

INVESTIGATION OF APPLICATION NICHE FOR
SUSTAINABLE WASTEWATER TREATMENT USING
MICROBIAL FUEL CELLS

by

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ABSTRACT

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Microbial fuel cells represent a sustainable wastewater treatment technology due to its simultaneous treatment of contaminants and electricity production. Selection of suitable substrates is important to identifying proper application of microbial fuel cell (MFC) technology. In this work, four identical MFCs were used to treat the wastes sampled from different stages of a cheese wastewater treatment process, and both treatment performance and energy balance were examined. The two MFCs treating liquid wastes achieved more than 80% removal of total chemical oxygen demand (TCOD), while the other two MFCs fed with sludge or cheese whey removed about 60% of TCOD. The suspended solids were greatly reduced in all MFCs. Nutrient removal mainly occurred with nitrite and ammonia reduction, while the phosphate decrease was insignificant. The MFC-2 treating the DAF (dissolved air flotation) effluent generated the highest Coulombic efficiency of 27.2 ± 3.6 % and the highest power density of 3.2 ± 0.3 W/m³. Because of the low contaminant concentrations in the DAF effluent, the MFC-2

consumed the least amount of energy of 0.11 kWh/m³. None of the tested MFCs achieved an energy-neutral balance, mainly because of the small connecting ports (which resulted in high recirculation energy) and the use of cathode aeration. Our results suggest that MFCs may be more suitable for treating low-strength wastewater in terms of both treatment and energy performance. Owing to the importance of nutrient (nitrogen and phosphorus) control in wastewater treatment operations, this work also reviews the removal and recovery of nutrients in various bioelectrochemical systems (BES) including microbial fuel cells and microbial electrolysis cells, discusses the influence factors and potential problems, and identifies the key challenges for nitrogen and phosphorus removal/recovery in a BES.

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Chapter 1 Literature Review and Background

1.1. Water/Wastewater Treatment Introduction

The proper disposal of wastewater from homes, businesses, and industries is very critical in preserving the quality of our surface water and groundwater so we may safely use them for drinking water, recreation, and fishing. Inadequate wastewater treatment diminishes water quality and aquatic life by lowering dissolved oxygen (DO) concentrations in the receiving waters. Low DO levels occur by eutrophication by algal blooms and microbial contamination resulting from incomplete wastewater treatment. The primary goal of the Clean Water Act (passed in 1972) is to “restore and maintain the chemical, physical and biological integrity of the nation’s waters” (U.S.E.P.A, 2004).

The proper treatment of wastewater is accomplished in metropolitan areas by collection using sewer systems and removal of pollutants using wastewater treatment plants (WWTP). Industries with highly concentrated streams may have their own wastewater treatment plants to handle their respective loadings while residential sources in rural areas may simply use a septic system. Wastewater treatment plants will likely use physical, chemical, and/or biological methods to remove water pollutants in the waste stream. Water pollutants may consist of organic matter, pathogens, nutrients (nitrogen and phosphorus), inorganic/organic chemicals, and elevated heat. WWTPs are designed to meet the operational requirements as well pollutant removal and thus are designed in a site specific manner. Though WWTPs differ from plant to plant, they typically use primary screening and sedimentation followed by secondary biological removal using techniques such as activated sludge, aerated trickling filter, rotating biological contactors,

etc... These conventional secondary treatment processes are vital to the treatment process, but consume a majority of the energy in the WWTP (Figure 1-1).

1.2. Energy Considerations in Water/Wastewater Treatment

Water and wastewater treatment facilities consume approximately 30 to 60% of a municipal government's energy budget and account for about three to four percent of the U.S.'s energy usage (WEF, 2009). The estimated electrical energy demand for the water

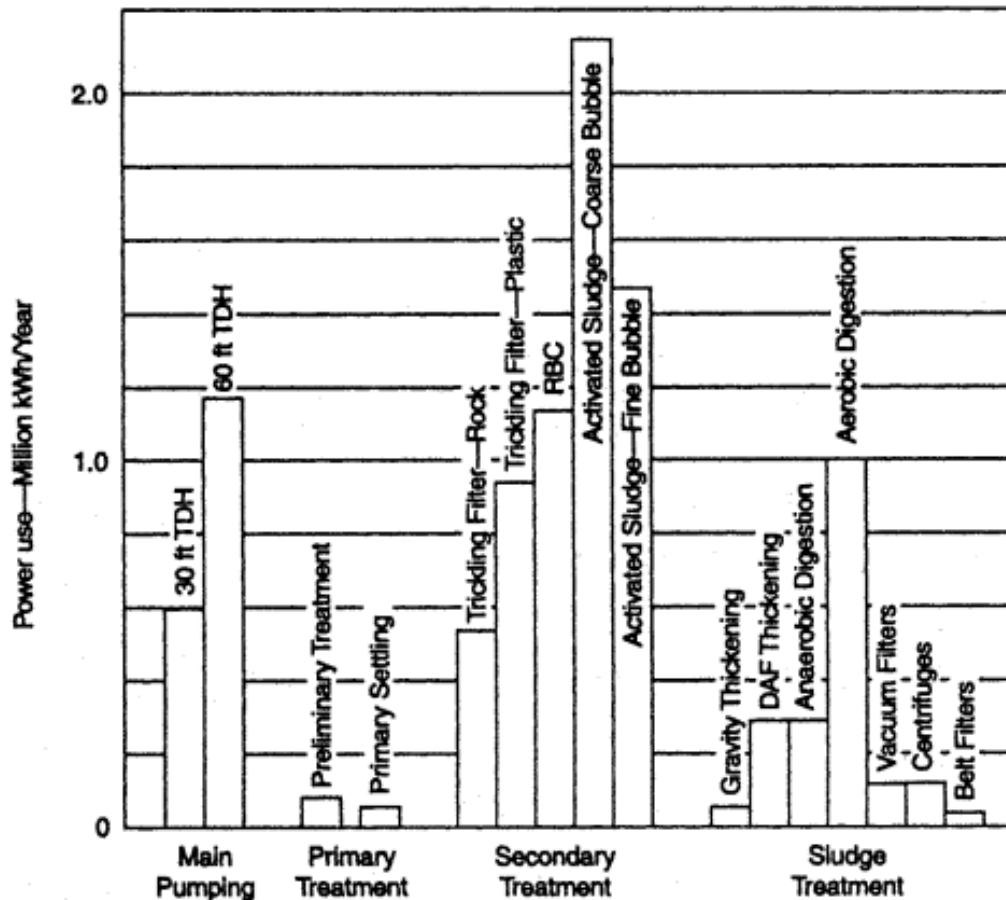


Figure 1-1. Typical energy use profile for 10-mgd (0.4 m³/s) WWTP processes (WEF, 2009)

and wastewater industry is approximately 100 billion kilowatt hours (kWh) per year (about \$7.5 billion per year) (U.S.E.P.A., 2010). The cost of energy is increasing because discharge requirements are becoming increasingly stringent, our infrastructure is aging,

and electricity prices are rising, causing the water and wastewater industry to become more and more energy intensive. Therefore, it is of great interest to develop sustainable low energy water and wastewater treatment systems to reduce energy costs and greenhouse gas emissions while maintaining removal of contaminants.

1.3. Nutrients Removal in Water/Wastewater Treatment

It is of great importance for domestic and industrial wastewater treatment operations to remove nutrients (i.e. nitrogen and phosphorus compounds) from wastewater to mitigate the effects of eutrophication (by oxygen depletion) in the receiving waters as well as the prevention of human disease.

Nitrogenous compounds in wastewater take the form of organic nitrogen and inorganic nitrogen (ammonia, nitrite, and nitrate). For example, nitrate, a commonly occurring groundwater contaminant released to the environment by nitrogen fertilizers, is linked to methemoglobinemia (blue baby syndrome) when ingested (Della Rocca et al., 2007). Otherwise, nitrogen is typically present in the form of ammonia in wastewaters. Phosphorus is most commonly subjected to wastewater/natural waters from fertilizer use (to boost agricultural human food production) in the forms of orthophosphate, polyphosphate, and organically bound phosphorus. It is considered the critical nutrient contributing to eutrophication to natural waters (Seviour et al., 2003) causing excessive algae blooms resulting in oxygen depletion and adverse effects to aquatic ecosystems (de-Bashan & Bashan, 2004). Beyond this, the human demand for the mining of phosphorus reserves continues to grow (at a growth rate of 3% per year) and the finite resource continues to dwindle (suggested to run out in 50 years) exemplifying the importance in recovering phosphorus from wastewater treatment operations (Gilbert, 2009).

1.3.1. Conventional Nitrogen Removal Technologies

In the United States, nitrogen and phosphorus control methodologies in wastewater treatment most commonly take the form of biological processes rather than physiochemical methods as they are reliable, environmentally sustainable, cost effective, and avoid the use of expensive chemicals (U.S.E.P.A., 1993). Biological nitrification and denitrification is a robust and effective method in converting ammonia nitrogen to nitrogen gas. While this has been proven in application worldwide, aerobic nitrifiers performing nitrification require the addition of free dissolved oxygen and facultative heterotrophic denitrifiers require external carbon electron donors (i.e. methanol, ethanol, acetic acid) to perform denitrification resulting in high energy inputs, increased operational costs, and post treatment (Feleke & Sakakibara, 2002; Gomez et al., 2003; Killingstad et al., 2002).

Efforts have been made to improve this process by reducing energy inputs and operational costs in the development of novel biological nitrogen control technologies. Anaerobic Ammonia Oxidation (ANAMMOX) is low energy (no external carbon source is needed and aeration energies can be reduced by 50%) nitrogen removal technology founded in the Delft University of Technology during the 1990s where ammonium is converted directly to nitrogen gas strictly under anoxic conditions by anaerobic ammonia oxidizing bacteria (AOB) using nitrite as the electron acceptor (van de Graaf et al., 1995; Zhu et al., 2008). This process has been implemented in full scale treatment of low carbon ammonium containing wastewaters, such as treating sludge digestion supernatant in the Netherlands (Fux et al., 2002).

Other low energy nitrogen removal technologies are listed as follows:

- Simultaneous Nitrification and Denitrification (SND): combines the process into a single reactor through applying the optimal DO concentration (Zhu et al., 2008)
- Single reactor system for High Ammonia Removal Over Nitrite (SHARON) process: limits DO by oxidizing ammonia to nitrite for survival of AOB and obstruction of nitrite oxidizing bacteria (NOB). This process has been applied to full scale treatment of ammonia rich wastewater (Hellings et al., 1998).
- Oxygen-Limited Autotrophic Nitrification-Denitrification (OLAND)
- Completely Autotrophic Nitrogen Removal over Nitrite (CANON)

1.3.2. Conventional Phosphorus Removal Technologies

Conventional biological phosphorus removal uses phosphate accumulating organisms (PAO) to store excess amounts phosphate within their cells in the form of intracellular polyphosphate at levels higher than normal to satisfy their metabolic growth requirements in a process known as Enhanced Biological Phosphorus Removal (EBPR) (Liu et al., 2010). This process utilizes anaerobic and aerobic conditions to enrich PAOs to successively accumulate polyphosphate, and finally remove the waste sludge biomass rich in phosphorus (Blackall et al., 2002). Although this method is the preferred biological method advantageous to the chemical precipitation of phosphorus, it has issues with consistent stability in operation (due to excessive aeration during starving events) and low anaerobic solids retention time (Blackall et al., 2002; Brdjanovic et al., 1998; Matsuo, 1994). There is also a growing demand to recover phosphorus mineral as its reserve supplies are diminishing calling for a growth in research for phosphorus recovery from wastewater (Gilbert, 2009).

1.4. Microbial Fuel Cells

Microbial fuel cells (MFCs) represent a prospective low energy wastewater treatment system that converts chemical energy stored in wastewater to electrical energy. The operation of MFCs does not require aeration for the removal of contaminants (BOD/COD, nutrients) as present conventional methods (activated sludge or nitrification)

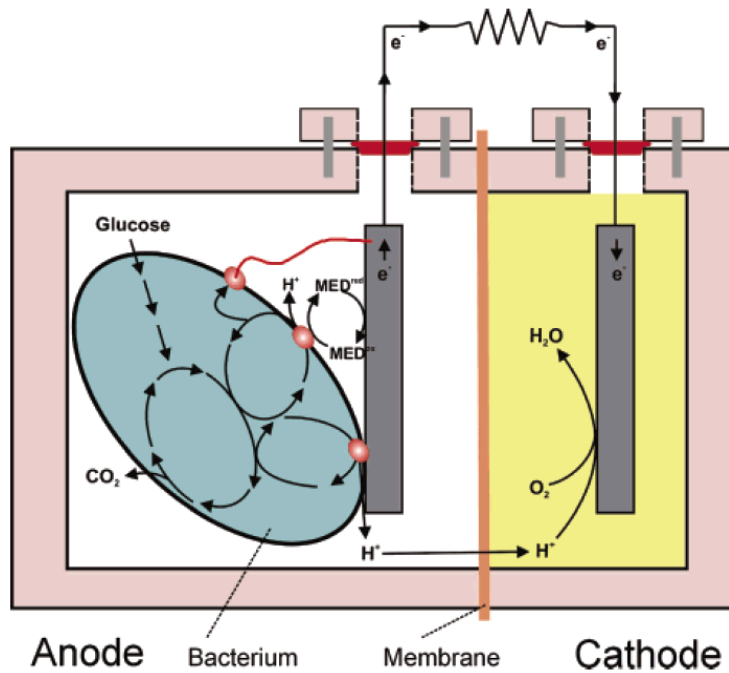
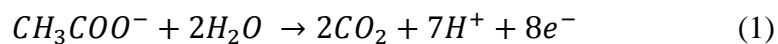


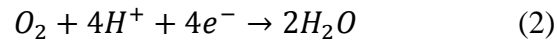
Figure 1-2 Two chamber microbial fuel cell reactor principle (Logan et al., 2006)

typically use. As shown in Figure 1-2, the MFC reactor is composed of an anode and cathode chamber containing electrodes which are electrically connected. Exoelectrogenic microorganisms (ability to transfer electrons extracellularly), such as *Geobacter sulfurreducens*

(Reguera et al., 2005), are cultivated onto the anode electrode where wastewater (organic or inorganic compounds) is anaerobically oxidized (Logan, 2009). For example, in Equation 1 below, acetate is oxidized by bacteria to produce electrons, protons, and carbon dioxide.



The electrons flow through the external circuit (a load) to the cathode electrode where the protons will migrate through a separator (usually a membrane) to both participate in a reduction reaction. For example, in Equation 2 below, oxygen is reduced by protons and electrons, producing water.



The low redox potential from anodic oxidation and higher redox potential from cathodic reduction ultimately drives the flow of electrons from the anode to cathode generating a voltage typically observed from 0.3-0.5 V depending on energy gain by bacteria and cathodic energy losses (Logan, 2009).

1.4.1. Microbial Fuel Cell Background

Other variations of the MFC have transpired from the basis of MFC technology. The Sediment Microbial Fuel Cell (SMFC) has been deployed in remote water bodies to drive low power sensors, replacing batteries (Tender et al., 2008). The addition of a small voltage (~0.4 V) to the system results in the application of Microbial Electrolysis Cells (MECs) with the generation of valuable products in the cathode such as methane, hydrogen, and hydrogen peroxide (Cheng et al., 2009; Liu et al., 2005; Rozendal et al., 2009). Desalination is also feasible within the MFC technology through Microbial Desalination Cells (MDCs) where salt anions and cations (through the use of anion and cation exchange membranes) are removed when passing through a salt chamber (separating anode/cathode) driven by electrical current generation from anodic oxidation (Cao et al., 2009b).

MFCs may be applied to a wide range of substrates (including, but not limited to): acetate, glucose, starch, cellulose, wheat straw, pyridine, phenol, *p*-nitrophenol, and complex solutions such as domestic wastewater, brewery waste, landfill leachate, chocolate industry waste, mixed fatty acids and petroleum contaminants (Franks & Nevin, 2010). The complexity of the substrate will have an important impact on the recovery of electrical energy production. A more complex substrate requires additional metabolic processes for degradation leading to energy losses causing decreased energy recovery. However, The MFC's ability to treat a diverse range of waste streams means that this technology may be applied to almost any waste stream (domestic, industrial, or residential) for effective contaminants removal and low carbon footprint.

Over the past decade, a significant amount of research has been conducted on optimization of MFC performance to bring the technology out of the laboratory (milliliter and liter scale) and into the field for pilot studies. A few pilot studies have been attempted. Researchers from the Advanced Water Management Centre at the University of Queensland constructed a 1000 L (12 tubular MFC modules) MFC pilot reactor installed at the Foster's brewery in Yatala (Queensland, Australia) with no results published. A 1000 L continuous flow MEC was built to treat winery wastewater, generate electricity, and produce hydrogen gas. The study reported low recovery of hydrogen (86.6% converted to methane gas) and 62% SCOD removal providing important considerations for the scale up of bioelectrochemical systems (Cusick et al., 2011). These pilot studies indicate some hindrances in terms of energy collection (based on a target current density of 1000 Am^{-3} recommended by Foley et al. (Foley et al., 2010)) for the full scale implementation. However, the MFC's primary function in wastewater treatment

may be considered to focus on a reduction in energy consumption and secondarily on energy production with the added benefit of less production of secondary sludge (He, 2013). Only with continued research in optimization of performance and materials while reducing costs will the MFC technology move closer to full scale treatment of wastewater.

1.4.2. Electricity Parameters

A critical understanding of the electrical parameters is needed to improve performance and minimize energy losses. MFCs generate an electrical current through microbial anodic oxidation and cathodic reduction. The MFC electrical performance must be expressed in established terminologies for the comparison of key performance parameters (Logan et al., 2006). Electricity is a broad term that in general refers to the electric current produced by exoelectrogenic bacteria in the anode chamber. Electricity in MFCs is quantified by the voltage (V), current (I), and power (P) produced by the cell.

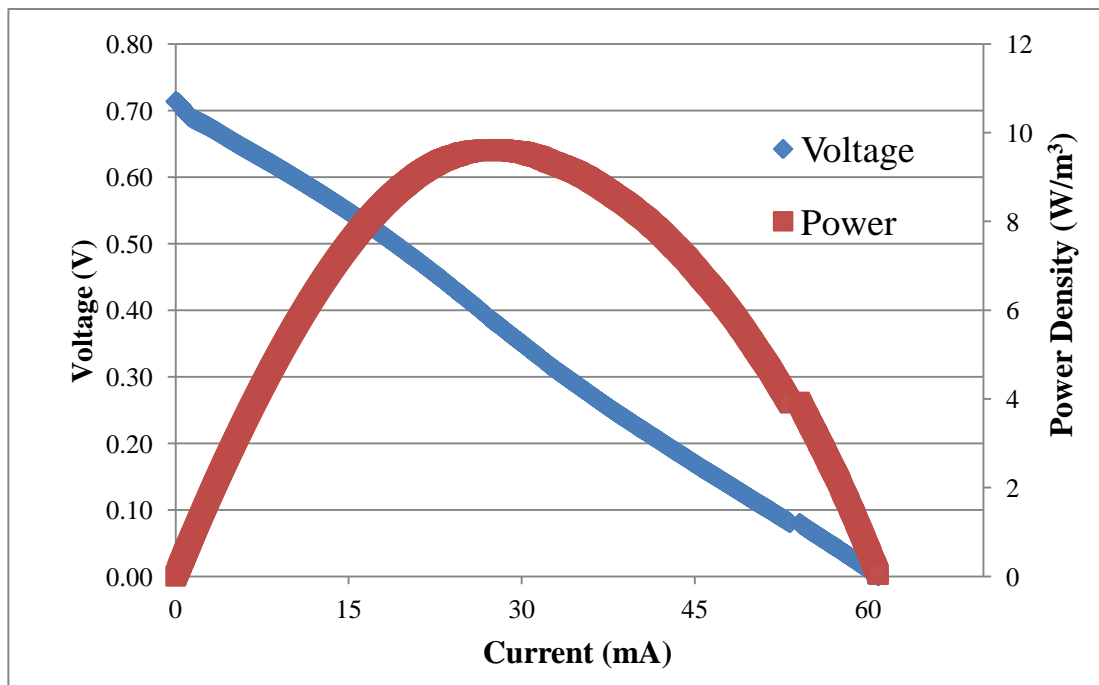


Figure 1-3. Typical polarization resistance curve

These parameters are commonly expressed in terms of current or power densities (such as A/m^3 or W/m^2) to normalize current or power to the volumetric size of reactor or the electrode surface area. To maximize power within the cell, a polarization resistance curve may be generated (see Figure 1-3) to determine the maximum power produce by the cell and the internal resistance (slope of voltage/current line) within the reactor. To maximize power the external resistance of the MFC is set to the internal resistance. For high current applications, such as desalination in MDCs, the external resistance may be set to a very small resistor to increase the flow of electrons.

To assess the efficiency of an MFC's ability to convert chemical energy into electrical current, the coulombic efficiency (CE) is applied as the ratio of the coulombs produced to the maximum coulombs stored as chemical energy in the following equation from (Logan et al., 2006):

$$\epsilon_{cb} = \frac{M \int_0^{t_b} I dt}{F b v_{An} \Delta COD}$$

where $M = 32$ (the molecular weight of oxygen), $F =$ Faraday's constant, $b = 4$ (the number of electrons exchanged per mole of oxygen), $v_{an} =$ anode liquid volume, $\Delta COD =$ change in COD concentration. CE is an indicator of "electron sinks" where electron acceptors other than the cathode are being utilized (i.e. oxygen diffusion or competition with other microorganisms).

1.4.3. Nutrient Removal/Recovery in Microbial Fuel Cells

Microbial Fuel Cells possess a capability of removing and recovering critical nutrients like nitrogen and phosphorus at a low energy footprint. As stated before, today's conventional nutrient removal technologies require high energy aeration for nitrification and EBPR. Microbial fuel cells and other bioelectrochemical (BES) variations (MEC or MDC) have been applied to remove and recover nitrogenous compounds in wastewater. Nitrogen control in MFCs has been achieved through incorporating biological nitrification-denitrification, simultaneous nitrification-denitrification and ammonia recovery. Phosphorus control has been implemented in BESs through phosphorus removal by algal biomass uptake and physiochemical recovery by struvite precipitation. A review of nutrient removal and recovery in BESs in the coming chapter will review pertinent BES technologies, discuss influence factors, and identify key challenges for further development of nutrient removal/recovery in BESs. MFCs and other BESs possess promising new technologies to meet the energy and contaminant removal demands of today's wastewater treatment.

Chapter 2 A Review of Nutrients Removal and Recovery in Bioelectrochemical Systems[†]

2.1. Introduction

In a bioelectrochemical system (BES), organic compounds are oxidized by microorganisms, and the electrons generated from this oxidizing process can be used to produce energy and other value-added compounds (Sleutels et al., 2012). Direct conversion of chemical energy into electric energy in a BES holds potential advantages over the existing technologies in terms of energy recovery from organic compounds, and the intensive studies of BES configuration/operation, microbiology, electrochemistry, and application have occurred in the past decade. The representative BES includes microbial fuel cells (MFCs), microbial electrolysis cells (MECs), and microbial desalination cells (MDCs). A BES can be potentially applied to treat wastewater, to power remote sensors, to act as a platform for studying fundamental microbial interaction with a solid electron acceptor/donor (e.g., in a micro-MFC), or to produce value-added compounds through electrochemical or electrosynthetic processes.

The use of the low-grade substrates such as wastewater as an electron source is attractive because of the increasing demand for sustainable water/wastewater treatment with a low carbon footprint (Rozendal et al., 2008). Various substrates including pure organics and domestic/industrial wastewaters have been examined in the BES for electricity generation (Pant et al., 2010), the BES size has been enlarged from milli-liter to liter-scale or even larger at a pilot scale, and its long-term performance outside the

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laboratory has been reported (Zhang et al., 2013a). However, at this stage the energy recovery in a BES is still too low to make it practically competitive, and a benchmark power density of 1000 W m^{-3} (Arends & Verstraete, 2012) was realized only in very small-scale reactors. The low energy recovery, as well as the low energy consumption (due the reduced use of aeration) in a BES, indicates that its primary function, if designed for energy recovery from wastewater treatment, may be contaminant removal, rather than energy recovery that would be a beneficial plus to offset energy use by the treatment process, thereby furthering energy benefits by using BES (He, 2013). In addition, because of a low conversion efficiency (from organic to electric energy), a BES will be more applicable to the low-strength wastewater, such as domestic wastewater.

The main goal of contaminant removal in a domestic wastewater treatment process is to reduce the concentrations of organic pollutants and nutrients (mainly nitrogen and phosphorus). BES can efficiently remove organic compounds within a reasonable time; however, the anaerobic condition in the anode of a BES does not effectively facilitate nutrient removal, which may require aerobic conditions (e.g., nitrification, and enhanced biological phosphorus removal). Therefore, nutrient removal has become a key challenge to develop BES for efficient wastewater treatment. Nitrogen and phosphorus are key elements for improving agricultural production; due to the depleting reserve, there is an increasing trend of research and development of wastewater treatment technologies to recover instead of remove nutrients from wastes (Rittmann et al., 2011). A BES capable of removing or recovering nutrients will certainly make it promising for future deployment. The objectives of this review paper are to examine the past research on nutrient removal/recovery in BES (with a focus on wastewater

treatment), introduce developed technologies, analyze removal efficiencies, and discuss the challenges for future development of BES for effective and efficient nutrient removal and/or recovery. The studies of nitrogen removal in biofilm-electrode reactors (BERs) are excluded because the denitrification in a BER relies on *in situ* produced hydrogen gas as an electron donor (Ghafari et al., 2008), which is different from a BES described here.

2.2. Nitrogen Removal and Recovery

2.2.1. Effect of Nitrogen on BES Performance

Nitrogen can affect the BES performance, especially electricity generation, through inhibiting effects on microbes, adjusting pH, and competition for electron donors/acceptors. It was reported that a concentration of total ammonia nitrogen (TAN) higher than 500 mg L⁻¹ could severely inhibit power production, and the maximum power density decreased from 4.2 to 1.7 W m⁻³ when the TAN concentration increased from 500 to 4000 mg L⁻¹ (Nam et al., 2010). It was concluded that a high concentration of free ammonia nitrogen had inhibited the activity of the anode-respiring bacteria. The researchers further demonstrated ammonia inhibition in a continuously-operated MFC, in which the maximum power density dropped from 6.1 to 1.4 W m⁻³ when the TAN concentration increased from 3500 to 10000 mg L⁻¹ (Kim et al., 2011a). By comparing with their previous study of the batch MFCs, the researchers found that the microorganisms in a continuously-operated MFC could adapt to a much higher TAN concentration. Ammonia inhibition is affected by the anolyte pH, and a low anolyte pH results in less free ammonia and thus little inhibitive effect; this was demonstrated in a

two-chamber MFC, in which increasing the concentration of ammonium nitrogen from 70 to 4000 mg L⁻¹ at a neutral analyte pH did not affect the MFC performance (Kuntke et al., 2011).

It is clear that the electrolyte pH in a BES is a key parameter, because of its effects on microbial metabolism and overpotential. Nitrogen compounds can influence the electrolyte pH through biological and chemical reactions. Biological nitrification releases protons that could buffer the high pH of a catholyte due to oxygen reduction, as demonstrated in an MFC with a buffer-free catholyte: adding the nitrifying bacteria and ammonium into the catholyte improved the voltage from 0.30 to 0.56 V and decreased the catholyte pH from 8.8 to 7.0 (You et al., 2009). Further studies by others confirmed that nitrification activity in the cathode could consume alkalinity and lower the pH (Virdis et al., 2010; Zhang & He, 2012b). The NH₄⁺/NH₃ couple was used to control the electrolyte pH: the ammonium ions were added into the anode compartment and then migrated into the cathode compartment across a cation exchange membrane to buffer the high pH; the volatilized NH₃ was returned to the anode compartment to maintain a reasonable analyte pH. In this way, the NH₄⁺/NH₃ couple acts as a proton shuttle between the anode and the cathode compartments (Cord-Ruwisch et al., 2011). This concept was further developed by employing an MEC and an additional gas exchange device to use hydrogen gas for driving the ammonia recycle (Cheng et al., 2013). Such a change promoted ammonia migration by current generation and developed a more efficient anodic biofilm.

Nitrogen compounds could also negatively affect the BES performance via competing for electron donors (e.g., organics) or acceptors (e.g., oxygen) with

microorganisms or electrodes. It was reported that in a single-chamber MFC, the presence of 4-8 mM nitrate decreased electricity generation, especially at lower external resistance where high current generation (and thus more electrons flowing) was expected (Sukkasem et al., 2008), likely due to the competition for electrons (in organic compounds) between the anode electrode (anode-respiring bacteria) and nitrate (denitrifying bacteria). Nitrification of ammonium in a cathode compartment may cause competition for oxygen between nitrifying bacteria and the cathode electrode, as shown in a two-chamber MFC, in which increasing ammonium concentration from 30 to 100 mg L⁻¹ (while maintaining a constant organic loading rate) decreased the cathode potential (Ryu et al., 2013).

Therefore, understanding of the nitrogen effects on BES performance is critical to maintain a healthy operation, and proper control of the nitrogen effects will be necessary under certain conditions. Development of effective nitrogen removal and recovery strategies will not only reduce the negative influence of nitrogen on BES performance, but also eliminate the contaminants and/or recover valuable nutrient resources.

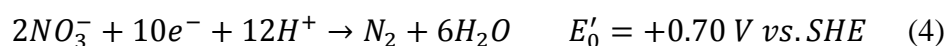
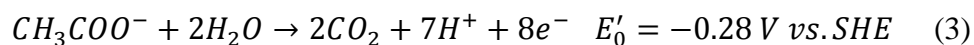
2.2.2. Nitrogen Removal

2.2.2.1. Background

Nitrogen is removed from wastewater usually by using biological processes such as nitrification (ammonia oxidized to nitrate) and denitrification (nitrated reduced to nitrogen gas) (Knowles, 1982). Ammonia can also be anaerobically oxidized, for instance using nitrite as an electron acceptor in an ANAMMOX process (Jetten et al., 2001), and this process can theoretically generate a positive electric potential under a standard condition; however, this thermodynamically favored process has a very slow kinetics to

be realized in a BES (He et al., 2009). Although a recent study reports an ANAMMOX-like process in an MEC (Zhan et al., 2012), further evidence will be required to prove the feasibility of anaerobic ammonia oxidation with an electrode as an electron acceptor in the presence of low dissolved oxygen. Therefore, ammonia removal in a BES is mainly through ammonia loss across a separator (Kim et al., 2008), or nitrification with supply of oxygen.

Nitrate can accept electrons from organic compounds to be reduced to nitrogen gas (e.g., in a conventional denitrification process (Knowles, 1982)). Such an electron-transferring process makes it possible to use nitrate as a terminal electron acceptor in a BES. The reduction of nitrate can generate a positive electric potential of 0.98 V when using organic compounds (e.g., acetate) as an electron source (Eq 3 and 4) (Madigan et al., 2010).



Unlike conventional denitrification that relies on heterotrophic denitrifying bacteria, bioelectrochemical denitrification is carried out by autotrophic denitrifying bacteria that are capable of accepting electrons from a solid electron donor (e.g, a cathode electrode). Such an anaerobic respiration process was demonstrated for the first time with *Geobacter* species: a pure culture of *Geobacter metallireducens* was found to be able to reduce nitrate to nitrite with an electrode as the only electron donor (Gregory et al., 2004). The similar phenomenon was also observed with the mixed culture under an applied electric current that reduced nitrate to nitrogen gas while accepting electrons from an

electrode (Park et al., 2004). Those findings encouraged the accomplishment of a denitrifying biocathode in an MFC, which demonstrated an effective nitrate reduction with simultaneous electricity generation (Clauwaert et al., 2007; Fang et al., 2011; Zhu et al., 2013).

2.2.2.2. Microbiology

The microbial community on a denitrifying biocathode is very complex, and consist of both functioning species involved in denitrification and other microbes appeared in the food web (e.g., those living on organic compounds synthesized during autotrophic denitrification). An analysis of a denitrifying biocathode in an MFC identified the enrichment of *Nitrosomonas* sp., which can oxidize ammonia to nitrite or reduce nitrite to nitric oxide (Chen et al., 2008). A long-term operated MFC with a denitrifying biocathode revealed the switch of the most abundant phylotype in the cathode community from *Betaproteobacteria* at the initial stage to *Gammaproteobacteria* at the final stage (Chen et al., 2010). A more thorough analysis of active bacterial community of the denitrifying biocathodes was conducted through comparing the communities between two enrichment approaches, an MFC with a loop connection (in which the anode effluent flowed into the cathode) and an MFC with separated anode and cathode streams (Wrighton et al., 2010). Their results showed that, the loop MFC had superior performance in both current generation and nitrogen removal rate, likely due to its greater bacterial richness and evenness, and it was identified that the members of the *Proteobacteria* and *Firmicutes* were dominant and active in the cathode denitrifying biofilm. Nitrate and nitrite can be used interchangeably as an electron acceptor in the cathode of an MFC, and *Oligotropha carboxidovorans* was found to be a dominant

species for autotrophic denitrification (Puig et al., 2011). The functional genes of the denitrification pathway were used to identify the key players in the bioelectrochemical denitrifying process of an MFC, and the results showed that the denitrifiers containing *nirS* gene (nitrite reductase) were dominant in the cathode biofilm and affected nitrous oxide reducer that was related to N₂O emission (Vilar-Sanz et al., 2013). Identification of relevant species during nitrogen removal and understanding of their functions/roles will be of great interest to future microbiological studies.

2.2.2.3 Reactor Process

Although nitrate can be bioelectrochemically reduced in an MFC, most wastewaters contain ammonia rather than nitrate. Ammonia can be “removed” from wastewater by moving it from the anolyte into the catholyte across cation exchange membrane driven by electricity generation; this process leads to the discovery of ammonia recovery in a BES, which will be addressed in the section 2.2.3. Here we mainly focus on the removal of total nitrogen, which requires the conversion of ammonia to nitrate that will facilitate the following bioelectrochemical denitrification. This is realized through incorporating an aerobic process (for nitrification) into an MFC system. The first demonstration of complete nitrogen removal in an MFC was with the aid of a separate biofilm-based aerobic reactor for nitrification (Virdis et al., 2008). In this system (Fig. 2-1A), the synthetic wastewater was first treated in the anode compartment of the MFC for organic removal, which also provided electrons to the cathode reduction reaction; the anode effluent then flowed into an aerobic bioreactor in which ammonia was biologically oxidized to nitrate; finally, nitrate was reduced to nitrogen gas in the cathode when the stream returned to the MFC (cathode). The system achieved a nitrogen removal

rate of $0.41 \text{ kg m}^{-3} \text{ d}^{-1}$ (net cathode volume) and a maximum power density of 34.6 W m^{-3} . It was found that the elevation of ammonium concentration in the cathode was due to ammonia diffusion through cation exchange membrane. Their subsequent design integrated the aerobic process into the cathode in which simultaneous nitrification and denitrification (SND) was accomplished (Fig. 2-1B) (Viridis et al., 2010). It was believed that, although oxygen was present in the cathode, denitrifiers might survive by taking advantage of biofilm and electrode structure that could create a micro-anoxic environment. Further analysis of the cathode biofilm stratification revealed that the nitrifying bacteria appeared in the outer layer of the biofilm and the putative denitrifying organisms occupied the inner layer, confirming the feasibility of SND in the cathode of an MFC (Viridis et al., 2011).

To simplify the reactor structure and reduce the cost associated with ion exchange membranes, SND was also investigated in several membrane-less MFCs. Those systems rely on an oxygen gradient to produce aerobic and anoxic zones within a bioreactor, through either active aeration or agitation of the electrolyte (e.g., by rotating a cathode electrode) (Sayess et al., 2013; Yu et al., 2011). Although nitrogen can be removed in those systems, the presence of a large amount of oxygen around the cathode would inhibit bioelectrochemical denitrification, and omitting membranes could encourage the contact between organic compounds and nitrate, thereby resulting in significant heterotrophic denitrification. Consequently, the benefit of using MFCs' electricity-generating feature for nitrogen removal would become weaker.

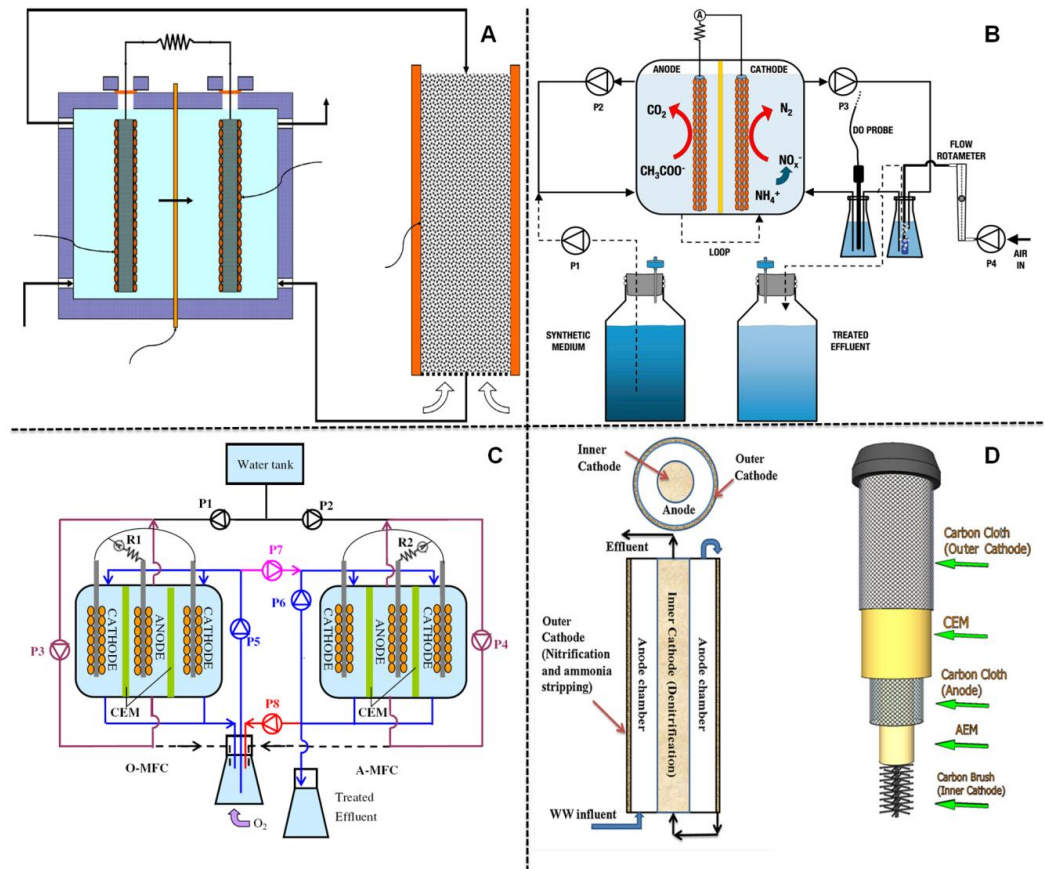


Figure 2-1. The MFC systems designed for complete nitrogen removal involving nitrification and bioelectrochemical denitrification: A) an MFC plus an external nitrifying bioreactor; B) simultaneous nitrification and denitrification in the cathode of an MFC; C) two MFCs with aerobic and anaerobic cathodes, respectively; and D) a tubular MFC with dual cathodes. Reproduced with permission from references (Virdis et al., 2010; Virdis et al., 2008; Xie et al., 2011; Zhang & He, 2012a).

Because of the high requirement of DO control for SND, several MFCs systems were designed to have separate aerobic and anoxic cathodes for nitrification and denitrification, respectively; in this way, DO will have less influence on denitrification. For example, a coupled MFC system consisted of two MFCs, one with dual aerobic biocathodes and the other containing dual anoxic biocathodes (Fig. 2-1C): the synthetic wastewater was fed into the anodes of the two MFCs individually, and the effluents were collectively sent to the aerobic biocathodes, whose effluents were then transferred into the anoxic biocathodes (Xie et al., 2011). Recently they scaled up the MFC system to a

scale of 50 L with comparable (or better) performance to the small-scale systems, strong encouragement for further development of the MFC system for nitrogen removal (Liang et al., 2013). This system was simplified to a dual-cathode MFC, which contains an aerobic cathode and an anoxic cathode on each side of the anode (Zhang & He, 2012b). Similarly to the prior system, in the dual-cathode MFC the synthetic wastewater flowed according to the orders of “anode-aerobic cathode-anoxic cathode”. However, the dual-cathode MFC adopted different ion exchange membrane installation: cation exchange membrane between the anode and the aerobic cathode, and anion exchange membrane between the anode and the anoxic cathode; such an arrangement may prevent ammonia loss to the final effluent (from the anode to the anoxic cathode). The batch-operated dual-cathode MFC was further developed to a continuously-operated system in tubular configuration (Fig. 2-1D), and it was found that nitrate removal involved both bioelectrochemical denitrification in the anoxic cathode and heterotrophic denitrification in the anode (Zhang & He, 2012a). When a conventional MFC was linked to the dual-cathode MFC for treating actual wastes, the cooperative system removed more than 80% of total COD and 50-70 % of total nitrogen from the digested sludge or landfill leachate with low energy consumption ($<0.06 \text{ kWh m}^{-3}$ or $0.1 \text{ kWh kg COD}^{-1}$) (Zhang & He, 2013). To reduce energy consumption by aeration, the active oxygen supply to the aerobic cathode was replaced by the passive oxygen supply in an MFC with its cathode exposed to the air for nitrification; in connection to another MFC containing an anoxic denitrifying cathode, this MFC system reduced the total nitrogen in a domestic wastewater by 76% (Zhang et al., 2013a).

Some MFC systems accomplished nitrogen removal but the removal process was not necessarily related to electricity generation (or as a part of electron-transfer process). For example, in a single chamber MFC, the nitrifying biofilm enriched on the air cathode oxidized ammonia to nitrate, which was reduced by heterotrophic denitrifiers with organic compounds (Yan et al., 2012). Nitrogen removal was further improved by increasing the gas-diffusion area of a single chamber MFC by adding more air cathodes or diffusion cloth (Yan & Regan, 2013). Another example is the bioelectrochemical systems containing algae. Algae are known to be capable of assimilating nutrients during their growth via photosynthetic activities (Leite et al., 2013). When algal growth was incorporated into a sediment MFC, more than 87% of nitrogen was removed, of which algal biomass contributed to 75% with the remaining removal by nitrification and denitrification (Zhang et al., 2011b). In an integrated photo-bioelectrochemical (IPB) system, algal bioreactor was used as the cathode compartment for providing dissolved oxygen and stripping off nutrients (Xiao et al., 2012). The IPB system achieved more than 98% of ammonia removal and 63% of total nitrogen removal; the inefficient uptake of nitrate by algae could be a major factor affecting the removal of total nitrogen.

In addition to wastewater, groundwater is also studied for nitrogen removal by using BES. Nitrate is one of contaminants appearing in groundwater with serious threats to human health (Manassaram et al., 2006), and can be removed via bioelectrochemical denitrification in an MFC (Puig et al., 2012). In a bench-scale two-chamber MFC, the concentration of nitrate in the groundwater sample was reduced from 28.32 ± 6.15 to 12.14 ± 3.59 mg L⁻¹, which was close to the regulated limit of 11.29 mg L⁻¹ (Pous et al., 2013). The use of MFCs for nitrate removal from groundwater would require a pump-

and-treat approach, which will be energy intensive, and thus development of *in situ* remediation technologies for nitrate removal is of strong interest because of potentially low cost. The researchers have applied the principle of microbial desalination cells (Cao et al., 2009a) to move nitrate from groundwater into the anode compartment of a BES; this transportation of nitrate ions is to balance the charge of the anolyte and driven by electricity generation (Fig. 2-2A). Nitrate can either act as a terminal electron acceptor for bioelectrochemical denitrification in the cathode (Zhang & Angelidaki, 2013), or be reduced through heterotrophic denitrification in the anode (Fig. 2-2B) (Tong & He, 2013). Applying an external voltage improved electric current generation, achieved nitrate decrease from 23.3 to 5.3 mg L⁻¹ within 24 hours, and prevented the undesired ions entering groundwater (Tong & He, 2013).

2.2.2.4 Influence Factors

Nitrogen removal in a BES is affected by multiple factors such as oxygen, electrolyte pH, carbon/nitrogen (C/N) ratio, electricity generation, and other operating parameters that are critical to BES performance. Understanding of those influence factors is critical to improving system performance and to stabilizing the operation of an effective process for nitrogen removal.

A key factor for successful nitrogen removal from wastewater in the MFC cathode is the concentration of dissolved oxygen (DO), especially in an MFC with an SND process. The researchers found that the optimal DO in the cathode was 4.35 mg L⁻¹, at which the MFC system obtained 94% removal of total nitrogen (Viridis et al., 2010). Another study reported that SND did not occur at the high DO in a membrane-less MFC, but their optimal DO was much lower at 0.5 mg L⁻¹ (Yu et al., 2011). Determining an

optimal DO becomes important, because a low DO would cause ammonia accumulation in the final effluent (incomplete nitrification), while a high DO would inhibit denitrification, resulting in nitrate accumulation.

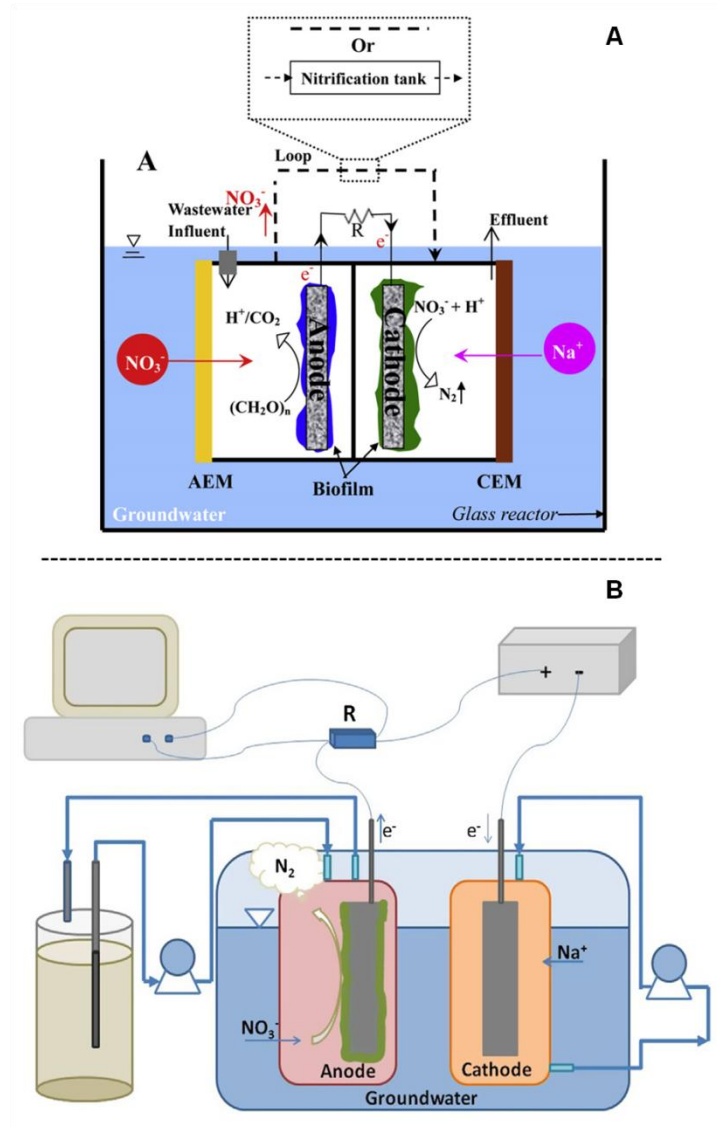


Figure 2-2. Nitrate removal from groundwater by using a BES: A) a BES having nitrate as a terminal electron acceptor in its cathode; and B) a BES removing nitrate via heterotrophic denitrification in its anode. Reproduced with permission from references (Tong & He, 2013; Zhang & Angelidaki, 2013).

The catholyte pH is another key factor affecting nitrogen removal. It was found that nitrate removal rate was doubled when the pH of the catholyte was maintained

around 7.2, indicating that proton supply limited the nitrate reduction in the cathode (Clauwaert et al., 2009). With nitrification concurrently or followed by denitrification, the catholyte pH may be better buffered because of proton production from ammonia oxidation (Zhang & He, 2012b). An interesting approach was developed to have the same electrochemically-active biofilm catalyzing organic oxidation and nitrate reduction in turn, in which alkalinity produced during the cathode reaction (nitrate reduction) could be used by the anode reaction (organic oxidation), thereby eliminating the need of external pH buffer (Cheng et al., 2012).

Although bioelectrochemical denitrification accepts electrons from a cathode electrode, those electrons originally come from organic compounds in the anode; thus, C/N ratio is expected to affect nitrogen removal through electron supply. In general, bioelectrochemical denitrification can be accomplished at a low C/N ratio (Virdis et al., 2008; Zhang & He, 2012a), although a high C/N ratio is also applicable (Xie et al., 2011); oversupply of organic compounds (beyond the anode capacity) may stimulate heterotrophic denitrification and thus inhibit bioelectrochemical denitrification (Zhang & He, 2013). Electron supply is affected by current generation, and a higher electric current or the flow of more electrons will benefit bioelectrochemical denitrification, which was demonstrated in a study that by reducing the external resistance from 712 to 10 Ω (to increase current generation), nitrate removal was improved from 52.1 to 66.4%, resulting in an improved removal of total nitrogen from 51.9 to 68.0% in a dual-cathode MFC (Zhang & He, 2012b). Inorganic carbon sources have a stronger influence on current generation than organic carbon, and a higher current will be more favorable to autotrophic denitrification than heterotrophic denitrification (Huang et al., 2013).

2.2.3. Nitrogen Recovery

Recovering nitrogen from wastes is considered as a more sustainable approach than removing it, due to the depleting natural resources and the significant cost of nitrogen fixation. The recovered nitrogen may be applied as a fertilizer to agricultural production. Nitrogen recovery in a BES is mainly through ammonia recovery. Although photobioreactors (containing algae) can also “recover” nitrogen via concentrating it in algal cells, further utilization of nitrogen in algae as a fertilizer would face great challenges. Ammonia recovery with phosphorus in struvite will be discussed in the section 3. Therefore, this section focuses on ammonia recovery via ammonium migration driven by electricity generation.

2.2.3.1 Ammonia Migration

The foundation for realizing ammonia recovery in a BES is the fact that ammonium ions can move across ion exchange membranes via either current-driven migration or diffusion. Early studies believed that MFCs followed the principle of hydrogen fuel cells in which to generate electricity, hydrogen ions move from the anode into the cathode via a cation (proton) exchange membrane to balance the charge. Later investigation found that in a wastewater anolyte, the concentration of protons was much lower than other cations such as sodium ions, and thus it was more likely that other cations instead of protons moved across the ion exchange membrane. Ammonium ions are usually present in domestic wastewater with a much higher concentration than protons (assuming wastewater has a neutral pH); therefore, ammonium ions can be one of the cations migrating through a cation exchange membrane. This was demonstrated in an MFC that used ammonium migration as a proton shuttle, and the researchers found that

ammonia/ammonium accounted for about 90% of ionic flux in their system (Cord-Ruwisch et al., 2011). Further development of this system added a gas-exchange device to recycle ammonia gas back to the anode for pH control; the success of recycling ammonia relied on the microbial-generated electric current that drove ammonium migration from the anode into the cathode against a strong concentration gradient (Cheng et al., 2013).

Ammonia migration driven by electricity generation was also demonstrated in other BES like MECs and MDCs. In an MEC, ammonia moving resulted in ammonium accumulation in the cathode to 318 mg L^{-1} , almost ten times the ammonium concentration in the anode (Villano et al., 2013). However, it was found that ammonium migration contributed only 2.5% of the overall charge transport in this MEC, much lower than the previous MFC studies, likely affected by ammonium concentration in the anode feeding solution. In an MDC-type reactor that was used to treat synthetic wastewater containing ammonium chloride, ammonium ions were transported from the middle chamber to an aerobic cathode for nitrification (Zhang et al., 2013b); however, there is a lack of rationale for using such an approach rather than an MFC that could achieve the similar results with a much simpler reactor structure/operation.

2.2.3.2 Ammonia Recovery

The feasibility of ammonia recovery in a BES was investigated through further understanding of ammonia moving mechanism, which revealed that ammonium was transported via both migration and diffusion, and the cathode could accumulate several grams of ammonium nitrogen per liter (Kuntke et al., 2011). The following study successfully recovered ammonia from urine via volatilization due to the high pH of the

catholyte and aeration, and subsequent adsorption by an acid solution in an MFC (Kuntke et al., 2012). The theoretical analysis of energy consumption and production suggested that ammonia recovery in an MFC had significant energy advantage (with a positive energy balance) over conventional ammonia stripping. A higher current density could greatly improve ammonia recovery in an MFC with 61% of ammonium transportation by electricity-driven migration (Haddadi et al., 2013).

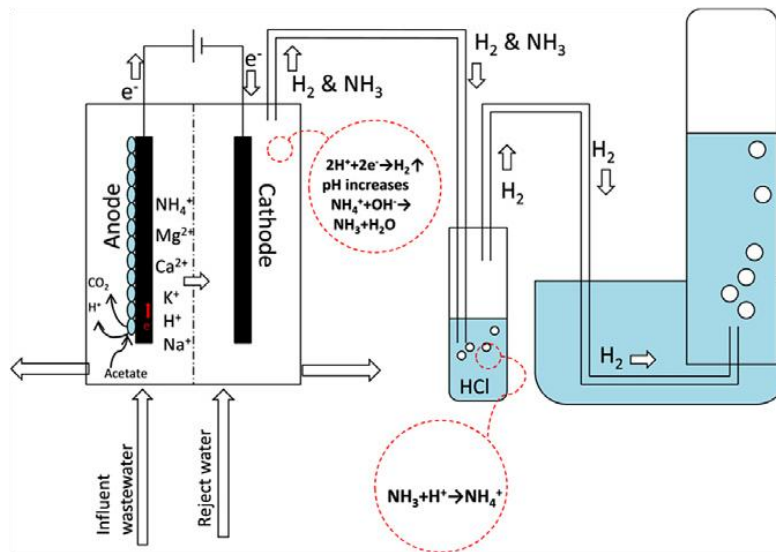


Figure 2-3. Ammonia recovery with hydrogen production by using a BES. Reproduced with permission from reference (Wu & Modin, 2013).

One of the key factors in ammonia recovery is the high pH of catholyte, which can drive ammonium to ammonia gas. This feature alone has also been used to recover ammonia from some special wastewaters such as reject water, which contains a high concentration of ammonium (~ 1000 mg/L) but a low amount of organic compounds (thus not suitable as an anode feeding solution). The concept was examined in an MEC with simultaneous hydrogen production and ammonia recovery: the catholyte pH increased to above 12 due to current generation, and the MEC recovered 96% of

ammonia in a synthetic reject water and 79% from a real reject water (Fig. 2-3) (Wu & Modin, 2013).

2.2.4 Nitrogen Removal/Recovery Rate

Nitrogen removal rates in BES are usually expressed based on the liquid volume of the anode, the cathode, or the total. To better facilitate a cross-wise comparison, we calculated the nitrogen removal rate based on the total liquid volume of the BES, and the results are summarized in Table 2-1, which includes the nitrogen removal rates in conventional nitrification/denitrification processes and ANAMMOX processes for comparison. The table also includes some results from ammonia recovery studies, since “recovery” also “removes” nitrogen from wastewater. Due to the significant difference in reactor structure and operation, microorganisms, and substrates, it is not very appropriate to draw any firm conclusions from this Table; however, we can see that in general nitrogen removal rates in BES are within the range of that in the conventional nitrification/denitrification processes, likely because of the similar microbial redox processes between the two. It was believed that bioelectrochemical denitrification was slower than heterotrophic denitrification (Clauwaert et al., 2007); thus, we may not expect higher removal rates in BES compared with conventional processes. Ammonia recovering processes seem to exhibit a higher removal rate than bioelectrochemical denitrification, suggesting a faster rate with physical/chemical treatment than biological treatment. The main advantages of nitrogen removal in a BES lie in lower requirement of organic compounds, possible energy recovery, and possible ammonia recovery, which may compensate for its removal rates.

Removal Mechanism	Removal rate (kg m⁻³ d⁻¹)	Reference
N-BD	0.051	(Viridis et al., 2008)
N-BD	0.013	(Xie et al., 2011)
N-BD	0.008	(Cha et al., 2009)
N-BD	0.003	(Zhang & He, 2012b)
N-BD	0.013	(Zhang & He, 2012a)
N-BD	0.037-0.199	(Zhang & He, 2013)
N-BD	0.042	(Ryu et al., 2013)
AR	0.132	(Kuntke et al., 2012)
AR	0.52	(Wu & Modin, 2013)
AR	0.061	(Haddadi et al., 2013)
SND (cathode)	0.0043	(Yu et al., 2011)
SND (air cathode)	0.049	(Yan et al., 2012)
SND (cathode)	0.1	(Viridis et al., 2010)
SND (cathode)	0.024	(Viridis et al., 2011)
Conventional ND	0.05-4	(Wang et al., 2009a)
ANNAMOX	6-12	(Wang et al., 2009a)

Table 2-1. The nitrogen removal rates in the BES and conventional nitrogen removing processes. N-BD: nitrification and Bioelectrochemical denitrification; AR: ammonia recovery; SN-BD: simultaneous nitrification and bioelectrochemical denitrification; and ND: nitrification and denitrification.

2.2.5 Challenges for Nitrogen Removal and Recovery

Having effective and efficient nitrogen removal and/or recovery in a BES will clearly be an additional benefit and make BES more advantageous over some existing technologies in meeting the stringent regulations of waste treatment. Further development of BES will need to address several key challenges.

- We need to choose between “removal” and “recovery”. The majority of the current treatment processes focus on “removal”, while “recovery” will benefit a sustainable treatment theme. We believe that BES application will be niche-based, and the choice between removal and recovery could be influenced by ammonia concentration in wastes: “removal” may be better applicable to low-strength ammonia streams such as domestic wastewater (primary effluent), and “recovery” can be used for concentrated wastes including sludge, landfill leachate, animal wastes, and others containing a large amount of ammonia.
- Because electric current can significantly affect both nitrogen removal and energy production in an MFC system, it is necessary to determine whether the major goal of such a system is nitrogen removal or energy recovery. With the maximum energy recovery, an MFC will generate a moderate electric current; while the maximum current generation will benefit ammonia migration and pH elevation, but result in little energy recovery. We think that at the current stage, nitrogen removal may be more valuable than energy recovery. An MFC system can be designed to consist of multiple MFC modules with different functions including nitrogen removal and energy recovery in separate MFCs (Zhang et al., 2013a).
- Incomplete denitrification can produce nitrous oxide, a very potent greenhouse gas that has 298 times the global warming potential as carbon dioxide. It is of particular concern to reduce the emission of this gas in wastewater treatment to reduce the effect on global warming as well as increase denitrification efficiencies. It was found that nitrous oxide (N_2O) accumulation accounted for a significant portion of the electron loss (~ 10%) during nitrate removal (Viridis et al., 2009),

and 30-40% of influent nitrogen was released as nitrous oxide in the MFCs (Virdis et al., 2010; Virdis et al., 2008). It is possible to adjust operating conditions to optimize bioelectrochemical denitrification and thus reduce the emission of nitrous oxide, but more detailed strategies warrant further investigation.

- Like other BES, the systems designed for nitrogen removal and/or recovery also face the challenges such as system scaling up, understanding of microbiological processes, demonstration of long-term operation and stability, capital investment and operational cost, and better assessment of economic and environmental benefits of using those systems (e.g., life cycle analysis).
- Last, we need to understand that in some conditions, BES will not be applicable. For example, when both electron donors and acceptors (nitrate) are present in the same stream, the use of BES for nitrogen removal may not be necessary (Cai et al., 2012), because conventional denitrification can well carry out nitrate reduction without an electrode (which is competing for electrons with nitrate). Another example is to use nitrite as an anode substrate in an MFC, which does not remove nitrogen compound and is not beneficial to electricity generation (Faraghi & Ebrahimi, 2012).

2.3. Phosphorus Removal and Recovery

2.3.1 Background

Phosphorus is another important inorganic nutrient and pollutant, and is usually removed via chemical precipitation or biological processes. Biological phosphorus

removal is more attractive because of its cost effectiveness. In the enhanced biological phosphorus removal (EBPR), phosphate accumulating organisms (PAO) are enriched through aerobic and anaerobic processes and store excess amounts phosphate within their cells in the form of intracellular polyphosphate at levels higher than normal to satisfy their metabolic growth requirements, and the accumulated polyphosphate can be removed with the waste sludge. Phosphorus has not been studied as much as nitrogen in a BES, but there is certainly a strong interest to investigate phosphorus removal/recovery because of its importance as both a contaminant and a valuable resource.

2.3.2 Phosphorus Removal in Photosynthetic Systems

As introduced earlier, photosynthetic processes have been studied for removing nitrogen from wastewater; phosphorus can also be removed in the same process with algal growth. In a photomicrobial fuel cell that combined the growth of microalgae, *Chlorella vulgaris*, in a sediment MFC, about 70% of phosphorus was removed with simultaneous organic (99.6%) and nitrogen (87.6%) removal (Zhang et al., 2011b). In a membrane-based IPB system, 82% of phosphate was removed in the cathode compartment where algal growth occurred (Xiao et al., 2012). In addition to algal growth within an MFC, an algal bioreactor can also be linked externally to an MFC, and this combination improved the removal of total phosphorus from 58% to 92% (Jiang et al., 2012). Further treatment of algal biomass to dispose or recover phosphorus will need more detailed investigation.

2.3.3 Phosphorus Recovery in Struvite

In light of the global phosphorus problems, recovering phosphorus from wastes has become an emerging subject (Rittmann et al., 2011). Phosphorus concentrations can

be high in industrial and domestic wastewaters bringing the potential to recover it as struvite mineral ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$). Early on, struvite precipitation in wastewater treatment plants posed as a nuisance scaling problem. Nowadays, it has gained much interest and research in terms of phosphorus recovery but is subject to economical problems and technical difficulties to move towards full scale implementation. There have been a few full scale trial tests as well as a significant amount of laboratory tests conducted most often using the fluidized bed reactor. The purity of the struvite mineral is vital to the reuse of the product which is dependent on the characteristics of the influent such as elemental concentrations to reach the minimum struvite ratio (Mg:N:P 1:1:1) as well as competition with other compounds (Corre et al., 2009).

Phosphorus recovery in struvite was first investigated in a two-chamber MFC, which used microbiologically-produced electricity to reduce FePO_3 in digested sludge for converting insoluble phosphate to soluble form, and then the mobilized phosphate was precipitated in struvite by adding magnesium and ammonia (Fig. 2-4A) (Fischer et al., 2011). Orthophosphate was recovered in yields of 48% and 82% from pure ferric phosphate hydrate and digester sludge, respectively. Struvite formation was accomplished within a BES by using a single-chamber MEC, in which up to 40% of soluble phosphate was removed with struvite precipitation at $0.3\text{-}0.9 \text{ g m}^{-2} \text{ h}^{-1}$ (Fig. 2-4B) (Cusick & Logan, 2012). The hydrogen-producing process in the MEC increased the localized pH adjacent the cathode electrode, which was important to struvite formation. A similar process was demonstrated in a single-chamber MFC that recovered both nitrogen and phosphorus in struvite from urine (Zang et al., 2012). The MFC system recovered 94.6% of phosphate, which was a limiting factor for struvite precipitation due to a much

lower concentration than nitrogen in urine. Another waste containing a large amount of phosphorus is animal wastewater such as swine wastewater that has also been studied in a single-chamber MFC for struvite precipitation (Ichihashi & Hirooka, 2012). It was found that 70-82% of phosphorus was removed and struvite precipitation only occurred on the cathode surface. Although the electrolyte pH was not very high (~ 8), it was believed that oxygen

reduction on the cathode increased the localized pH, which facilitated struvite formation.

The role of an MFC in struvite precipitation was investigated through having ammonia, phosphorus and magnesium added into a buffer solution, and then a piece of electrode was added into this solution, none of which showed struvite precipitation; when sodium hydroxide was added to elevate the pH to 8.62, precipitation appeared. Thus, MFC operation is necessary to create a high-pH zone around the cathode electrode to form struvite precipitation (Hirooka & Ichihashi, 2013). On the other hand, struvite

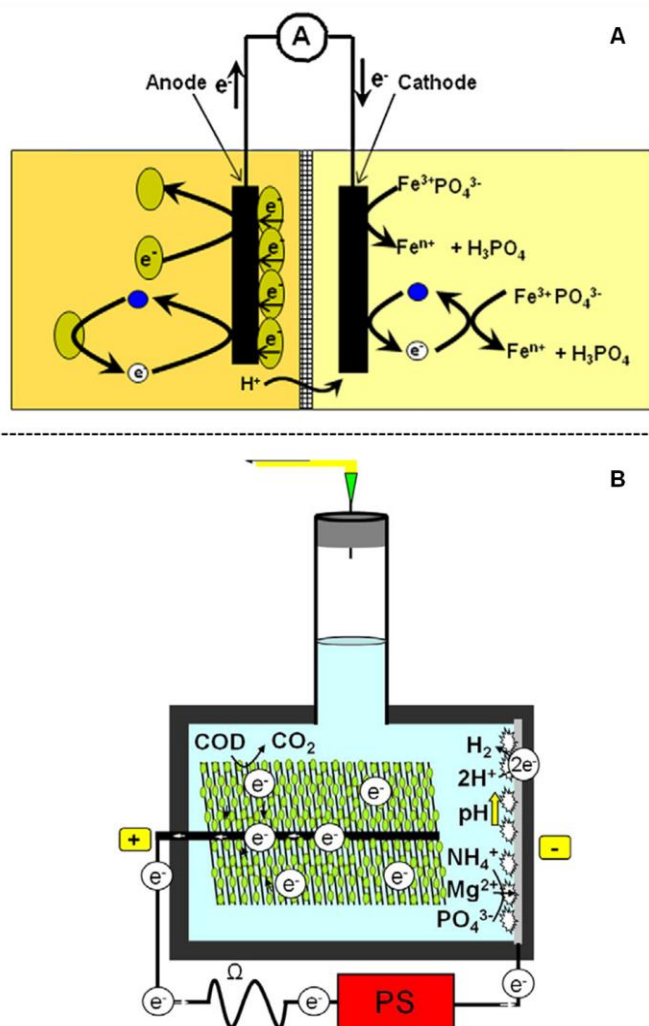


Figure 2-4. Phosphorus recovery as precipitates by using a BES: A) a two-chamber system; and B) a single-chamber system. Reproduced with permission from references (Cusick & Logan, 2012; Fischer et al., 2011).

precipitation decreased electricity generation in the MFC, because of the coverage of the cathode electrode by the precipitates that impeded the mass transfer of ions and oxygen. After removing the precipitates, the cathode electrode restored its performance almost to the initial level (Hirooka & Ichihashi, 2013).

2.3.2 Challenges for Phosphorus Removal and Recovery

Clearly there were much fewer studies on phosphorus than nitrogen in BES, possibly because phosphorus removal is exclusively through precipitation and phosphorus compounds are not involved in electron transfer processes via redox reactions like nitrogen. However, due to the depleting mining resource and stricter discharge regulation, phosphorus removal and recovery is not less important than nitrogen. Likewise, future investigation and development of BES for phosphorus removal and recovery will need to address some challenges.

- It will be of great interest to investigate how the electricity-generating process in a BES can affect phosphorus removal and recovery, in addition to the pH effect as a result of electrochemical reactions. It was reported that a low current could improve biological phosphorus release and uptake (Zhang et al., 2012), but the exact reasons were not clear. The current in those cases was at a level of a few milliamps, which is achievable in a BES. Exploring such a process may implement BES inside biological phosphorus removal reactors, thereby avoiding the difficulty of developing standalone BES and accelerating the BES development and application.
- The electrolyte pH in a BES is critical to forming precipitation. Most studies discussed in this section adopted single chamber configuration, which has one

electrolyte shared by the anode and the cathode. Such a configuration could buffer the pH via both the anode reaction (accumulating protons) and the cathode reaction (generating hydroxide ions), and thus impede the pH increase in the cathode. Future design of BES may consider two-chamber configuration, which have better separation between the anolyte and the catholyte; the supply of phosphorus (and other ions such as ammonium and magnesium) can be conducted through recirculating the anode effluent into the cathode, and/or ion flux across ion exchange membranes.

- Although most studies claim struvite precipitation in the BES, recent opinions pointed that the optimal pH for struvite formation is close to neutral, rather than alkaline (Hao et al., 2013). The “struvite” reported could be phosphate-based compounds containing little struvite, but that does not mean those precipitates cannot function as fertilizers. Those findings indicate that it may not be necessary to “chase” struvite during phosphorus recovery in a BES, especially in a situation that one or more key elements of struvite (e.g., magnesium or ammonia) are not well supplied. Other precipitates such as calcium phosphate have similar fertilization efficiency as struvite.
- Because precipitates are normally formed on the cathode electrode, collection of those precipitates and replacement/regeneration of the cathode electrode will be a great challenge in future BES application. Designing removable cathode electrodes may be a possible solution, in which the electrodes covered by the precipitates can be moved out of the BES for regeneration while new electrodes

can be inserted. Alternatively, multiple BES may be operated in turn, some under operation while others on idle (for regenerating electrodes).

- There is a lack of information on a systematic level of BES designed for phosphorus removal and recovery. For example, it is not clear how the BES will perform in a long-term operation and how seriously the precipitates will affect current generation (the decreased current could negatively affect further precipitation). Like other BES, system scaling up and economical analysis of using BES for phosphorus removal and recovery needs further studies.

2.4. Conclusions

Incorporating nutrients removal/recovery into a BES will make it more advantageous over the current technologies, and the available literature has demonstrated the feasibility of nutrient removal/recovery at a bench scale. This is an interesting and also important subject in BES development, and more investigation should be conducted to address some key challenges, especially at the level of systematic development and demonstration. Nutrient removal/recovery should be niche-based application (depending on the specific situations such as wastewater characteristics and the main function of BES), and future studies should take appropriate application niche into their consideration of BES development and investigation.

2.5. Acknowledgements

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Chapter 3 Understanding the Application Niche of Microbial Fuel Cells in a Cheese Wastewater Treatment Process[‡]

3.1. Introduction

The dairy industry is one of the most polluting industries in terms of the volume of water used for production and disposal (Vourch et al., 2008). The increasing demand for cheese and other dairy products results in increased volumes of wastewater that needs to be efficiently treated to meet stringent regulatory standards before being discharged. Dairy wastewaters are typically treated by means of aerobic and anaerobic biological treatment (Arvanitoyannis & Giakoundis, 2006; Malaspina et al., 1995), including activated sludge, trickling filters, aerobic lagoons, anaerobic lagoons, sequencing batch reactors (SBR), anaerobic sludge blankets (UASB), anaerobic filters, constructed wetlands, or a combination of these. Physical/chemical treatment is also applied with membrane technology or coagulation/flocculation (Arvanitoyannis & Giakoundis, 2006; Vourch et al., 2008). While aerobic treatment can provide a good effluent quality, such methods consume a great deal of energy. On the contrary, anaerobic treatment produces energy through biogas production but is susceptible to further treatment of effluent due to inadequate organic oxidation, incomplete nutrient removal, and vulnerability to shock loading, oils, greases, and temperature (Kushwaha et al., 2011). Therefore, it is of strong interest to develop energy-efficient treatment methods for dairy wastewater.

As an emerging concept, microbial fuel cells (MFCs) perform microbial oxidation of a wide range of substrates while simultaneously producing bioelectricity (Logan et al.,

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2006; Rabaey & Verstraete, 2005). The direct electricity generation in MFCs is a potential advantage over anaerobic digestion (Pham et al., 2006). Where aerobic treatment such as an activated sludge process has been assessed to consume 0.3 kWh/m³ or 0.6 kWh/kg COD (McCarty et al., 2011), MFCs can greatly reduce energy consumption (<0.1 kWh/m³) (He, 2013) and produce much less secondary sludge (Freguia et al., 2007). In a recent study, we found that MFCs could theoretically achieve a positive energy balance proving MFCs to produce more energy than they consume while treating actual municipal wastewater (Zhang et al., 2013a). Furthermore, MFCs may contribute to the prevention of eutrophication of receiving waters by removing nitrogen through bioelectrochemical reactions (Clauwaert et al., 2007; Yan et al., 2012).

A considerable amount of interest has recently transpired from researchers using MFC technology to treat dairy wastes (Kassongo & Togo, 2011; Mathuriya & Sharma, 2009; Nasirahmadi & Safekordi, 2012; Tremouli et al., 2013; Velasquez-Orta et al., 2011). For example, a single chamber, open-air cathode MFC achieved substantial dairy wastewater degradation of COD (95.5%), proteins (78.1%), carbohydrates (92.0%), and turbidity (99.0%) with the production of a maximum power density of 1.1 W/m³ (Mohan et al., 2010). Another study found that the dual-chamber MFCs treating dairy wastewater produced a higher power density (3.2 W/m³) and a 3.7 fold increase in Coulombic efficiency under an anaerobic anodic metabolism rather than an aerobic metabolism (E. Elakkiya & Matheswaran, 2013). The use of a spiral anode in an annular single-chamber MFC resulted in a Coulombic efficiency of 26.9 % and a maximum power density of 20.2 W/m³ from dairy wastewater (Mardanpour et al., 2012). There has also been much interest in researching the use of cheese whey (a high strength cheese processing

byproduct) as substrates in MFCs. It was concluded in a study of MFCs treating diluted cheese whey that a pretreatment step was required for the cheese whey to increase both Coulombic efficiencies and power densities (Antonopoulou et al., 2010). A further study implemented a filter sterilized pretreatment step that achieved almost a two-fold increase in power density and determined that the HRT increases linearly with the strength of the substrate (Stamatelatou et al., 2011).

Those prior studies usually focus on a single type of substrate. Because of the complex composition of dairy wastewater and the promising application of MFC technology as a key component of a treatment process, it will be interesting to examine how MFCs can be integrated into a process of treating dairy wastewater. The objective of this research is to find the optimal point where MFCs can be applied within a cheese plant wastewater treatment process to meet effluent quality standards and reduce energy consumption. This work reports the results of a case study analyzing the performance of multiple lab-scale MFC reactors treating two wastewaters (DAF influent and DAF effluent; DAF: dissolved air flotation) and two wastes (sludge and cheese whey) from a cheese processing wastewater treatment (Schreiber Foods, West Bend, WI). We analyzed energy production, energy consumption, organic reduction, nutrient removal (N and P), and Coulombic efficiency. To our knowledge, this is the first study that examines MFCs in parallel treating different wastes from an industrial wastewater treatment process.

3.2. Materials and Methods

3.2.1. MFC Setup

Four identical tubular MFCs (MFC-1, MFC-2, MFC-3, and MFC-4) with differences in anode substrates were constructed by using a cation exchange membrane (CEM, 17 x 25 cm, Ultrex CMI7000, Membranes International, Inc., Glen Rock, NJ) (Figure 3-1A and Figure 3-2), similarly to our prior work (Zhang et al., 2010). Each MFC

had a diameter of 5 cm and a length of 30 cm and contained a 20-cm carbon fiber brush (Gordon Brush Mfg. Co., Inc., Commerce, CA, USA) as the anode electrode, resulting in an anode liquid volume of about 500 mL. Prior to use, the carbon

brushes were pretreated by being immersed in

acetone for 24 hours and then heat treated at 450 °C for 30 minutes (Wang et al., 2009b).

The cathode electrode was carbon cloth (542 cm², PANEX®30-PW03, Zoltek, Corporation, St. Louis, MO, USA) that wrapped around the CEM tube. The cathode catalyst was activated carbon powder (9 mg AC/cm², Thermo Fisher Scientific, USA),

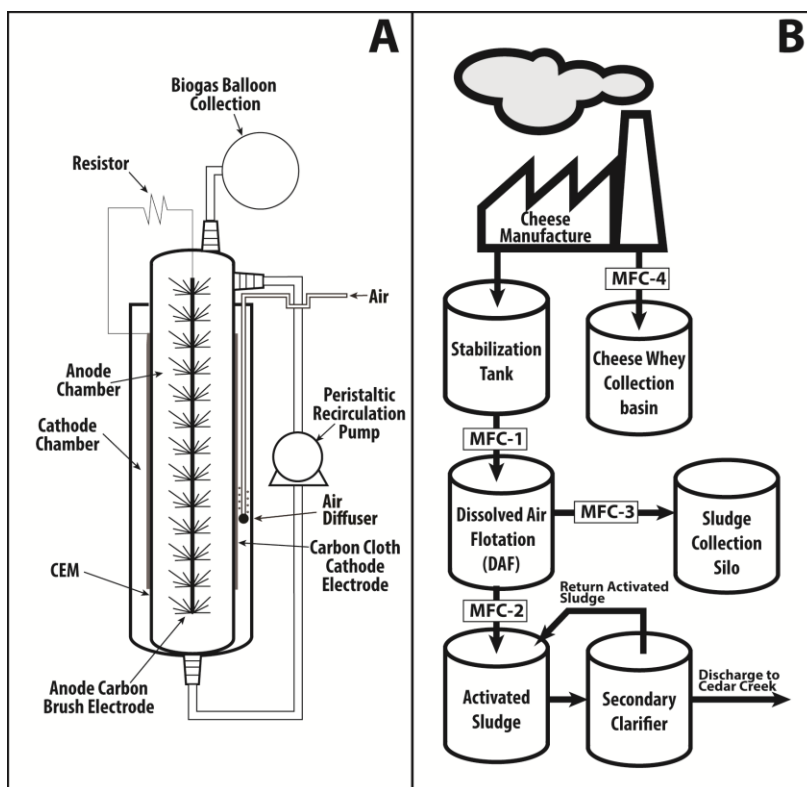


Figure 3-1. (A) Schematic of the tubular MFC design, (B) the flow diagram of the cheese wastewater treatment process with the sampling locations for MFC substrates.

which was prepared by mixing with a 2% polytetrafluoroethylene (PTFE, 7 μL PTFE/ mg AC) solution, applied to the cathode electrode surface, and heat treated for 30 minutes at 350 $^{\circ}\text{C}$. The anode and cathode electrodes were connected by using titanium wire to an external circuit across a resistor of 66 Ω , determined as internal resistance by a polarization curve, unless stated otherwise. The MFC was housed vertically in a PVC tube acting as a cathode chamber with a diameter of 9 cm and a working volume of about 800 mL, which was aerated by the air.

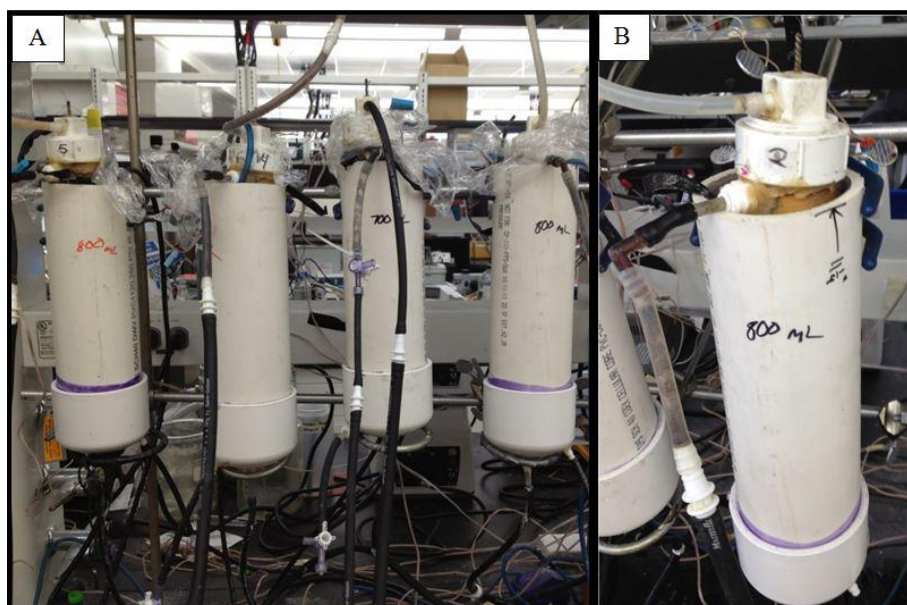


Figure 3-2. Picture of 4 MFC reactors in lab (A) and close up view (B)

3.2.2. MFC Operation

The MFCs were operated at a room temperature (~ 21 $^{\circ}\text{C}$). The anodes were inoculated with 20 mL digested sludge from a local wastewater treatment plant (South Shore Water Reclamation Facility, Milwaukee, WI, USA). To start MFCs (before feeding the cheese wastes), the anodes were initially fed with a nutrient solution containing:

sodium acetate, 1 g; NH_4Cl , 0.15 g; MgSO_4 , 0.015 g; CaCl_2 , 0.02 g; NaHCO_3 , 0.1 g; KH_2PO_4 , 0.53 g; K_2HPO_4 , 1.07 g; and trace element, 1 mL per L (Angenent & Sung, 2001). The analyte was recirculated by a peristaltic pump at 150 mL/min. The catholyte (100 mM phosphate buffer solution) was replaced at the end of a cycle when the pH increased above 9. After the startup period, the MFCs were fed with different wastes from the cheese wastewater treatment process: the DAF (dissolved air flotation) influent for the MFC-1, the DAF effluent for the MFC-2, the sludge (diluted by 4 times) for the MFC-3, and the cheese whey (diluted by 10 times) for the MFC-4 (Figure 3-1B). The MFC-1 was operated in a batch mode with an average hydraulic retention time of 6.4 days, and 21 mM NaHCO_3 buffer was added to the influent of each batch cycle to maintain a neutral pH. The MFC-2 was operated in either a batch mode or a continuous mode using a flow rate of 0.3 mL/min that resulted in an HRT of 28 h. The organic loading rate during the continuous operation varied between 0.27 and 0.74 kg $\text{TCOD}/\text{m}^3/\text{day}$. The MFC-3 was operated in a batch mode for a retention time of 12.9 ± 1.4 days; a NaHCO_3 solution varying from 18.75 to 74.4 mM was added to the sludge to buffer the pH. Before feeding, the sludge was homogenized by blending the sample. The MFC-4 was operated in a batch mode for a retention time of 11.9 ± 2.5 days; similarly, the NaHCO_3 solution varying from 42.52 to 59.53 mM was added to the cheese whey sample to buffer its pH.

3.2.3. Measurement and analysis

The MFC voltage was recorded every 5 minutes by a digital multimeter (2700, Keithley Instruments Inc., Cleveland, OH, USA). The pH was measured by using a benchtop pH meter (Oakton Instruments, Vernon Hills, IL, USA). The concentrations of

total chemical oxygen demand (TCOD), soluble chemical oxygen demand (SCOD), and phosphate (PO_4^{3-}) were measured by using a colorimeter according to the instructions of the manufacturer (Hach Company, Loveland, CO). The total suspended solids (TSS) and volatile suspended solids (VSS) were measured according to standard methods (Clesceri et al., 1998). Power densities and current densities were calculated based on the anode liquid volume. Coulombic efficiency (CE) was calculated according to the previous work (Logan et al., 2006). Energy consumption in the MFCs was mainly due to the recirculation of the anolyte. The power requirement by the pump was estimated as (Kim et al., 2011b):

$$P = \frac{Q\gamma E}{1000}$$

where P is power requirement (kW), Q is flow rate (m^3/s), γ is $9800 \text{ N}/\text{m}^3$, and E is the hydraulic pressure head (m).

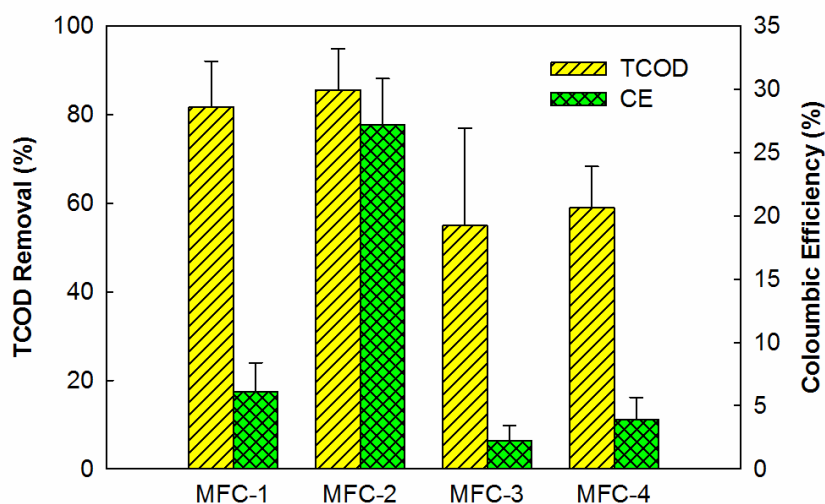


Figure 3-3. The TCOD removal efficiencies and Coulombic efficiencies of the tested MFCs.

3.3. Results

3.3.1. Contaminant Removal

Due to the difference in substrates and MFC operation, we present the results of contaminant removal in the four MFCs separately in the following.

	pH	TCOD (mg/L)	SCOD (mg/L)	TSS (mg/L)	VSS (mg/L)
Raw Wastes					
DAF _{influent} (MFC-1)	7.2±0.2	2201.6±508.8	635.9±262.3	959.3±224.1	790.9±225.7
DAF _{effluent} (MFC-2)	7.3±0.2	377	371.5	N/A	N/A
DAF _{effluent} (MFC-2) ^a	7.5±0.3	645.9±113.7	536.9±100.2	71.4±26.4	59.0±29.8
Sludge (MFC-3) ^b	6.4±0.4	16485.4±4458.2	N/A	7870±1793.1	6596.9±1935.9
Whey (MFC-4) ^c	4.2±0.4	11346.8±424.8	7143.2±2191.6	354.2±450.8	326.7±435.3
Treated Effluents					
MFC-1	5.7±0.6	405.2±182.1	135.4±24.3	156.0±85.8	133.5±79.9
MFC-2	6.7±0.5	54.3±34.9	49.5±14.4	N/A	N/A
MFC-2 ^a	7.0±0.2	141.8±113.7	125.6±100.2	19.9±14.7	16.0±11.7
MFC-3 ^b	5.9±0.4	7565.0±4172.8	N/A	2306.3±1087.1	2060±933.4
MFC-4 ^c	6.2±0.4	4670.0±1138.8	3628.0±1064.5	229.8±92.6	208.3±81.1
^a The MFC-2 under continuous operation					
^b Those values were from the sludge diluted by 4 times					
^c Those values were from the cheese whey waste diluted by 10 times					
N/A: not measured					

Table 3-1. Characteristics of the raw wastes collected from different stages of a cheese wastewater treatment process (upper part), and the treated effluents from different MFCs (lower part).

The MFC-1 was fed with a DAF influent and operated in a batch mode with an average HRT of 6.4 d. It removed 80.3±11.6 % of TCOD and 75.1±10.7 % SCOD (Figure 3-3), with a reduction of the TCOD concentration from 2201.6±508.8 to 405.2±182.1 mg/L and the SCOD concentration from 635.9±262.3 to 135.4±24.3 mg/L (Table 3-1). The MFC-1 also decreased the concentration of the suspended solids by 82.1±12.4 % of TSS and 80.9±14.4 % of VSS. There was no significant change in the concentration of the total phosphate.

The MFC-2 was fed with the DAF effluent, and operated under either a batch or a continuous mode. During the batch operation (with an average HRT of 34 h), the MFC-2 removed 85.6 ± 9.3 % of TCOD and 86.7 ± 3.9 % of SCOD (Figure 3-3 and 3-4B), resulting in final concentrations of 54.3 ± 34.9 mg TCOD/L and 49.5 ± 14.4 mg SCOD/L in the anode effluent (Table 3-1). We did not measure the SS concentration during the batch operation. During the continuous operation (with an HRT of 28 h), the MFC-2 achieved 80.4 ± 11.6 % of TCOD removal and 79.0 ± 11.5 % of SCOD removal (Figure 3-4C), resulting in the final concentrations of 141.8 ± 113.7 mg TCOD/L and 125.6 ± 100.2 mg SCOD/L in the effluent. The MFC-2 also reduced 75.5 ± 13.6 % of the TSS and 71.8 ± 21.4 % of the VSS. Due to variable organic concentrations in the cheese wastewater, the MFC-2 experienced different organic loading rates during its continuous operation, and we observed lower removal efficiencies at higher organic loading rates (Figure 3-5). There was no significant removal of total phosphate under both operations.

The MFC-3 was used to treat the waste sludge from the DAF process in a batch mode. At a long HRT of 13 d, the MFC-3 reduced the TCOD from 16485.4 ± 4458.2 to 7565.0 ± 4172.8 mg/L (Table 3-1), a 54.9 ± 21.9 % removal (Figure 3-3). The TSS concentration was decreased by 71.8 ± 10.1 % and the VSS was reduced by 69.9 ± 9.0 % with the final concentrations shown in Table 3-1.

The MFC-4 was treating the cheese whey waste that did not enter the wastewater treatment process. At an HRT of 12 d, the MFC-4 achieved 59.0 ± 9.3 % of TCOD reduction (Figure 3-3) and 54.1 ± 22.6 % of SCOD reduction. The

concentrations of organic compounds decreased from 11346.8 ± 424.8 to 4670.0 ± 1138.8 mg TCOD/L and from 7722.0 ± 2042.3 to 3252.5 ± 755.5 mg SCOD/L (Table 3-1).

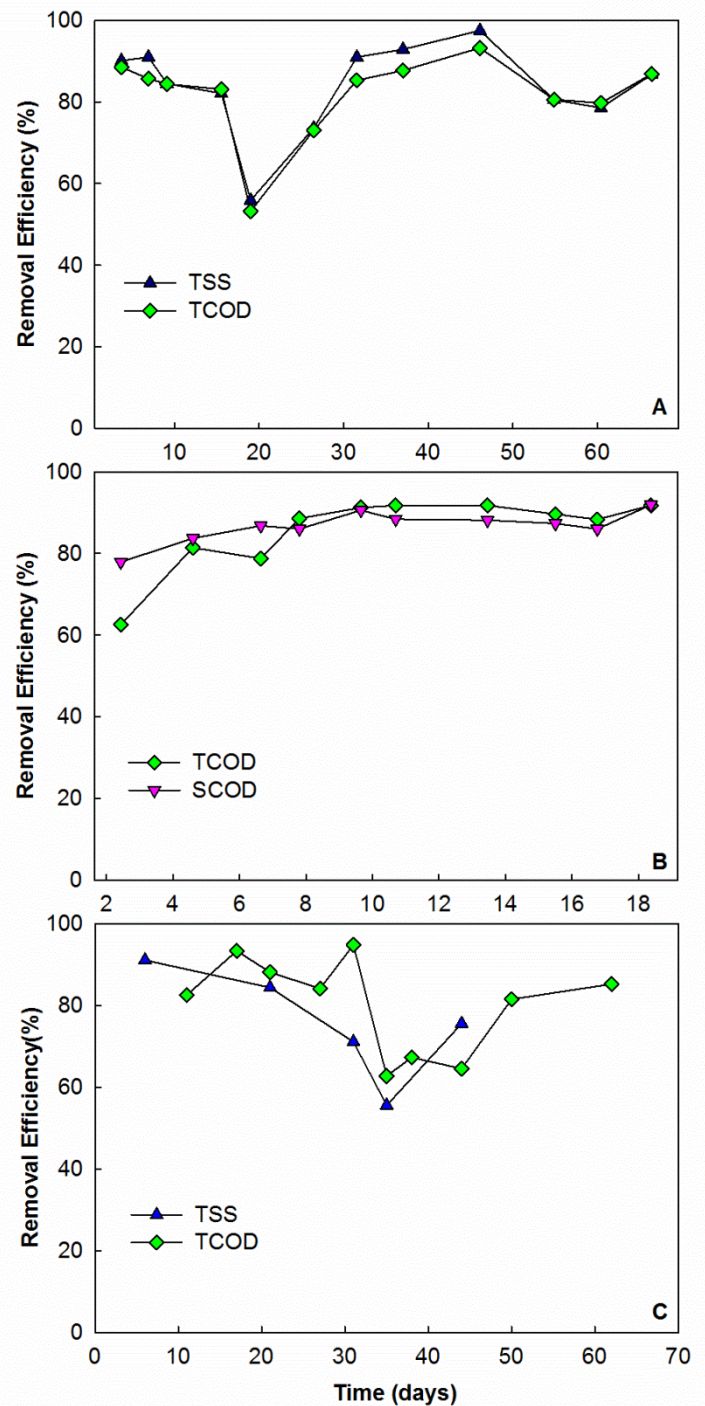


Figure 3-4. Current generation in the tested MFCs under the batch operation: (A) MFC-1, (B) MFC-2, (C) MFC-3, and (D) MFC-4.

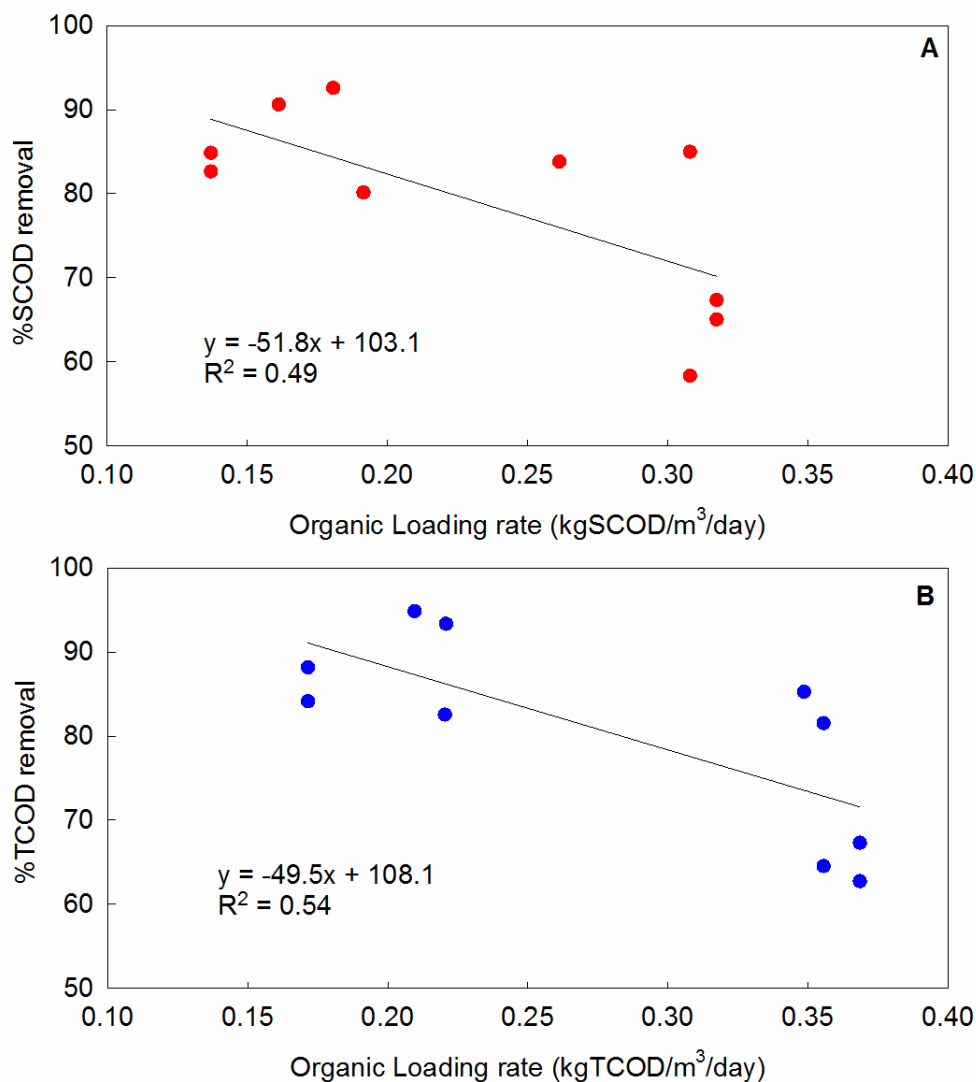


Figure 3-5. (A) SCOD and (B) TCOD removal efficiencies for MFC-2 during continuous operation with respect to organic loading rate.

3.3.2. Electricity Generation

Electricity is a broad term that may refer to voltage, current, power and electric energy. Herein the data of current and power are presented, while the energy results are described in the next section.

To start the reactors, the four MFCs were fed with acetate, which was replaced by the designated substrates after stable current generation was achieved (Figure 3-6).

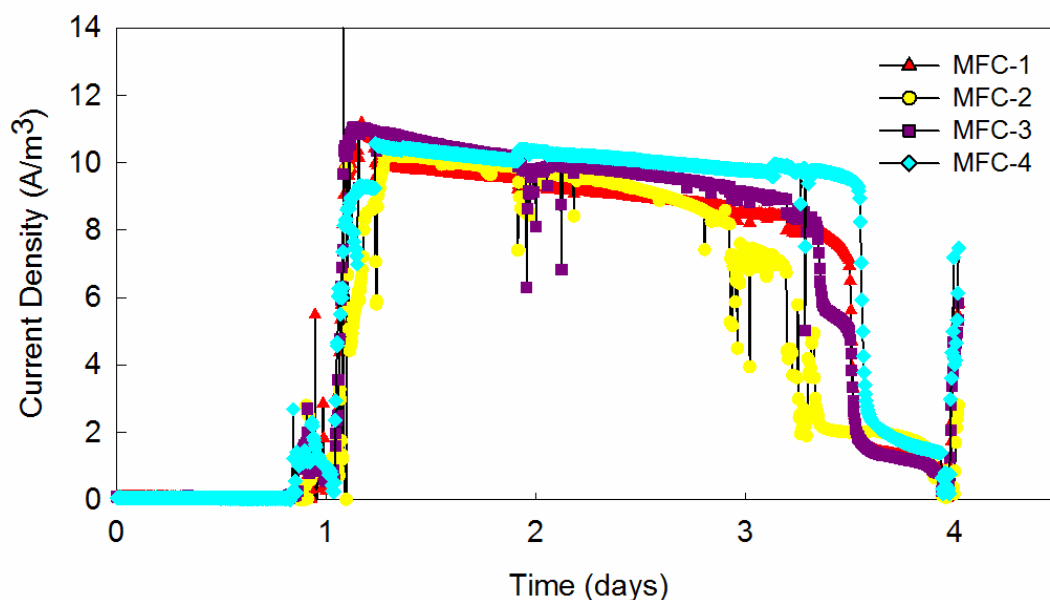


Figure 3-6. MFC 1, 2, 3 and 4 voltage plot during initial Sodium Acetate (1 g/L) feeding

All the MFCs produced electric current from the wastes with a significant difference (Figure 3-7). The two MFCs treating DAF wastewaters (influent and effluent) generated higher current densities than the other two. The MFC-1 produced a

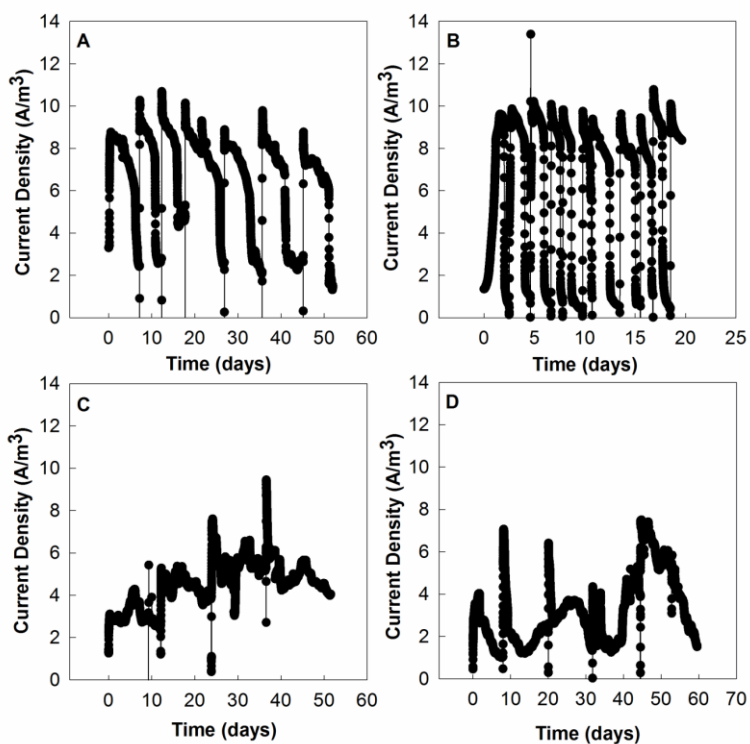


Figure 3-7. Current generation in the tested MFCs under the batch operation: (A) MFC-1, (B) MFC-2, (C) MFC-3, and (D) MFC-4.

peak current density of 9.5 ± 0.7 A/m^3 (Figure 3-7A) and a peak

power density of 3.0 ± 0.5 W/m^3 ; the average current density during a batch was 6.4 ± 2.3

A/m³ with an average power density of 1.5±0.9 W/m³. The peak current density and the peak power density in the MFC-2 was 10.1±0.9 A/m³ and 3.2±0.3 W/m³, respectively (Figure 3-7B); while the average current and power densities were of 6.1±3.7 A/m³ and 1.7±1.2 W/m³. When the operation was switched to continuous feeding, the MFC-2 generated an average power density of 1.9±0.6 W/m³ and an average current density of 7.4±1.4 A/m³ (Figure 3-8). The MFC-3 treating sludge waste generated a peak power density of 1.7±0.9 W/m³ (average of 0.7±0.3 W/m³) and a peak current density of 7.0±2.0 A/m³ (Figure 3-7C) (average of 4.5±1.1 A/m³). The MFC-4 treating cheese whey produced a peak power density of 1.3±0.5 W/m³ (average 0.4±0.4 W/m³) and a peak current density of 6.1±1.4 A/m³ (Figure 3-7D) (average 3.1±1.6 A/m³).

Coulombic efficiency (CE) represents the conversion efficiency of organic compounds to an electric charge. As shown in Figure 3-3, the MFC-2 achieved the highest CE among the four MFCs, with 27.2±3.6 % based on TCOD or 27.0±1.3 % based on SCOD. The continuous operation of the MFC-2 decreased the CE to 12.2 % based on TCOD and 15.0 % based on SCOD. The MFC-1 had a much lower CE of 6.1±2.3 % based on TCOD, but the CE based on SCOD was 27.6±15.5 %, comparable with that of the MFC-2 in a batch mode. Both the MFC-3 and the MFC-4 exhibited very low CEs of 2.2±1.2 % and 3.9±1.7 % (based on TCOD), respectively.

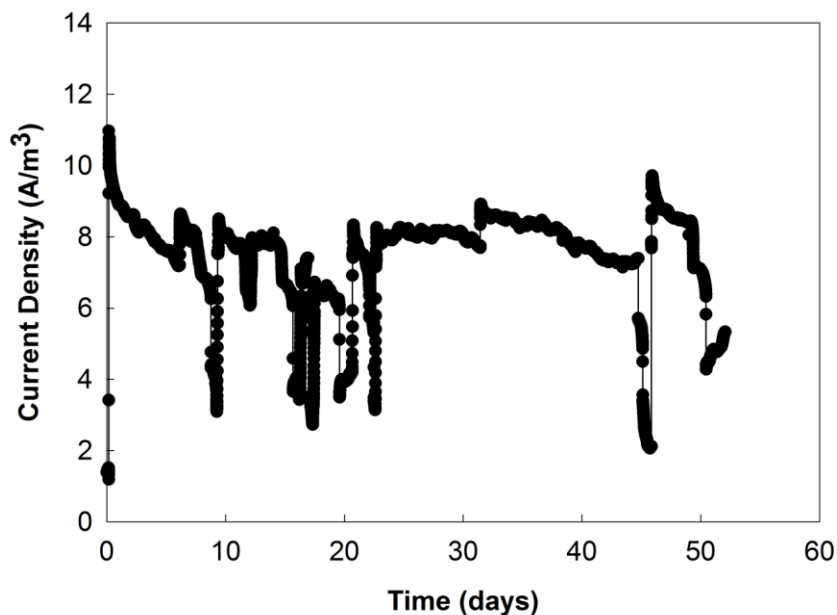


Figure 3-8. Current generation in the MFC-2 during the continuous operation.

3.3.3. Energy Performance

Energy performance, including energy production and consumption, is a key parameter when assessing the performance of MFC technology. The energy production in the present MFCs was calculated by integrating power with time; the energy consumption was estimated from the pumping recirculation system and catholyte aeration. The energy consumption by the feeding pump is negligible compared with the recirculation energy, according to our calculations and previous studies (Zhang et al., 2013a). The data are presented in either kWh/m³ wastewater treated or kWh/kgCOD removed (Table 3-3).

	Energy Production		Energy Consumption		Balance	Balance ^b	Balance ^c
	(kWh/m ³)	(kWh/kg COD)	Recirculation (kWh/m ³)	Aeration (kWh/m ³)			
MFC-1	0.26	0.15	0.20	0.25	-0.19	-0.08	0.06
MFC-2	0.07	0.21	0.05	0.06	-0.04	-0.01	0.02
MFC-2^a	0.05	0.10	0.04	0.06	-0.05	-0.02	0.01
MFC-3	0.88	0.10	1.64	1.39	-2.15	-1.28	-0.76
MFC-4	1.18	0.17	1.51	2.24	-2.57	-1.77	-0.33

^a The MFC-2 under a continuous operation
^b Assuming that large ports are used for hydraulic connection, resulting in a lower hydraulic head loss of 0.013 m than 0.027 m in the actual experiment
^c Energy balance without aeration energy consumption

Table 3-2 Energy production and consumption in the MFCs treating different wastes.

When expressed in kWh/m³, the MFCs treating DAF wastewaters produced less energy than the ones fed with sludge or cheese whey: the MFC-1 and the MFC-2 generated 0.26 and 0.07 kWh/m³, respectively, much lower than 0.88 and 1.18 kWh/m³ from the MFC-3 and the MFC-4. The continuous operation of the MFC-2 resulted in the lowest energy density of 0.05 kWh/m³. However, the four MFCs produced similar energy densities when expressed in kWh/kg COD (Table 3-3). The energy consumption by the recirculation pumps of the MFC-3 and the MFC-4 was much higher than that of the MFC-1 and the MFC-2; likewise, they also consumed more energy in aeration than the other two MFCs. Although all four MFCs had negative energy balances because they consumed more energy than what they could produce, the ones of the MFCs with DAF wastewaters exhibited less negative.

3.4. Discussion

The four MFCs effectively reduced the concentrations of organic contaminants with difference affected by the characteristics of the substrates. The raw DAF influent contained a relatively high amount of solids and organics due to the leftover milk solids (e.g., proteins, fats, carbohydrates, and lactose) from the cheese manufacturer. The MFC-1 was able to remove a considerable percentage of the TCOD, SCOD, and SS from the

DAF influent; however, in accordance with the Wisconsin Department of Natural Resource's NPDES (National Pollutant Discharge Elimination System) effluent limits for this site (Table 3-4), the MFC-1 effluent would not meet the regulatory limits for both organic and SS concentrations and thus a post-treatment would be necessary.

Furthermore, the long HRT (6.4 d) for the treatment is not feasible for practical application. For comparison, the DAF process was able to efficiently remove 95% of the solids in a short HRT of about one hour. The MFC-2 treated the DAF effluent from the DAF process that had low SS and the majority for the COD to be soluble and readily biodegradable. With a much shorter HRT (34-h in batch and 28-h in continuous operation) than the MFC-1, the quality of the MFC-2 effluent in the batch operation was close to meeting the discharge requirements; however, the continuous operation did not produce an effluent within the discharge limits and the effluent must be polished by post-treatment or an extended HRT. Both the MFC-3 treating the sludge waste and the MFC-4 treating the cheese whey waste had low organic removal under an extended HRT of 12-13 d, resulting in the effluents needing further treatment. In general, our findings suggest that the MFC technology applied to the treatment of high strength and high solids wastes/wastewater may not be capable of efficient and practical treatment (Ge et al., 2013), and low-strength wastewater appears to be an optimal substrate.

pH	BOD	TSS	NH ₃	PO ₄ ³⁻
6-9	19 mg/L (Nov-April) 10 mg/L (May-Oct)	19 mg/L (BOD Nov-April) 10 mg/L (May-Oct)	7.9 mg/L daily max	0.7-1 mg/L

Table 3-3. Wisconsin DNR NPDES Effluent Limits for Schreiber Foods, Inc. WWTP

The energy production per volume (kWh/m³) by the MFCs was directly related to the organic loading rate, HRT, and volume of wastewater treated. For example, the MFC-1 produced a higher energy density (0.26 kWh/m³) than the MFC-2 (0.07 kWh/m³)

because of both high organic concentration in the MFC-1 influent and the greater HRT (6.4 d vs. 34 h) that resulted in a much lower volume of the treated water than a shorter HRT within the same time period. The MFC-3 and the MFC-4 produced higher energy densities per volume because of longer HRTs and high organic loading. However, the energy density per COD removed (kWh/kg COD) was similar for each MFC, indicating essentially similar conversion from organic compounds to electric energy (not the electric charge reflected by the CE). Energy consumption by the MFCs was also correlated with HRT; a longer HRT led to longer operation of anolyte recirculation and aeration of the catholyte, which are major energy consumers. This explains the increase in recirculation and aeration consumption energy for the MFC-1, the MFC-3, and the MFC-4. Because the energy consumption by anolyte recirculation is associated with hydraulic head loss, we found that the size of connection ports can significantly affect hydraulic head loss and thus energy requirement. The present MFCs used a port at a diameter 0.40 cm, resulting in a hydraulic head loss of 0.027 m; if we replace it with a larger port (0.64 cm) used in our other MFCs, the hydraulic head loss is estimated to be 0.013 m, thereby greatly reducing the energy requirement of recirculation and making the energy balance close to zero (Table 3-3). In addition, energy consumption may be further reduced by omitting aeration if methods such as catholyte dripping and air cathodes are used, as shown in our previous studies (Zhang et al., 2013a; Zhang et al., 2010). An energy balance neglecting the aeration would produce a positive energy balance for the MFC-1 and the MFC-2 (Table 3-3). However, the energy balances of the MFC-3 and the MFC-4 will remain negative even without aeration, likely due to a long operating time that requires a significant energy input.

The results of this work collectively suggest that MFCs should not be a standalone process and future application must consider appropriate integration with the existing treatment methods. For example, the DAF process is a vital component in the Schreiber wastewater treatment process that removes a significant amount of both solids and nutrients (which the MFCs cannot handle well). For this application of cheese wastewater treatment, the MFC technology seems feasible to be installed after the DAF and to replace the activated sludge as the secondary wastewater treatment with additional energy benefits. Because of the significantly lower SS concentration in the MFC effluent compared with the activated sludge treatment, the post-treatment such as precipitation can be minimized, resulting in less capital investment and operating expense associated with energy and sludge disposal.

3.5. Conclusions

This study has demonstrated effective treatments of cheese wastes in MFCs with differences affected by the characteristics of the wastes and operating conditions. The DAF effluent was found to be the optimal substrate for the MFC treatment because of low concentrations of contaminants. As a result, the MFC treating the DAF effluent achieved the lowest energy consumption, a practical HRT, a higher CE, and the treated water quality close to the discharge limits. The results indicate that MFCs should be properly integrated into the existing treatment process, for example, in connection with a DAF process, instead of being deployed as a standalone method. This study provides a preliminary benchmark for determining which stage of the wastewater treatment process may be applicable to MFC technology with an aim to reduce energy consumption while complying with wastewater treatment standards.

3.6. Acknowledgements

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Chapter 4 Conclusions and Perspectives

The recent years have certainly seen promising improvements in research and development of Microbial Fuel Cells by researchers across the world—all of whom share the common goal to scale up this technology in the efforts to reduce the energy demand of wastewater treatment sector. It is conventional wisdom to assume that MFC technology is not going to be the answer for all wastewater treatment operations. Indeed each waste stream, whether it is industrial, domestic, or residential, will have a unique composition and complexity. In turn, a unique wastewater treatment system must be designed to handle the specific loading of organics, nutrients, and other contaminants. It is crucial that we recognize where MFC technology may or may not be effective in wastewater treatment operations. For example, the slow anaerobic metabolic nature of MFC microbial consortia suggests long operating times (HRT) will be needed to treat wastes of high organic loads implying the necessity for a pre-treatment step.

To make the technology economically viable for commercialization, power outputs must continue to increase while reducing the costs of construction materials. This

has been proven effective in diverting the use of costly noble metals for cathode catalysts (such as the cost-effective use activated carbon for cathode catalyst (Zhang et al., 2009)) . To gain commercial interest, researchers must pay more attention to the life cycle analysis of MFC materials. It will be important to establish the relationship between performance stability and material degradation over time to provide a lifetime for MFC technology. For example, Zhang et al conducted a yearlong study of an activated carbon air cathode concluding that cathode performance degraded (by 22%) over time due to clogging of the activated carbon micropores. With the use of electrochemical techniques (linear sweep voltammetry, electrochemical impedance spectroscopy, etc...) they determined the performance reduction was attributed to increase in diffusional resistance over time (Zhang et al., 2011a). Moreover, innovative engineering techniques must be continually applied to MFC pilot scale studies to prove the applicability of this technology and encourage interest from commercial investors.

Works Cited

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