewater and recover resources in the form of electricity/hydrogen gas, and nitrogen and phosphorus compounds. Microbial electrolysis cell (MEC) is a type of BES that is used to treat wastewater and generate hydrogen gas. An additional voltage is supplied to the MEC for producing hydrogen. In the long run, this may not be sustainable as it relies on fossil fuels to provide that additional energy. Thus, it is important to explore alternative renewable resources that can provide energy to power MEC. Waste heat is a byproduct of many industrial processes and widely available. This was utilized as a renewable resource by converting waste heat to electricity using a device called thermoelectric generator (TEG). TEG converted simulated waste heat from an anaerobic digester to power an MEC. The mutual benefit for MEC and TEG was also explored by connecting the system electrically and hydraulically. Cost-estimation of the system was performed to understand the economic viability and functions of the system were developed. The present system provides a sustainable method for wastewater treatment and resource recovery which can play an important role in human health, social and economic development and a strong ecosystem.
Dedication

This dissertation is dedicated to my parents (Deepmala Jain and Abhay Kumar Jain) and grandparents (Rajni Devi Tiwari, Mohan Bai Saklecha, Manohar Lal Tiwari, and Harakchand Ji Saklecha) who all have valued education above everything else.
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As I begin to think about all the people that have been a great support in this journey, I already feel this might become the longest section of my dissertation. I would like to start with the biggest reason I am here, my mother. She is the one person who knew, even when I was not sure, that I am going to go to the United States for higher education. She is hugely supported in this endeavor with my father. He not only arranged that financially I have all the things for a comfortable life here when he might not have sufficient things for himself but also made sure to provide moral support and love at all the hard times. I know no amount of gratitude can ever compensate for all that you have provided all these years yet I thank both of you and would try to fulfill as many dreams of yours as possible.

Being an international student, it is always difficult to find directions for your future career. After one semester here, I was scared as I could not find an advisor. It was then, Dr. Zhen (Jason) He, offered me to work in his lab, just to explore my interests. I have not thought at that time that it was just the beginning of a long-lasting relationship I am going to have with him. But his strong belief and the commitment to see me advance gave me the confidence to change my degree from Master’s to Doctorate under his guidance. Dr. He has always encouraged me to think outside the box, guided when I got lost and was always there holding the light when I could only feel darkness ahead. Whether I wanted to go for an internship or a study abroad program, Dr. He has always provided support. Even all my committee members have been very supportive of me during this entire journey. From being my temporary advisor when I arrived at Virginia Tech to staying on my committee all the way to the end of my degree, Dr. Andrea Dietrich has seen me grow. I learned a lot in the Aquatic Chemistry class with her and thoroughly enjoyed during WaterIGEP social activities. Dr. Zhiwu (Drew) Wang has always offered constructive suggestions on research projects as well as practical advice on career building. I am really thankful to Dr. Haibo Huang for sitting with me for long sessions, patiently listening to all my doubts and providing technical and moral support. Outside of my committee, I am actually grateful to have such a wonderful Environment and Water Resources department. I can proudly say that each faculty member strives to make every student feel welcome and I am thankful for the support system they provide. I would like to thank Dr. William Knocke, with who I got to spent a lot of time when I took his classes, being his teaching assistant for three out of the five spring semesters and during the organization of Open House. He is a wealth of knowledge and
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Things could not have run as smoothly as they did without the enormous help from staff members. Julie Petruska, the former lab manager for the EWR department, has always kept us safe while we worked with different chemicals and equipment in the lab. I was fortunate to get her help during my time as the teaching assistant of the Unit Operations and Processes Laboratory. I could not thank her enough for all the assistance and it would be impossible to do all those tasks myself. I am thankful to Dr. AJ Prussin, the current lab manager, for assisting me with setting up my research project and always guiding to ensure lab safety. If I could complete this dissertation, it is not without the help of Elizabeth (Jody) Smiley. Thank you, Jody, for always being available to train on all the equipment and machines needed to perform my research. For any the administrative work, there was one person who was just an email away, Elizabeth (Beth) Lucas! From helping with setting up all the meetings to just cheering me up, Beth was always there. Thank you, Beth, for your extensive support. I would like to appreciate the help of staff members at the Christiansburg Wastewater Treatment Plant. They were always supportive whenever I needed to collect any samples for anaerobic sludge from the digester and secondary effluent. I would also extend my thanks to Jim from Bulls and Bones Brewhaus for collecting and storing the brewery wastewater sample for me.

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Ut Prosim
Forever a Hokie!
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Attribution

Dr. Zhen He worked as the principal investigator. Each co-author is duly credited for their contribution to this work in the list below.

**Zhen (Jason) He, Ph. D.**
Professor, Department of Energy, Environment and Chemical Engineering, Washington University in St. Louis, St. Louis, MO 63130
Adjunct Professor, Department of Civil and Environment Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA 24060
Co-author: Chapter 1 – 6

**Shiqiang (Nick) Zou, Ph. D.**
Postdoctoral Scholar, Department of Civil and Environment Engineering, Stanford University, Stanford, CA 94305
Co-author: Chapter 1

**Haibo Huang, Ph. D.**
Assistant Professor, Department of Food Science & Technology, Virginia Polytechnic Institute and State University, Blacksburg, VA 24060
Co-author: Chapter 6
1 Introduction

1.1 Background

Energy and water supply are the two most important challenges facing humanity. With the world population expected to surpass 9 billion by 2050, these two parameters can largely decide the economies of the nations in the future (Finley & Seiber, 2014; Hussey & Pittock, 2012). The interactions and interdependence of energy and water on each other further add to the complexity of the challenge. Meeting this challenge necessitates an interdisciplinary train of thought. The solutions should ensure security, sustainability, and economic viability. Our planet is largely dependent on fossil fuels for meeting energy demands. Currently, fossil fuels supply 80% of the world’s primary energy needs (Mohr et al., 2015). In the US, a quarter of the total fossil fuel consumption is used for electricity and heat production (USEPA). The global energy consumption increases by about 2% per annum (Shafiee & Topal, 2008). The growth of energy demand is higher in developing economies such as China and India. As the developing part of the world progresses, the growth would further increase. However, out of the three fossil fuels – oil, coal and gas, it is estimated that only coal will be available after 2042 and the rest two would be depleted (Shafiee & Topal, 2009). In addition to the large dependence, the use of fossil fuel as an energy source is the major source of greenhouse gas (GHG) emissions. US EPA estimated 65% of global GHG emissions are generated from fossil fuel consumption (USEPA). The global rise of temperature and adverse effects of climate change are exacerbated by the increase in GHG emissions. The limited reserves of fossil fuels, in addition to the harmful environmental effects of GHG, make it imminent to find alternative – renewable and sustainable, energy sources (Sharma & Ghoshal, 2015).

Wastewater treatment, an indispensable process to prevent the mixing of contaminated water with clean water bodies, is energy-intensive, consuming up to 3% of the total electrical energy demand in the US (USEPA, 2006). This energy is often supplied by fossil fuels. Wastewater may contain up to 1.93 kWh m$^{-3}$ chemical energy and 7.0 kWh m$^{-3}$ thermal energy (McCarty et al., 2011) whereas the activated sludge process, commonly used for the domestic wastewater treatment, consumes about 1.1 kWh m$^{-3}$ energy as per Electric Power Research Institute (EPRI)
Clearly, wastewater possesses more energy than required for its treatment. However, current conventional wastewater treatment technology consumes a huge amount of energy without recovering any energy available within the wastewater. Such an operation may not be sustainable in the long-term; especially for the developing nations. The provision of clean water and sanitation is the sixth goal in the United Nations’ Sustainable Development Goals (SDG) initiative. To realize that goal, it is necessary to develop technologies that could support wastewater treatment without becoming a burden on the economy.

1.2 Bioelectrochemical System

1.2.1 History

A new system, called as bioelectrochemical system (BES), is emerging as a sustainable solution for the wastewater treatment and recovery of energy and resources (Pant et al., 2012). In BES, microorganisms are used to treat different types of wastewater which in addition to contaminant removal, generate electrons. The electrons can be used for the production of electricity or other value-added products such as hydrogen, in a (bio)electrochemical cell setup. The concept of electrochemical energy system involving a biological part is not new, however, and was first founded in 1911. M C Potter of the University of Durham discovered microorganisms could dissociate organic compounds to generate an electric effect (Potter & Waller Augustus, 1911). Microorganisms act as a catalyst to release the chemical energy stored in the bonds of organic compounds. This energy, in the presence of the electrochemical setup of the cell, could be converted to electrical energy. In the specialized galvanic cell with platinum electrodes, Potter could achieve a potential difference of 0.3-0.5 V. This fascinating interaction between the microbes and the electrodes was explored further in the 20th century, albeit sporadically (Fig.1.1). Two decades from the first discovery, an electrical half-cell was built (Cohen, 1931). Six cells were stacked in this study which produced an output voltage of 35 V (2 mA current) using glucose as a substrate. The thermodynamics behind the bioelectrochemical energy conversion was explained in a report in 1964 (Del Duca & Fuscoe, 1964). The report identified the applications of this biochemical energy within four major areas – power sources, detectors of specific contaminants in low concentrations, sensors, and catalysts for the generation of electrochemical reactions. It is interesting to note that more than half a century later, with the development of BES for multi-application in various fields, these remain the main applications
of the system. A complete biological fuel cell was realized in 1977 using immobilized *Clostridium butyricum* as biocatalyst at the anode (Karube et al., 1977). They reported a current generation of 1.1-1.2 mA simultaneously producing 0.6 mol of hydrogen and 0.2 mol of formic acid. A microbial fuel cell (MFC) with *Proteas vulgaris* was used to study glucose metabolism and stoichiometry of product formation in 1985 (THURSTON et al., 1985). Research on MFC garnered higher interest in the 1990s with a patent for the bioelectrochemical desulfurization process (Kim et al., 1990) and the use of graphite as an electrode for electricity production with carbohydrates in MFC (Allen & Bennetto, 1993). These developments led the foundation for BES, which was instrumental in the current bloom in the research in the field. The past two decades observed exponential growth of the field with a focus on treatment and recovery from waste streams.

**Figure 1.1** Brief timeline of bioelectrochemical system (BES) development

### 1.2.2 BES Components

In a typical BES, there are two electrodes – anode and cathode. Microorganisms oxidize the organic compounds present in the wastewater in the anode chamber and transfer the electrons to the anode electrode. The electrons move from anode to cathode via an external electric circuit.
and reduce an electron acceptor like oxygen or proton. Cathode catalysts play a key role in reducing the overpotential for the chemical reaction. Membrane, generally separating the two chambers, allow the transfer of selective ions through them. In this way, an electric circuit is completed and microorganisms convert chemical energy present in the wastewater to electrical/gaseous energy. Fig. 1.2 shows the schematic of a typical BES. Thus, the four main components of a typical BES can be described as — microorganisms, anode, cathode, and membranes.

Figure 1.2 Schematic of a typical BES (Jain et al., 2020)

1.2.2.1 Microorganisms
Microorganisms are one of the key components in the “bio” electrochemical system and responsible for electron generation (Mu et al., 2010). The microbes actively engaged in the transfer of electrons in the system are also called electrochemically active bacteria (EAB) or electrogenic bacteria. EAB use anaerobic respiration to transfer electrons from organic compounds to the electrode. They could be exoelectrogenic bacteria such as *Geobacter* and *Shewanella*, which have the ability to transfer electron directly with their conductive pilli (nanowires) (Logan, 2008) or *Escherichia coli* which need artificial electron mediator such as neutral red (Park et al., 1999) for the electron transfer. The mechanism of electron transfer in EAB is an area of active research as the diversity of them is still being discovered (Popov, 2015).

### 1.2.2.2 Anode

One of the performance characteristics of BES is its power output. Electrode materials can have a huge impact on the system performance as they act as the electron transfer station in the BES. It is important for the electrodes – both anode and cathode, to have high conductivity and large active surface area for a high rate of reaction and transfer (Park & Zeikus, 2002; Rabaey et al., 2005). Anodes typically represent the biological part over the different types and configurations of BES. As microorganisms are present in the anode chamber of the BES, the anode electrode should also able to offer a compatible surface for the growth of biofilms. Carbon has been the most preferred form of electrode in the case of anode. Carbon offers multiple advantages – cheap, biocompatible and stable for chemical reactions and microorganisms (Zhou et al., 2011). Some of the materials used as anodes are carbon brush, carbon cloth, graphite rod, carbon paper, and carbon felt. Carbon brush has been used extensively in the BES as it provides high surface area and low resistance (Feng et al., 2010). Depending on the configuration of the BES, carbon paper and cloth can be attractive as they provide a flat surface to reduce the distance between electrodes. Other materials have also been investigated such as carbon nanotubes, metals such as copper, nickel, stainless steel and cobalt (Baudler et al., 2015), however, carbon remains the most versatile electrode material for the anode.

### 1.2.2.3 Cathode

Cathodes play an important role in the BES as the reduction reaction at the cathode can determine the resource being recovered and the rate can represent the performance of the system. It has been found that cathodes have a higher impact on the power density of the system.
compared to the anode (Fan et al., 2008). Thus, the material and design of the cathode can play a
crucial role in a BES. Carbon material has been used commonly in the cathode. However, plain
carbon electrode such as carbon cloth or carbon paper, may not be effective as the reaction rate is
very slow on its own due to the presence of high overpotential (Kundu et al., 2013). Cathode
catalysts are used to reduce the energy loss due to overpotential, and various cathode catalysts
have been studied in BES: electrocatalysts such as platinum (Pt), palladium (Pd), nickel (Ni),
stainless steel, activated carbon, graphene, carbon nanotube; photoelectrocatalysts such as TiO$_2$
and Cu$_2$O; and biocatalysts including both enzymes and microorganisms (Liu et al., 2014).
Platinum (Pt) offers the most practical catalysts to increase the reduction rate because of its low
potential (Zhou et al., 2011). Pt is bind to carbon in the form of a paste often using a binder such
as Nafion or PTFE [poly(tetrafluoroethylene)]. Pt is a noble-metal, has a high cost and low
availability. Furthermore, the surface of Pt could be poisoned in the presence of sulfur species
(Pillay et al., 2010). Non-noble catalysts are actively researched for the cathode electrode. First-
row transition metals such as nickel (Hu et al., 2009) and stainless steel (Selembo et al., 2009)
have been investigated for their easy availability and low overpotential and have shown
promising results. Cathode cost and efficiency can be the deciding factors, as the system moves
towards industrial application.

1.2.2.4 Membranes

Membranes are a key part of BES, acting as the separator between chambers and facilitating ion
exchange (Jain et al., 2020). The electric field generated with the flow of electrons leads to the
migration of ions from one chamber to the other. Depending on the type of membrane used, they
can allow selective ions to pass through (ion exchange membranes (IEMs)) and reclaim high-
quality water (filtration/forward osmosis (FO) membranes). Membranes can also help to
maintain the purity of products formed in a BES such as hydrogen gas and increase the yield by
protecting the products from being consumed by other processes. Integration of membranes with
BES has led to multi-application of the system such as producing high-quality effluent, filtration,
and desalination (Yuan & He, 2015). However, membrane integration is not free from
challenges. Membrane fouling, scaling, reduced efficiency due to the pH gradient between
chambers, and relatively high cost of materials are some of the drawbacks from the use of
membranes.
1.2.3 BES Types

In general, BES can be grouped into four categories: microbial fuel cells (MFCs) for the production of electricity (Santoro et al., 2017); microbial electrolysis cells (MECs) for hydrogen generation (Logan et al., 2008); microbial desalination cells (MDCs) for water desalination and recovery (Sevda et al., 2015), and microbial electrosynthesis cells (MES) for the production of organic compounds from reduction of carbon dioxide (Rabaey & Rozendal, 2010). Fig. 1.3 represents the different types of BES with their key functions. MFCs are representative BES and have received the most attention in research and development. They have been studied for treating both municipal and industrial wastewater, producing bioenergy, and sensing contaminants (Santoro et al., 2017). When an external voltage is applied to the electrical circuit, an MFC is converted into an MEC that can achieve proton reduction to hydrogen gas (Liu et al., 2005; Rozendal et al., 2006). Hydrogen is a carbon-free, clean fuel, which can be stored and transported, and hence, could be more valuable than electrical energy (from MFCs). MFCs can also be modified to desalinate water in an MDC, which contains one or more desalination chambers using pairs of anion exchange membrane (AEM) and cation exchange membrane (CEM). MDCs follow the similar principle of electrodialysis (ED) but can achieve desalination at a much lower energy consumption because of bioenergy production from the organic oxidation (Sevda et al., 2015). Microbes are not only used for the treatment of wastewater (oxidation reaction) but have also been explored for reducing carbon dioxide in MES that can use bioelectricity to produce compounds such as methane, acetate, and ethanol (Bajracharya et al., 2015).
The focus of this work is on one particular type of BES – microbial electrolysis cell or an MEC. MEC is a cutting edge and promising alternative technology for wastewater treatment and value-added compounds production (such as hydrogen) from the oxidation of organic compounds present in wastewater (Escapa et al., 2016). MEC was discovered by two research groups independently when they identified that bacteria could produce hydrogen in a BES through a process similar to electrolysis (Liu et al., 2005; Rozendal et al., 2006). MEC has been referred by other names in the past such as a biocatalyzed electrolysis cell (BEC) or a bio-electrochemically assisted microbial reactor (Ditzig et al., 2007; Liu et al., 2005; Rozendal et al., 2006). Hydrogen
(H₂) is a very promising fuel, with several technical and environmental advantages (Das, 2009). It is the only carbon-free fuel, producing water when combusted, and has the highest heating value on a weight basis (142 kJ/g) on earth. It has been used as fuel for space shuttle and rockets in the form of liquid hydrogen (Kundu et al., 2013). Using H₂ gas for energy production protects the environment from GHG emissions, acid rain, and ozone layer depletion. It is an essential component of metallurgy, fertilizers, chemical and petrochemical industries (Scholz, 1993). Thus, the production of biohydrogen from bio-waste and waste streams using bio-electrohydrogenesis is attractive and favorable.

The basic principle of an MEC is the same as outlined for the BES. The EAB in the anode of an MEC oxidizes organic compounds to produce carbon dioxide, electrons, and protons. The electrons are transferred to the anode electrode by the microorganisms. For an MEC, when electrons reach the cathode electrode, they reduce the protons to produce hydrogen gas. The reduction reaction in the MEC, however, is not spontaneous. An additional voltage (0.14V) is theoretically required to produce hydrogen at the cathode at standard conditions (Rozendal et al., 2006). Practically, an applied voltage 0.2-0.8V is used in the process to overcome the overpotentials caused by microorganisms, ohmic and other losses (Kadier et al., 2016). This is considerably low compared to 1.8-2.3V required for water electrolysis (Bockris et al., 1985). The difference between an MFC and an MEC in here is that the cathode chamber of the MFC is aerobic while MEC is completely anaerobic and thus different products are obtained. The absence of oxygen promotes the growth of obligate anaerobic bacteria such as Geobacter spp., as no oxygen is diffused to the anode. The redox half-reactions occurring at the anode and the cathode of an MEC, when acetate is oxidized at the anode, is:

Anode: $\text{CH}_3\text{COO}^- + 4\text{H}_2\text{O} \rightarrow 2\text{HCO}_3^- + 8e^- + 9\text{H}^+$  \(1.1\)

Cathode: $2\text{H}^+ + 2e^- \rightarrow \text{H}_2$  \(1.2\)

Accordingly, to produce hydrogen at the cathode a potential of $E^\circ = 0.42V$ is required at standard conditions ($T = 25 \, ^\circ C, P = 1 \, \text{bar}, \text{pH} = 7$) (Logan et al., 2008). The potential generated at the anode by microorganisms is about 0.28V. Thus, with an addition of 0.14V, theoretically, hydrogen can be produced.
Many reports suggest that MECs may have techno-economical and environmental advantages over MFCs (Escapa et al., 2016; Foley et al., 2010; Sleutels et al., 2012) depending on the value-added product obtained (hydrogen, ethanol, hydrogen peroxide, etc.). Though MECs may be technically better than MFCs, they still need an external source of power for hydrogen production. Supplying the power externally using conventional energy sources would put a burden on energy demands and makes the process less-sustainable as a full-scale technology. Therefore, alternate sources of energy that are environmentally-friendly such as solar, wind or waste heat, are needed to supply the additional power (Zhang & Angelidaki, 2014).

1.3 Alternative power sources

Alternative renewable energy could be supplied by many sources such as solar, wind, microbial fuel cells, waste heat, etc. The resource being used should have certain characteristics to be used. First, it should be feasible to power MEC with that source. As there is a minimum threshold beyond which hydrogen production is observed (>0.4 V), the energy source should be able to supply sufficient power. Second, it should be continuous, that is, there should not be an intermittent supply of power. An intermittent supply may lead to a decline in microorganism’s growth and poor performance of the system. Third, the resource should be economical. As wastewater treatment is a mass-scale activity, a huge capital cost for the renewable resource may prevent the industrial application of the technology.

Dye-sensitized solar cells (DSSC) have been investigated to be used as a power source for MEC (Ajayi et al., 2010; Ajayi et al., 2009; Chae et al., 2009). A DSSC converts light energy falling on the photo-electrode into electrical energy with a counter electrode and electrolyte between the electrodes to complete the setup. The photo-electrode consists of the dye-sensitized coating. The electrolyte consists of iodide/tri-iodide oxide redox couples which act as the electron mediator between the two electrodes. In an MEC-DSSC integrated system, light energy falling on the photo-electrode is absorbed by the dye. The absorbed energy excites electrons to the conduction band of titanium dioxide where charge separation takes place and the excited electrons flow through the cathode for proton reduction. Anode on the other side, transfer the electrons from the bacterial oxidation to the counter electrode of the DSSC. The electrons with the help of redox mediator are used to regenerate the dye molecules. The DSSC was able to produce 0.6-0.8 V of
open-circuit voltage. Hydrogen production varied in the range of 0.07 – 0.14 m$^3$ m$^{-3}$ d$^{-1}$ from a single MEC (Ajayi et al., 2009; Chae et al., 2009).

MFC, another type of BES, which generates electricity has also been used to power an MEC. In an MFC, the anodic reaction is the same as the MEC, with EAB oxidizing the organic matter and producing carbon dioxide, protons, and electrons. The difference, between the two systems – MFC and MEC, is that in an MFC, oxygen is reduced at the cathode whereas protons are reduced at the cathode in an MEC. The cathode of an MFC is, thus, aerobic. For use as a power source, the anode of the MFC is connected to the cathode to provide electrons for hydrogen evolution reaction whereas electrons from the anode of the MEC are transferred to the cathode of the MFC to complete the circuit. The MFCs could reach an open circuit voltage of 0.8 V (Sun et al., 2008). The hydrogen production rate was comparatively low with a range of 0.0145 – 0.0149 m$^3$ m$^{-3}$ d$^{-1}$ (Sun et al., 2009; Sun et al., 2008).

These alternative power sources allow the system to be less dependent on fossil-fuel based energy sources. These systems, though, have their own challenges. For example, both DSSC-MEC and MFC-MEC systems are interdependent on each other. If one of the systems performs poorly, the other is negatively affected. Solar energy is weather dependent and may not be able to provide uniform power. Thus, it is important to continue to research alternative renewable resources for power supply. Waste heat, a byproduct of industrial processes, is an attractive option. Thermal energy available in the waste heat can be converted to electrical energy by the means of a device called thermoelectric generator (TEG).

1.3.1 Thermoelectric generator (TEG)
A TEG module utilizes the “Seebeck effect” to transfer the thermal energy difference between a heat source and a heat sink to electricity (Hamid Elsheikh et al., 2014). A thermoelectric device consists of p- and n-type semiconductor junctions which are attached to each other by a conducting material (Bell, 2008). When one side of the junctions is heated and the other side is cooled, due to the temperature differential, electrons/hole pairs are created on the hot side and absorb energy (heat). On the cold side, the electron/hole pairs are combined and release energy (heat). A voltage potential, called Seebeck voltage, is thus created driving the electron/hole pair flow. The net voltage is formed at the bottom of the element legs and extracted as power. This
Seebeck effect forms the basis of the operation of the TEG devices. The efficiency is directly related to the temperature difference (ΔT) with higher efficiency at a larger temperature difference. Though higher ΔT areas have been widely studied and used in applications such as internal combustion engines and spaceships, the low ΔT fields have not been as well (Zou et al., 2018). TEG is a simple, solid-state device with a noise-free stable operation and minimum maintenance which reduces the burden on the WWT facility staff.

TEG has shown some feasibility as a power source for MEC with liquid (hot water) as the heat source (Chen et al., 2016). Anaerobic digestion is a common treatment process for various types of wastewater. A surplus of heat energy from the process is released in the environment. This waste heat from the anaerobic digester (AD) can be a promising source of energy. The gaseous heat can be directly used as a heat source for TEG without losing efficiency in heating a liquid. This utilizes the waste heat from AD and supplies the additional energy required by MEC, in a sustainable manner. Thus, MEC integrated with TEG is expected to be a viable solution for wastewater treatment, waste heat utilization, and energy recovery.

1.4 Outline
As BES continues to develop, it is important to narrow the focus of the system. The cathode can provide extra treatment in terms of physical and chemical space. Other functions of the BES such as nutrient, energy and water recovery are crucial to the overall success of the technology. The application niches of BES are discussed for developing technology in a particular direction. The main focus of this work is to investigate the feasibility of TEG as a power source for MEC and to further develop its application within the system. Furthermore, to realize the technology at full scale, it is important to understand the economic feasibility and scalability of the technology. A techno-economic analysis can reflect the current status of the technology and the areas that should be focused on improving the technology to achieve commercial success. This work is expected to advance the application of microbial electrolysis cell technology. Hence, more focus is given on the applied side of the technology compared to the fundamental knowledge. This dissertation contains a total of six (6) chapters. The specific aims of this work are as follows:

As the first specific aim (SA1), this work describes the ability and availability of cathode in the BES for enhanced treatment of contaminants, challenges pertaining to the cathode treatment and future directions.
The second specific aim (SA2) is to develop the application niche of BES technology. As the BES developed over the years, multiple applications have been explored. It is important to understand the viable avenues and focus on the limitations of the technology to bring it to commercial competitiveness.

The third specific aim (SA3) of this dissertation is to assess the feasibility of TEG to be used as a power source for MEC specifically investigating the waste gaseous heat from an AD to be converted to useful energy form as electricity. Different cold sources were explored to understand TEG characteristics.

The fourth specific aim (SA4) is to study the effect of electrical as well as a hydraulic connection between TEG and MEC on the performance of the overall system. Different operation parameters were varied to optimize system performance.

The fifth specific aim (SA5) is to perform the techno-economic analysis (TEA) for the MEC technology for a small-scale treatment facility. Cost estimation of the technology can assist in the conceptual design of a large-scale system and provide directions for future research. TEA for a brewery wastewater treatment using MEC was performed and costs were compared to an AD.
References


2

Cathode-enhanced treatment in bioelectrochemical systems

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2.1 Abstract

Bioelectrochemical systems (BES) have been intensively studied as a new technology for wastewater treatment. However, the treatment efficiency of BES anodes is limited and the anode effluent usually cannot be for direct discharged or reused. To enhance the treatment, BES cathodes may be used for additional treatment of selected contaminants. This has been investigated in a number of approaches, which can be grouped into cathode-stimulated treatment and cathode-supported treatment. The former involves electron transfer directly to reduce contaminants like nitrate or dye compounds, while the latter can accomplish contaminant removal by aerobic oxidation, algal growth, production of strong oxidants for advanced oxidation, and/or membrane treatment. This paper aims to provide a concise view and discussion on the cathode-promoted wastewater treatment in BES, analyze challenges pertaining to the cathode treatment, and offer suggestions on the future development of BES for maximized treatment performance.
2.2 Introduction

Along the BES development, wastewater treatment is considered a basic function and also of great importance to possible implementation of this technology. Organic removal is a primary goal for wastewater treatment, and in BES the removal efficiency is highly variable depending on several factors such as the composition and strength of wastewater, hydraulic retention time, reactor configurations, temperature, etc. Most removal occurs in the BES anode for producing electrons (Pandey et al., 2016). In general, BES can achieve good removal of organic matter from low-strength wastewater or simple organic substrates, while the removal efficiency would become much lower when dealing with high-strength wastewater or complex organic compounds (Pant et al., 2010). Nutrients such as nitrogen and phosphorus, however, can hardly be removed in the anode of BES, because their removal (if via biological pathways) would need to involve aerobic conditions. Therefore, the effluent from the BES anode is a partially treated stream, which still contains residue compounds such as organics and nutrients. This has been demonstrated in several previous studies of MFCs treating actual domestic wastewater, in which the removal of both organic and ammonium compounds were significantly enhanced with cathodic treatment (Ge & He, 2016; Zhang et al., 2013). In many cases, such as a stream cannot be either directly discharged or reused for non-potable purposes.

To enhance the treatment of wastewater in BES while avoiding the addition of more reactors, we can consider to take advantage of the cathode of BES for further treatment. A cathode can provide more physical space to host biological processes for extended treatment, and cathodic reduction reaction can be used to accomplish the removal of several types of contaminants that cannot be removed in the anode. Integration of membrane in the cathode will be able to reject a wide range of contaminants including pathogens and deliver a high quality effluent. Although cathodes have been investigated for wastewater treatment, there have not been any strong attentions or focuses in the past BES studies. This paper aims to provide a concise perspective on cathode-promoted wastewater treatment in BESs, discuss and analyze several major cathodes stimulated or supported treatments, and encourage more efforts to explore this approach for improving BES effluent quality.
2.3 Cathode Stimulated Treatment

Cathode-stimulated treatment is realized by accepting electrons from a cathode electrode; thus, it is a reduction reaction process. In theory, any compounds that can be reduced will be able to act as electron acceptors to a BES cathode; however, in reality such a reduction is only feasible in the presence of an appropriate catalyst, either abiotic or biological, which can reduce the activation energy and thus facilitate electron transfer from a cathode electrode to a terminal electron acceptor. In addition to commonly used electron acceptors such as oxygen (for electricity generation) and protons (for hydrogen production), there have been various compounds that can be removed by cathodic reduction reactions, including recalcitrant compounds, metals, nitrogen compounds, and carbon dioxide (Fig. 2.1). Because carbon dioxide is not a contaminant (despite a greenhouse gas and recently intensive research of microbial electrosynthesis (Bajracharya et al., 2017)), we will not discuss its reduction in BES here.

![Figure 2.1](image)

**Figure 2.1** Cathode-stimulated treatment of recalcitrant compounds, metals, nitrogen compounds, and/or carbon dioxide.

Although many recalcitrant compounds require an oxidation removal process, a few can be removed by reduction. For example, nitrobenzene, a widely used industrial compound, can be cathodically reduced to aniline that is less toxic and more biodegradable, and this approach could
significantly reduce organic dosage compared to conventional anaerobic degradation (Mu et al., 2009). Many dye compounds have been studied for reduction-based removal and decolorization in BES (Solanki et al., 2013). Perchlorate, an emerging drinking contaminant, can act as a sole electron acceptor in the cathode of an MFC (Butler et al., 2010). Despite potential benefits of low energy consumption, there is a key issue in BES removal of those compounds: incomplete removal. As mentioned above, nitrobenzene is reduced to aniline. Sulfanilic acid was found to be a major product of dye reduction in the BES cathode (Solanki et al., 2013). Thus, post-treatment such as aerobic treatment may still be needed. In addition, some studies applied co-substrates to enhance decolorization of dye compounds by adding easily degraded organic compounds into the cathode (Cao et al., 2010; Pan et al., 2017). Such an approach is questionable, because those added organic compounds are electron donors and will compete with the cathode electrode for electron donation, thereby lowering the efficiency of the cathodic electron transfer.

Metals, especially heavy metals, are important contaminants produced from various industries; they are toxic, not biodegradable, and widely distributed, and their removal is usually involving immobilization and/or filtration (Fu & Wang, 2011). Many metal compounds will change their soluble state to an insoluble state after reduction reactions, and such a process can be conducted by a BES cathode (Nancharaiah et al., 2015). A classic example is chromium: hexavalent chromium (Cr(VI)) is carcinogenic and mutagenic, and also highly soluble in water; cathodic reaction of Cr(VI), catalyzed by microorganisms or abiotic catalysts, produces Cr(III) that is much less toxic and also less soluble, and thus can be removed via precipitation (Tandukar et al., 2009). In recent years, more efforts have been devoted to recovery of valuable metals such as gold and silver, a step beyond removal. More details about BES removal and recovery of metals can be found in several review papers (Nancharaiah et al., 2016; Nancharaiah et al., 2015). What has been missing in the vast literature on this subject is how to effectively and efficiently collect the recovered metals. Abiotic reduction of metals by accepting electrons from a cathode electrode is expected to deposit metals on the surface of the cathode electrode, in a way like electroplating. However, many BES studies employed microorganisms to catalyze metal reduction, resulting in intracellular metal deposition. By using a fluorescent probe, researchers found that less than half of total chromium accumulated within the bacterial cells, consisting of a
composite of Cr(III) ions and other forms of chromium-complex (Xue et al., 2017). Thus, there could be two ways to collect the recovered metals: (1) intracellular accumulation of metals may allow the collection by harvesting microbial cells (with further extraction); and (2) deposition on the cathode electrode may be extracted for metal collection. However, both methods could affect the operation of BES (e.g., loss of microorganisms and periodic replacement of cathode electrodes). Furthermore, metal precipitated on the wall and separator of a BES reactor will require an appropriate removal method without significant influence on BES operation.

Unlike recalcitrant and metal compounds that are mostly presented in industrial wastewaters, nitrogen is a key inorganic contaminant in domestic wastewaters and can be in the forms of ammonia, nitrite, nitrate, etc. Cathodic reduction of nitrate was firstly demonstrated in a BES containing a pure culture Geobacter metallireducens that could reduce nitrate to nitrite with an electrode as the sole electron donor (Gregory et al., 2004). This finding was extended to a mixed-culture BES achieving a removal rate of 0.080 kg NO$_3^-$-N m$^{-3}$ and a conclusion that bioelectrochemical nitrate reduction did not involve hydrogen gas as an electron donor (Clauwaert et al., 2007). Since then, there have been many more studies of nitrate reduction in BES, as summarized in several review papers (Kelly & He, 2014; Rodriguez Arredondo et al., 2015; Sevda et al., 2018). The characteristics of water/wastewater can impose a strong effect on BES nitrate reduction. In general, two types of streams have been investigated for nitrate removal in BES cathodes. First, domestic wastewater in which nitrogen is in the form of ammonia must go through a nitrification process that converts ammonia to nitrate. This requires either a separate nitrifying reactor or combined nitrification and bioelectrochemical denitrification in a cathode (Virdis et al., 2010). Precise control of dissolved oxygen is a key to successful combination of nitrification and denitrification. Second, nitrate is a common contaminant in groundwater and in this scenario, bioelectrochemical denitrification can be directly applied. However, deployment of BES for groundwater nitrate removal must consider the associated energy demand, depending on how/where the treatment system will be installed. It was estimated that a specific energy consumption of 0.341 and 1.602 kWh kg NO$_3^-$-N$^{-1}$ could be obtained from in situ and ex situ MFC treatments, respectively, with pumping energy as the main contributor (Cecconet et al., 2018).
2.4 Cathode Supported Treatment

Cathode supported treatment occurs in the cathode compartment but does not directly accept electrons from the cathode electrode. That is, such a treatment takes advantage of the physical space of a cathode compartment, and may have positive or negative effects on the cathode electrode/reactions. Several examples of such treatments, such as loop operation, algal bioreactor, advanced oxidation, and membrane integration, are summarized in Table 2.1.

Table 2.1 Examples of cathode supported treatments and their interaction with cathode electrode

<table>
<thead>
<tr>
<th>Type</th>
<th>Treatment Processes</th>
<th>Interactions with cathode electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loop operation</td>
<td>• Organic oxidation by aerobes</td>
<td>• Compete for oxygen with cathode electrode</td>
</tr>
<tr>
<td></td>
<td>• Nitrification and/or denitrification</td>
<td>• May decrease pH and improve aerobic biocatalysis</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Increase the biofouling on cathode electrode</td>
</tr>
<tr>
<td>Algal bioreactor</td>
<td>• Nutrients (N and P) uptake by algae</td>
<td>• Provide dissolved oxygen to cathode reaction</td>
</tr>
<tr>
<td></td>
<td>• Nitrification by aerobic bacteria</td>
<td>• Increase the biofouling on cathode electrode</td>
</tr>
<tr>
<td></td>
<td>• Organic removal by algae and bacteria</td>
<td></td>
</tr>
<tr>
<td>Advanced oxidation</td>
<td>• Organic oxidation by radicals or strong oxidants</td>
<td>• Cathode reduction reactions generate radicals or strong oxidants</td>
</tr>
<tr>
<td></td>
<td>• Removal of recalcitrant compounds</td>
<td>• Incomplete oxygen reduction for H₂O₂ production</td>
</tr>
<tr>
<td>Membrane integration</td>
<td>• High-quality effluent after membrane</td>
<td>• Electric potential helps alleviate membrane fouling</td>
</tr>
<tr>
<td></td>
<td>• Rejection of a wide range of contaminants</td>
<td>• Draw solutions in forward osmosis facilitate cathode reactions with high conductivity</td>
</tr>
</tbody>
</table>

Loop operation was created to use the cathode compartment as a secondary treatment unit by flowing the anode effluent into the cathode. This helps address the issue of insufficient organic removal by the anode. It was reported that treating the anode effluent in the cathode could enhance the COD removal from 75% to 92% (Lefebvre et al., 2011). A more significant benefit is the improved transfer of protons from the anode to the cathode that compensates the alkalization of a catholyte and results in smaller pH difference between the two electrodes,
thereby eliminating the pH adjustment (Clauwaert et al., 2009). One study observed that a loop operation has increased the maximum power generation by 180% in a batch mode and 380% in a continuous mode as compared to a negative control (Lefebvre et al., 2011). However, introducing organic compounds in the anode effluent into the cathode also brings in electron donors, which will compete with the cathode electrode for terminal electron acceptors (e.g., oxygen). This competition can inhibit the cathodic reaction. Furthermore, fast growth of heterotrophic bacteria on organic matter will form biofilm on the surface of the cathode electrode and this biofouling would further decrease the cathode efficiency. Thus, using the cathode for improving organic removal may not be an ideal approach in BES. If organic concentration can be reduced to a very low level that does not significantly affect the cathodic reaction, then nitrogen compounds can be removed in the cathode via autotrophic nitrification (though still competing with the cathode electrode for oxygen) and bioelectrochemical denitrification as described previously (Virdis et al., 2010). Therefore, a loop operation could be effective for organic removal in the anode and nitrogen removal in the cathode with benefits of decreasing catholyte pH.

Because aeration is a key energy consumer, alternative approaches for providing dissolved oxygen have been studied, and among them algal bioreactors are of strong interest. Cultivation of algae in the cathode will not only provide oxygen, but also consume nitrogen and phosphorus by algal growth, resulting in increased nutrient removal. In addition to electric energy production, such BES also produce algal biomass that may be converted into bioenergy. A preliminary analysis revealed that algal biomass could contribute to 71-86% of total energy production in an MFC with an algal cathode, leading to a theoretically energy positive treatment system (Xiao et al., 2012). More details about algal-cathode BES can be found in several review papers (ElMekawy et al., 2014; Lee et al., 2015; Xiao & He, 2014). BES with an algal cathode require special consideration in reactor design, because of the need for illumination that supports algal growth. Integrating BES into open-pond or photobioreactor has been explored, and interaction between algae and bacteria in a cathode community warrants further investigation (Luo et al., 2017).
BES cathodes may also play a role in removing bio-refractory organic compounds and emerging contaminants. Incomplete oxygen reduction via a two-electron pathway can generate hydrogen peroxide (Rozendal et al., 2009), which can then react with Fe$^{2+}$ to produce hydroxyl radical, one of the strongest oxidants used in advanced oxidation processes. This has been investigated in a BES-Fenton system, for example to achieve complete degradation of Orange II, a dye commonly used in the textile, food and cosmetics industry (Feng et al., 2010). Production of hydrogen peroxide in the cathode requires precise control of reaction pathway to avoid four-electron reduction of oxygen to water. The use of gas diffusion layer in a composite cathode electrode made of carbon black and graphite has achieved a high H$_2$O$_2$ yield of 11.9 mg L$^{-1}$ h$^{-1}$ cm$^{-2}$ (Li et al., 2016). After Fenton oxidation, the residue hydrogen peroxide can be removed by alternate switching between MFC and MEC operation (Zhang et al., 2015). Like conventional Fenton treatment, a BES-Fenton system also faces the problems such as high chemical dosage and sludge production/disposal. The generated H$_2$O$_2$ can also be used for in situ treatment of contaminants, as demonstrated in a study that obtained the accelerated reduction of Cr (VI) with electrogenerated H$_2$O$_2$ (Liu et al., 2011).

Membrane is an excellent barrier to reject a wide range of contaminant and produce a high-quality effluent. Integration of various membranes into BES, such as dynamic membrane, micro-ultrafiltration membrane, and forward osmosis membrane, has been actively studied (Yuan & He, 2015). Installing membrane in the anode of a BES has experienced serious biofouling and lack of appropriate anti-fouling strategies without affecting the anode microbial process. Thus, having membrane in the cathode becomes a viable option. A study using membrane/biocathode assembly achieved the removal of 91% of bacterial cells and a water effluent with a turbidity of <0.1 NTU (Malaeb et al., 2013). Because the majority of organic matter has been removed by the anode, biofouling due to microbial growth would be less serious in the cathode. In addition, aeration can also act as fouling control in an aerobic cathode. The unique feature of BESs, electricity generation, was found to be able to reduce the deposition of sludge on membrane surface by enhancing the electrostatic repulsive force between them, resulting in less membrane fouling (Wang et al., 2013). This is further demonstrated in a BES with a conductive filtration cathode, in which the accumulated negative charges on the cathode created electrostatic
repulsion to reduce foulants (Liu et al., 2013). When forward osmosis (FO) membrane is integrated into BESs forming osmotic BESs (Qin & He, 2017), a cathode hosts draw solution that generates an osmotic pressure and extracts water from the anode. FO-based BES potentially have low fouling and low energy demand; however, regeneration of draw solute in an energy efficient way will be a key to the successful operation.

2.5 Outlook

Despite the potential advantages of using cathodes to improve wastewater treatment, we must also understand the challenges associated with this approach. First, there is always a tradeoff between contaminant removal and energy recovery in BES. Because electrons are involved in the removal of many contaminants, the more electrons flow, the better will be the contaminant removal. As a result, BESs will need to be operated under a mode for high current generation, which does not produce much power or energy. The benefit from enhanced contaminant removal may compensate for low energy production. The second challenge is how to overcome the cathode limitation to accommodate both high current generation and contaminant removal. Although those two tasks are correlated, the detailed interactions between the two should be further investigated. For example, some intermediates or end-products of contaminant removal may limit further current generation by covering the cathode surface (e.g., metal deposition) or poisoning the catalysts. Third, intrusion of undesired electron acceptors/donors can deteriorate the BES performance. Supplying an anolyte to the cathode can introduce electron donors (e.g., organics and ammonia) and thus create competition for terminal electron acceptors (e.g., oxygen). To minimize such an effect, it is important to reduce the concentration of organic matter to as low as possible before entering the cathode, or to increase the oxygen supply at the expense of energy consumption. Fourth, some cathode-supported treatments may be better conducted outside the cathode. Although an electrical field may reduce foulants, installation of membrane will complicate the cathode structure and operation/maintenance. In addition, fouling can hardly be avoided and it will be difficult to apply anti-fouling/membrane cleaning strategies inside the cathode. Likewise, algal growth may be better conducted in a separate photobioreactor that receives the cathode effluent, because of the special requirement for illumination and difficulty in harvesting algal biomass within the cathode.
Future design of BESs for utilizing cathode treatment should not neglect the anode, and a synergistic linkage between the anode and the cathode would lead to a functional BES with maximized treatment performance. We present two examples of such systems in Fig. 2.2. When domestic wastewater is treated in BES, organic compounds are mostly removed in the anode via anaerobic oxidation and electron production; then, the anode effluent is supplied to the cathode, where ammonium nitrogen can be removed via multiple biological pathways (Fig. 2.2A). Because cathodic reduction of a recalcitrant compounds like dye does not always completely degrade the contaminant, the cathode effluent can be transported to the anode, where further oxidation may occur and also provide some electrons to cathodic reduction reaction (Fig. 2.2B). Additional organic matter may need to be added to the anode to ensure sufficient electron supply. Clearly, more efforts should be invested to explore efficient ways to use cathodes for enhancing wastewater treatment in BES.

Figure 2.2 Two examples of cathode enhanced treatment in BES: (A) enhancing nitrogen removal from domestic wastewater; and (B) enhancing the removal of dye compounds from industrial wastewater.
References


“NEW” resource recovery from wastewater using bioelectrochemical systems: moving forward with functions

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3.1 Abstract

Bioelectrochemical systems (BES) have been extensively studied for resource recovery from wastewater. By taking advantage of interactions between microorganisms and electrodes, BES can accomplish wastewater treatment while simultaneously recovering various resources including nutrients, energy and water (“NEW”). Despite much progress in laboratory studies, BES have not been advanced to practical applications. This paper aims to provide some subjective opinions and a concise discussion of several key challenges in BES-based resource recovery and help identify the potential application niches that may guide further technological development. In addition to further increasing recovery efficiency, it is also important to have more focus on the applications of the recovered resources such as how to use the harvested electricity and gaseous energy and how to separate the recovered nutrients in an energy-efficient way. A change in mindset for energy performance of BES is necessary to understand overall energy production and consumption. Scaling up BES can go through laboratory scale, transitional scale, and then pilot scale. Using functions as driving forces for BES research and development will better guide the investment of efforts.
3.2 Introduction

The early efforts in the 20th century have demonstrated the feasibility of electricity generation in BES via microbial reaction with an electrode, but the research activities during that period (“Yesterday”) were low and mostly in the scope of scientific discovery. In the past 15 years (“Today”), BES research and development has been blooming as indicated by the number of journal publications (Fig 3.1). There has been much progress in both fundamental research and system development. A strong interest is always about microorganisms: 1) who they are: various molecular techniques are employed to reveal microbial ecology in BES and identify the dominant species affected by operational parameters (Logan & Regan, 2006); 2) what they are doing: microorganisms play different roles in BES, such as fermentation, hydrolysis, anaerobic respiration, and electrode-respiration (Pham et al., 2009); 3) how they do it: electron transfer between microorganisms and an electrode may be accomplished by direct electron transfer, mediated electron transfer, and/or nanowires (Lovley, 2006). To support microbial activities and facilitate electron transfer (e.g., via reducing internal resistance), electrode/catalyst materials are a key component of BES, and numerous materials, at micro or nano-scale, have been studied for their performance in BES (Zhou et al., 2011). Unlike hydrogen fuel cells that accept pure gaseous substrates, BES are designed to treat mixed substrates in liquid, usually in the form of wastes. Thus, three-dimension configurations are preferred for BES; no matter what configurations, plate type or tubular, BES configuration has not been changed significantly after 15 years’ intensive research. A major advancement in BES configuration is that there are more efforts of system scaling up (Logan, 2010). The function of BES has been greatly expanded from its origin of electricity generation to hydrogen production, desalination, synthesis of higher value compounds, and various waste treatments (Wang & Ren, 2013).
After so much progress and so many studies, the questions to be often asked are: what is “Tomorrow” of BES research/development and how can we get there? Tomorrow is ahead of us, so we will need forward thinking. There could be a number of approaches to help us get to “Tomorrow”, and one of them is the identification of appropriate application niches for BES and using the identified function to guide further research and development.

A critical function of BES, beyond waste treatment, is resource recovery from wastewater (Fig. 3.2). It is well recognized that wastewater contains valuable resources, which can be recovered for various applications and offset the operating cost of wastewater treatment (Lee et al., 2013). The most readily available resource is chemical energy that can be recovered via biogas production in anaerobic digestion; thermal energy in wastewater has a greater potential than chemical energy, but its recovery needs more efficient technologies and can be affected by the specific locations/climate (McCarty et al., 2011). Nutrients, mainly nitrogen and phosphorus,
require extensive efforts/input for their removal from wastewater, and their recovery may be accomplished by using algal treatment or struvite precipitation (Cai et al., 2013; Le Corre et al., 2009). The largest resource in wastewater is probably “water”. Wastewater reuse, for either potable or non-potable applications, is realized by various membrane technologies (Tchobanoglous et al., 2003). The abovementioned major resources in wastewater, Nutrients, Energy, and Water, are recognized as “NEW”. In addition, there is an increasing interest in carbon recovery from wastewater for producing biopolymer, bioplastic, or other valuable compounds (Valentino et al., 2017).

![Diagram of Bioelectrochemical System](image)

**Figure 3.2** Paradigm of resource recovery from wastewater using bioelectrochemical systems

The unique characteristics of BES technology such as direct electron harvest from waste organic matter will allow BES to play an important role in resource recovery from wastewater, and there have been many prior efforts on this subject. Identifying an appropriate application niche can guide the further research and development of BES technology. This feature paper aims to provide a concise discussion and subjective analysis of BES for resource recovery from wastewater. Instead of a comprehensive review of BES or overall discussion/overview of technical details, this paper will focus on several issues that either are keys to the success of recovering a specific resource in BES or have not been well evaluated in the prior studies.
3.3 Resource recovery

3.3.1 Energy recovery

3.3.1.1 Electrical energy

Recovery of useful energy is the primal goal of BES research (Rabaey & Verstraete, 2005), and energy can be generated in the form of either electricity in MFCs or gas in MECs (microbial electrolysis cells). A vast amount of effort has been devoted to improving energy production in BES, while little is focused on “usefulness” of the recovered energy (Sun et al., 2016). No matter what type of energy data are reported in a publication, the ultimate goal is practical use of energy. Thus, we need to invest more effort in examining the application of the recovered energy. Fortunately, there have been some early explorations on this issue. A convenient use of energy produced in an MFC is to power another BES such as an MEC in its hydrogen production, thereby avoiding energy input from an external resource (Sun et al., 2008).

Electricity generated from a microbial desalination cell (MDC) system was used to power an electrodialysis (ED) system for further desalination of the MDC effluent (Zhang & He, 2012). In a 200-L MFC system treating actual primary effluent, about 200 mW was extracted by a power management system and used to drive a 60-W DC pump for periodic catholyte recirculation (Ge & He, 2016). Several studies reported “energy neutral” operation of MFC systems, in which no external energy was required to power (mainly) the pumping system. For example, with special design of the feeding system, a 90-L MFC system treating brewery wastewater was able to produce more energy than what its pumps needed, achieving a self-sustained operation (Dong et al., 2015). Despite the initial success and great promise of applying the produced energy from BES, one must understand that energy loss occurs during extraction, storage, and application. In the aforementioned MDC system, less than 50% of the produced energy was finally used in driving the ED (Zhang & He, 2012). Therefore, efficient extraction of BES energy for further applications is of critical importance to the successful implementation of BES technology for energy recovery.

BES are low-voltage systems, and energy extraction usually involves DC-DC converters. The high-efficiency DC-DC converters would become “very low-efficiency” at a low output voltage of BES. Power management systems (PMS) are employed to extract energy from low-voltage
BES, and the early success was mostly in powering sensors by energy produced from sediment-type MFCs (Donovan et al., 2011). More details about PMS can be found in an excellent review about energy harvesting for MFCs (Wang et al., 2015). Most reported PMS were based on capacitors and could boost voltages for external applications (Fig. 3.3). Capacitors can be quickly charged and discharged, but this fast speed may encounter challenges in BES energy extraction. BES rely on biological processes, which are normally slower compared to chemical energy conversion processes. The discrepancy between slow energy generation in BES and fast charging in capacitors create an issue of energy loss, because capacitors can self-discharge in a long period of time. This was demonstrated in the study of using MDCs to power ED, in which the supercapacitor-based extraction had a much lower efficiency of 41.8% than that of the rechargeable battery-based extraction (86.6%) (Zhang & He, 2012). Thus, PMS design for BES energy extraction should take the “slow electricity generation” feature into consideration.

Another important issue is how to extract energy at its maximal level. It is well known that BES, more specifically MFCs, have a maximal power output point where the internal resistance of the system equals its external resistance. To capture the maximum power output point, maximum power point tracking (MPPT) may be used as a potentially effective approach that can be incorporated into PMS for energy harvesting. Using diode-based boost converter or other enhanced converters, energy extraction from MFCs can be accomplished at any operating points including the peak power point, and significantly improved compared to regular charge pumps (Wang et al., 2015). Those PMS have yet to be examined in the scaled BES system for their long-term stability and efficiency.
3.3.1.2 Gaseous energy

Another kind of energy to recover in BES can occur in the form of gas such as hydrogen and methane gas, which can be produced in MECs. One of the early MECs studies reported a hydrogen production rate of 0.02 m$^3$ m$^{-3}$ d$^{-1}$ and predicted that the optimization could lead to a production of 10 m$^3$ m$^{-3}$ d$^{-1}$ (Rozendal et al., 2006). Why do we need hydrogen production in MECs if we can directly produce electricity in MFCs, considering that electricity is a more popular form of energy for practical applications? A life-cycle assessment of three technologies, including anaerobic digestion (AD), MFCs, and MECs, suggested that MFCs would not provide significant benefits over conventional technologies in terms of factors such as human health, ecosystem quality, climate change, and resource utilization; however, MECs may have significant benefits over anaerobic digestion and MFCs from the economical and environmental...
aspects (Foley et al., 2010). The detailed benefit will vary depending on the target product from MECs such as hydrogen peroxide, hydrogen gas, and/or methane (Escapa et al., 2016). Moreover, hydrogen gas has a high energy content and is considered as a promising fuel with zero carbon emission. At last, hydrogen gas may be stored and transported, once the challenge for its storage is overcome (toward the hydrogen fuel cells – based applications).

A debate in MEC design and development is whether an effective separator such as ion exchange membrane is needed. The MECs in early stages all contained ion exchange membrane to create two different environments. With the appearance of membrane-less MFCs (Liu & Logan, 2004), membranes were started to be omitted from MECs in so called “single-chamber MECs” (Call & Logan, 2008). This omission of membranes can have some obvious benefits, for example decreasing both the internal resistance and pH difference in electrolyte (that can cause potential loss) (Rozendal et al., 2007). In addition, membrane-less MECs also simplify the reactor design and reduce the capital cost, in which the cost of the membrane is a key contributor. As a result, membrane-less MECs can potentially outperform membrane-based MECs. However, lacking an effective separator between the anode and the cathode also creates significant drawbacks: first, the anode substrates such as organic matter can get in contact with the cathode electrode and act as electron donors competing for electron acceptors with the cathode electrode; second, microorganisms (from a bioanode) will colonize on the cathode electrode and deteriorate the efficiency of HER catalysts if being used; third, in the presence of microorganisms (either via contamination from the anode or the use of a biocathode), methanogens will be cultivated and use the produced hydrogen gas to generate methane gas (Clauwaert et al., 2009). In a pilot-scale membraneless MEC treating winery wastewater, hydrogen production was observed in the initial stage of the operation and then methane production became overwhelming after 40 days of the operation with nearly complete inhibition of hydrogen production in the remaining operating period (Fig. 3.4) (Cusick et al., 2011). Those results also indicate that it would take some time (e.g., ~ 40 days in this pilot study) to develop methanogenic population; thus, a short-term study of membraneless MECs, even with “exceptional hydrogen production performance”, may not be sufficient to demonstrate the methanogenic effects. Although it is possible to inhibit methanogenesis in a single-chamber MEC, for example via active harvest of hydrogen gas using low-pressure vacuum (Lu et al., 2016), those methods will need long-term examination with more detailed analysis of the associated maintenance issue and energy consumption. To obtain
high-purity hydrogen gas in MECs, we believe that an effective separator such as ion exchange membrane is still needed at this stage of MEC development. The cost of membranes will become lower with rapid development of material science. Given the fact of evolvement of methanogens, a biocathode may not be a good option, unless strict selection of desirable organisms can be conducted and those organisms can be maintained during MEC operation. Even in the presence of membranes, microorganisms will still occur during a long-term operation and some organic compounds could move across the membrane into the cathode compartment. Thus, in situ control of microbial contamination such as chemical inhibition or a low pH condition may be considered; those methods have been investigated in the anode of an MEC (Chae et al., 2010), and can also been applied to the cathode. The presence of membrane will minimize the effects of those controlling methods on the anodic activities.
What if we can not get rid of methane production in an MEC? Then we will have to live with it. Methane can be produced in either the anode or the cathode (two-chamber MECs) or a single-chamber MEC. Much research has been focused on direct production of methane, especially in single-chamber MECs, likely a result of unsuccessful inhibition of methanogens. Inocula exhibit clear effects on methane production, for example it was found that bog inoculum performed better compared to the anaerobic sludge inoculum with respect to methane production and reducing hydrogen recycling (Siegert et al., 2015). In two chamber MECs, methane is produced

Figure 3.4  Gas production in a pilot-scale membraneless MEC winery wastewater: (a) gas composition; and (b) gas production rate. Reproduction with permission from (Cusick et al., 2011)
as the end product in the cathode with high energy conversion efficiency, for example 75% of the electrical input was captured as methane energy (Villano et al., 2013). MECs can be integrated with anaerobic digestion (AD) process to make the process efficient and economical as the effluent of AD consists of dilute organic acids that can serve as ideal substrates for the electroactive bacteria in MECs. In addition to hydrogen-based methane production pathway, researchers also found the evidence of methane production by direct electron transfer (Cheng et al., 2009). In some cases, both hydrogen and methane are produced in a mixture gas, which can become (bio)hythane, an alternative fuel with higher fuel and heat efficiency (Ghimire et al., 2017). This was observed in a single-chamber MEC treating swine wastewater that produced a mixture of hydrogen (77%) and methane gas (13%) (Wagner et al., 2009). (Bio)hythane can be transported with the current infrastructure used for biogas or directly used in methane-fueled vehicles (Huang et al., 2017). Because (bio)hythane has a preferred range of ratio between methane and hydrogen, it is important to achieve such a ratio via certain strategies. A recent study of a 19-L MEC employed several operational strategies by varying the key operational factors such as anolyte recirculation rate, external resistance, and hydraulic residence time, and successfully achieved the desired methane/hydrogen ratio (Luo et al., 2017).

3.3.2 Nutrient recovery

3.3.2.1 Ammonia recovery

Nitrogen is one of the major pollutants present in wastewater and its removal is important to protect the receiving water bodies from eutrophication. Conventional biological nitrogen removal is accomplished by oxidizing ammonia to nitrite and nitrate, which is then reduced to nitrogen gas (Ahn, 2006), and this is an energy/chemical intensive process because of the need for aeration and organic matter. Although new removal processes such as short-cut nitrification/denitrification and anammox have been developed, those technologies are still focused on “removal”. Ammonia is a vital compound for life and a major component of fertilizers. Thus, recovery of ammonia, instead of removal, will represent a sustainable approach for nutrient resource management. BES have been studied to produce energy and recover ammonia from various wastewaters (Kelly & He, 2014; Rodriguez Arredondo et al., 2015; Xiao
et al., 2016). To achieve ammonia recovery, ammonium ions in wastewater migrate into the cathode driven by electron movement, and high catholyte pH (as a result of cathodic reduction reaction) facilitates the conversion of ammonium into ammonia gas, which is then separated by stripping. This recovery process can be highly energy efficient. It was reported that ammonia recovery would require 4.9 kWh kg\(^{-1}\) N in an MFC (Qin et al., 2017) or 1.3 kWh kg\(^{-1}\) N in an MEC with passive aeration (Qin et al., 2018). A recent study has demonstrated ammonia recovery in a scaled-up system (5 L) with 31% ammonia removal and 31% ammonia recovery by using TransMembraneChemiSorption (TMCS) membrane module in a two-stage treatment of urine waste (Zamora et al., 2017).

A question about ammonia recovery in BES is: what do we do with the recovered ammonia? Although Haber-Bosch process requires 8–12 kWh for synthesizing one kg of ammonia, ammonia is generally a low cost and readily available chemical. Recovering ammonia from wastewater using BES needs to identify the potential applications of the recovered ammonia to justify the benefits of such an approach. There could be several potential applications. First, fertilizer is still an attractive option for the recovered ammonia. Most studies obtained a solution containing a high concentration of ammonia, and application of this solution as fertilizer will require either transport to the field or locating BES adjacent the application field. Alternatively, turning the recovered ammonia into solid will greatly expand the range of application field because of easier transport, and this has been investigated in a three-chamber cell with a middle chamber concentrating ammonium bicarbonate salt in the solid form (Thompson Brewster et al., 2017). Second, the recovered ammonia can be used to cultivate pure microbial culture for producing value-added products. One example is microalgae, which has been used to produce biofuels and value added biochemical for food, medical and research uses (Miledge, 2011). Wastewater has been used to cultivate algae, but complex composition of wastewater organics and presence of various bacteria create challenges for growing pure strains of algae (Cai et al., 2013; Li et al., 2011). Thus, obtaining relatively pure ammonia from wastewater would benefit growth of selected algal species. Third, it was demonstrated that the recovered ammonia from an MEC cathode could be used as a draw solute for a forward osmosis (FO) system that extracted water from the MEC anolyte effluent (Qin & He, 2014). This innovative approach presents a synergistic link between BES and FO technologies for simultaneous recovery of multiple resources. Fourth, ammonia is also an energy source and can be converted into electricity by
using ammonia fuel cells. In this way, the recovered ammonia will not need transport and the produced electricity can be readily applied to various devices.

3.3.2.2 Phosphorus recovery

Another important nutrient present in wastewater is phosphorus. Recovery of phosphorus has been advanced to practical applications through struvite recovery (Le Corre et al., 2009; Ren et al., 2017; Yuan et al., 2012). Struvite is a slow-releasing fertilizer, containing the equal molar ratio among ammonium, phosphate, and magnesium (El Diwani et al., 2007). Sometimes, ammonium may be replaced by potassium and magnesium can be substituted by another metal such as cadmium, zinc, or nickel (Ronteltap et al., 2007). Struvite recovery has been studied in both MECs and MFCs, mainly by taking advantage of high pH catholyte to precipitate struvite (Cusick & Logan, 2012; Ichihashi & Hirooka, 2012). It was reported that a single-chamber MEC performed better with up to 40% phosphorus removal whereas an MFC recovered about 27% in its cathode. To increase the concentration of phosphorus for better struvite recovery, an FO system was employed to concentrate the MEC effluent (Zou et al., 2017). A key challenge for struvite recovery in BES is separation and collection. In BES, struvite may form precipitation in the reactor (e.g., bottom and wall), on membrane/separator (if used), and on electrodes. This will not only make separation/collection very difficult, but also cause scaling on membrane/separator and electrodes, resulting in deteriorated performance in a long-term operation. Therefore, it may be better to accomplish struvite precipitation outside BES. Several studies have examined two-stage processes to separate struvite precipitation from BES. For example, one recovered phosphorus with 96% efficiency and 90% purity before a BES that was used to recover ammonia (Zamora et al., 2017). A hybrid MEC-FO system accomplished the recovery of water (54.2% ± 1.9%), ammonium nitrogen (99.7% ± 13%), and phosphorus (79.5% ± 0.5%), where phosphorus was recovered via chemical precipitation outside the MEC (Zou et al., 2017). Similar challenges of separation and collection can be expected in recovery of metal or organic matter (e.g., via microbial electrosynthesis) in BES (Luo et al., 2015).
3.3.3 Water recovery

Recovery of reusable water in BES can be accomplished via integration of various membranes, such as micro/ultrafiltration membranes and forward osmosis (FO) membrane (Yuan & He, 2015). Such an integration can be conducted by installing membrane inside BES (e.g. in an anode, in a cathode, or as a separator), or externally linking a membrane unit to BES through hydraulic connection. The presence of membrane can also result in the rejection of a wide range of contaminants such as soluble organics and pathogens (Wang et al., 2013). As described in a previous review paper, the mutual benefits between BES and membrane include enhanced water treatment, high-quality water extraction, stable water flux, fouling resistance, and enhanced electricity generation (Yuan & He, 2015). The quality of recovered water is largely depending on the membranes, influent quality, and the treatment processes. In general, we believe the recovered water can be used for non-potable purpose such as landscaping or agricultural irrigation. A common challenge for membrane-based treatment processes is fouling. In BES, if membrane has a direct contact with the anodic process, then it will be difficult to impose fouling control/alleviation strategies, because of potential effects of chemical/physical fouling control methods on anaerobic microbial processes. Incorporating anti-fouling materials in membrane can help reduce fouling. Fouling control can also be implemented through operational strategies. For example, an MFC containing ultrafiltration membrane in its anode employed fluidized granular activated carbon (GAC) to control fouling and was able to maintain TMP below 10 kPa whereas in the control experiment TMP increased to 25 kPa in 20 days after GAC fluidization was stopped (Li et al., 2014). However, a long-term operation with fluidized GAC may damage membrane via abrasion. Installing membranes in the cathode that accepts the anode effluent as a catholyte would experience much less fouling because of significantly lower concentrations of organics and microbes; in addition, active aeration can also reduce membrane fouling (Yuan & He, 2015). Electricity generation in an MFC may help with the mitigation of fouling in the cathode chamber, possible due to two reasons: 1) oxygen reduction in the cathode can produce \(H_2O_2\), which could remove foulant via oxidation; and 2) the negatively charged microbial cells might be repulsed by the electric field (Liu et al., 2014). Seeking an effective method for fouling control will be a key task for water recovery in BES, and a rule of thumb is to have membranes away from microbial processes, either in an abiotic cathode or outside BES (i.e. external connection).
Operation of FO membrane is very different from ultra/microfiltration membranes, because of the need for a draw solution, which has a high concentration of draw solute to create a high osmotic pressure for water movement (Cath et al., 2006). Since the use of FO membrane as a separator in an MFC in 2011 (Zhang et al., 2011), there have been many studies to integrate FO into BES for resource recovery (Qin & He, 2017). Draw solutions also create unique challenges for FO-based BES: what kind of chemicals can be used as a draw solute in BES and how to reduce reverse solute flux (RSF)? When FO membrane is employed as a separator between an anode and a cathode, draw solution also acts as a catholyte and thus the choice of an appropriate draw solute can greatly affect the cathodic performance. In a study that compared four different draw solutes, phosphate buffer solution was demonstrated to be the best, due to its high conductivity and buffering capacity; glucose was the worst because of little conductivity that inhibited electricity generation (Ge & He, 2012). Another criterion for a draw solute is easy regeneration, an approach to recover draw solutes and produce final water effluent. One example is to use polyacrylic acid sodium salts (polyelectrolyte) as a draw solute and recover it through pH adjustment (Yang et al., 2017). Bioelectricity generation in BES is able to inhibit RSF. It was found that the higher coulomb production in an osmotic MFC could lead to higher reduction of RSF, and thus improving current generation by lowering electrolyte pH would increase RSF reduction (Qin et al., 2016).

3.4 Universal Barriers

3.4.1 A mind for energy

A key interest in BES technology lies in “energy”. Despite much progress in BES research and development, there lacks a strong mind for energy when evaluating the system. We have pointed out previously that most BES studies did not properly present energy data, and we must go beyond “power density” when presenting energy performance (He, 2017; He, 2013). Lacking energy data have created some dilemmas, for example we simply do not know how much energy our BES can produce or consume, and without such information we do not know whether our BES is energy efficient or not. In 2014, we proposed a new parameter to describe energy data, normalized energy recovery (NER) that has a unit of kWh m⁻³ treated wastewater or kWh kg⁻¹ removal COD (Ge et al., 2014). This is a system-dimension independent parameter, and allows
us to make comparison among different BES or between BES and other treatment technologies. NER can be calculated by normalizing power production over unit volume of the treated wastewater or unit mass of the COD removed:

\[ \text{NER}_v = \frac{P_{\text{production}}}{Q_{\text{feeding}}}, \]  

(3.1)

or

\[ \text{NER}_{\text{COD}} = \frac{P_{\text{production}}}{R_{\text{COD}}}, \]  

(3.2)

where \( Q_{\text{feeding}} \) is the wastewater feeding rate (m³ wastewater h⁻¹), \( P_{\text{production}} \) is the produced power, and \( R_{\text{COD}} \) is the COD removal rate (kg COD h⁻¹). NER can also be calculated for MECs in which hydrogen gas is produced and the total energy recovery can be estimated based on heat combustion of hydrogen gas. In addition to energy recovery, we also need to know energy consumption of a BES, which can be described by specific energy consumption, or SEC. There are multiple contributors to SEC, such as pumping systems, mixing systems, aeration, and/or external power supply. More details about NER and SEC calculation can be found in our recent review paper (Zou & He, 2018).

Researchers have started to incorporate NER into their energy data expression. For example, one study analyzed the physiologic and chemical effects of different electron acceptors on exoelectrogens in a two-chamber MFC that delivered a NER of 0.025 kWh m⁻³ (Yang et al., 2014). A 45-L MFC system using single-chamber MFCs reported a mean NER of 0.36 kWh kg⁻¹ COD for treating primary effluent of a wastewater treatment plant (Hiegemann et al., 2016). A recent study has provided an in-depth analysis of energy production and consumption in various BES including electricity production, hydrogen production, nitrogen recovery, desalination and chemical production (Zou & He, 2018). It found that while MFCs have mostly negative energy balance, MECs’ energy balance could be positive because of hydrogen production that greatly contributes to energy recovery. Detailed analysis of energy consumption was also conducted. In a BES for ammonia recovery, much energy is invested in the stripping of ammonia using aeration, which can be optimized to reduce energy consumption (Fig 3.5). In this system, power supply consumed more energy compared to the aeration and an MFC might perform better as there is no requirement of power supply. We must admit that energy analysis of a laboratory-scale BES does not provide a complete energy picture, and it is not fair to compare laboratory-scale BES to the existing treatment systems for claiming “energy benefits” due to the lack of
pre/post-treatment, solid handling, and other necessary units in laboratory-scale BES. However, it is still important to analyze and present energy data with laboratory-scale BES, as the first step toward understanding energy issues and possibly guiding BES development.

![Specific energy consumption (SEC) for different aeration flow rate in an MEC. Reproduction with permission from (Zou & He, 2018)](image)

**Figure 3.5** Specific energy consumption (SEC\textsubscript{NH\textsubscript{4}-N}) for different aeration flow rate in an MEC. Reproduction with permission from (Zou & He, 2018)

### 3.4.2 Scaling up

One of the most important challenges for the BES technology is to demonstrate its techno-economic feasibility at a large scale (i.e. significantly beyond laboratory scales). Most laboratory studies are based on the BES reactors at a scale of few milliliters or liters, using simple substrates such as acetate or glycerol, under well controlled conditions such as temperature and pH, and for a limited amount of operating period. There have been several efforts of scaling up BES to treat actual wastewater and examine the key operational/performance parameters such as different flow modes, electrode connections and pollutant removal (Hiegemann et al., 2018; Liang et al., 2013). An example of a scaled MFC is a stackable horizontal MFC (SHMFC) developed with a capacity of 1000 L and consisting of four modules of 250 L each to treat wastewater; this system
achieved the maximum power of 116 mW and 79% COD removal and 71% removal of TN (Feng et al., 2014). It was found that the internal area specific resistance of this large MFC (2.3 × 10^4 Ω·cm^2) was much higher than that of a 28-mL cubic MFC (840-910 Ω·cm^2) and thus resulted in the low electricity generation. MECs have also been scaled up to treat actual wastewater. A 175-L MEC treating low temperature wastewater was able to remove 63.5% COD, but its hydrogen production relative to the anode surface area was much smaller compared to the small MEC (Cotterill et al., 2017). Those efforts indicate that the laboratory-scale results can not be translated linearly to the large-scale systems. Therefore, more efforts are required to investigate and understand the scaling up related issues.

Despite the use of “pilot scale” in several studies, there is no strict definition on how large can be considered as a pilot scale. In general, a pilot system should be able to provide sufficient information (both design and system performance) to help develop a full-scale system, and no significant change of design parameters should be expected from a pilot system to a full-scale system. Given the special characteristics of BES such as varied electrode space when the system scale is changed, BES scaling up should move through several stages of development. We suggest three stages, laboratory scale, transitional scale, and pilot scale. Laboratory scale is a size that can be hosted within a laboratory, for instance < 100 L. BES at a laboratory scale is used for fundamental studies of basic design and operational factors and can be fed with synthetic wastewater. Transitional scale is a size that is significantly larger than laboratory scale but much smaller than pilot scale, for example 100–500 L. At this scale, BES is too large for a laboratory study and will need to be tested onsite (preferably). It should be operated with actual wastewater and under a less controlled condition (e.g., temperature and pH). The function of a transitional scale system is to bridge the findings of laboratory-scale systems to pilot systems without significant investment of finance, time, and manpower. The success of a transitional-scale system will lead to the design of a pilot system, which will be larger than 1000 L or have a treatment capacity > 2 m^3 d^-1. The values of this scale classification are still arbitrary.

The difficulties for scaling up BES are obvious: graduate students are not trained mechanics to build a large system (and sometimes, reactor leaking can kill a project), it will require significant amounts of financial resource and time, and operation of large systems will face many uncertainties that can affect the system performance (and you will not obtain “beautiful data” like that from laboratory-scale systems). However, we must invest more efforts into system
scaling up, likely through collaboration with industry that might already have had appropriate expertise and equipment for building large-scale systems. There are several rules to consider when scaling up a BES. First, keep it simple. Compared to the existing wastewater treatment systems, BES technology is considered to a very complicated unit, involving more components such as electrodes and separator/membrane. Complication of a treatment system will not only increase the capital investment, but also demand more maintenance. Thus, it is important to keep a BES as simple as possible. We often create a “novel system” by incorporating different components into BES, such as membrane filtration and/or other chemical/biological processes. Integration of multiple processes into one may reduce footprint but it also adds more complication. During scaling up an integrated BES, we should re-evaluate whether it is appropriate to integrate and/or how to better integrate to facilitate system construction. Second, keep it cheap. Development of many treatment technologies is driven by cost, including both capital and operating costs. BES technology is expected to have a lower operating cost than aerobic treatment, because of its anaerobic process in the anode. But its capital cost is expected to be much higher, due to the use of electrodes/separator/membrane and reactor construction. Capital cost is highly location and treatment capacity related. Our initial analysis of a 200-L MFC system suggested that it could be cost-competitive in decentralized treatment with a capacity lower than 10000 gpd (Ge & He, 2016). Selection of cost effective materials is a key to reducing the capital cost of BES. For example, nanomaterials have been extensively studied as cathodic catalysts in BES, but scaled BES rarely use nanomaterial-based catalysts because of their high cost. Third, keep it moving. This “moving” refers to the movement of liquid/substrates, instead of reactor components. Mass transfer limitation plays a critical role in the system performance and providing appropriate mixing can reduce this limitation. This will require careful consideration in reactor design (e.g., not to have leak of liquid/substrate, and precise determination of the distance between electrodes/sepators) and/or operation (especially when having the anolyte effluent into the cathode).

3.5 Conclusions

BES research has shown immense development in the last two decades with a great promise in many potential applications and also controversial opinions on its feasibility. It is critically
important to move forward with BES to demonstrate its technical and economic feasibility. To do this, we should identify the functions of BES and use “function” to guide research and development. Recovering energy, nutrient, and/or water in BES will need to focus more on harvest/collection and reuse. Energy performance of a BES, especially energy consumption, must be properly incorporated into data expression of BES studies. Scaling up BES can go through three stages of development, laboratory scale, transitional scale, and pilot scale.
References


Powering Microbial Electrolysis Cells by Electricity Generation from Simulated Waste Heat of Anaerobic Digesters using Thermoelectric Generators


4.1 Abstract

Waste heat from anaerobic digesters can be converted to electricity using thermoelectric generators (TEG). Herein, such energy was employed to power a microbial electrolysis cell (MEC) for producing hydrogen gas. Four TEG units could deliver a voltage of ~0.5 V, sufficient to drive the MEC that achieved a hydrogen production rate of $0.48 \pm 0.13 \text{ m}^3 \text{m}^{-3} \text{d}^{-1}$. This rate was further improved to $0.75 \pm 0.05 \text{ m}^3 \text{m}^{-3} \text{d}^{-1}$ when the temperature difference for TEG was increased from 18 to 28 °C. There was no significant difference between the TEG-powered MEC and power supply-supported MEC (at 0.6 V), in terms of current generation, hydrogen production, and organic removal. Ambient air was also studied as a cold-side source for TEG, although some challenges were encountered to maintain a large temperature difference. Those results encourage further exploration of using TEG as a feasible power supply for sustainable MEC operation.
4.2 Introduction

Wastewater treatment is an energy intensive process consuming up to 3% of the total electricity demand in the U.S. (USEPA, 2006). Yet as the population continue to increase, the energy consumption for wastewater treatment would increase with the increase in wastewater generation, if the conventional technology is used. It is, thus, necessary to develop technology for wastewater treatment that are both efficient and sustainable. One of the key challenges for the application of MECs is the use of external energy to drive hydrogen evolution reaction (HER). The analysis has revealed that the external power supply can contribute to more than 94% of the total energy demand by an MEC (Zou & He, 2018). This is a significant amount of energy consumption which makes the MEC operation unsustainable in the long run. To address this issue, alternative external power sources have been investigated, in particular from renewable sources such as solar power, BES, and waste heat (Zhang & Angelidaki, 2014). For example, dye-sensitized solar cells have been used to provide solar energy as an external source for MECs, which could achieve hydrogen production of 0.07 – 0.14 m³ m⁻³ d⁻¹ with an applied photovoltage of 0.7 V (Ajayi et al., 2010; Ajayi et al., 2009; Chae et al., 2009). MFCs, a similar bioelectrochemical system to MECs but capable of producing electricity, are also used to power MECs (Sun et al., 2009; Sun et al., 2008). It was found that in such a system MECs and MFCs could influence each other as the bioanodes of both systems are sensitive to changes in the electric charge (Sun et al., 2008).

Waste heat from anaerobic digesters (AD) is also an attractive source of energy but has not been well explored for MEC applications. Sludge contains a high amount of energy in the form of organics, for example 1 kg of dry sludge may contain up to 18,000 kJ of energy (Kaur et al., 2019). For treatment plants with a large AD capacity, biogas is burned in the combustion engines for production of power and there is waste heat generated from exhaust gas and cooling waters (Bacenetti et al., 2019; Lansche & Müller, 2012). A part of that heat is used for the self-heating of the digesters. However, there is a surplus of heat energy being discharged by the plants. For small treatment plants, for example Christiansburg Wastewater Treatment Facility (Christiansburg, VA, US) treating a total of 3 million gallons per day (MGD), the methane production in the AD is not enough to be economically feasible to have a separate infrastructure for electricity generation from biogas. As a result, the methane gas is burned to release waste
heat into the atmosphere. Thus, the excess heat at large-scale facilities and the waste heat from small-scale facilities can be a potential source of energy.

Waste heat can be converted directly to electricity by using a thermoelectric generator (TEG) (Hsu et al., 2011; Niu et al., 2009). A TEG utilizes the “Seebeck effect” to transfer the thermal energy difference (between a heat source (hot side) and a heat sink (cold side) to electricity (Hamid Elsheikh et al., 2014). The efficiency is directly related to the temperature difference (ΔT) with higher conversion at a higher temperature difference. It was reported that a small wastewater treatment plant (WWTP) with a treatment capacity of 3 MGD could produce as much as 70,986 kWh energy per year by converting wastewater thermal energy to electric energy using TEG (Zou et al., 2018). However, using mainstream wastewater as a heat source can be challenging given its large quantity (thus a high requirement for TEG size) and also depend on geographic location (temperature). Therefore, the waste heat from AD can be a stable source of energy, regardless the location of the WWTP, and converting waste heat from AD using TEG may create opportunities to power small-scale devices such as MECs that can be used to further treat AD effluent.

TEG has been coupled with MECs for hydrogen production to demonstrate some feasibility (Chen et al., 2016). However, the prior study used liquid (water bath) as the heat source, while the heat released from AD is usually in a gaseous form. Herein, a TEG-MEC coupled system was investigated for direct electricity generation from the gaseous waste heat of anaerobic digesters and for the application of the generated electricity to the MEC as the external source of power. The objectives of the study were to investigate: i) the feasibility of waste gaseous heat as a heat source for thermoelectric generator; ii) use of thermoelectric generator as a power source to power an MEC; and iii) examine the effects of different cold side sources (liquid and gas) on the MEC performance.

4.3 Materials and Methods

4.3.1 TEG-MEC system setup
A two-chamber MEC was constructed with carbon brush (5 cm, Gordon Brush Mfg. Co. Inc., Commerce, CA, USA) as an anode electrode and carbon cloth (5cm x 2 cm, Zoltek Companies,
Inc., MO, USA) coated with 0.5 mg cm$^{-2}$ Pt/C (Millipore Sigma, St. Louis, MO, USA) as the cathode electrode, separated by anion exchange membrane (AEM, AMI-7001, Membrane International, Inc., Ringwood, NJ, USA). Before use, the carbon brush and carbon cloth were soaked in acetone for 24 hours and heat treated in a muffle furnace (Model 550 Isotemp Series, Fisher Scientific, Pittsburgh, PA, USA) for 30 minutes at 450 °C. An external resistor of 8 ohms was used in the electrical circuit of the MEC, connected to a power supply or TEG. The positive side of the power source (positive pole in case of power supply and red lead in the case of TEG) was connected to the anode electrode and the other side to the cathode electrode with resistor in between (Fig. 4.1). Each chamber of the MEC was 8 cm × 3.2 cm × 0.9 cm and had a liquid volume of 22 mL.

![Diagram of TEG and MEC system](image)

**Figure 4.1** Schematic of the TEG integrated MEC system using simulated gaseous waste heat (hot) and water (cold).

The TEG unit (Model TEG2-126LDT, Bi$_2$Te$_3$ based, designed specifically for low temperature difference) was purchased from TECTEG MFR. (Ontario Canada), with a dimension of 40 × 40 × 5.1 mm. The 126 P- and N- type semiconductors were pre-mounted on ceramic plates with graphite sheet on both sides and no perimeter seal to avoid thermal bridging. An electric heating fan (Grainger, Fountain Inn, SC, USA) with two adjustable heat settings was used to simulate gaseous waste heat emission from anaerobic digesters. The TEG unit was fixed in a flat-plate reactor with the hot side being exposed to the hot air from the heater fan and the cold side
embedded into a water chamber (40 x 40 x 5 mm). The fan could be set to two heat settings allowing a hot side temperature of either 51 °C or 43 °C. Tap water in a reservoir bottle was used for recirculation in the cold side of TEG. The cold side temperature rose to 33 °C and remained in equilibrium at that temperature.

4.3.2 TEG-MEC system operation

The MEC was operated at room temperature of ~26 ºC and in a batch mode with each cycle of 12-h long. The anode of the MEC was inoculated with anaerobic sludge from an anaerobic digester located in Peppers Ferry Regional Wastewater Treatment Plant (Radford, VA, USA), and was fed with a synthetic solution containing (per liter): 1.5 g acetate; NH₄Cl, 0.15 g; NaCl, 0.5 g; MgSO₄, 0.015 g; CaCl₂, 0.02 g; NaHCO₃, 0.5 g; and trace element, 1 mL (He et al., 2005). The catholyte was prepared with 50 mM phosphate buffer solution consisting of K₂HPO₄ and KH₂PO₄. The MEC was started with being powered by a power supply at an applied voltage of 1.0 V and once its hydrogen production became stable, the power source was switched to TEG.

TEG was firstly characterized for electricity generation with two temperature differences. For TEG characterization, only one TEG unit was used. The theoretical internal resistance and maximum power output was quantified by polarization tests. Then, four TEG units were connected in series to power the MEC. A comparative analysis of the MEC powered by TEG and a power supply was conducted by connecting the MEC to the power supply at a voltage of 0.6V, comparable to that achieved with four TEGs in a series. In some tests, to reduce the temperature of cold side water (to stimulate water at the outdoor temperature in a wastewater treatment facility) the reservoir bottle was kept in a cooler where the water temperature was in equilibrium at 23 °C. Ambient air was also studied as a cold source by using an air pump.

4.3.3 Measurement and analysis

The MEC was characterized for electricity generation, hydrogen production rate (HPR) and chemical oxygen demand (COD) removal (R_{cod}). Coulombic efficiency (CE), cathodic hydrogen recovery (R_{cat}) and hydrogen yield rate (Y_{H2}) were calculated to quantify the MEC performance according to previous studies (Luo et al., 2017; Sun et al., 2009; Yang et al., 2017). The voltage
across the resistors (both MEC and TEG units) was recorded every 2 min by a digital multimeter (2700, Keithley Instruments Inc., Cleveland, OH, USA). The concentration of COD was measured by using a spectrophotometer according to the manufacturer instructions (DR 890, HACH Company, USA). The solution pH was measured by using a benchtop pH meter (OAKTON Instruments, Vernon Hills, IL USA). Hydrogen gas was collected from the cathode of MEC using a water displacement method where the gas produced in the cathode displaces an equivalent volume of water (Argun et al., 2008; Wang & Wan, 2008). After collection, hydrogen gas was quantified for its volume by using a syringe. The contents of the cathodic produced gas were analyzed by using a HP 5890 Series II Plus gas chromatograph (GC) equipped with a thermal conductivity detector (TCD), with helium as the carrier gas. Thermometers were used to measure the temperature of water and surface temperature of TEG. The power and current density for the TEG module was obtained by dividing the power and current by the surface area of TEG (16 cm² per unit).

4.4 Result and Discussion

4.4.1 TEG Characterization

The TEG unit was examined for electricity generation at two small temperature differences, 18 and 10 °C. The temperature of water (cold side) remained ~ 33 °C, higher than the room temperature due to the effect of hot air. To create temperature differences, the hot air was measured at either 51 °C or 43 °C. Due to the technical limitation, precise control of hot air temperature was not possible in the present study. Clearly, the higher ΔT was, the higher OCV would be. The TEG unit produced relatively stable open circuit voltage (OCV) of 0.12 V at ΔT=18 °C, double that at ΔT=10 °C (0.06 V) (Fig. 4.2a). Similar results were obtained in a low-temperature waste heat TEG study using forced convection cooling that demonstrated linear characteristics for increase of OCV with increasing temperature gradient (Gou et al., 2010). The output voltage is dependent on the heat transfer. With a fixed cold-side temperature, the increase of the hot-side temperature expects to increase heat flux which in turn generates a higher voltage. It was observed that some fluctuation occurred in the OCV output, likely related to the supply of hot air that could experience some inconsistency due to inherent issues with the fan. In addition, the current TEG unit had a hot side open to the atmosphere, making it difficult to supply consistent heat because of unpredictable air flow and heat loss. This certainly warrants further
optimization of TEG module design to better accommodate flow of heat (either air or liquid). The improved electricity generation with a higher temperature difference was further demonstrated by polarization tests (Fig. 4.2b). The maximum power density at $\Delta T=18 \, ^\circ C$ was 108 mW m$^{-2}$, much higher than 31 mW m$^{-2}$ at $\Delta T=10 \, ^\circ C$. An evaluation of TEG based on mathematic modeling for conversion of wastewater heat to electricity found similar results that 10 °C of temperature difference could create a fourfold increase in the power production (Zou et al., 2018). The estimated internal resistance of a single TEG unit at $\Delta T=18 \, ^\circ C$ was 12.9 Ω, smaller than 13.7 Ω at $\Delta T=10 \, ^\circ C$. To drive HER for hydrogen production in an MEC, a theoretical minimum of 0.14 V is required and in practice (based on published literature) the applied voltage is often greater than 0.4 V to overcome the overpotential (Sun et al., 2008). Because the OCV of one TEG unit at $\Delta T = 18 \, ^\circ C$ was approximately 0.12 V, four TEGs were connected in series to produce an OCV of ~ 0.5 V (Fig. 4.2c), which could be more applicable. When a 5.6 Ω resistor was connected to the TEG circuit, 18 mA of current was generated.
Figure 4.2 Characterization of TEG module at two temperature differences: a) Open circuit voltage; b) polarization curves; and c) Open circuit voltage with four TEGs connected in series.

4.4.2 TEG powered MEC for hydrogen production
Next, four TEGs were connected in series and used as a power source to drive the MEC for hydrogen production. For comparison, the MEC was also investigated for its performance supported by a regular power supply (PS) that provided 0.6 V (close to what the four TEGs could provide). The TEG-powered MEC generated a current of 1.51 ± 0.05 mA, comparable to 1.49 ± 0.01 mA from the PS-powered MEC (Fig. 3a). This result proves that TEG can perform similarly to PS as a feasible power source for an MEC. Like OCV (Fig. 4.2a), the current generation by the TEG-powered MEC exhibited some fluctuation (Fig. 4.3a), likely due to some (minor) instability in its voltage supply by the TEGs as explained earlier. The Coulombic efficiency obtained with the TEG-powered MEC was 56.9 ± 12.5 % with COD removal efficiency of 37.6 ± 3.2 % (Fig. 4.3b). The high CE value indicates that the MEC was able to recover a large amount of electrons stored in the removed acetate. The CE and COD removal efficiency obtained in the PS-MEC system was 72.9 ± 12.9 % and 31.1 ± 4.7 %, respectively. The low COD removal efficiency was related to the short batch time of 12 hours for a relatively high initial COD concentration (>1,000 mg L⁻¹). Although the PS-MEC system had a higher average CE than that of the TEG-powered MEC, there is no statistical difference between the two. This is not unexpected due to similar voltage input between TEG and PS.
Figure 4.3 Comparison between TEG-powered MEC and power supply (0.6 V) – supported MEC: a) current generation; and b) Coulombic efficiency (CE), COD removal ($R_{\text{cod}}$), Cathodic hydrogen recovery ($R_{\text{cat}}$), hydrogen production rate (HPR), and hydrogen yield rate.

Hydrogen production rate (HPR) of the TEG-powered MEC was $0.48 \pm 0.13 \, \text{m}^3 \, \text{m}^{-3} \, \text{d}^{-1}$, comparable to $0.36 \pm 0.13 \, \text{m}^3 \, \text{m}^{-3} \, \text{d}^{-1}$ from the PS-powered MEC (Fig. 4.3b). The HPR obtained in the TEG-MEC system is about four times higher than that from an MEC powered by a dye
sensitized solar cell (DSSC), despite that DSSC could supply an even higher voltage (0.7 V open circuit voltage) (Ajayi et al., 2009). In an MFC-MEC coupled system, the highest HPR achieved was 0.0149 m³ m⁻³ d⁻¹ (Sun et al., 2008). Those cross-comparisons may not be accurate, due to the difference in MEC configuration and operation. However, the advantages of using TEG as a power source, compared to MFCs or DSSCs, can be understandable. Both MFCs and DSSCs would require relatively complex operation: MFCs have bioanodes that are biological systems, and DSSCs need reduction of oxidized mediators for exciting the electrons to inject to the conduction band. In addition, both MFCs and DSSCs presented in the previous studies can be influenced by the electron production from the anode of MECs that are supported by those power sources. Because of those mutual effects between MECs and its power sources (MFCs or DSSC), a performance drop in the MEC could deteriorate the overall system performance. This issue would be avoided by using TEGs that work on the principal of temperature difference, independent of MEC performance. Therefore, it is reasonable to conclude that TEG can be a feasible alternative source of power for MECs.

4.4.3 Effects of cold sources on MEC

In the present study, the temperature of the cold-side water was at 33 °C affected by the hot air. However, the temperature of the treated effluent (e.g., secondary effluent) in a wastewater treatment plant could be much lower (except some special regions where ambient temperature is high). To mimic a colder water condition, the water reservoir that supplied water to the cold side of the TEGs was kept in a cooler, where the temperature of the water stabilized at ~ 23 °C. This has created a temperature difference of 28 °C for the TEGs and as a result, current generation was significantly increased to ~3.5 mA (Fig. 4.4a). This current was more than double of that obtained at a temperature difference of 18 °C, although fluctuations in current were still observed likely because of the issues with hot side instability. In general, the performance of the MEC with respect to CE, R_cod, and HPR increased with an increase of temperature difference. The CE was observed to be 77.8 ± 10.4 % and cathodic hydrogen recovery was recorded as 52.1 ± 5.29 %. Higher current generation resulted in higher CE which was 5% higher; however, R_cat was reduced, implying that the efficiency of conversion of current to hydrogen became less, compared to that at a temperature difference of 18 °C. It has been found in earlier studies that an
increase of voltage up to a certain value could enhance the COD removal due to the possible increase in the activity of electrochemically-active microorganisms (Ding et al., 2016).

Improvement of 15% in COD removal was obtained in a study when the voltage was increased from 0.5 V to 0.75 V (Escapa et al., 2012). In the present study, the COD removal efficiency was increased to 64.1 ± 10.8 % at a temperature difference of 28 °C, 33% higher than that at 18 °C difference. Such an increase in organic removal benefited from a higher current generation. The HPR increased to 0.75 ± 0.05 m³ m⁻³ d⁻¹, about 1.5 times higher than when the temperature difference was 18 °C. Those results are encouraging because of improved MEC performance under a more realistic condition.
Figure 4.4 Enhanced MEC performance when a colder water was used in the cold side of TEG: a) comparison of current generation between at $\Delta T = 28 \, ^\circ\text{C}$ and $\Delta T = 18 \, ^\circ\text{C}$; and b) Coulombic efficiency ($\text{CE}$), COD removal ($\text{R}_{\text{cod}}$), Cathodic hydrogen recovery ($\text{R}_{\text{cat}}$), hydrogen production rate ($\text{HPR}$), and hydrogen yield rate at $\Delta T = 28 \, ^\circ\text{C}$.

Another cold source is ambient air. In cold regions or wintertime, the temperature of ambient air can be very low, thereby creating a large temperature difference from the hot waste heat from AD. In the present study, the ambient air temperature was ~26 °C. To examine its feasibility as a cold source, the cold-side water was replaced with ambient air. It was observed that the current generation of the MEC with this TEG setup (hot air – cold air) was 0.70 ± 0.02 mA, much lower than that obtained from the TEG of hot air – cold water at a similar temperature difference (Fig. 4.5a). Because the heat transfer takes place through convection and heat transfer coefficient for liquid is generally higher than gases, the actual heat transfer in the TEG system with gas-solid boundary layer components might be poorer compared that with liquid-solid boundary layer components. Due to the worse heat transfer, the electricity generation from the TEG became less, resulting in a decreased MEC performance. Consequently, Coulombic efficiency, COD removal, and hydrogen production all became lower (Fig. 4.5b). The COD removal efficiency decreased by 12% to 25.9 ± 4.5 %, compared to that with cold water that had a temperature difference of 18 °C. Hydrogen production rate was also about 3.5 times lower at 0.13 ± 0.05 $m^3\, m^{-3}\, d^{-1}$ in this system. However, cathodic recovery (60.47 ± 9.38 %) became high implying the conversion efficiency of the current generated to hydrogen was relatively high. Though the performance was poor, the functioning of this system is a proof of concept that ambient air could also function as a cold-side source and the TEG could be improved as discussed in the following section.
Figure 4.5 The MEC performance with ambient air as a cold-side source for TEG: a) comparison of current generation between using water at $\Delta T = 18 \, ^\circ C$ and using air at $\Delta T = 20 \, ^\circ C$; and b) Coulombic efficiency (CE), COD removal ($R_{\text{cod}}$), Cathodic hydrogen recovery ($R_{\text{cat}}$), hydrogen production rate (HPR), and hydrogen yield rate using air at $\Delta T = 20 \, ^\circ C$. 

![Graph showing MEC performance](image-url)
4.4.4 Perspectives

Development of alternate energy sources for powering MEC is critically important to the long-term deployment and sustainability of the MEC technology. In this study, the simulated gaseous waste heat from anaerobic digesters was explored as a power source for MECs. Although promising results have demonstrated the feasibility of this approach, there are several challenges to be addressed with future efforts. First, the instability of TEG voltage output must be addressed so that MECs can have a more consistent performance. As mentioned earlier, this instability could be related to the supply of gaseous heat, which should be collected and channeled directly to the surface of the TEG. In this study, a heating fan was used that could not precisely represent the gaseous heat emission from anaerobic digester. In realistic conditions, the energy released from the combustion of methane could be at higher temperatures and it should be captured near the source for maximizing the temperature difference. The hot side of TEGs should be designed to better host the movement of hot air, for example in a chamber/channel instead of being open to the atmosphere. Second, although the use of ambient air as a cold source was not very successful in the present study, it still remains a potentially viable approach because ambient air is readily available and it can avoid the need for building water pipes. Once the hot side air is constrained in chamber/channel, the effect of heat on the cold side air may be minimized and thus the use of simple fan (instead of energy intensive air pump) may be able to achieve replacement of cold side air to maintain a large temperature difference. Third, because of multiple TEG units are involved, it may be possible to maximize heat usage by optimizing the arrangement of TEG units (to better capture heat). It will also be of interest to examine TEG connection (e.g., in series and/or parallel) to minimize the internal resistance for maximal voltage output. Fourth, the temperature of hot side source is relatively stable, but the cold side temperature will be highly variable depending on the season and geographical locations. This temperature may also directly affect MEC operation via changing its influent temperature. Thus, it is important to study the effects of temperature variation on the TEG/MEC performance, especially during a long-term operation. Fifth, MECs may also be integrated with TEGs through hydraulic connection, in addition to electrical connection. This can be realized by using AD effluent (e.g., thermophilic AD that can have a temperature > 50 °C) as a hot-side source. In this way, AD effluent will not only provide heat energy to TEG for electricity generation that powers MECs, but also supply (residue) organic matter to the MEC anode for producing electrons to
HER. This would enhance the treatment efficiency of the MEC due to a higher temperature of the anolyte as well as the overall contaminant removal capacity of the facility (through AD-MEC cooperation, in a way similar to a temperature phased AD system).

4.5 Conclusions

This study has demonstrated that (simulated) gaseous waste heat from anaerobic digesters could be employed as a heat source for thermoelectric generators to generate electricity powering microbial electrolysis cells. The MEC powered by TEG exhibited similar performance in terms of current generation, hydrogen production, and organic removal. Using colder water would enhance TEG electricity generation. However, there were some challenges with using gas as either heat or cold sources, resulting in fluctuation in electricity generation. Future studies are needed to improve the sustainability of TEG output, explore new heat/cold sources, and examine temperature variation due to seasonal changes.
References


Improving Hydrogen Production in Microbial Electrolysis Cells through Hydraulic Connection with Thermoelectric Generators

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5.1 Abstract

Using alternative power sources to drive hydrogen production in microbial electrolysis cells (MECs) is important to implementation of MEC technology. Herein, thermoelectric generators (TEG) were to power MECs using simulated waste heat. With the MEC anolyte as a cold source for TEG, current generation of the MEC increased to $2.46 \pm 0.06 \ mA$ and hydrogen production reached $0.14 \ m^3 \ m^{-3} \ d^{-1}$, compared to the TEG-MEC system without hydraulic connection ($1.16 \ pm 0.07 \ mA$ and $0.07 \ pm 0.01 \ m^3 \ m^{-3} \ d^{-1}$). A high recirculation rate of 30 mL min$^{-1}$ doubled both current generation and hydrogen production with 10 mL min$^{-1}$, benefited from a stronger cooling effect that increased the TEG voltage output. However, the optimal recirculation rate was determined as 20 mL min$^{-1}$ because of comparable performance but potentially less energy requirement. Reducing anolyte hydraulic retention time to 4 h has increased hydrogen production to $0.25 \ pm 0.05 \ m^3 \ m^{-3} \ d^{-1}$ but decreased organic removal efficiency to $69 \ pm 2\%$. Adding three more TEG units that captured more heat energy further enhanced hydrogen production to $0.36 \ m^3 \ m^{-3} \ d^{-1}$. Those results have demonstrated a successful integration of TEG with MEC through both electrical and hydraulic connections for simultaneous wastewater treatment and energy recovery.
5.2 Introduction

Microbial electrolysis cells (MECs) can treat wastewater while simultaneously harvesting energy in the form of hydrogen gas or other value added products (Hua et al., 2019). To overcome the thermodynamic barrier (theoretical 0.14 V) of HER, an additional voltage is typically required to achieve hydrogen production (Rozendal et al., 2006). In practice however, for high-efficiency hydrogen production, the required voltage is often equal to or greater than 0.6 V (Call & Logan, 2008; Cheng & Logan, 2007). There have been several large-scale MEC systems that were tested outside laboratory and with actual wastewater. For example, a 100-L MEC treating domestic wastewater was investigated for a period of one year and it was found that the energy recovered from the hydrogen production, with a hydrogen production rate of 0.007 m$^3$ m$^{-3}$ d$^{-1}$, was about half of that required for the system operation (Heidrich et al., 2014). Another 120-L MEC fed with domestic wastewater was estimated to consume 0.64 kWh kg-COD$^{-1}$ (Heidrich et al., 2013), lower than energy consumption by a typical aerobic treatment of domestic wastewater (1.5 kWh kg-COD$^{-1}$) (Metcalf et al., 2004).

One of the key challenges for MEC implementation is the energy input, which is often provided by fossil fuels. This external energy can constitute as much as 94% of the total energy demand by an MEC (Zou & He, 2018). To address this challenge, renewable and sustainable power sources have been explored to replace fossil fuel based energy. Waste heat is an attractive resource of energy that may be used to power MECs, especially considering that the source of waste heat can be co-located with MECs in a wastewater treatment plant. Waste heat can be converted to electricity by using thermoelectric generators (TEG) (Hsu et al., 2011; Niu et al., 2009). Those devices employ semi-conducting materials to convert the thermal energy present in a medium by creating a potential difference between a hot source and a (cold) sink, allowing TEG to capture the thermal energy even at a low temperature difference ($\Delta T$) (Hamid Elsheikh et al., 2014). For example, a set of TEGs were able to generate an open circuit voltage of 38.6 V at a $\Delta T$ of 30 °C, providing 12.41 W of electrical power via converting waste heat from the exhaust pipes of an automobile to electricity, and the voltage would increase by 6.4 V for every 5 °C of $\Delta T$ (Hsu et al., 2011). A low $\Delta T$ of 4 °C could reach an open circuit voltage of 1.4 V from the TEG and a model predicted that with a temperature difference of 50 °C, the TEG system will produce 31 V as open circuit voltage (Gou et al., 2010). A theoretical analysis reported that using
TEG to harvest energy from warmer wastewater could deliver 1094 to 70,986 kWh to a small-scale wastewater treatment plant with an annual saving of $163 to $6076 (Zou et al., 2018).

TEG has also been investigated to power MECs where hot water was used as a heat source while atmospheric air acted as a cold source (Chen et al., 2016). As mentioned previously, waste heat is usually in the form of flue gas, which has a much higher temperature than wastewater. Thus, another study demonstrated that the simulated waste thermal heat could also be utilized to power an MEC (Jain & He, 2020). In that study, the synergy between MEC and TEG was via “electrical connection” (which provides an electrical potential to drive HER). When a low-temperature water is used as a sink and passes through the cold side of TEG, there is a rise in the temperature of the water. This “warmer” water could benefit the anode of an MEC because of a higher microbial activity at a higher temperature (Ahn & Logan, 2010). This intrigues us to explore the use of wastewater as a cold sink for TEG and then feed the “TEG-heated” wastewater to the MEC anode. In this way, MEC and TEG are connected both hydraulically (through wastewater) and electrically. The specific objectives of the present study were to investigate: 1) the feasibility of using a cold side solution as the anolyte for the MEC; and 2) the effect of operation parameters (recirculation rate and hydraulic retention time) on the performance of the coupled system.

5.3 Materials and Methods

5.3.1 TEG-MEC system setup

A two-chamber MEC was constructed with a carbon brush (5 cm, Gordon Brush Mfg. Co. Inc., Commerce, CA, USA) as an anode electrode and carbon cloth (5 cm x 2 cm, Zoltek Companies, Inc., MO, USA) coated with 0.5 mg cm⁻² Pt/C (Millipore Sigma, St. Louis, MO, USA) as the cathode electrode, separated by anion exchange membrane (AEM, AMI-7001, Membrane International, Inc., Ringwood, NJ, USA). Before use, the carbon brush and carbon cloth were soaked in acetone for 24 hours and then heat treated in a muffle furnace (Model 550 Isotemp Series, Fisher Scientific, Pittsburgh, PA, USA) for 30 minutes at 450 °C. Each chamber of the MEC was 8 cm × 3.2 cm × 0.9 cm and had a liquid volume of 22 mL. An external resistor of 8
ohms was used in the electrical circuit of the MEC for high current generation. The external voltage was provided by TEG except in one case where power supply was used for comparison.

The TEG unit (Model TEG2-126LDT, Bi$_2$Te$_3$ based, designed specifically for low temperature difference) was purchased from TECTEG MFR. (Ontario Canada), with a dimension of 40 × 40 × 5.1 mm. The 126 P- and N-type semiconductors were pre-mounted on ceramic plates with graphite sheet on both sides and no perimeter seal to avoid thermal bridging. An electric heating fan (Grainger, Fountain Inn, SC, USA) was used to simulate gaseous waste heat emission from anaerobic digesters. The hot side of the TEG unit was exposed to the hot air from the heater fan that was used to simulate waste heat and its cold side was embedded into a water chamber (40 x 40 x 5 mm) that allowed water to flow through. The fan allowed to maintain a hot side temperature of 44 °C. The cold side of the TEG used either the MEC anolyte or tap water (for comparison).

5.3.2 **TEG-MEC system operation**

The MEC and TEG were connected electrically and hydraulically (Fig. 5.1). For electrical connection, the positive side (red lead) of the TEG was connected to the anode of the MEC. The negative side (black lead) was connected to the cathode of the MEC with a resistor in between. The synthetic wastewater flowed through the cold side of the TEG and the effluent from TEG passed through the anode of MEC, to complete the hydraulic connection between the two units, before being discharged. The MEC was operated at room temperature of ~23 °C and in a continuous mode with adjusted hydraulic retention time (HRT) and recirculation rate. The anode of the MEC was inoculated with anaerobic sludge from an anaerobic digester located in Peppers Ferry Regional Wastewater Treatment Plant (Radford, VA, USA), and was fed with a synthetic solution containing (per liter): 0.45 g acetate; NH$_4$Cl, 0.15 g; NaCl, 0.5 g; MgSO$_4$, 0.015 g; CaCl$_2$, 0.02 g; NaHCO$_3$, 0.5 g; and trace element, 1 mL (He et al., 2005). This synthetic solution was to mimic a domestic wastewater. The catholyte was prepared with 50 mM phosphate buffer solution consisting of K$_2$HPO$_4$ and KH$_2$PO$_4$. The MEC was started with being powered by a power supply at an applied voltage of 1.0 V and once its hydrogen production became stable, the power source was switched to the TEG.
Three TEG units were connected in series, both electrically and hydraulically, to power the MEC. A comparison of the MEC performance powered by TEG and a power supply was conducted by connecting the MEC to the power supply at a voltage of 0.6 V, comparable to that obtained with three serial TEGs. Then, the MEC was connected hydraulically to TEG with the anolyte from the MEC recirculating through the TEG. Three anolyte recirculation rates, $10 \text{mL min}^{-1}$, $20 \text{mL min}^{-1}$ and $30 \text{mL min}^{-1}$, and three anolyte HRTs – $4 \text{h}$, $8 \text{h}$, and $12 \text{h}$ were applied to examine their effects on the MEC performance. In the later stage of the experiments, three more TEG units were added, making a total of six TEGs in series.

5.3.3 Measurement and analysis

The MEC was characterized for current generation, hydrogen production rate (HPR) and COD removal ($R_{\text{COD}}$). Coulombic efficiency (CE), coulombic recovery (CR) and cathodic hydrogen recovery ($R_{\text{cat}}$) were calculated to quantify the conversion of organic compounds to electrons and then from electrons to hydrogen gas, according to previous studies (Ge et al., 2013; Luo et al., 2017). The voltage across the resistor was recorded every 2 min by a digital multimeter (2700,
Keithley Instruments Inc., Cleveland, OH, USA). The concentration of COD was measured by using a spectrophotometer according to the manufacturer instructions (DR 890, HACH Company, USA). The solution pH was measured by using a benchtop pH meter (OAKTON Instruments, Vernon Hills, IL USA). Hydrogen gas was collected from the MEC cathode using a water displacement method (Argun et al., 2008; Wang & Wan, 2008) and quantified for its volume by using a syringe. The contents of the cathodic produced gas were analyzed by using a HP 5890 Series II Plus gas chromatograph (GC) equipped with a thermal conductivity detector (TCD), with helium as the carrier gas. Although the MEC was operated in a continuous mode, the data of current generation was analyzed over a period of 12 h for a uniform comparison under different operational conditions, unless otherwise noted.

5.4 Result and Discussion

5.4.1 Enhanced MEC performance by hydraulic connection

We first compared the MEC performance driven by a power supply and TEG in the absence of hydraulic connection. The serial TEGs were able to produce a voltage of 0.56 V from a temperature difference ($\Delta T$) of 12 °C using tap water as a cold source. Thus, a voltage of 0.6 V was provided by the power supply (PS). At an anolyte HRT of 12 h, the PS-MEC generate a peak current of $1.58 \pm 0.16$ mA, higher than $1.16 \pm 0.07$ mA from the TEG-MEC (Fig. 5.2). As a result, the total coulomb production by the PS-MEC was 62 C, also higher than 47 C from the TEG-MEC over a period of 12 h. Both MECs could remove ~90% of COD, resulting in a decrease of the COD concentration from 364 to 35 mg L$^{-1}$. The PS-MEC produced hydrogen gas at a higher rate of $0.09 \pm 0.02$ m$^3$ m$^{-3}$ d$^{-1}$ than that of the TEG-MEC ($0.07 \pm 0.01$ m$^3$ m$^{-3}$ d$^{-1}$). Those results support the previous finding that TEG can be a feasible power source to drive MECs for hydrogen production (Jain & He, 2020).
Figure 5.2 Current generation from the MEC driven by power supply or TEG in the absence of hydraulic connection, or by TEG with hydraulic connection (HRT = 12 h; anolyte recirculation rate = 20 mL min\(^{-1}\)).

Next, a hydraulic connection was established between TEG and MEC, by changing the cold source for the TEG from tap water to the MEC anolyte in a recirculating loop as shown in Fig. 5.1. This change has clearly enhanced the MEC performance. The peak current increased to 2.46 ± 0.06 mA (Fig. 2), resulting in a total Coulomb production of 101 C in 12 hours, more than twice of that from the TEG-MEC without hydraulic connection. This improvement was related to a larger temperature gradient in the TEG-MEC with hydraulic connection. The temperature of the recirculating anolyte was ~ 28 °C, creating a temperature difference of ~16 °C. For comparison, the tap water used in the TEG-MEC without hydraulic connection had a temperature of 32 °C. Therefore, the MEC anode has acted as a “cooling” unit for the cold source (anolyte) during the recirculation. The lost heat might be possibly released from the anolyte via ion
exchange membrane that provided a large surface area for heat emission, but this warrants further investigation.

**Figure 5.3** Comparison of major parameters between the TEG-MEC with and without hydraulic connection (HRT = 12 h; anolyte recirculation rate = 20 mL min⁻¹).

More comparisons of performance parameters between the TEG-MEC systems with and without hydraulic connection are presented in Fig. 5.3. The TEG-MEC with hydraulic connection achieved a higher COD removal efficiency of 94 ± 1%, compared to 89 ± 1% without hydraulic connection. The enhanced COD removal was likely benefited from a stronger microbial degradation activity under a higher temperature. As mentioned earlier, the recirculating anolyte had a temperature of 28 °C, while the anolyte in the MEC that did not have hydraulic connection had a temperature of 23 °C (room temperature). Thus, the rise in the temperature of the anolyte from 23 °C to 28 °C was beneficial for the anode community to increase COD removal and hydrogen production. Because of generally high COD removal in both systems, the increase in COD removal efficiency was not as significant as Coulombic efficiency, which increased from 29 ± 1% (no hydraulic connection) to 56 ± 2% (hydraulic connection). The enhanced conversion of organic compounds to electrons (as reflected by CE) resulted in the enhanced hydrogen
production. The hydrogen production rate of the TEG-MEC with hydraulic connection was 0.14 ± 0.02 m$^3$ m$^{-3}$ d$^{-1}$, double that of the system without hydraulic connection. The hydrogen production obtained from the TEG-MEC with hydraulic connection was ten-fold higher compared to that of an integrated MFC-MEC system (0.0145 – 0.0149 m$^3$ m$^{-3}$ d$^{-1}$) (Sun et al., 2009; Sun et al., 2008) and comparable with the MEC powered by DSSC (0.07-0.14 m$^3$ m$^{-3}$ d$^{-1}$) (Ajayi et al., 2009; Chae et al., 2009). The cathodic hydrogen recovery efficiency ($R_{\text{cat}}$) remained similar between the two systems (12 ± 1% vs. 13 ± 1%), indicating that the two cathode electrodes/performances performed similarly and thus the main difference between two TEG-MEC systems was due to the anode performance as explained earlier.

5.4.2 Effect of anolyte recirculation rate

The anolyte recirculation rate can play a key role in maintaining both TEG temperature gradient (“cooling effect”) and MEC anode performance (higher anodic activity). Thus, we further studied its effect by varying the recirculation rate at 30 mL min$^{-1}$, 20 mL min$^{-1}$ and 10 mL min$^{-1}$. The results show that a higher recirculation rate could lead to higher current generation (Fig. 5.4a). For example, a recirculation rate of 30 mL min$^{-1}$ resulted in an average current generation of 2.66 ± 0.03 mA, much higher than 1.18 ± 0.05 mA with 10 mL min$^{-1}$. Likewise, the total Coulomb production with 30 mL min$^{-1}$ was 110 C, more than twice of that with 10 mL min$^{-1}$ (47 C). The difference of electricity generation between 20 and 30 mL min$^{-1}$ was not as much as that between 10 and 30 mL min$^{-1}$. It seems that a higher recirculate rate exhibited a stronger “cooling effect”, which then led to a bigger temperature gradient for the TEG. At 30 mL min$^{-1}$, the anolyte flowing out of the TEG had a temperature 26 °C, lower than 32 °C from the one at 10 mL min$^{-1}$. Because of technical limitation, we could not measure the temperature of the anolyte within the anode chamber of the MEC. Thus, we hypothesize that a faster movement of the anolyte has carried more heat energy to the MEC, where heat loss occurs, and the returning anolyte to the TEG has a lower temperature, resulting in a larger temperature gradient allowing the TEG to generate a higher voltage that in turns leads to higher current generation in the MEC.
Figure 5.4 Comparison of the MEC performance at three recirculation rates, 10, 20 and 30 mL min\(^{-1}\): (a) current generation; and (b) other performance parameters (CE = coulombic efficiency; Rcod = COD removal efficiency; Rcat = cathodic hydrogen recovery; HPR = hydrogen production rate) (HRT = 12 h).
The increased heat loss within the MEC at a higher recirculation rate did not affect the organic removal in the MEC. Three recirculation rates resulted in similar COD removal efficiency, 93 ± 2%, 94 ± 1%, and 96 ± 2% at 10, 20, and 30 mL min⁻¹ (Fig. 5.4b). Because of the different current generation, Coulombic efficiency increased from 27 ± 2%, to 41 ± 2% and then to 44 ± 3%, when the recirculation rate increased from 10 to 20 and then to 30 mL min⁻¹. Hydrogen production was strongly affected by current generation and thus a higher current generation would result in more hydrogen production. The higher recirculation rates at 20 or 30 mL min⁻¹ led to higher HPR of 0.11 ± 0.02 or 0.13 ± 0.02 m³ m⁻³ d⁻¹, more than twice of 0.04 ± 0.01 m³ m⁻³ d⁻¹ with 10 mL min⁻¹. The cathodic recovery had minor difference among three recirculation rates, varied at 8 ± 1%, 10 ± 1%, and 11 ± 1% and for 10, 20, and 30 mL min⁻¹. One can see that although the recirculation rate of 30 mL min⁻¹ exhibited the best performance, the difference of COD removal and hydrogen production was not significant between 20 and 30 mL min⁻¹. However, energy consumption due to recirculation of the anolyte could be very significant between 20 and 30 mL min⁻¹. Therefore, 20 mL min⁻¹ was selected as the optimum recirculation rate and used for the following experiments.

5.4.3 Effects of anolyte hydraulic retention time

Next important operational parameter to the system performance was the anolyte hydraulic retention time (HRT). Varying HRT will change organic loading rate and thus the availability of carbon for electricity production. We selected three HRTs, 12 h, 8 h and 4 h, which are typical for biological treatment of domestic wastewater. As expected, the current generation showed an inverse relation with increasing HRTs, at 2.93 ± 0.09 mA (4 h), 2.66 ± 0.07 mA (8 h), and 2.31 ± 0.02 mA (12 h) (Fig. 5.5a), resulting the total Coulomb production of 127, 115, and 97 C, respectively, for an operational period of 12 h. This is due to a higher organic loading rate at a lower HRT. However, the capacity of microbial degradation in the MEC anode did not increase proportionally with the increased COD loading rate, leading to the decreased COD removal efficiency from 93 ± 3% (HRT 12 h) to 83 ± 2% (HRT 8 h) and then to 69 ± 2% (HRT 4 h) (Fig. 5.5b). Thus, to ensure a good treatment performance, the anolyte HRT should be maintained above 8 h in the present MEC. Despite the decreased COD removal efficiency with a lower HRT, CE increased significantly from 38 ± 5% (12 h) to 73 ± 3% (8 h) and then to 97 ± 3% (4
Such a dramatic increase in CE, when the current generation only increased by 26% (from HRT 12 h to 4 h), seems improper. As discussed in a recent paper (Wang & He, 2020), the calculation of CE is based on the removed COD and thus the removal efficiency could greatly affect CE values and may cause misleading in some cases. To avoid such misleading, we also calculated Coulombic recovery (CR) based on the total COD input. CR still increased with the decreased HRT, but not as dramatically as CE. When the HRT decreased from 12 to 4 h, CR increased from 51 ± 2% to 67 ± 4%, indicating that the conversion from organic compounds to electrons increased. This increased conversion to electron and thus current generation resulted in the increased HPR from 0.11 ± 0.02 m³ m⁻³ d⁻¹ at the HRT of 12 h to 0.20 ± 0.03 m³ m⁻³ d⁻¹ at 8 h HRT and to 0.25 ± 0.05 m³ m⁻³ d⁻¹ for the HRT of 4 h. Interestingly, $R_{\text{cap}}$ became significantly higher at a lower HRT, increased from 10 ± 1% (HRT 12 h) to 17 ± 1 % (HRT 4 h). These results indicate that a shorter HRT could enhance hydrogen production but at a cost of poor treatment performance. The improved hydrogen production was mainly due to the MEC anode activity (more organic input), instead of TEG, because the temperature of the anolyte did not change much, varying between 27 and 28 °C for three HRTs. Therefore, the effect of the anolyte HRT was mostly on the MEC performance and the TEG was not affected.
Figure 5.5 The MEC performance affected by the anolyte HRT (4, 8, and 12 hours): (a) current generation; and (b) other performance parameters (CR = coulombic recovery; CE = coulombic efficiency; Rcod = COD removal efficiency; Rcat = cathodic hydrogen recovery; HPR = hydrogen production rate) (Recirculation rate = 20 mL min$^{-1}$ for all three HRTs).
5.4.4 Perspectives

Despite the promise of this TEG-MEC system for simultaneous wastewater treatment and hydrogen production, there are several challenges to address with the further investigation. Hydrogen production in the MEC should be further improved with more voltage output from the TEG. Under the condition of “fixed” temperature difference between the hot and cold sources, the number of TEG units can be increased. For example, when we added three additional TEG units (totally six TEG units in series), current generation was increased to $3.01 \pm 0.07$ mA with a hydrogen production rate of $0.36 \pm 0.05$ m$^3$ m$^{-3}$ d$^{-1}$ (HRT of 8 h and recirculation rate of 20 mL min$^{-1}$). Thus, there is additional energy available for thermoelectric conversion. Adding TEG units will increase the capital cost and result in other issues such as a longer HRT inside TEG. It should also be noted that the increase in hydrogen production may not be linear though, as the MEC performance could be limited by its internal factors such as anodic microbial conversion or could even deteriorate when the applied voltage is too high (Ding et al., 2018). To avoid overly applied voltage, there is also possibility that the extra energy produced from TEG could be used to power other parts of the treatment system such as pumps. The optimal number of TEG units can be determined via techno-economic assessment of the TEG-MEC system. Hydraulic connection introduces microbes/organic compounds into the TEG and a long-term operation may cause microbial growth inside the TEG. Such biofouling could increase heat transfer resistance and thus reduce TEG voltage output. Although the MEC anode contains biofilm that can decrease the chance of microbial loss compared to suspended growth, it is still necessary to examine biofouling effects during long-term operation with actual wastewater. Like the previous TEG-MEC system, the hot side of the current TEG was open to the air. Design of a closed hot side will greatly trap the heat energy from the simulated waste heat and increase the voltage output. Some full-scale TEG units already have such a design and therefore this issue should be relatively easy to address. The challenge for scaling up TEG-MEC system will lie in MEC scaling up, because TEG is an abiotic unit and has a simpler structure. The actual energy consumption by this system, mostly due to pumping (feeding and recirculation), will need to be better evaluated once the system is scaled up.

5.5 Conclusions
This study has demonstrated the synergy between TEG and MECs through hydraulic connection: the MEC take advantage of the heat flux into the cold-side solution in the TEG that benefits its anodic microbial activities and meanwhile, it acts as a cooling unit for the TEG to increase voltage output. A higher anolyte recirculation rate could increase the cooling effect and lead to higher voltage output from the TEG that eventually benefited the MEC hydrogen production. Decreasing the anolyte HRT for a higher organic loading rate improved hydrogen production but decreased organic removal efficiency, mainly through affecting the MEC anode microbial activity. Hydrogen production could be further increased by adding more TEG units to capture more heat energy, but the optimal number of TEG units linked to MECs will need a more comprehensive techno-economic assessment. Future studies should aim to address several challenges such as optimized TEG-MEC setup, biofouling inside the TEG, improved design for better capture of heat energy, and system scaling up.
References


6

Techno-Economic Analysis of Microbial Electrolysis Cell for the Treatment of Brewery Wastewater and Hydrogen Production

6.1 Introduction

The United Nations World Water Development Record 2014 report noted the interconnection and interdependence between water and energy (UNESCO, 2014). The report emphasized the imminent need to develop sustainable and renewable energy sources and universal access to water and sanitation. Moving forward, the 2017 report focused on one important component of water – wastewater (UNESCO, 2017). It pointed to the challenges of increased wastewater generation especially in low-income, developing countries and considering wastewater as a valuable resource rather than a costly problem. Currently, conventional wastewater treatment technologies are energy and cost-intensive. It is estimated that for the treatment of one cubic meter of wastewater ~0.6 kWh of energy is required (McCarty et al., 2011). In developed countries such as the United States, between 1-3% of the total electrical energy consumption is used for wastewater treatment (USEPA, 2006). Whereas in the same cubic meter of wastewater, about 1.93 kWh of energy stored in the form of chemical energy. Thus there is a potential to tap the energy stored in wastewater which can make the process cost-effective and sustainable.

Bioelectrochemical systems (BESs) have emerged as a novel technology for simultaneous wastewater treatment and resource and energy recovery (Pant et al., 2012). The basic components of a BES include microorganisms, electrodes (anode and cathode), cathode catalysts, and membranes. In a BES, electrogenic microorganisms oxidize organics in the anode chamber and generate electrons that travel to the cathode through an external circuit. An electron acceptor at the cathode accepts the electrons and gets reduced. In the basic microbial fuel cell (MFC), oxygen is the electron acceptor and the flow of electrons through the circuit generates electricity (Logan et al., 2006). Oxygen can be supplied to the cathode either by having air-cathodes or aerating the cathode chamber. Aeration, in this case, while may be cheaper than activated sludge (AS) process, may still prove to be expensive. Additionally, the electricity should be used
directly or stored in batteries, which may not be energy-efficient for a small power generation. Microbial electrolysis cell (MEC), another type of BES differs from MFC in a way that, an external power is provided to reduce protons at the cathode to generate hydrogen gas (Hua et al., 2019). In the MEC, both anode and cathode chambers are anaerobic. Thus, integrating MEC in the existing infrastructure should be relatively easier compared to MFC where the anode is anaerobic and the cathode is aerobic.

Hydrogen is one of the most promising sustainable fuels as it is a carbon-free, high energy alternative (Mazloomi & Gomes, 2012). Hydrogen can be stored and transported. Biological hydrogen production using organic wastes is attractive as it is less expensive, less energy demanding and an environmentally-friendly process reducing dependency on fossil fuels (Münster & Meibom, 2011). The external energy required for hydrogen production using an MEC (0.14 V theoretical; ~0.6 V practical) is much less than electrolytic water splitting (1.23 V theoretical), currently used in industries for hydrogen production (Cheng & Logan, 2007; Rozendal et al., 2006).

Over the past decade, MECs have been extensively analyzed for technical development and parameter optimization. Researchers have studied different substrates that can be used in MECs, hydrogen production rates for various substrates (Kadier et al., 2014), ion exchange membranes, electrode materials (Leong et al., 2013; Zhou et al., 2011), cathode materials and catalysts (Kundu et al., 2013), the surface area of electrodes, the spacing between the electrodes (Cheng & Logan, 2011) and various applications of MECs (Zhang & Angelidaki, 2014). The period observed a few pilot-scale studies to evaluate the technology at a scaled-up level (Gil-Carrera et al., 2013; Heidrich et al., 2014). However, there are several challenges still concerning the technology. System performance at scaling-up, cost of the components and lack of techno-economic data are some of the issues faced by the technology.

In a study, comparing MEC with MFC and anaerobic digester in a life cycle assessment, MEC was found to be the most favourable amongst the three (Foley et al., 2010). To be implemented in the industry, MECs should be technically as well as economically viable. Lack of data on potential capital costs limits the interests of the industry. With the limited economic data available, it has been reported that municipal wastewater treatment using MEC will involve huge capital costs for infrastructure development. In a study, the economic feasibility of MEC was investigated, estimating the allowable capital cost per cubic meter of the anodic chamber (Escapa
et al., 2012). Based on their analysis, it was concluded that the organic loading rate (OLR) for MECs should be higher than 2000 g-COD (chemical oxygen demand) m\(^{-3}\) d\(^{-1}\) for bringing down the acceptable cost of MEC at $1370 (€ 1220) per m\(^3\). In another study, an economic analysis was reported for a treatment plant treating 15,000 m\(^3\) wastewater every day (Aiken et al., 2019). It was found that at the current performance, MECs are not viable for such large-scale applications and recommended to have an OLR between 800-1400 g-COD m\(^{-1}\) d\(^{-1}\). Treating domestic wastewater (DWW) using MEC has several disadvantages such as larger infrastructure requirement and lower organic content (~350 g-COD m\(^{-3}\) d\(^{-1}\)) in the wastewater. It has been reported that substrates with higher concentration and biodegradability provide a better MEC performance (Escapa et al., 2016). Industrial wastewater such as brewery wastewater (BWW) contains very high biodegradable organic content in their wastewater. Another advantage with industrial wastewaters such as BWW is the quantity generated is comparatively very less from DWW. This could be ideal as the initial investment cost would be much less as a small infrastructure would be required and the high biodegradability of the substrate would give a better MEC performance.

In this study, we present the economic cost of MEC technology for the treatment of industrial wastewater which is high in concentration and highly biodegradable. For simplicity, only BWW is considered in this work. Anaerobic digestion (AD) is the preferred process for the treatment of high-strength industrial wastewater. In this work, a comparative economic analysis is carried out between an AD and an MEC for the treatment of BWW. Though there have been attempts to evaluate MEC for its economic feasibility for municipal wastewater, a techno-economic assessment (TEA) for the treatment of high – strength wastewater using MEC has not been carried out to the best of our knowledge. A TEA can help in understanding the cost limiting factors for the development of MEC for commercialization. The restrictive use of MEC and similar other BES technology at scaled-up levels limits the cost estimation of the technology. However, the economic assessment based on the best available data can pave a way for the advancement of the technology to overcome the restrictions. Thus, the main objective of this study was to provide a techno-economic assessment of BWW treatment using an MEC and comparative analysis with AD.
6.2 Methodology

6.2.1 Case Study Description

For this assessment, an MEC study treating real brewery wastewater was chosen (Lu et al., 2016). The wastewater fed to the MEC had COD of 1100 mg L⁻¹. Three cathode catalysts were selected for comparison analysis namely: carbon cloth with platinum/carbon coating (PtC); nickel foam (NiF) and stainless steel mesh (SS). All other components of the MEC are considered to be the same. The anode used in all the reactors is carbon brush. A low-cost Rhinohide membrane which acts as a separator was used between the anode and the cathode. The characteristic performance data for each cathode catalyst as described in Table 6.1 was used for projections. The treatment capacity for this study is based on the annual volume production of 200,000 beer barrel (bbl). Ballast Point Brewing Company used to operate a plant in Daleville, Virginia with this capacity and Deschutes planned to open a new brewery in Roanoke, Virginia having a capacity of 200000 bbl. A brewing facility produces about 10 units of wastewater for each unit of beer produced (Shao et al., 2008). The treatment capacity is thus considered to treat 0.2 million gallons of wastewater every day (MGD).

Table 6.1 Performance parameters of brewery wastewater treatment (Lu et al., 2016)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>PtC-MEC</th>
<th>NiF-MEC</th>
<th>SS-MEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coulombic Efficiency (CE)</td>
<td>66%</td>
<td>63%</td>
<td>71%</td>
</tr>
<tr>
<td>COD removed (ΔCOD)</td>
<td>870 (g m⁻³)</td>
<td>870 (g m⁻³)</td>
<td>870 (g m⁻³)</td>
</tr>
<tr>
<td>Current Density (Iₐ)</td>
<td>3.67 (A m⁻²)</td>
<td>2.23 (A m⁻²)</td>
<td>2.16 (A m⁻²)</td>
</tr>
<tr>
<td>Hydrogen Production Rate</td>
<td>2.08 (m³ m⁻³ d⁻¹)</td>
<td>1.13 (m³ m⁻³ d⁻¹)</td>
<td>1.13 (m³ m⁻³ d⁻¹)</td>
</tr>
</tbody>
</table>

For economic evaluation at large-scale, a model prepared for cost estimation of MEC for municipal wastewater was used (Aiken et al., 2019). One of the important parameters to characterize MEC performance is Coulombic efficiency (CE) (Logan, 2008). CE is the amount
of electrons flowing in the circuit compared to the theoretical amount that can be generated from the degraded substrate.

\[ CE = \frac{8.1}{F \cdot Q \cdot \Delta COD} \]  

where \( Q \) is the flow rate which reflects the size of the treatment capacity; \( I \) is the current (current \( I \) divided by anode surface area, \( A \)); \( \Delta COD \) is the COD removed from the system; \( 8 \) is the number of electrons in a mole of oxygen, and \( F \) is the Faraday’s constant. The equation 4.1 can be rearranged to calculate the anodic surface area for a given current density and flow rate:

\[ A = \frac{CE \cdot F \cdot Q \cdot \Delta COD}{8 \cdot I_A} \]  

With the performance data from Table 6.1, the anodic surface area was calculated for the treatment of 0.2 MGD of wastewater. The reactor had a cassette-type configuration and anode surface area was used as a base for estimating the quantity of other materials. In every cassette, there were two frames of carbon brush anode on either side of the cathode. The cathode chamber, placed in the middle of the cassette had a membrane (Rhinohide membrane (separator)) on both sides separating it from the anode. For a comparison with the established technology, AD, commonly used for the treatment of high-strength wastewater, is used. The cost of the digester is based on a case study operating a similar system (Pullen, 2015). Natural gas generated is assumed to be sold to a third party for a fair comparison. The capital and operating cost that differs for the two technology are considered for the economic assessment and other costs common to both are not used for comparison in this analysis.

6.2.2 TEA Model
This study is focused on evaluating the economic viability of using MEC in the industrial wastewater treatment process. It discusses the difference in cost due to the inclusion of MEC in the process. A detailed estimation of the cost for the complete wastewater treatment plant is beyond the scope of this work. The total costs consist of capital cost, operating cost and revenue from the sale of produced gas. The TEA model is based on the Excel spreadsheet and uses experimental data, engineering knowledge, and economic data. The cost of components and the sources are listed in Appendix A. The cost was estimated based on the price from manufacturers and literature when the price was not available. The produced gas will be stored in a tank. The cost of the compressor and storage unit were also included in the capital cost. The total installation cost consists of 10% of the tank, pipes, and pumps each and 5% of the cost of the compressor unit (Escapa et al., 2012). Operating costs included in this analysis were labor and electricity cost. The price of electricity is 6.9 cents per kWh of electricity used based on the US Energy Information Administration data. The source of revenue is from the sale of produced gas. The cost of hydrogen is taken as $3.9 per kg H₂, the target production cost from electrolysis by US DOE (Dixon et al., 2016) while methane is priced as $0.22 per cubic meter (USEIA). If the water is not treated by brewery before discharge, they have to pay a surcharge to the treatment facility for such high concentration wastewater. The surcharge is based on the facility treating the wastewater. For this report, the cost for BOD is used as $0.3896 per pound and TSS as $0.4326 per pound based on the charges available from King County Industrial Waste Program (King-County, 2019). This cost is added to revenue as part of the cost saved by treating the wastewater on the facility itself.

For the economic evaluation, the net present value (NPV) was used. The NPV can be calculated as:

\[
NPV = \sum_{i=0}^{n} \frac{C_i}{(1 + r)^t} - C_0
\]

(6.3)

where \(C_i\) is the cash flow for a particular year \(i\), \(r\) is the discount rate, \(n\) is the operating life of the plant and \(C_0\) is the initial investment. A twenty-year operational period \((n)\) is considered with no
salvage value for the comparison. The discount rate \( (r) \) was assumed to be 4 \% for a water resources project (OMB).

### 6.2.3 Sensitivity Analysis

There are many factors involved in the estimation of cost that directly affects the techno-economic evaluation of the technology. For example, an increase in the electricity price can reduce the profit margin, whereas an increase in the price of gas will increase the profit. There are some parameters whose prices are uncertain at this point due to the lack of commercialization of the technology. It consists of parameters like electrode cost, membrane cost, membrane duration, etc. A sensitivity analysis was carried out to understand the effects of these variations on economics. Five scenarios are discussed in this context as represented in Table 6.2. Scenario 1 involves a change in the hydrogen production rate. As this study is based on the results of a lab-scale study, it is expected that the performance at full-scale operation will be inferior compared to the controlled environment of the lab. A 50\% reduction in the hydrogen gas yield is tested. It is also possible that the advancement in technology can improve the performance of the system. This scenario also analyzes the case when hydrogen production is 50\% higher compared to the present performance. For Scenario 2, the annual replacement of Rhinohide separator was considered. The membrane may not last for 20 years, however annual replacement is used as a conservative estimate. In Scenario 3, the separator used in the present configuration is replaced by an anion exchange membrane. Though in the case studies hydrogen had 98-99\% purity without an ion exchange membrane, in the long run, microbes from the anode could use the hydrogen produced at the cathode to generate methane. For producing pure hydrogen, it is highly recommended to keep the anode and cathode environment completely separate. This scenario can estimate the effects of including ion-exchange membranes on the cost of the system. For Scenario 4, the replacement of the electrodes was considered. As there are no full-scale long time operations for MEC available, the durability of the materials is not known. In this scenario, the replacement of anode and cathode was considered every 7 years. In Scenario 5, the cost of the materials specific to MEC (anode, cathode, membrane) is considered to be reduced to half. As technology makes progress and full-scale operations take place, the increase in demand can reduce the cost of the materials. This scenario analyzes the effect of cost reduction of materials...
on the economics of the system. In practical application, many of these may overlap, however, to understanding the impact they have on the overall economics, they are evaluated separately here.

Table 6.2 Description of Scenarios

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scenario 1</td>
<td>Change in Hydrogen Production Rate</td>
</tr>
<tr>
<td>Scenario 2</td>
<td>Annual replacement of membrane</td>
</tr>
<tr>
<td>Scenario 3</td>
<td>Use of Ion Exchange Membrane</td>
</tr>
<tr>
<td>Scenario 4</td>
<td>Electrode Replacement</td>
</tr>
<tr>
<td>Scenario 5</td>
<td>Material Cost</td>
</tr>
</tbody>
</table>

6.3 Results and Discussions

6.3.1 Base Case Performance

The initial investment cost for all the three MEC cases varied greatly. The total capital cost for MEC follows the trend of PtC-MEC>NiF-MEC>SS-MEC. As can be expected, the capital cost for MEC with PtC as the catalyst was the highest at $15,066,000. The capital cost reduced significantly for the MECs with NiF and SS as the cathode catalyst. For each of them, the cost was a magnitude lower than PtC-MEC at $3,902,000 for NiF-MEC and $1,689,000 for SS-MEC. Fig. 6.1 represents the material cost for various components for the three MEC systems. Cathode constitutes the highest percentage of the total cost for the case of PtC –MEC and NiF-MEC. Due to such a high value of cathode (92%) for the PtC case, the cost for other components such as membrane; pipes and pumps; and anode is dwarfed. Tank cost was the highest component of the total cost of the system for SS and the second highest for the other two catalysts. In fact, for the case of SS, the tank cost (61%) was much higher than the combined anode and cathode cost (10%). The anode was inexpensive and thus didn’t contribute significantly to the total capital cost of the system. Total capital cost for AD including biogas to biomethane upgradation facility
was similar to MEC with SS as cathode catalyst at about $1,523,000. The equipment and installation of biogas to biomethane upgrade facility constitute a significant portion of the total cost for the AD. Table 6.3 shows the capital cost for the four different cases.

![Pie chart showing capital cost for different cases of MEC and AD](image)

**Figure 6.1** Capital cost for the three MEC cases (MEC with: PtC = Pt/C as cathode catalyst; NiF = nickel foam as cathode catalyst and SS = stainless steel as cathode catalyst)

The high capital cost of the MEC acts as a barrier towards the implementation of the technology on a large scale. However, it should be noted that with certain cathode catalysts for MECs such as NiF and SS, the initial investment is not too high for a small scale facility. In fact, as noted for the case of SS as a cathode catalyst, the total capital cost is similar to that of AD. On top of that, MECs provide the benefit of producing hydrogen which is a clean fuel with no harm of
generating greenhouse gas emission from its use. The total capital cost for BWW treatment with MEC using non-precious metal as cathode catalyst was similar to that estimated for municipal wastewater treatment ($2,135,000 when scaled down to 750 m$^3$) (Aiken et al., 2019). However, hydrogen production was much higher in the case of BWW.

Table 6.3 Capital Cost for the three MECs and AD (All cost in USD)

<table>
<thead>
<tr>
<th>Parameter/Reactor</th>
<th>PtC-MEC</th>
<th>NiF-MEC</th>
<th>SS-MEC</th>
<th>AD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode</td>
<td>12,800</td>
<td>20,000</td>
<td>23,400</td>
<td>NA</td>
</tr>
<tr>
<td>Cathode</td>
<td>13,895,400</td>
<td>2,573,200</td>
<td>149,700</td>
<td>NA</td>
</tr>
<tr>
<td>Membrane</td>
<td>32,000</td>
<td>50,200</td>
<td>58,400</td>
<td>NA</td>
</tr>
<tr>
<td>Tank</td>
<td>576,200</td>
<td>864,200</td>
<td>1,037,000</td>
<td>627,200</td>
</tr>
<tr>
<td>Compressor &amp; Storage</td>
<td>434,400</td>
<td>236,000</td>
<td>236,000</td>
<td>336,000</td>
</tr>
<tr>
<td>Biogas Upgrade Facility</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>300,000</td>
</tr>
<tr>
<td>Pipes and Pumps</td>
<td>25,000</td>
<td>25,000</td>
<td>25,000</td>
<td>25,000</td>
</tr>
<tr>
<td>Installation Cost</td>
<td>90,200</td>
<td>133,400</td>
<td>159,300</td>
<td>235,200</td>
</tr>
<tr>
<td>Total Capital Cost</td>
<td>$15,066,000</td>
<td>$3,902,000</td>
<td>$1,688,800</td>
<td>$1,523,200</td>
</tr>
</tbody>
</table>

Two parameters were considered for operating cost – electricity and labor. The labor price was fixed at $45,000 per annum based on the data from the US Department of Labour (USDOL, 2018). Electricity costs varied for different cases. The system requirements for MEC with PtC were the highest which was reflected in the electricity cost of $72,500. Electricity cost for NiF-MEC and SS-MEC was similar at $44,000 and $43,000, respectively. AD costs the least with respect to electricity at only $14,000 per annum. Generally, the biogas generated from the digester is used to provide energy for the system, however, for comparison with the MEC system, electricity is assumed to be taken from the grid.
As the hydrogen production rate of PtC was the highest, so was the revenue generated from the sale of hydrogen. PtC-MEC generated ~$200,000 per annum whereas revenue from NiF-MEC and SS-MEC was about $109,000 (similar hydrogen production rate). AD generated biogas which was upgraded to natural gas. The revenue from the sale of natural gas was estimated at about $83,500. Even with hydrogen production for PtC-MEC at twice the rate of hydrogen production for NiF-MEC and SS-MEC, the NPV for the PtC-MEC was lowest at $2,741,000 for a twenty-year time period. The NPV increased remarkably for NiF-MEC and SS-MEC with $13,050,000 for NiF-MEC and $15,280,000 for the case of SS-MEC. This is directly in relation to the initial investment cost which followed the inverse trend. In this comparative analysis, the NPV is positive for all the alternatives. However, it should be noted that, this is not an all-inclusive estimation and the other cost which are not compared here should be taken into consideration for evaluating the viability of the project. Of the three cathodes used, PtC involves the use of platinum which is an expensive, precious metal and has negative environmental impacts incurred during mining/extraction (Rabaey & Keller, 2008). Furthermore, sulfides commonly present in wastewater can poison platinum. It can, therefore, be suggested to not use PtC for such applications where clearly equally beneficial if not better alternatives are available. NPV for the AD was the highest with a value of $15,517,000. AD is a proven technology and more favored by industries, yet this cost comparison evidently makes a case for MECs to be adapted as a full-operation technology specifically in small-scale operations such as brewery wastewater treatment. Table 6.4 summarizes the economic parameters for the three MECs and AD.

**Table 6.4** Summary of the parameters for each of the alternatives estimated (All cost in USD)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>PtC-MEC</th>
<th>NiF-MEC</th>
<th>SS-MEC</th>
<th>AD</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Capital Cost</strong></td>
<td>15,066,000</td>
<td>3,902,000</td>
<td>1,689,000</td>
<td>1,523,000</td>
</tr>
<tr>
<td><strong>Operating Cost</strong></td>
<td>117,000</td>
<td>89,000</td>
<td>88,000</td>
<td>59,000</td>
</tr>
<tr>
<td><strong>Revenue</strong></td>
<td>200,000</td>
<td>109,000</td>
<td>109,000</td>
<td>84,000</td>
</tr>
<tr>
<td><strong>Profit</strong></td>
<td>83,000</td>
<td>20,000</td>
<td>21,000</td>
<td>24,000</td>
</tr>
<tr>
<td><strong>Net Present Value</strong></td>
<td>2,741,000</td>
<td>13,050,000</td>
<td>15,280,000</td>
<td>15,500,000</td>
</tr>
</tbody>
</table>
6.3.2 Sensitivity Analysis

6.3.2.1 Change in hydrogen production

When hydrogen production was reduced to half, the NPV changed for each of the systems. The change was the most significant for PtC-MEC where NPV decreased by $1,806,000. For NiF-MEC and SS-MEC, the reduction in NPV was about $953,000 and $944,000, respectively. These figures can be understood better when compared on the percent change. In the case of PtC-MEC, there was a 66% reduction in the NPV value, which signified that hydrogen production holds a deciding role in accounting the capital cost of the system. Whereas in the case of NiF-MEC and SS-MEC, the effect of change in hydrogen yield was only about 7% and 6%, respectively. As the initial investment is much lower for NiF-MEC and SS-MEC, hydrogen production has a low impact on the system.

When hydrogen production was doubled, it is expected that NPV will improve. Results for PtC saw a dramatic change as in the previous case. The NPV jumped to $5,009,000 increasing by a staggering 83%. As the change in capital cost is very low (compressor and storage unit), the increase in the revenue is directly reflected in the NPV. For NiF-MEC and SS-MEC, the NPV increased by 10% to $14,311,000 and 8% to $16,550,000, respectively. This result emboldens the previous finding that change in hydrogen production has a lower impact on NPV for NiF-MEC and SS-MEC.

6.3.2.2 Annual Replacement of Membrane

As it is unlikely that membrane (Rhinohide) can last for 20 years, an annual replacement for the membrane was considered in this scenario. The replacement of the membrane will put an additional burden on the economics of the system. However, the impact of annual replacement was not very drastic. The NPV decreased 16%, 5% and 5%, respectively for PtC-MEC, NiF-MEC and SS-MEC. As membrane comprises at most 4% of the total cost (for the case of SS-MEC), the notion of escalating cost too high because of the inclusion of membrane should be
reconsidered (Sleutels et al., 2012). The details of NPV for all the scenarios are presented in Table 6.5 (Fig. 6.2) along with the % change from the base case.

6.3.2.3 Ion Exchange Membrane

Replacement of the Rhinohide membrane (separator) by anion exchange membrane will increase the capital cost of the system. Assuming the performance is not changed, the NPV of the system observed a negative change. The impact on the cost of PtC-MEC was higher compared to NiF-MEC and SS-MEC. The NPV for PtC-MEC decreased by 22% whereas there was a 7% decrease observed in the case of NiF-MEC and SS-MEC. The cost of the membrane has come down in the past decade and with the advancement in technology and increasing demand of the membrane, the cost will further come down. This is beneficial as the application of the ion exchange membrane ensures there is no mixing between the biological and abiotic components of the system.

6.3.2.4 Electrode replacement

The lifetime of components used in MEC is unknown as there has been no full-scale application for the technology. In this scenario, anode and cathode were assumed to be replaced every seven years. This had the most dramatic and varied effect on the system. The NPV for PtC-MEC system went down to -$25,000,000, an astronomical shift of 1000%. This is not so surprising as, for the PtC-MEC case, the cathode is the major cost contributor (93%) and its replacement will add a significant amount to the total cost of the system. There was a high decrease in the case of NiF-MEC as well, with NPV reducing by 40% to $7,900,000. Though, the NPV was still positive for NiF-MEC implying the investment was still viable. SS-MEC experienced the least amount of change (2%) for an NPV of $14,975,000. As the total contribution of anode and cathode to the system is only 10%, the replacement of these two components didn’t have a very significant negative impact on the overall economics. It is clear from the results of this Scenario that PtC may not prove to be a sustainable solution in the long run.
6.3.2.5 Material cost

The advancement in technology and production at mass-scale can bring down the cost. In this case, the cost for each of the anode, cathode, and membrane was reduced to half. The anode and membranes are already inexpensive, however, reduction in cathode cost would have a major effect on the NPV of the system. The reduction in material cost had a significant impact on PtC-MEC with NPV increasing to $9,720,000, a change of 250% from the base case. NiF-MEC changed by 10% to $14,400,000 whereas there was only a 1% increase observed in the case of SS-MEC ($15,440,000). Thus, a reduction in the cost of components specific to MEC is beneficial for the system, in general. However, it should also be noted that the NPV for MEC with low investment cost at the beginning is resilient against the changes in the system.

![Comparison of net present value (NPV) for the base case and the five scenarios](image)

**Figure 6.2** Comparison of net present value (NPV) for the base case and the five scenarios (1a: Hydrogen yield decrease; 1b Hydrogen yield increase)
Table 6.5 Comparison of NPV for different scenarios and their percent change from the base case (1a: Hydrogen yield decrease; 1b Hydrogen yield increase)

<table>
<thead>
<tr>
<th>Scenario</th>
<th>PtC-MEC</th>
<th>NiF-MEC</th>
<th>SS-MEC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NPV (USD)</td>
<td>Change (%)</td>
<td>NPV (USD)</td>
</tr>
<tr>
<td>Base</td>
<td>2,741,000</td>
<td>NA</td>
<td>13,050,000</td>
</tr>
<tr>
<td>1a</td>
<td>935,000</td>
<td>-65</td>
<td>12,097,000</td>
</tr>
<tr>
<td>1b</td>
<td>5,009,000</td>
<td>83</td>
<td>14,311,000</td>
</tr>
<tr>
<td>2</td>
<td>2,314,000</td>
<td>-16</td>
<td>12,400,000</td>
</tr>
<tr>
<td>3</td>
<td>2,124,000</td>
<td>-22</td>
<td>12,103,000</td>
</tr>
<tr>
<td>4</td>
<td>-25,067,000</td>
<td>-1014</td>
<td>7,900,000</td>
</tr>
<tr>
<td>5</td>
<td>9,720,000</td>
<td>250</td>
<td>14,404,000</td>
</tr>
</tbody>
</table>

6.4 Conclusion

MEC can be a promising, sustainable alternative for industrial wastewater treatment. The results demonstrate that using MEC for full-scale operations can be economically and environmentally beneficial. The use of non-precious cathode catalysts such as nickel foam and stainless steel for MEC could make it competitive with the existing technologies such as anaerobic digestion. Capital cost with Pt/C as cathode catalyst is quite high and it is recommended that Pt/C should be avoided as a cathode catalyst. The MEC with SS as a cathode catalyst was the most robust against changes such as a decrease in hydrogen production, replacement of components and separator with ion-exchange membranes. The advancement in technology can bring the cost of
material down which can further increase the economic value of the MEC system. This cost comparison evidently makes a case for MECs to be adapted as a full-scale operation technology.
References


King-County. 2019. King County's Industrial Waste Program: www.kingcounty.gov/services/environment/wastewater/industrial-waste/fees.aspx. King County, WA.


USEIA. Natural Gas. Washington D.C.


Appendix A

Table A1 List of components with material, price and source

<table>
<thead>
<tr>
<th>Component</th>
<th>Material</th>
<th>Cost</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode</td>
<td>Carbon brush</td>
<td>$7.8/Carbon brush</td>
<td>The Mill-Rose Company, OH, US</td>
</tr>
<tr>
<td>Cathode</td>
<td>Platinum/Carbon on Carbon Cloth</td>
<td>$45/m² carbon cloth</td>
<td>Zoltek Corporation, MO, US</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$160/g Platinum/carbon</td>
<td>Sigma-Aldrich Corporation, MO, US</td>
</tr>
<tr>
<td>Cathode</td>
<td>Nickel Foam</td>
<td>$200/m²</td>
<td>Xiamen TOB New Energy Technology Co. Ltd., China</td>
</tr>
<tr>
<td>Cathode</td>
<td>Stainless Steel Mesh</td>
<td>$10/m²</td>
<td>Jingsi Hardware Mesh Co. Ltd., China</td>
</tr>
<tr>
<td>Membrane</td>
<td>Rhinohide© Battery Separator</td>
<td>$1.95/m²</td>
<td>Entek Ltd, UK</td>
</tr>
<tr>
<td>Membrane</td>
<td>Anion Exchange Membrane</td>
<td>$40/m²</td>
<td>Hangzhou Lontech Environment Technology Co. Ltd., China</td>
</tr>
</tbody>
</table>