Integrated Membrane and Microbial Fuel Cell Technologies for Enabling Energy-Efficient Effluent Re-use in Power Plants

Namita Shrestha^a, Govinda Chilkoor^a, Lichao Xia^b, Catalina Alvarado^b, James Kilduff^{b*}, John J. Keating IV^c, Georges Belfort^c, Venkataramana Gadhamshetty^{a,d*}

^aCivil and Environmental Engineering, South Dakota School of Mines and Technology,
501 E Saint Joseph Blvd, Rapid City, SD 57701

^bCivil and Environmental Engineering, Rensselaer Polytechnic Institute, 110 8th Street,
Troy, NY, 12180

^cHoward P. Isermann Department of Chemical and Biological Engineering, Rensselaer
Polytechnic Institute, 110 8th Street, Troy, NY, 12180

^aSurface Engineering Research Center, South Dakota School of Mines and Technology,
501 E Saint Joseph Blvd, Rapid City, SD 57701

*Corresponding author:
Rensselaer Polytechnic Institute
110 8th Street
CEE Dept., Room 4049 JEC Building
Troy, NY 12180
Email: kilduff@rpi.edu

South Dakota School of Mines and Technology
501 E Saint Joseph Blvd
Rapid City, SD 57701
Email: venkata.gadhamshetty@sdsmt.edu

Abstract

Municipal wastewater is an attractive alternative to freshwater sources to meet the cooling water needs of thermal power plants. Here we offer an energy-efficient integrated microbial fuel cell (MFC)/ultrafiltration (UF) process to purify primary clarifier effluent from a municipal wastewater treatment plant for use as cooling water. The microbial fuel cell was shown to significantly reduce chemical oxygen demand (COD) in the primary settled wastewater effluent upstream of the UF module, while eliminating the energy demand required to deliver dissolved oxygen in conventional aerobic treatment. We investigated surface modification of the UF membranes to control fouling. Two promising hydrophilic monomers were identified in a high-throughput search: zwitterion (2-(Methacryloyloxy)-ethyl-dimethyl-(3-sulfopropyl ammonium hydroxide, abbreviated BET SO_3^-), and amine (2-(Methacryloyloxy) ethyl trimethylammonium chloride, abbreviated $\text{N}(\text{CH}_3)_3^+$). Monomers were grafted using UV-induced polymerization on commercial poly (ether sulfone) membranes. Filtration of MFC effluent by membranes modified with BET SO_3^- and $\text{N}(\text{CH}_3)_3^+$ exhibited a lower rate of resistance increase and lower energy consumption than the commercially available membrane. The MFC/UF process produced high quality cooling water that meets the Electrical Power Research Institute (EPRI) recommendations for COD, a suite of metals (Fe, Al, Cu, Zn, Si, Mn, S, Ca and Mg), and offered extremely low corrosion rates (<0.05 mm/yr). A series of AC and DC diagnostic tests were used to evaluate the MFC performance.

Keywords: municipal wastewater, power plant cooling, microbial fuel cell, ultrafiltration, surface modification, wastewater reuse

1.0 Introduction

A 500 MW wet-cooled power plant consumes nearly 4 million gallons of freshwater per day (Gadhamshetty et al., 2014). Thermal power plants in the U.S. comprise 86% of total fresh water withdrawals (EPRI, 2011). Water reclaimed from secondary and tertiary effluents of publicly owned treatment work (POTWs) serve as an excellent source of cooling water in power plants (Chien, 2010). POTWs within a 25 mile radius could fulfill 90% of cooling water needs; those within a 10 mile radius could meet 80% of cooling water needs of proposed power plants (Chien, 2010). For example, 74% of the power plants in Texas (USA) have access to reclaimed water within 25 miles (Stillwell and Webber, 2014). The use of reclaimed water in thermal power plants becomes desirable in arid regions that suffer from water scarcity issues, especially during hottest days of the year (Prisciandaro et al., 2016). However, POTWs configured with aerobic processes require energy inputs of 0.5 to 2.0 kWh/m³ to maintain sufficient dissolved oxygen (DO) to support microbial activity during treatment (Gude, 2015).

Microbial fuel cells (MFC) (Rozendal et al., 2008) eliminate this energy requirement and can even generate electricity from wastewaters, with minimal requirements for chemical supplements and dissolved oxygen (Pant et al., 2010). Within the past decade, MFC technologies have advanced from bench scale reactors (1-10 mL) to the pilot scale (250 L), achieving 97% removal of soluble chemical oxygen demand (sCOD) from wastewater (**Table S1**). The recent literature describes new approaches for integrating MFC technology with membrane bioreactors (MBRs) (Wang et al., 2011; Yuan and He, 2015) (Xu et al., 2015) and hollow fiber MBRs (Tian et al., 2015).

The Electric Power Research Institute has specified water quality criteria for cooling water (**Table 1**) to minimize corrosion, fouling, and scaling in cooling water recirculation systems (CWRS) (EPRI, 2012). For example, nutrients (N and P) in reclaimed water can promote precipitate formation (e.g., calcium phosphate), support biofouling, and increase pressure drop in CWRS (Bell and Conley, 1987). High temperatures (40-60 °C) favor precipitation of calcium carbonate, calcium phosphate, and magnesium silicate, leading to scale formation and reducing heat transfer efficiency in CWRS (Bell and Conley, 1987). Evaporation losses in cooling towers reduce overall water volume, concentrating pollutants, and aggravating mineral deposition (Li et al., 2011). Heavy metals (Cu, Fe, and Zn) encourage incrustation upon turbine blades (Metrohm, 2014). Pathogenic viruses and fecal coliforms pose human health risks. The metal components exposed to the reclaimed water, especially in the warm and aerobic conditions found in CWRSSs, are susceptible to biofouling (Frayne, 1999) and microbial corrosion (Howell and Saxon, 2005).

TABLE 1

Reclaimed water is often treated with: chemical inhibitors such as mono-chloramine (Chien et al., 2012), phosphate-based chemicals (Hsieh et al., 2010), poly-maleic acid (Liu et al., 2014), and tolytriazole (Frayne, 1999; McCoy, 1974) to mitigate corrosion; chlorine (Chien et al., 2012) to arrest biological growth; and anti-scalants such as polyacrylic acid, phosphonates and polyphosphates to inhibit deposition. We hypothesize that an MFC module integrated with an ultrafiltration (UF) module can reclaim wastewater as high quality, cooling water in an energy efficient manner (**Figure 1**), meeting Electric Power Research Institute (EPRI) and Environmental Protection Agency (EPA) standards for chemical oxygen demand (COD) (30 mg/L), pH (6.5-7.5), and a suite of dissolved and suspended solids, including coliform, metals,

and nutrients (**Table 1**) (USEPA, 2004). However, residual macromolecular COD and sloughed particulates (including microbes) in MFC effluent can foul UF membranes (Marshall et al., 1993). To address this, we investigated surface modification of UF membranes using hydrophilic monomers.

-----FIGURE 1-----

The high throughput and photo (UV)-induced graft polymerization (HTP-PGP) described in our earlier studies (Zhou et al., 2010; 2009c; Zhou et al., 2011) is an effective route to discover new surfaces that enhance wetting and anti-fouling properties of UF membranes. The current study used HTP-PGP to identify three candidate hydrophilic monomers (a zwitterion, an amine, and a polyethylene glycol) to improve the performance of poly (ether sulfone) (PES) membranes. We anticipate that the MFC/UF configured with the anti-fouling membranes will be compact, modular and easily automated; will offer high removal rates for turbidity, organic matter, and microorganisms; and will operate at low-pressure and handle variable loading rates (Lainé et al., 2000). UF systems have lower operating costs than nano-filtration and reverse osmosis technology, in part because they operate at lower pressures, and in part because they do not reject salts, avoiding concentration polarization (Gao et al., 2011). This study evaluates UF performance using MFC effluent; the objectives of this study were to: i) evaluate the performance of a sequential MFC/UF train, configured with anti-fouling membranes, to enable wastewater reuse as cooling water; and, ii) screen and identify suitable surface chemistries that yield high flux, low energy consumption, high rejection, anti-fouling UF membranes for treating the MFC effluent. Further, reclaimed wastewater is known to offer corrosion risks to metals in power plants. We evaluated corrosion characteristics of mild steel exposed to MFC effluent at 25

$^{\circ}\text{C}$ and 40°C , typical temperatures encountered in CWRS, and compared the corrosion profiles with that of primary clarifier effluent.

2.0 Materials & Methods

2.1 *Anti-fouling UF membranes.*

First we used high-throughput screening (HTP) with photo-initiated graft polymerization (HTP-PGP method (Zhou et al., 2009c)) to screen and select the best monomer candidates from a 24-monomer library using both static and dynamic fouling tests. Then, the PGP method was applied to graft the three best candidates, which were tested at the bench scale in a dead end cell.

2.1.1. *High throughput screening.*

High throughput screening was done to evaluate the monomers shown in **Figure S1**. PES specimens housed in each well of an AcroPrep^{TM}, 96-well filter plate were modified by photo-initiated graft polymerization (Zhou et al., 2009c). Each filter plate had 16 control wells and each monomer was evaluated in triplicate. The efficacy of graft polymerization in offering a fouling resistant surface was quantified by a fouling index, $\text{F.I.} = (R_{\text{fouled}} - R)_{\text{mod}} / (R_{\text{fouled}} - R)_{\text{control}}$, which compares the increase in resistance (R) due to fouling ($R_{\text{fouled}} - R$) of the modified membrane (mod) to that of the ungrafted membrane as a control. Resistance after fouling was measured relative to membrane resistance tested with pure water or buffer (used for protein solutions). Optimum performance occurs when the F.I. approaches 0, which indicates little fouling of the modified membrane (Zhou et al., 2009a). In static adsorption tests, MFC effluent was pipetted into each well and allowed to equilibrate for 72-hours, after which it was discarded, and the membrane resistance was measured using reagent-grade water. In dynamic filtration tests, BSA was pipetted into each well and allowed to equilibrate for 72-hours, after which BSA

solution was filtered for 2 minutes. Solution mass flux ($\text{kg m}^{-2} \text{s}^{-1}$) was computed from gravimetric measurements of solution throughput $J_w = M/At$; then, membrane resistance was computed using transmembrane pressure drop ΔP and solution flux, $R = \Delta P/\mu J_w$. The static adsorption tests and dynamic filtration tests were performed independently for 24 monomers.

2.1.2 Bench scale evaluation.

Bench scale filtration tests were done using the membrane filtration system shown in **Figure S2**. The MFC effluent was tested with modified and unmodified membranes (**Table 2**), using the same commercially available base PES membranes. After grafting, different surface chemistry and anti-fouling characteristics were obtained as a result of differences in the nature of grafted monomers and monomer concentration.

-----TABLE 2-----

Both modified and unmodified UF membranes were tested at a constant pressure with same initial flux using the protocol described previously (Cho et al., 2000; Taniguchi et al., 2003b) and summarized in **Figure S3**. Briefly, UF membranes were first compacted at 45 psi with reagent-grade water until flux changed less than $10^{-5} \text{ kg m}^{-2} \text{s}^{-1}$ per g throughput, after which membrane permeability was measured using reagent-grade water or phosphate buffer saline (PBS) solution and used to compute membrane resistance (R_m). The mass throughput of MFC effluent (pH 7.1) was monitored gravimetrically to calculate total fouling resistance (R_t). Following hydraulic cleaning, the resistance (R_H) was measured by filtering reagent-grade water or PBS solution, and finally, the UF membrane was chemically cleaned with 0.05 M NaOH and resistance (R_{ch}) was measured with reagent-grade water. Chemicals and feed solution concentrations used in the UF filtration experiment are summarized in **Table S2**.

2.1.3 Modeling.

In the absence of significant osmotic pressure, solution flux, J_w [$\text{kg m}^{-2} \text{s}^{-1}$], is proportional to the transmembrane pressure, ΔP [Pa], and inversely proportional to the total resistance, R_T [$\text{Pa m}^2 \text{s kg}^{-1}$]: $J_w = \Delta P / \mu R_T$, where μ is viscosity [$\text{kg m}^{-1} \text{s}^{-1}$]. The total resistance includes the intrinsic membrane resistance, R_m , assumed constant after compaction, and any resistance due to fouling, R_f . The resistance due to fouling may result from some combination of complete or partial pore blockage, pore constriction due to adsorption or adhesion onto pore walls, and cake formation on the membrane surface. These so-called “classical” fouling mechanisms act to reduce the accessible number of pores, reduce the effective pore cross sectional area, or introduce a resistance in addition to the membrane resistance, respectively. A summary of individual fouling mechanisms can be found in Kilduff *et al.* (Kilduff et al., 2002).

Ho and Zydney (Ho and Zydney, 2000) and later Duclos-Orsello and Ho (Duclos-Orsello et al., 2006) developed models to incorporate classical fouling mechanisms. The combined pore blockage-cake formation model is summarized in Supplemental Information. The model includes parameters to describe the rate of pore blockage, α_b [$\text{m}^2/\text{kg solute}$], and cake formation, α_c [$\text{Pa m}^4 \text{s kg}^{-2}$], and the initial resistance of the cake deposit, $R_{c,0}$ [$\text{Pa m}^2 \text{s kg}^{-1}$]. The model exhibits a smooth transition from pore blockage at the beginning of filtration, to cake formation as time progresses; fouling resistance as a result of cake formation that has been studied by Ye *et al.* (Ye et al., 2005) and Katsoufidou *et al.* (Katsoufidou et al., 2008), among others.

2.2 MFC Module.

The test and control MFCs were based on the two-compartment MFCs described in our earlier studies (**Figure S4a, S4b**) (Fogg et al., 2015; Shrestha et al., 2016). Details of MFC experimental design are tabulated in **Table S3**. The test MFC used primary clarifier effluent

(COD = 828 mg/L; pH = 7.07) from a wastewater reclamation facility in Rapid City, SD. The test MFC is herein referred as a WW_{MFC}. The WW_{MFC} was operated in 17 consecutive cycles of fed-batch operation extended over 120 days. At end of an each cycle, planktonic microbes were eliminated by draining the spent-anolyte, gently washing the anode with 50 mM phosphate, and replenishing the anode with 180 mL of fresh media (**Figure S5**). The spent anolyte of WW_{MFC} from the cycles 6 to 17 was stored at 4 °C and was subsequently used as the UF feed.

The MFC that used acetate as the electron donor (ACE_{MFC}) (as a control for WW_{MFC}) was based on minimal media (acetate, 6 g L⁻¹; NH₄Cl, 0.62 g L⁻¹; KCl, 0.26 g L⁻¹; NaH₂PO₄•H₂O, 4.904 g L⁻¹; Na₂HPO₄•7H₂O, 9.152 g L⁻¹; vitamin mix, 10 ml L⁻¹; and trace minerals). The anode was inoculated with an enriched microbial consortia (biofilm age = 360 days) from active MFCs in our laboratory (Fogg et al., 2015). The catholyte was 50 mM ferricyanide buffered with 50 mM phosphate buffer solution (PBS). Graphite felt, used as both the cathode and the anode, was pretreated with acetone for 12 hours, soaked in a mixture of ammonium peroxydisulfate and concentrated sulphuric acid for 15 minutes, and heated at 450 °C for 30 minutes (Fogg et al., 2015).

2.3 Analytical Methods, Data acquisition, AC and DC electrochemical tests.

The anolyte samples were collected using a gastight syringe to measure pH (Orion™ Star log R pH), electrical conductivity (Oakion Con 700), soluble COD (Method 5220 (Clesceri et al., 1998); Hach COD system, Loveland, Colorado), and metals (Ca, Al, Cu, Fe, Zn, Si, S, Mn) (Agilent 7900 inductively coupled plasma mass spectrometer (ICP/MS)). Voltage data were acquired using a DAQ/54 module (I/O Tech Inc., Cleveland OH) across an external load. The polarization data at each resistance were recorded every hour to obtain a voltage value under steady state conditions. Electrochemical impedance spectroscopy (EIS) tests were performed

using a Gamry reference 600 workstation, at open circuit potential (OCP), using an alternating current signal with an amplitude of ± 10 mV, and a frequency range of 10 kHz to 0.01 Hz. The EIS spectra were obtained on days 36, 58 and 75 using the anode as the working electrode (WE), and the cathode as the reference electrode (RE) and counter electrode (CE). Individual resistances were obtained by external equivalent circuit fitting analysis (maximum error tolerance of 2%) of the EIS data, using a modified Randle's circuit (**Figure S6**). Gamry Echem Analyst software was used to analyze the EIS results. DC cyclic voltammetry was carried out using a PGSTST302N workstation (Metrohm USA, Inc, Riverview, FL), using anode in the test MFCs as the WE, Ag/AgCl as the RE, and cathode as the CE. Cyclic voltammetry tests were carried out in a potential region of ± 1 V, at a scan rate of 10 mV/s, and with 120 days old biofilm in the anode. Differential pulse voltammetry (DPV) tests were performed using a 50 mV pulse size.

2.4 Corrosion Tests.

The corrosion characteristics of low carbon steel (LCS) were evaluated in a Gamry Paracell (V = 0.5 L, **Figure S7**). Details of the experimental design are tabulated in **Table S3**. Coupons having a defined composition (C, 0.13-0.20%; Mn, 0.30-0.90%, Si, 0.15-0.30%, P, 0.04%; S, 0.50%; Fe, 98.06-99.42%) were exposed to three different electrolytes: (i) primary clarifier effluent, ii) the MFC effluent, and iii) distilled water. Corrosion was evaluated at two different temperatures (25 °C or 40 °C) using a water bath. The LCS represents a technologically relevant metal used in the CWRs of the power plants (Lister, 2007). The Paracell used a graphite plate as the CE, Ag/AgCl as the RE, and LCS as the WE. The RE was immersed in a bridge tube and its tip was positioned in line with exposed surface of the WE (2.85 cm²). We used a Gamry reference 600 workstation to carry out the tests for the corrosion potential/open

circuit potential (OCP) measurements, linear polarization resistance, CV, cyclic polarization and Tafel analysis. The measurements were obtained after achieving a steady-state OCP condition. Temporal values for the OCP were monitored during the course of 72 hours. Linear polarization resistance tests were performed using a ± 1 mV (vs. OCP) window and a scan rate of 0.125 mV/s, initial delay of 1200 s, and voltage stability of 0.1 mV/s. The Tafel tests were carried out in the potential range of ± 1 V (vs. OCP) using a scan rate of 1mV/s. The EIS tests were performed under OCP conditions.

3.0 Results and Discussion

3.1 Anti-fouling UF membranes

3.1.1 *High throughput screening.*

Results of high throughput screening are shown in **Figure 2(a)**; 14 of the 24 initial monomers performed better than the unmodified surface with F.I. < 1 based on static tests. Dynamic tests were conducted to verify the performance of modified surfaces identified under static adsorption (**Figure 2(b)**). These tests yielded three monomer candidates (BET SO₃⁻, N(CH₃)₃⁺, and PEG) (**Table 2**); however, the PEG candidate was subsequently excluded due to membrane degradation during modification.

-----FIGURE 2-----

3.1.2 *Bench scale evaluation.*

A membrane flux of 0.050 kg m⁻²s⁻¹ was used in bench scale evaluation; this value is higher than used in practice but is often used in bench scale studies to accelerate fouling (Cho et al., 2000; Ho and Zydney, 2000; Katsoufidou et al., 2007; Taniguchi et al., 2003a; Zhou et al., 2009b). Water permeability determined before fouling resistance is shown in **Figure 3**. In

comparison to the AR membrane, the modified membranes have lower membrane permeability (**Figure 3**), suggesting that grafted monomers narrow or partially block membrane pores (Taniguchi et al., 2003b). Reduction in permeability by either monomer is small when grafted from 0.2 M solution; when grafted from 0.6 M solution, the BET SO_3^- exhibits a significant reduction in membrane permeability.

-----FIGURE 3-----

The flux, fouling resistance, and the energy consumption during filtration of MFC effluent is shown in **Figure 4** for membranes modified with BET- SO_3^- and $\text{N}(\text{CH}_3)_3^+$ using two monomer concentrations, 0.2 and 0.6 M. Flux decline during filtration of MFC effluent through BET- SO_3^- and $\text{N}(\text{CH}_3)_3^+$ membranes modified from 0.2 M monomer solution was similar to the as-received membrane (**Figure 4(a)**). When modified from 0.6 M monomer solution, the membrane modified with $\text{N}(\text{CH}_3)_3^+$ exhibited somewhat lower rate of flux decline, as shown in **Figure 4(b)**. However, flux decline does not reveal differences in membrane resistance; the modified membranes offered lower fouling resistance and hence lower energy consumption as compared to the as-received membrane (**Figure 4c and 4d**). Modified membranes also exhibited good flux recovery after hydraulic cleaning, above 90%. Recovery was not improved by further washing in 0.05 M NaOH.

-----FIGURE 4-----

Flux decline caused by the MFC effluent was compared to three model foulants, NOM, BSA, and sodium alginate. All the feed solutions exhibited similar flux decline trends; fouling resistance of the feeds followed the order $\text{BSA} > \text{NOM} > \text{SA} \approx \text{MFC}$ for both modified surfaces (data not shown). Compared to other feed solutions through either 0.2 or 0.6 M monomer modified membranes, MFC effluent had the lowest energy consumption.

3.1.3 Modeling.

The combined pore blockage and cake formation model (Ho and Zydney, 2000) agrees well with our flux and fouling resistance measurements with good model fits (Lines in **Figure 4**). Model parameters are tabulated in **Table 3**. For the MFC effluent, 0.2 and 0.6 M monomer modified membranes have lower $R_{c,0}$ than the as-received membrane. The BET SO_3^- modified membrane fouled faster, as reflected in the higher pore blockage and cake formation rate constants α_b and α_c .

-----TABLE 3-----

3.2 COD Removal.

The MFC achieved 94% COD removal from the primary clarifier effluent (**Figure 5a**), significantly reducing the COD load on the downstream UF. MFC performance is on par, or better, than contemporary pretreatment systems used upstream of UF filters. For instance, COD removal in granular filters is much lower, on the order of 50% (Bourgeois et al., 2001). Similarly, COD removal by the MFC used here is competitive with rates reported in other UF studies, which ranged from 34 to 95%, with and without pretreatment. Feeds included kraft black liquor (Bhattacharjee et al., 2006), olive mill wastewater (El-Abbassi et al., 2011), soy protein (Cassini et al., 2010), and fermentation broths (Kim et al., 1997). The pH of the anolyte in the WW_{MFC} (6.5 to 7.5; **Figure 5b**) meets EPA criteria for cooling water. Here we confirm that MFC/UFs can generate the cooling water from wastewater without additional buffers or chemical supplements.

-----FIGURE 5-----

3.2.1 Effect of Biofilm Age and Current Density.

The COD concentration in the MFC effluent (55 mg/L) (**Figure 5a**); EPA criteria for cooling water (50 mg/L) is met after UF filtration (**Table 1**). The average values of the initial and final concentrations for the COD in the ACE_{MFC} were (1117.75±62.5) mg/L and (270.25±103.75) mg/L; and the WW_{MFC} were (806±21.25) mg/L and (105.25±50) mg/L, respectively. The COD removal efficiency in both the ACE_{MFC} and WW_{MFC} increased with increasing duration of the fed-batch operation, and at higher current densities (R_{ext}) (**Figure 5a**). For WW_{MFC}, with $R_{ext} = 10 \Omega$ and BA = 45 days, the COD removal was limited to 50%; with $R_{ext} = 1 \Omega$ and BA = 77 days, the COD removal increased to 90% (**Figure 5a**). The COD removal rate, $|\Delta COD/\Delta t| = 31.4 \text{ mg L}^{-1} \text{ d}^{-1}$ in the WW_{MFC} at $R_{ext} = 1 \Omega$, which was 30% higher than at $R_{ext} = 10 \Omega$. For the ACE_{MFC}, $|\Delta COD/\Delta t| = 26.3 \text{ mg L}^{-1} \text{ d}^{-1}$ at $R_{ext} = 1 \Omega$, which was 23% higher than the $R_{ext} = 10 \Omega$ (**Figure 5a**). In presence of a mature biofilm (i.e., higher BA), the lower R_{ext} , results in a more positive anodic potential, and a higher current flux (Ren et al., 2011).

3.2.2 Conductivity, pH, and power density.

The conductivity of the anolyte in the WW_{MFC} was between 1.12 and 1.8 mS/cm throughout 120 days of fed-batch operation. The MFC effluent therefore meets EPA guidelines for conductivity (of 0.6 to 2.7 mS/cm) (USEPA, 2004) (**Figure 6a**). The pH of the anolyte in the WW_{MFC} was between 6.5 and 7.5, at both $R_{ext} = 1 \Omega$ and $R_{ext} = 10 \Omega$, throughout the fed-batch operation. Considering that we did not use any external buffers in WW_{MFC}, it is interesting to note that the pH profiles for the WW_{MFC} are comparable to that of the ACE_{MFC}, and both met EPA and EPRI guidelines for pH of cooling water (**Figure 6b**). Preliminary results shown in **Figure 6a** indicate that conductivity in the anolyte decreases with increasing time of the fed-

batch operation. For the WW_{MFC} and ACE_{MFC} , the conductivity reduced by 62% and 84%, respectively, within 44 days; and by 79% and 88%, respectively, in 119 days of the fed-batch operation (**Figure 6a**). While the pH remained in the range of 6.3 to 7.3 (**Figure 6b**), the temporal profile for the pH also appears to follow a decreasing trend (**Figure 6b**) as observed by others (Cheng and Logan, 2011; Dong et al., 2015; Rozendal et al., 2008). To establish a correlation between the pH, conductivity, and power density, we carried out additional experiments by poisoning the anode potential (E_{anode}) at a fixed value (-0.15 V vs Ag/AgCl), and compared the temporal profiles (**Figure S8**). During the first three days, the pH changed from 7.14 to 7.19, the conductivity increased from 1.32 mS/cm to 6.5 mS/cm, and the power density increased from 5.75 mW/m² to 85.47 mW/m² (**Figure S8**). A subsequent decrease in power density to 12.44 mW/m² was correlated to decrease in pH and conductivity to 7.09 and 1.54 mS/cm respectively. Because the test MFCs did not encounter carbon starvation or pH inhibition during the first three days, the results suggest a strong correlation between the three parameters. Prior MFC studies have suggested a relationship between the solution conductivity and the electric power densities (Cheng et al., 2007; Cheng and Logan, 2011; Rozendal et al., 2008), attributable to reduced ohmic losses in conductive solutions.

-----FIGURE 6-----

3.2.3 Metal removal in MFCs.

We measured the metal concentrations for nine different elements (Fe, Al, Cu, Zn, Si, Mn, S, Ca and Mg) in the primary clarifier effluent and the MFC effluent. The measured values for four metals (Al, 1 mg/L; Zn, 0.3 mg/L; Cu, 0.1 mg/L (Henze and Comeau, 2008) and Ca, 1.5-16 mg/L) in the primary clarifier effluent met EPA (USEPA, 2004) and EPRI criteria (Ellis, 2013; Pescod, 2015). Except for Fe (2.72 mg/L) and S (81.50 mg/L), the values for all the nine

metal concentrations in the MFC effluent fall within EPRI limits (**Table 1, 4**). The results indicate that the MFC operations have exerted a minimal influence on the metal removal from the wastewater (**Table 4**). Kimura et al. (Kimura et al., 2004) found that metal concentrations in this range did not interact strongly with dissolved organic matter to foul UF membranes. If metal concentrations in wastewater exceed prescribed limits, treatment in the MFCs could be improved by designing them as bio-cathodes to precipitate the heavy metals (Mathuriya and Yakhmi, 2014) or by removing them via capacitive deionization (Forrestal et al., 2015) or desalination (Cao et al., 2009; Luo et al., 2012). Depending on their form (dissolved, complexed with organic matter, or particulate) some removal may be expected in downstream UF (Tortora et al., 2016).

----- TABLE 4 -----

3.2.4 Electrochemical impedance: WW_{MFC} vs ACE_{MFC} .

The EIS tests were used to discern the performance differences between the WW_{MFC} and ACE_{MFC} . The EIS data was fitted with an EEC to yield precise values for the ohmic resistance (R_u), charge transfer resistance (R_p), and the capacitance (C) for the test MFCs (**Figure 7**). As expected, the electrochemical impedance in the test MFCs decreased with the increasing biofilm age (**Figure 7**). For example, in the WW_{MFC} , the R_p decreased from $6.73 \text{ k}\Omega\cdot\text{cm}^2$ (BA = 36 days) to $1.82 \text{ k}\Omega\cdot\text{cm}^2$ (BA = 58 days) over 22 days, and further decreased to $1.53 \text{ k}\Omega\cdot\text{cm}^2$ (BA = 75 days) in the subsequent 17 days (**Figure 7**). Similarly, in ACE_{MFC} , the R_p ($0.11 \text{ k}\Omega\cdot\text{cm}^2$) for BA = 75 days was 2 fold lower than that for BA = 36 days ($0.27 \text{ k}\Omega\cdot\text{cm}^2$) (**Figure 7**). During long-term MFC operation, the growth of electrochemically active biofilm on the anode surface is expected, decreasing the anodic polarization resistance (Ramasamy et al., 2008), and optimizing

electricity generation from the wastewater. Further, as discussed in section 3.6, increasing biofilm age resulted in increasing power densities in the test MFCs. As shown in **Figure 7**, for BA = 75 days, the R_p values for the ACE_{MFC} ($R_p = 0.11 \text{ k}\Omega\cdot\text{cm}^2$), using simple carbon substrate, is an order of magnitude lower than the WW_{MFC} ($1.53 \text{ k}\Omega\cdot\text{cm}^2$) with complex carbonaceous matter. Compared to the ACE_{MFC}, the Nyquist plots for WW_{MFC} extend into the low frequency region, implying slow bio-electrochemical oxidative processes with the wastewater. Nevertheless, as discussed in Section 3.4, the power density profiles in the WW_{MFC} became comparable to the ACE_{MFC}. There were no significant differences between the ohmic losses (R_u) in the ACE_{MFC} compared to the WW_{MFC} (**Figure 7**). The ohmic losses were at least 10 fold lower compared to the polarization losses (**Figure 7**). Further, the R_u values decreased significantly within the first 75 days of the fed-batch operation. In the ACE_{MFC}, the R_u ($0.13 \text{ k}\Omega \text{ cm}^2$) decreased by 28% as the biofilm age increased from 36 to 75 days; similarly, in WW_{MFC}, the R_u ($0.09 \text{ k}\Omega \text{ cm}^2$; BA = 75 days) decreased by nearly 60% over 39 days of fed-batch operation ($0.23 \text{ k}\Omega \text{ cm}^2$; BA = 36 days).

-----FIGURE 7-----

3.2.5 Voltammetry Tests.

The major findings from the CV results for the ACE_{MFC}, WW_{MFC}, and the controls (Figure 8a-8d) are summarized in **Table S4**. The controls did not yield any peaks during the CV tests. The ACE_{MFC} has exhibited a redox peak at -0.37 V (vs. SHE) for BA = 120 days, implying that the redox-active species is likely Ferredoxin (-0.398 vs. SHE) (Cammack et al., 1977; Smith and Feinberg, 1990). In the WW_{MFC}, for BA = 120 days, the CV peak was observed at -0.19V (vs. SHE), reflecting the redox characteristics of the cytochrome outer membrane cytochromes (OmcB) (-0.19 V vs SHE) (Fricke et al., 2008; Magnuson et al., 2001). We observed a similar

peak for the WW_{MFC} using planktonic microbes (without biofilm) at -0.195 V (vs SHE) (**Figure S9b**). The literature suggests that the *G. sulfurreducens* uses an OmcB to transfer electrons to a solid electron acceptor. Further, the prior CV studies with *G. sulfurreducens* have established a linear relationship between the peak current and the scan rate.

We carried out additional CV tests for the two test MFCs, for BA = 120 days, using four different scan rates (1, 5, 10 and 50 mV/s) with 15 minutes of equilibration between each scan (**Figure 8a, 8c**). The redox peak occurs approximately at a potential of -0.492 V (vs. Ag/AgCl). As shown in **Figure 8a** and **8c**, peak size increased with increasing scan rate, which can be attributed to the size of the diffusion layer and the time taken to record the scan. The results indicate the peak current is proportional to the square root of the scan rate (**Figure 8b, 8d**). The lower scan rates yield definitive peaks, facilitating the identification of possible redox mediators. Data in **Figures 8b** and **8d** suggest a linear relationship between the peak current (i_p) and the square root of the scan rate (v), implying a diffusion-controlled processes during electron transfer from the outer-membrane cytochromes to the redox enzymes in wastewater. The ratio of anodic peak current (i_{pa}) and cathodic peak current (i_{pc}) in the two test MFCs was less than unity (**Figure 8b, 8d**), implying that the participating redox-active species follow quasi-reversible reactions.

-----FIGURE 8-----

Compared to the CV tests, the DPV provides improved sensitivity and facilitates the identification of characteristic peaks, while canceling out non-faradic, capacitive current (background current). In the ACE_{MFC} with BA=125 days, the CV tests showed a cathodic peak at -0.625 V (vs. Ag/AgCl) with the peak height 1.15 mA (**Figure S10b**), while the DPV tests showed a well-defined peak at -0.625 V (vs. Ag/AgCl) with a peak height of 9.37 mA (**Figure**

S10a). For the WW_{MFC} with BA = 125 days, the CV tests exhibited a peak at -0.58 V (vs. Ag/AgCl) with the peak height of 0.011mA (**Figure S10d**), while the DPV results indicated a peak at -0.594 V (vs. Ag/AgCl) with a peak height of 2.39 mA (**Figure S10c**). The peak height in the DPV is related to the abundance of the electroactive species in the cell. DPV on both the test MFCs contained a broad peak at redox potentials similar to that obtained in CV. The increased peak current in the DPV tests (compared to CV) implies their potential for a greater accumulation of charge that can be effectively transferred to the anode.

3.3. Corrosion

Our results suggest that, compared to the primary clarifier effluent (WW), the MFC effluent introduces minimal corrosion risks to metal components in the CWRS. The corrosion rates of the low carbon steel (LCS) exposed to MFC effluent lies in the range of 0.009 and 0.06 mm/yr and meets the recommended standards shown in **Table 1**. The results indicate that the corrosion rates at ambient conditions (25 °C) are lower than the rates measured at 40 °C. The corrosion rates of the four waster systems decreased as: $WW_{40} > WW_{25} > MFC_{40} > MFC_{25}$. Lower corrosion rates for the MFC effluent, in comparison to the WW, are further corroborated with the polarization resistance (R_p) profiles: $WW_{25} < WW_{40} < MFC_{40} < MFC_{25}$ (**Figure 9a**). Higher R_p , corresponds to lower corrosion rates, indicating the MFC_{25} and MFC_{40} pose the least risk for corrosion. The R_p for the WW_{40} ($3.04 \text{ k}\Omega \cdot \text{cm}^2$) was at least 10 fold lower than the WW_{25} ($30.78 \text{ k}\Omega \cdot \text{cm}^2$); and the corrosion rate for WW_{40} (0.28 mm/yr) was 7368 fold higher than WW_{25} (0.000038 mm/yr). The OCP values for the WW_{40} and WW_{25} were negative compared to the MFC_{40} and MFC_{25} (**Figure 9b**), indicating the lower potential for the corrosion of LCS exposed to the MFC effluent. In the Nyquist plots for the test MFCs, the real axis value at the high frequency intercept corresponds to the solution resistance, and the real axis value at the low

frequency intercept corresponds to the total impedance, equivalent to the sum of the polarization resistance and the solution resistance. The Nyquist plots corroborate that low steel carbon exposed to WW₄₀ is least resistant to corrosion (at different time scales: 2, 6, 16, 24, 30, 42, 60 h), in comparison to WW₂₅, MFC₄₀ and MFC₂₅ (**Figure 9c**). The external electrical circuit analysis yielded the precise values for charge transfer resistance (R_{ct}) and ohmic resistance (R_u) of the relevant electrochemical reactions affecting the corrosion. The R_{ct} in WW₂₅ (2.25 k Ω .cm²) was 9 fold lower than that for MFC₂₅ (21.1 k Ω .cm²).

-----FIGURE 9-----

3.4 WW polarization performance.

The electric power generated from the wastewater treatment can be used to meet the energy requirements required to maintain the flow and pressure drop for the UF operation (Figure 1). During the initial phases of the fed-batch operation, the polarization tests did not indicate significant differences between the test MFCs. However, the power densities in both the test MFCs increased with increasing biofilm age, and the performance difference between the test MFCs was amplified within first 50 days of the operation (**Figure S11**). For example, for BA = 77 days, the peak current density for WW_{MFC} and ACE_{MFC} was 221.8 mA/m² and 237.9 mA/m², respectively, and the corresponding peak power density were 37.8 mW/m² and 87.2 mW/m² (**Figure S11**). However, considering that the chemical energy available during the oxidation of COD in the wastewater can be captured as electric current, it is promising to note that the peak current density for the WW_{MFC} (431.24 mA/m²) was only 1.5 fold smaller than the ACE_{MFC} (636.2 mA/m²); the corresponding peak power density (143.2 mW/m²) in the WW_{MFC} was 2.2 fold smaller than ACE_{MFC} (311.61 mW/m²) (**Figure S11**). A detailed life-cycle analysis

is underway to assess and compare the overall environmental benefits of using the reclaimed water from the MFC/UF systems with the conventional cooling water sources.

3.5 MFC/UF effluent quality

Table 4 summarizes results for the 15 water quality parameters measured for i) the MFC effluent (upstream; **Figure 1**) and ii) UF effluent (i.e., reclaimed water) (downstream; **Figure 1**) from eleven different UF configurations (**Table 2**). The measured pH (6.23 to 6.8) and the conductivity (1.02-1.56 mS/cm) of the reclaimed water met EPRI guidelines defined in **Table 1**. The results indicate that the COD removal after UF ranges between 91-98%, and in most cases the COD concentration in the reclaimed water meets the EPRI standard of 50 mg/L (the one exception is the BET-SO₃⁻ membrane with flux > 281 L m⁻² h⁻¹). The MFC/UF unit configured with the UF membrane #11 unit (HTP-PGP, N(CH₃)₃⁺; flux = 84 L m⁻² h⁻¹) achieved 97% COD removal, generating reclaimed water with a COD concentration as low as 17.8 mg/L. The results imply that the COD remnants in the reclaimed water generated by the MFC/UF effluent will not exert an excess demand in presence of disinfectants (e.g., ClO₂) typically used to control microbial growth in CWRS (DiFilippo and Maulbetsch, 2003). Except for Fe and S, the metal concentration in the reclaimed water generated by all the eleven MFC/UF effluents meets EPRI standards (**Table 4**). As discussed in Section 3.3, the results indicate that the MFC effluent offers minimal corrosion risks to the metal components in CWRS.

4.0 Conclusions

We demonstrate the feasibility of using an integrated microbial fuel cell/ultrafiltration as a decentralized module for generating cooling water from municipal wastewater without additional buffers or chemical supplements. The MFC/UF process generated high quality cooling

water that meets EPRI recommendations for pH, conductivity, COD, and metals. The current study has established that the MFC effluent, in comparison to the municipal wastewater, poses minimal corrosion risks to metal components at both 25 °C and 40 °C. However, further studies are required to evaluate the corrosion characteristics of the MFC effluent in realistic flow conditions similar to those encountered in cooling water recirculation systems, especially in the presence of disinfectants. We also anticipate that monovalent ions (e.g. Cl), divalent metals (e.g. Fe, Ca, Mg, S, Zn) and trivalent metals (e.g. Al) in the anolyte can be separated from the anode compartment through electrodeposition to contaminate the electrolyte in cathode chamber. The cation exchange membrane in the current study is also known to promote transport of cationic species (e.g. Fe^{2+} , Ca^{2+}) to the cathode. In such cases, the MFCs can be configured with a desalination unit or a capacitive desalination unit, but at an expense of reduction in the overall power output.

Supporting information includes details on monomer library used for HTP-PGP testing and synthesis; hardware, start-up characteristics, AC EIS circuit, anodic polarization, polarization response and CVs for fuel cells; and corrosion reactor.

5.0 Acknowledgements

We acknowledge the funding support from NYSERDA and Electric Power Research Institute (EPRI). Gadhamshetty acknowledges the partial funding support from National Science Foundation CAREER Award (#1454102), NASA award (NNX16AQ98A) and the South Dakota Board of Regents under the auspices of the Surface Engineering Research Center (SERC).

6.0 References

- Bell, R., Conley, E., 1987. Recommended practices for operating and maintaining steam surface condensers, Electric Power Research Institute.
- Bhattacharjee, S., Datta, S., Bhattacharjee, C., 2006. Performance study during ultrafiltration of Kraft black liquor using rotating disk membrane module. *Journal of Cleaner Production* 14(5), 497-504.
- Bourgeois, K.N., Darby, J.L., Tchobanoglous, G., 2001. Ultrafiltration of wastewater: effects of particles, mode of operation, and backwash effectiveness. *Water research* 35(1), 77-90.
- Cammack, R., Rao, K.K., Barger, C.P., Hutson, K., Andrew, P., Rogers, L., 1977. Midpoint redox potentials of plant and algal ferredoxins. *Biochem. J* 168, 205-209.
- Cao, X., Huang, X., Liang, P., Xiao, K., Zhou, Y., Zhang, X., Logan, B.E., 2009. A new method for water desalination using microbial desalination cells. *Environmental science & technology* 43(18), 7148-7152.
- Cassini, A., Tessaro, I., Marczak, L., Pertile, C., 2010. Ultrafiltration of wastewater from isolated soy protein production: a comparison of three UF membranes. *Journal of Cleaner Production* 18(3), 260-265.
- Cheng, S., Dempsey, B.A., Logan, B.E., 2007. Electricity generation from synthetic acid-mine drainage (AMD) water using fuel cell technologies. *Environmental science & technology* 41(23), 8149-8153.
- Cheng, S., Logan, B.E., 2011. Increasing power generation for scaling up single-chamber air cathode microbial fuel cells. *Bioresource technology* 102(6), 4468-4473.
- Chien, S.-H., 2010. Use of impaired waters in power plant cooling tower system: Review of regulations and feasibility analysis, University of Pittsburgh.
- Chien, S.-H., Chowdhury, I., Hsieh, M.-K., Li, H., Dzombak, D.A., Vidic, R.D., 2012. Control of biological growth in recirculating cooling systems using treated secondary effluent as makeup water with monochloramine. *Water research* 46(19), 6508-6518.
- Cho, J., Amy, G., Pellegrino, J., 2000. Membrane filtration of natural organic matter: comparison of flux decline, NOM rejection, and foulants during filtration with three UF membranes. *Desalination* 127(3), 283-298.
- Clesceri, L.S., Greenberg, A.E., Eaton, A.D., 1998. Standard methods for the examination of water and wastewater, American Public Health Association, Washington, DC.
- DiFilippo, M., Maulbetsch, J., 2003. Use of Degraded Water Sources as Cooling Water in Power Plants, Electric Power Research Institute, California Energy Commission.
- Dong, Y., Qu, Y., He, W., Du, Y., Liu, J., Han, X., Feng, Y., 2015. A 90-liter stackable baffled microbial fuel cell for brewery wastewater treatment based on energy self-sufficient mode. *Bioresource technology* 195, 66-72.
- Duclos-Orsello, C., Li, W.Y., Ho, C.C., 2006. A three mechanism model to describe fouling of microfiltration membranes. *JOURNAL OF MEMBRANE SCIENCE* 280(1-2), 856-866.
- El-Abbassi, A., Khayet, M., Hafidi, A., 2011. Micellar enhanced ultrafiltration process for the treatment of olive mill wastewater. *Water research* 45(15), 4522-4530.
- Ellis, T.G. 2013. Chemistry of Wastewater http://www.eolss.net/eolssamplechapters/c06/e6-13-04-05/E6-13-04-05-TXT-04.aspx#3._Wastewater_Composition. (accessed Jan, 2015).
- EPRI, 2011. Water Use for Electricity Generation and Other Sectors: Recent Changes (1985-2005) and Future Projections (2005-2030)

- EPRI. 2012. Water Treatment for Power Plant Cooling Towers: A supplement to the EPRI 2012 RFI for those unfamiliar with the power industry.
http://mydocs.epri.com/docs/PublicMeetingMaterials/0712/watertreatment_RFI_Final.pdf.
- Fogg, A., Gadhamshetty, V., Franco, D., Wilder, J., Agapi, S., Komisar, S., 2015. Can a microbial fuel cell resist the oxidation of Tomato pomace? *Journal of Power Sources* 279, 781-790.
- Forrestal, C., Stoll, Z., Xu, P., Ren, Z.J., 2015. Microbial capacitive desalination for integrated organic matter and salt removal and energy production from unconventional natural gas produced water. *Environmental Science: Water Research & Technology* 1(1), 47-55.
- Frayne, C., 1999. *Cooling water treatment: Principles and practice*, Chemical Publishing Company.
- Fricke, K., Harnisch, F., Schröder, U., 2008. On the use of cyclic voltammetry for the study of anodic electron transfer in microbial fuel cells. *Energy & Environmental Science* 1(1), 144-147.
- Gadhamshetty, V., Gude, V.G., Nirmalakhandan, N., 2014. Thermal energy storage system for energy conservation and water desalination in power plants. *Energy* 66, 938-949.
- Gao, W., Liang, H., Ma, J., Han, M., Chen, Z.-l., Han, Z.-s., Li, G.-b., 2011. Membrane fouling control in ultrafiltration technology for drinking water production: a review. *Desalination* 272(1), 1-8.
- Gude, V.G., 2015. Energy and water autarky of wastewater treatment and power generation systems. *Renewable and Sustainable Energy Reviews* 45, 52-68.
- Henze, M., Comeau, Y., 2008. *Wastewater characterization. Biological wastewater treatment: principles, modelling and design*. IWA Publishing, London, 33-52.
- Ho, C.C., Zydney, A.L., 2000. A combined pore blockage and cake filtration model for protein fouling during microfiltration. *Journal of Colloid and Interface Science* 232(2), 389-399.
- Howell, A., Saxon, G. 2005. The practical application and innovation of cleaning technology for condensers, pp. 109-117, American Society of Mechanical Engineers.
- Hsieh, M.-K., Li, H., Chien, S.-H., Monnell, J.D., Chowdhury, I., Dzombak, D.A., Vidic, R.D., 2010. Corrosion control when using secondary treated municipal wastewater as alternative makeup water for cooling tower systems. *Water Environment Research* 82(12), 2346-2356.
- Katsoufidou, K., Yiantsios, S.G., Karabelas, A.J., 2008. An experimental study of UF membrane fouling by humic acid and sodium alginate solutions: the effect of backwashing on flux recovery. *Desalination* 220(1-3), 214-227.
- Katsoufidou, K., Yiantsios, S.G., Karabelas, A.J., 2007. Experimental study of ultrafiltration membrane fouling by sodium alginate and flux recovery by backwashing. *JOURNAL OF MEMBRANE SCIENCE* 300(1-2), 137-146.
- Kilduff, J.E., Mattaraj, S., Sensibaugh, J., Pieracci, J.P., Yuan, Y.X., Belfort, G., 2002. Modeling flux decline during nanofiltration of NOM with poly(arylsulfone) membranes modified using UV-assisted graft polymerization. *Environmental Engineering Science* 19(6), 477-495.
- Kim, J.-S., Kim, B.-G., Lee, C.-H., Kim, S.-W., Jee, H.-S., Koh, J.-H., Fane, A., 1997. Development of clean technology in alcohol fermentation industry. *Journal of Cleaner Production* 5(4), 263-267.

- Kimura, K., Hane, Y., Watanabe, Y., Amy, G., Ohkuma, N., 2004. Irreversible membrane fouling during ultrafiltration of surface water. *Water research* 38(14), 3431-3441.
- Laîné, J.-M., Vial, D., Moulart, P., 2000. Status after 10 years of operation—overview of UF technology today. *Desalination* 131(1), 17-25.
- Li, H., Hsieh, M.-K., Chien, S.-H., Monnell, J.D., Dzombak, D.A., Vidic, R.D., 2011. Control of mineral scale deposition in cooling systems using secondary-treated municipal wastewater. *Water research* 45(2), 748-760.
- Lister, D.H., 2007. *Power Plant Materials*. Thermal Power Plants 1.
- Liu, W., Chien, S.-H., Dzombak, D.A., Vidic, R.D., 2014. Scaling Control for Heat Exchangers in Recirculating Cooling Systems Using Treated Municipal Wastewater. *Industrial & Engineering Chemistry Research* 53(42), 16366-16373.
- Luo, H., Xu, P., Roane, T.M., Jenkins, P.E., Ren, Z., 2012. Microbial desalination cells for improved performance in wastewater treatment, electricity production, and desalination. *Bioresource technology* 105, 60-66.
- Magnuson, T., Isoyama, N., Hodges-Myerson, A., DAVIDSON, G., Maroney, M., Geesey, G., Lovley, D., 2001. Isolation, characterization and gene sequence analysis of a membrane-associated 89 kDa Fe (III) reducing cytochrome c from *Geobacter sulfurreducens*. *Biochem. J* 359, 147-152.
- Marshall, A., Munro, P., Trägårdh, G., 1993. The effect of protein fouling in microfiltration and ultrafiltration on permeate flux, protein retention and selectivity: a literature review. *Desalination* 91(1), 65-108.
- Mathuriya, A.S., Yakhmi, J., 2014. Microbial fuel cells to recover heavy metals. *Environmental Chemistry Letters* 12(4), 483-494.
- McCoy, J.W., 1974. *The chemical treatment of cooling water*, Chemical Publishing Company New York.
- Metrohm. 2014. Power plant analysis. <http://pdf.directindustry.com/pdf/metrohm/power-plant-analysis-quality-control-power-plants-process-water-turbine-oils-fuels-operating-materials/15372-665762.html>. (accessed December, 2014).
- Pant, D., Van Bogaert, G., Diels, L., Vanbroekhoven, K., 2010. A review of the substrates used in microbial fuel cells (MFCs) for sustainable energy production. *Bioresource technology* 101(6), 1533-1543.
- Pescod, M.B. 2015. Wastewater characteristics and effluent quality parameters. <http://www.fao.org/docrep/t0551e/t0551e03.htm>. (accessed December, 2015).
- Prisciandaro, M., Capocelli, M., Piemonte, V., Barba, D., 2016. Process analysis applied to water reuse for a “closed water cycle” approach. *Chemical engineering journal* 304, 602-608.
- Ramasamy, R.P., Ren, Z., Mench, M.M., Regan, J.M., 2008. Impact of initial biofilm growth on the anode impedance of microbial fuel cells. *Biotechnology and bioengineering* 101(1), 101-108.
- Ren, Z., Yan, H., Wang, W., Mench, M.M., Regan, J.M., 2011. Characterization of microbial fuel cells at microbially and electrochemically meaningful time scales. *Environmental science & technology* 45(6), 2435-2441.
- Rozendal, R.A., Hamelers, H.V., Rabaey, K., Keller, J., Buisman, C.J., 2008. Towards practical implementation of bioelectrochemical wastewater treatment. *Trends in biotechnology* 26(8), 450-459.

- Shrestha, N., Fogg, A., Franco, D., Wilder, J., Komisar, S., Gadhamshetty, V., 2016. Electricity generation from defective tomatoes. *Bioelectrochemistry*.
- Smith, E.T., Feinberg, B., 1990. Redox properties of several bacterial ferredoxins using square wave voltammetry. *Journal of Biological Chemistry* 265(24), 14371-14376.
- Stillwell, A.S., Webber, M.E., 2014. Geographic, technologic, and economic analysis of using reclaimed water for thermoelectric power plant cooling. *Environmental science & technology* 48(8), 4588-4595.
- Taniguchi, M., Kilduff, J.E., Belfort, G., 2003a. Modes of natural organic matter fouling during ultrafiltration. *Environmental Science & Technology* 37(8), 1676-1683.
- Taniguchi, M., Kilduff, J.E., Belfort, G., 2003b. Low fouling synthetic membranes by UV-assisted graft polymerization: monomer selection to mitigate fouling by natural organic matter. *Journal of Membrane Science* 222(1), 59-70.
- Tian, Y., Li, H., Li, L., Su, X., Lu, Y., Zuo, W., Zhang, J., 2015. In-situ integration of microbial fuel cell with hollow-fiber membrane bioreactor for wastewater treatment and membrane fouling mitigation. *Biosensors and Bioelectronics* 64, 189-195.
- Tortora, F., Innocenzi, V., Prisciandaro, M., Vegliò, F., di Celso, G.M., 2016. Heavy Metal Removal from Liquid Wastes by Using Micellar-Enhanced Ultrafiltration. *Water, Air, & Soil Pollution* 227(7), 1-11.
- USEPA. 2004. Guidelines for water reuse, EPA/625/R-04/108. USEPA and US Agency for International Development, Washington, DC.
- Wang, Y.-K., Sheng, G.-P., Li, W.-W., Huang, Y.-X., Yu, Y.-Y., Zeng, R.J., Yu, H.-Q., 2011. Development of a novel bioelectrochemical membrane reactor for wastewater treatment. *Environmental science & technology* 45(21), 9256-9261.
- Xu, L., Zhang, G.-q., Yuan, G.-e., Liu, H.-y., Liu, J.-d., Yang, F.-l., 2015. Anti-fouling performance and mechanism of anthraquinone/polypyrrole composite modified membrane cathode in a novel MFC-aerobic MBR coupled system. *RSC Advances* 5(29), 22533-22543.
- Ye, Y., Le Clech, P., Chen, V., Fane, A.G., Jefferson, B., 2005. Fouling mechanisms of alginate solutions as model extracellular polymeric substances. *Desalination* 175(1), 7-20.
- Yuan, H., He, Z., 2015. Integrating membrane filtration into bioelectrochemical systems as next generation energy-efficient wastewater treatment technologies for water reclamation: a review. *Bioresource technology* 195, 202-209.
- Zhou, M., Liu, H., Kilduff, J.E., Langer, R., Anderson, D.G., Belfort, G., 2009a. High throughput synthesis and screening of new protein resistant surfaces for membrane filtration. *AIChE Journal* 56(7), 1932-1945.
- Zhou, M., Liu, H., Kilduff, J.E., Langer, R., Anderson, D.G., Belfort, G., 2009b. High-Throughput Membrane Surface Modification to Control NOM Fouling. *Environmental Science & Technology* 43(10), 3865-3871.
- Zhou, M.Y., Liu, H.W., Kilduff, J.E., Langer, R., Anderson, D.G., Belfort, G., 2010. High Throughput Synthesis and Screening of New Protein Resistant Surfaces for Membrane Filtration. *Aiche Journal* 56(7), 1932-1945.
- Zhou, M.Y., Liu, H.W., Kilduff, J.E., Langer, R., Anderson, D.G., Belfort, G., 2009c. High-Throughput Membrane Surface Modification to Control NOM Fouling. *Environmental Science & Technology* 43(10), 3865-3871.

Zhou, M.Y., Liu, H.W., Venkiteshwaran, A., Kilduff, J., Anderson, D.G., Langer, R., Belfort, G., 2011. High throughput discovery of new fouling-resistant surfaces. *Journal of Materials Chemistry* 21(3), 693-704.

Table 1. Power plant cooling system water quality criteria

Constituent	Units	US-EPA 2004	Current EPRI Standards (1998)
pH		6-9	NA*
COD	mg/L	50	NA*
Mg	mg/L	NA	35000
Ca (as CaCo ₃)	mg/L	50-450	NA*
Si	mg/L	NA	150
M Alkalinity	mg/L	60-280	NA*
Fe (total)	mg/L	NA	<0.5
Mn	mg/L	NA	<0.5
Cu	mg/L	NA	<0.1
Al	mg/L	NA	<1
S	mg/L	NA	5
Zn	mg/L	NA	NA
NH ₃	mg/L	2-15	<2
P	mg/L	10-400	NA
Cl ⁻	mg/L	20-350	NA
Conductivity	mS/cm	0.600-2.7	NA
Corrosion rate	mm/yr	<0.254 (Hsieh et al., 2010)	

Table 2. Experimental UF Conditions

Run	Membrane	Structure
1,2,11	$\text{N}(\text{CH}_3)_3^+$	
3,4,10	PEG	
5,6,9	BET SO_3^-	
7,8	30kDa PES (Control)	

NOTE: Monomer concentration was 0.2 M for runs 1 through 6 and 0.6 M for runs 9 through 11

Table 3. Model parameters for MFC flux and fouling resistance measurements.

Monomer concentration	0.2 M			0.6 M		
Variables	AR	BET SO ₃ ⁻	N(CH ₃) ₃ ⁺	AR	BET SO ₃ ⁻	N(CH ₃) ₃ ⁺
α_b , [m ² /kg solute]	2.61E-03	4.08E-03	3.41E-03	4.04E-03	6.63E-03	4.19E-03
α_c , [Pa m ⁴ s kg ⁻²]	2.91E+03	3.08E+02	3.19E+02	2.81E+03	9.40E+02	7.36E+02
$R_{c,o}$, [Pa m ² s kg ⁻¹]	1.43E+06	7.28E+05	3.88E+05	9.11E+05	2.99E+04	9.99E+00
$R_m+R_{c,o}$, [Pa m ² s kg ⁻²]	3.19E+06	1.40E+06	7.28E+05	2.70E+06	5.67E+05	5.99E+05
Q_o , [kg/s]	1.55E-05	1.60E-05	1.50E-05	1.74E-05	1.92E-05	1.90E-05

Table 4. Water Quality Parameters.

Constituent	Units	Wastewater	SD	Ultrafiltration												
				MFC effluent	SD	1	2	3	4	5	6	7	8	9	10	11
pH		7.06	0.02	6.84	0.07	6.23	6.80	6.33	6.51	6.70	6.20	6.71	6.47	6.63	6.44	6.70
COD	mg/L	827.8	39.05	55.25	11.11	0.00	40.25	0.00	0.00	70.25	22.75	48.58	36.92	61.08	45.25	17.75
Mg	mg/L	121.64	0.03	341.5	0.00	39.92	39.94	40.73	38.98	37.68	27.77	38.55	21.89	24.94	24.93	23.36
Ca (as CaCo3)	mg/L	2445	449.97	195.3	137.4	10.58	10.83	11.09	11.84	11.34	12.35	7.56	13.86	12.85	16.38	16.38
Si	mg/L	14.67	3.40	2.73	1.19	8.86	7.75	8.24	7.63	7.53	6.26	7.21	5.82	7.81	5.94	5.98
M Alkalinity	mg/L	620.0		600.0		-	-	-	-	-	-	-	-	-	-	-
Fe (total)	mg/L	1.13	0.48	2.72	3.82	3.83	3.38	3.26	3.18	3.16	2.48	3.02	4.71	4.36	4.54	4.38
Mn	mg/L	0.45	0.24	0.03	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cu	mg/L	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.02	0.02	0.01
Al	mg/L	0.35	0.20	0.03	0.04	0.01	0.01	0.02	0.03	0.01	0.00	0.01	0.05	0.01	0.03	0.03
S	mg/L	154.5	80.96	81.50	50.49	82.93	84.93	94.91	82.93	94.11	70.96	80.54	69.77	55.01	61.39	66.18
Zn	mg/L	1.92	2.71	0.03	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.00
NH ₃	mg/L	0.15	-	0.02	-	-	-	-	-	-	-	-	-	-	-	-
P	mg/L	1.11	-	0.85	-	-	-	-	-	-	-	-	-	-	-	-
Cl ⁻	mg/L	118.50	-	105.70	-	-	-	-	-	-	-	-	-	-	-	-
Conductivity	mS/cm	1.80	-	1.45	-	1.02	1.14	1.04	0.90	0.89	0.95	1.45	1.56	1.34	1.23	1.34
Corrosion rate	mm/yr	0.0890	-	0.0088	-	-	-	-	-	-	-	-	-	-	-	-

NOTE: Details on membrane run 1 to 11 found in Table 2. SD = standard deviation.

Figure 1. An integrated membrane and microbial fuel cell technology for enabling wastewater reuse in power plants. In this study, the MFCs were operated in a fed-batch mode. The spent-analyte (treated wastewater) from Cycles 6-17 was combined and used as the feed in the membrane module.

Figure 2. High throughput screening using MFC effluent: (a) static fouling test results, and (b) dynamic fouling test results both show selected monomers based on fouling index as a function of normalized resistance. Experimental details in Table 2.

Figure 3. Membrane permeability measured using ultra-pure water. For AR, the average membrane permeability is $5.20 \times 10^{-7} \text{ kg.m}^{-2}.\text{s}^{-1}.\text{Pa}^{-1}$. For BET SO_3^- , the permeability of 0.2 and 0.6 M monomer modified membrane is 4.55×10^{-7} and $3.17 \times 10^{-7} \text{ kg.m}^{-2}.\text{s}^{-1}.\text{Pa}^{-1}$, respectively. For $\text{N}(\text{CH}_3)_3$, the permeability of 0.2 and 0.6 M monomer modified membranes is 4.66×10^{-7} and $4.47 \times 10^{-7} \text{ kg.m}^{-2}.\text{s}^{-1}.\text{Pa}^{-1}$, respectively.

Figure 4. MFC effluent filtration results. Flux: (a) and (b); fouling resistance: (c) and (d); energy consumption: (e) and (f). Membranes: 0.2M monomer (a), (c) and (e); 0.6 M monomer (b), (d) and (f). Mass throughput of about 25g corresponds to a run time of about 1 and 0.5 hours. Symbols are experimental data, and black lines are fits of the combined pore blockage and cake filtration model. Experimental details in [Table 2](#).

Figure 5. COD Results: a) Temporal profile of COD; b) pH corresponding to COD. Experimental details in [Table S3](#).

Figure 6. Conductivity and pH results: a) Conductivity Vs days; b) pH Vs days for corresponding conductivity test. Experimental details in [Table S3](#).

Figure 7. Nyquist plots for WW_{MFC} and ACE_{MFC} for biofilm ages 36, 58 and 75 days. Inset graph shows a clear view of the high frequency region. Experimental details in Table S3.

Figure 8. Voltammetry test results: a) ACE_{MFC} at different scan rates (mV/s), biofilm age 120 days; b) Plot of Square root scan rate(mV/s) Vs peak current (A) for ACE_{MFC}; c) WW_{MFC} at different scan rates (mV/s) biofilm age 120 days; d) Plot of Square root scan rate(mV/s) Vs peak current for WW_{MFC}

Figure 9. The comparison of MFC effluent and primary clarifier effluent: a) Average polarization resistance and corrosion resistance of the low steel carbon sample; b) Open circuit potential of the corrosion cell using wastewater and MFC effluent at 25 and 40°C; c) Nyquist plot of the low steel carbon samples at 60 h for 25°C and 40°C. Experimental details in [Table S3](#).