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Article

Minimum Performance Requirements for Microbial Fuel Cells to Achieve Energy-Neutral Wastewater Treatment

Zachary A. Stoll ¹, Jan Dolfig ²  and Pei Xu ^{1,*} 

¹ Department of Civil Engineering, New Mexico State University, Las Cruces, NM 88003, USA; zstoll9@gmail.com

² School of Engineering, Newcastle University, Newcastle upon Tyne NE1 7RU, UK; jan.dolfig@newcastle.ac.uk

* Correspondence: pxu@nmsu.edu; Tel.: +1-575-646-5870

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Abstract: Microbial fuel cells (MFCs) have recently achieved energy-positive wastewater treatment at pilot scale. Despite these achievements, there is still a limited understanding as to whether all wastewaters contain sufficient amounts of energy and, if so, whether MFCs can capture a sufficient amount of energy to offset electrical energy requirements in the wastewater treatment process. Currently, there are no tools or methods available that can determine whether an MFC can be energy-neutral *a priori*. To address this, we derived a simple relationship by setting the electrical energy requirements of a wastewater treatment facility equal to the net energy output of the MFC, such that the resulting expression describes the minimum chemical oxygen demand (COD) removal needed to achieve energy-neutral treatment. The resulting equation is simply a function of electrical energy requirements, Coulombic Efficiency, and cell voltage. This work provides the first ever quantitative method for determining if the MFCs are feasible to achieve energy-neutral treatment for a given wastewater and what level of performance is needed.

Keywords: microbial fuel cell; wastewater treatment; energy-neutral treatment; water-energy; organic degradation; chemical oxygen demand removal; energy analysis; electrical energy demand

1. Introduction

Energy and water security have become global challenges in recent years due to climate change, water shortages, rising energy demand, and increasing material costs [1]. Water and wastewater treatment are expensive and energy intensive processes that collectively cost over \$4 billion [2], consuming 3–4% of the total U.S. energy budget each year [3]. Implementing more energy efficient treatment systems is seen as a strategy to simultaneously improve sustainability and reduce operating expenses. For example, a 10% reduction in annual energy consumption would save 5 billion kilowatt-hours and \$400 million in energy costs [2]. With approximately half of a wastewater treatment plant's energy budget being used for aeration [4], implementing anaerobic treatment processes has been employed to significantly reduce treatment costs and energy consumption.

One emerging aeration-free treatment technology is the microbial fuel cell (MFC), which can treat wastewater and generate electricity at the same time. In the last decade, MFCs have been studied extensively in the laboratory, but so far only a few on-site pilot-scale (>10 L) bioelectrochemical systems have been built and tested, attaining varying levels of success [5–11]. Recent pilot studies have demonstrated that MFCs can be self-sufficient [5,7,12], in the sense that the energy captured from the MFCs could be used to power the feed and/or recirculation pump(s).

Aside from pumping energy, there are additional electrical energy sinks within a wastewater treatment plant (WWTP) such as mixing (e.g., aerated grit chambers, biological aeration), filtration, disinfection and other ancillary needs such as lighting and monitoring. Because the oxidation of organics in the anode chamber of MFCs is an anaerobic process, the MFCs have the advantage of generating very little biomass. Indeed, researchers have observed sludge yields in MFCs ranging from 0.07 to 0.22 gVSS/gCOD (gram of volatile suspended solids per gram of chemical oxygen demand removed), which is lower than yields for aerobic systems (0.54 gVSS/gCOD) [13,14]. Therefore, sludge production should be minimal in MFCs, resulting in lower energy costs for sludge handling.

Despite being considered as a potential technology to achieve energy-neutral treatment, to the best of our knowledge, the MFC has not been explicitly considered in its ability to offset pumping and additional electrical energy sinks, leaving a knowledge gap as to how much energy an MFC would need to generate to be energy-neutral. At this time, no energy analysis framework exists for determining if MFCs can achieve energy-neutral treatment and the interdependency between the factors that determine performance and energy consumption has not been established. Therefore, it is not possible to answer questions such as: Is it more beneficial to have an MFC system with a 10% higher Coulombic Efficiency or a 10% higher voltage? What is the minimum theoretical chemical oxygen demand (COD) removal needed to achieve energy-neutral treatment for a given reactor?

The purpose of this study is to begin to develop a quantitative understanding of what performance requirements are needed for an MFC to achieve energy-neutral treatment. We choose to evaluate energy-neutral wastewater treatment as minimum standard, because it represents a concrete point, where energy sinks equal energy sources, providing a well-defined baseline and minimum goal to aim for. In this paper, we develop a relationship that describes the COD removal needed in order for MFCs to achieve energy-neutral treatment based on the minimum cell voltage (E_{MFC}) and Coulombic Efficiency (CE). We assume that the secondary aerobic treatment system is replaced by MFCs in a given facility and adopt values for electrical energy requirements based on literature values. We develop general equations for the MFC's energy output and then set this equal to the electrical energy requirements at the WWTP to describe energy-neutral treatment. With the resulting expression, the feasibility of attaining energy-neutral treatment is discussed, as well as new research opportunities.

2. Materials and Methods

2.1. Steady-State Energy Sinks

To begin the derivation, we assume a wastewater treatment plant with an influent lift station that pumps water to the entrance works with coarse screening and grit removal. Water flows by gravity to primary clarifiers, through the MFC module then to disinfection. We consider only the energy required for treatment within the facility and do not include energy required for collection and conveyance. The total energy use ($N_{WWTP, T}$, kWh/day) can be calculated by multiplying the normalized energy usage (N_{WWTP} , kWh/m³) by the flow rate (Q , m³/s) such that:

$$N_{WWTP, T} = N_{WWTP} \cdot Q \cdot 86,400 \frac{s}{d} \quad (1)$$

2.2. Steady-State Energy and Power Generation

We realize that an array of MFCs would be needed to treat large volumes of wastewater and that the MFCs would be configured and connected together in a way that optimizes performance. However, for the initial efforts of this paper, we will model a single MFC, assuming a mature biofilm with an air cathode treating wastewater at a steady state. The MFC power (P_{MFC} , W) and energy generated (N_{MFC} , kWh/day) can be expressed according to Logan et al. [15]:

$$P_{MFC} = E_{MFC} \cdot I_{SS} \quad (2)$$

$$N_{MFC} = E_{MFC} \cdot I_{SS} \cdot t \cdot \frac{1 \text{ kW}}{1000 \text{ W}} \quad (3)$$

where E_{MFC} (V) is the cell voltage, I_{SS} is the steady-state current (A) and t is time (h/day).

The steady-state current for a continuous flow MFC can be derived from the definition of Coulombic Efficiency (CE) as described by Logan et al. [15]:

$$I_{SS} = F \cdot Q \cdot CE \cdot \Delta COD \cdot \frac{\text{mol } e^-}{8 \text{ gCOD}} \quad (4)$$

where F is Faraday's constant (96,485 C/mol), Q is the flow rate in m^3/s , CE is a percent expressed as a decimal, and ΔCOD is in g/m^3 . Thus,

$$N_{MFC} = E_{MFC} \cdot F \cdot Q \cdot CE \cdot \Delta COD \cdot \frac{\text{mol } e^-}{8 \text{ gCOD}} \cdot t \cdot \frac{1 \text{ kW}}{1000 \text{ W}} \quad (5)$$

2.3. Requirements for Energy-Neutral Wastewater Treatment

To determine the conditions in energy-neutral treatment will occur, the WWTP energy utilization rate (Equation (1)) is set equal to the energy output rate from the MFC (Equation (5)) such that:

$$N_{WWTP, T} = N_{MFC} \quad (6)$$

$$N_{WWTP} \cdot Q \cdot 86,400 \frac{\text{s}}{\text{d}} = E_{MFC} \cdot F \cdot Q \cdot CE \cdot \Delta COD \cdot \frac{\text{mol } e^-}{8 \text{ gCOD}} \cdot \frac{1 \text{ kW}}{1000 \text{ W}} \cdot t \quad (7)$$

Assuming the MFC runs for 24 h per day and that all the flow coming into the WWTP is treated by the MFC, the equation simplifies to

$$N_{WWTP} = \zeta \cdot E_{MFC} \cdot CE \cdot \Delta COD \quad (8)$$

where the constant $\zeta = 0.00345$ is the combined value of the constants on left and right-hand side of Equation (7), and has unit of $\text{C} \cdot \text{kWh} \cdot \text{s}^{-1} \cdot \text{gCOD}^{-1} \cdot \text{W}^{-1}$. This equation indicates that the MFC voltage (i.e., the difference in anode and cathode potentials), the CE (moles of electrons transferred to the anode divided by total moles of electrons available) and ΔCOD removed (i.e., total moles of electrons available) are the variables that determine the MFC's energy output (kWh/day).

Solving for ΔCOD yields Equation (8), which expresses the minimum COD removal needed for energy-neutral treatment as a function of N_{WWTP} , E_{MFC} , and CE . We believe this equation is useful in determining if a given wastewater stream has sufficient energy for an MFC to capture and determine what performance the MFC must achieve (cell voltage and CE) in order to be energy-neutral.

$$\Delta COD = \frac{N_{WWTP}}{\zeta \cdot E_{MFC} \cdot CE} \quad (9)$$

3. Results and Discussion

The purpose of this paper is to present a set of equations that can help determine what performance requirements needed to be energy-neutral, with the hopes that these equations will help determine if an MFC (or array of MFCs) can capture sufficient energy to offset energy demands at a wastewater treatment facility. The equations were developed in the previous section and the following sections determine: (1) the range of energy utilization at WWTPs (N_{WWTP}); and (2) the performance range MFCs typically operate in (the E_{MFC} , ΔCOD and CE parameters). Once the value range for each parameter is determined, they can be plugged into Equation (9) and the results are analyzed.

3.1. Energy Utilization at WWTPs

Several independent sources have determined the electrical energy usage for WWTPs. Using data from the U.S Environmental Protection Agency (EPA) Star Energy's database, researchers from the Lawrence Berkeley National Lab (LBNL) calculated the weighted-based average energy consumption of WWTPs as a function of the design capacity [4]. For WWTPs producing less than 7750 m³/day (2 million gallons per day, MGD), average energy intensity use is the highest and estimated to be 0.87 kWh/m³, whereas medium sized facilities with design capacities 27,000–60,500 m³/day (7–16 MGD) consume less energy per unit volume of wastewater treated (0.53 kWh/m³). The largest facilities (>60,500 m³/day) benefit the most from the economies of scale requiring only 0.42–0.45 kWh/m³, however, the law of diminishing returns is apparent, with WWTPs > 60,500 m³/day not consuming considerably more energy per unit volume of wastewater treated than facilities over 378,500 m³/day (100 MGD).

In comparison, Klein et al. surveyed several WWTPs in California and found the electrical energy use ranged from 0.53 to 0.78 kWh/m³. The California energy usage benchmark was also cited as being 0.69 kWh/m³ [16]. Yonkin et al. surveyed 174 WWTPs in New York State with capacities ranging from <3785 m³/day (1 MGD) to >284,000 m³/day (75 MGD) and also determined the average electrical energy used as a function of design capacity [17]. For WWTPs producing less than 3785 m³/day, average energy usage is significantly higher (0.9 kWh/m³) than the national average (0.32 kWh/m³) and all larger facilities (0.28 to 0.41 kWh/m³). Averaging all of these values yields an electrical energy use of 0.58 kWh/m³.

It is known that approximately half of the energy consumption at a WWTP is due to the aeration energy requirements for oxidizing biochemical oxygen demand (BOD) and ammonia (NH₃) in the activated sludge process [4]. Typical design values for air needed to oxidize BOD and NH₃ are 1.1 kg O₂/kg BOD and 4.6 kg O₂/kg NH₃, respectively [18]. According to Metcalf and Eddy [19], the average BOD and NH₃ concentrations for medium strength wastewater are 350 and 45 mg/L, respectively. If it is assumed that the effluent BOD and NH₃ values are 30 and 0 mg/L for surface water discharge, respectively, then for a given flow rate the energy required to oxidizing the BOD comprises 63% of the total aeration requirement. For this paper, we assume that MFCs will replace the activated sludge process and will offset the BOD aeration requirements, but not the ammonia aeration requirements. Therefore, the electrical energy requirements of a WWTP using an MFC instead of activated sludge are 69% of the values calculated by Yonkin et al. and Klien et al. (Figure 1). Thus, the electrical energy use (N_{WWTP}) at an "average" WWTP is 0.40 kWh/m³. We will use this value for N_{WWTP} for the remainder of the paper.

Note that the purpose of this paper is to provide a framework that will aid in developing a quantitative understanding of the conditions needed for an MFC to achieve energy-neutral treatment. Simplifying assumptions were made in this initial effort, such as the relative amount of oxygen needed for NH₃ oxidization was held constant at 37%, and the MFCs normalized energy utilization was held constant regardless of volume. However, Equation (8) is flexible in that it allows each term to be modified according to site-specific conditions. For example, the N_{WWTP} term can be modified on the left-hand side of Equation (8), which could be developed to quantify how MFC efficiency changes with volume, configuration, specific surface area (cathodic surface area/MFC volume), biofilm composition and other parameters. Additionally, the site-specific information pertaining to the relative amount of energy required to oxidize BOD for a given WWTP could also be used to further tune the N_{WWTP} term. These adjustments are outside the scope of this paper but warrant further investigation.

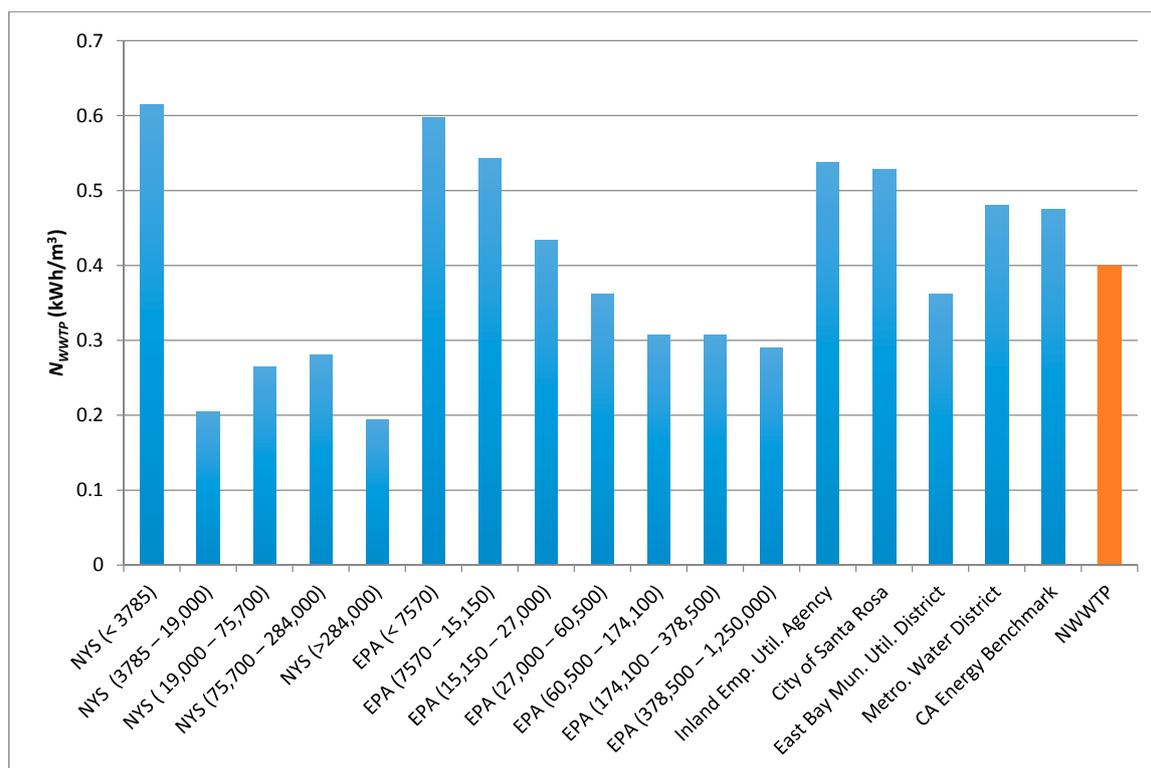


Figure 1. Energy consumption per unit volume (N_{WWTP}) for a given wastewater treatment plant (WWTP). NYS, New York State; EPA, United States Environmental Protection Agency; CA, California. Values inside parentheses indicate flow (m³/day).

3.2. Empirical Values for E_{MFC} , ΔCOD and CE in MFC Studies Using Real Wastewater

Literature values for E_{MFC} , ΔCOD and CE are presented in Table 1 for MFCs that treat real wastewater. We chose to not to evaluate MFCs that treat synthetic wastewater because it is known that the biofilm composition is different in MFCs that use real wastewater [20], and that higher performance is generated with synthetic wastewater, typically with more negative anode potentials and less positive cathode potentials [21,22].

The fuel cell voltage is the difference between the anode potential and the cathode potential. The electrode material, operating temperature, electrode spacing/reactor configuration, wastewater composition and microbial community at each electrode influence the respective electrode potentials. As such, the E_{MFC} values will vary study to study but tend to range between 0.17 and 0.50 V, with an average of 0.32 V, for MFCs treating real domestic wastewater. Higher voltages are not typically seen when treating wastewater so E_{MFC} above 0.50 V may not be practical, with a major reason being that real wastewater (compared to synthetic wastewater) contains more complex organic compounds that take longer for the biofilm to degrade. Slower organic biodegradation rates indicate less COD is consumed over a given time period, thus the transfer of electrons to the anode is slower, which typically results in lower anode potentials and lower E_{MFC} .

In general, electrons (energy) liberated from a substrate can either be used for biosynthesis of cellular compounds (e.g., proteins/enzymes, lipids, DNA (deoxyribonucleic acid), sugars, etc.) or to create energy carrier molecules (e.g., ATP (adenosine triphosphate) and NADH (nicotinamide adenine dinucleotide)). It is the formation of latter compounds that require electrons be transferred down an electrochemical gradient within the cell to a terminal electron acceptor (i.e., ATP synthesis via the electron transport chain). In MFCs and other bioelectrochemical cells, the terminal electron acceptor is the anode. As such, the CE is the fraction of electrons that are liberated from the substrate and transferred to the anode electrode. The remaining electrons do not get transferred to the anode as

they are tied up in the other biochemical processes mentioned above. Literature values of the CE for MFCs treating real wastewater range from 14% to 38%, and have an average of 24%. Lower CE values typically indicate that the exoelectrogens within the biofilm are using more of the energy extracted from the substrate for biosynthesis, not energy production, whereas higher CEs would indicate the opposite.

Table 1. Summary of typical MFC cell voltages (E_{MFC}) and Coulombic Efficiencies (CE) for MFCs treating real wastewater and assumed COD removals for high, medium and low strength wastewaters. Maximum Power Point values (MPP) are provided for reference.

Parameter	Value	P at MPP (W/m ²)	Volume (mL)	COD _{IN} (mg/L)	Δ COD (mg/L)	Notes	Ref
E_{MFC} (V)	0.17	2.4×10^{-5}	50	256	166	SC-MFC; No membrane	[23]
	0.19	2.9×10^{-5}	50	256	180	SC-MFC; ETFE membrane	[23]
	0.24	0.85 mW	100	410	-	HRT = 8.8 h; N1C config.	[24]
	0.27	0.95	7	-	92%	SC-MFC; 20 °C config.	[25]
	0.28	1.20	7	-	92%	SC-MFC; 30 °C config.	[25]
	0.28	0.94	130	210	71	SPA-U config.; Pt cathode	[26]
	0.30	0.59	7	-	92%	SC-MFC; 10 °C config.	[25]
	0.30	0.12	130	232	-	SC-MFC; $R_{ext} = 1000 \Omega$	[27]
	0.31	0.55 mW	100	410	-	HRT = 8.8 h; S2C config.	[24]
	0.33	0.33	130	303	-	SC-MFC; SEA config.; $R_{ext} = 1000 \Omega$	[28]
	0.33	0.30	28	292	-	HRT = 4 h; 23 °C; Pt cathode	[29]
	0.34	0.32	170	545	447	SC-MFC; Pt-NS; $R_{ext} = 100 \Omega$	[30]
	0.37	0.28	130	303	-	SC-MFC; SPA config.; $R_{ext} = 1000 \Omega$;	[28]
	0.40	0.16	170	330	195	SC-MFC; AC-CS; $R_{ext} = 300 \Omega$;	[30]
	0.42	0.89	130	210	59	SEA-U config.; Pt cathode	[26]
	0.45	0.21	27	300	-	SC-MFC; $R_{ext} = 1000 \Omega$; pH 8	[21]
	0.32	Average of literature values					This study
CE	0.13	0.89	130	210	59	SEA-U config.; Pt cathode	[26]
	0.14	-	26	439	-	SC-MFC; HRT = 2 h; $R_{ext} = 1000 \Omega$	[31]
	0.14	-	4000	280	196	Tubular MFC	[32]
	0.15	1.20	7	-	92%	SC-MFC; 30 °C config.	[25]
	0.17	0.95	7	-	92%	SC-MFC; 20 °C config.	[25]
	0.17	0.15	140	410	193	SC-MFC; HRT = 2.2 h; N1C config.	[24]
	0.18	0.10	140	410	134	SC-MFC; HRT = 2.2 h; S2C config.	[24]
	0.19	0.16	170	330	195	SC-MFC; AC-CS; $R_{ext} = 300 \Omega$	[30]
	0.22	-	26	439	-	SC-MFC; HRT = 2 h; $R_{ext} = 100 \Omega$	[31]
	0.23	0.28	130	303	242	SC-MFC; SPA config.; $R_{ext} = 1000 \Omega$	[28]
	0.25	0.59	7	-	92%	SC-MFC; 10 °C config.	[25]
	0.25	0.10	140	410	197	SC-MFC; HRT = 4.4 h; S2C config.	[24]
	0.26	0.30	28	292	-	HRT = 4 h; 30 °C; Pt cathode	[29]
	0.26	0.32	170	545	447	SC-MFC; Pt-NS; $R_{ext} = 100 \Omega$	[30]
	0.29	41 W/m ³	76	14,000	8260	TC-MFC; saline DWW; CEM	[33]
	0.29	0.11	140	410	267	SC-MFC; HRT = 8.8 h; S2C config.	[24]
	0.31	0.14	140	410	221	SC-MFC; HRT = 4.4 h; N1C config.	[24]
	0.31	0.33	130	303	182	SC-MFC; SEA config.; $R_{ext} = 1000 \Omega$	[28]
	0.36	0.13	140	410	283	SC-MFC; HRT = 8.8 h; N1C config.	[24]
	0.38	0.30	28	292	-	HRT = 4 h; 23 °C; Pt cathode	[29]
0.24	Average of literature values					This study	
COD _{IN} (mg/L)	2250	Assumed value for high strength WW					This study
	750	Assumed value for medium strength WW					This study
	250	Assumed value for low strength WW					This study
COD _{OUT} (mg/L)	100	Assumed lower limit of MFC COD removal					[31,34–36]
Δ COD (mg/L)	2150	Assumed value for COD removal with high strength WW as the substrate					This study
	650	Assumed value for COD removal with medium strength WW as the substrate					This study
	150	Assumed value for COD removal with low strength WW as the substrate					This study

Notes: SC, single chamber; TC, two chamber; ETFE, ethylene tetrafluoroethylene; HRT, hydraulic retention time; SPA, spaced electrode assembly; R_{ext} , external resistance; SEA, separator electrode assembly; SPA, closely spaced electrodes; S2C, a full brush evenly spaced between two cathodes; N1C, trimmed brush anodes near a single cathode; Pt, Platinum; NS, no separator; AC-CS, activated carbon cathode/cloth separator; DWW, domestic wastewater; CEM, cation exchange membrane; AC-CS, activated carbon cathode with cloth separator; Pt-NS, Pt cathode with no separator.

Several studies have shown that power density decreases significantly at COD concentrations below 100 mg/L [31,34–36]. As such, we assume the treated effluent COD is 100 mg/L and assume a high (2250 mg/L), medium (750 mg/L) and low-strength wastewater (250 mg/L). Examples of high-strength wastewaters (>2000 mg/L COD) include industrial wastes such as brewery, and food processing wastewater, as well as centrate streams in WWTPs. Medium and low-strength wastewaters include various domestic wastewaters.

3.3. Electrical Energy Generation from an MFC Using Average Values at Fixed CODs

In this section, we begin testing the model by using literature values for the right-hand side of Equation (8) (E_{MFC} , CE , and ΔCOD) to solve for values of N_{WWTP} and compare our calculated values with the average N_{WWTP} value of 0.40 kWh/m³ calculated in the section above. Values of N_{WWTP} were calculated at the three high, medium and low ΔCOD concentrations (2150, 650 and 150 mg/L) using Equation (8) and the average of the literature values for E_{MFC} (0.32 V) and CE (0.24). The N_{WWTP} for the high, medium and low-strength wastewaters is calculated to be 0.55, 0.17 and 0.04 kWh/m³, respectively. In comparison to the average energy utilization of 0.40 kWh/m³, only the high-strength wastewater would contain enough energy to offset a WWTP's energy requirements, if averaged E_{MFC} and CE values are used.

Equation (8) could be used to calculate the E_{MFC} and CE that the MFC would need to be energy-neutral (0.40 kWh/m³) and check if these values seem reasonable. As such, assuming medium strength wastewater ($\Delta COD = 650$ mg/L), the E_{MFC} and CE would need to increase such that their products equaled 0.18. This could be accomplished by generating higher voltages ($E_{MFC} = 0.77$ V and $CE = 24\%$), being more efficient ($E_{MFC} = 0.32$ V and $CE = 57\%$) or a combination of both ($E_{MFC} = 0.50$ V and $CE = 37\%$) to obtain a N_{WWTP} of 0.40 kWh/m³. According to our literature review summarized in Table 1, the ranges of E_{MFC} and CE are within what is typically seen (albeit at the higher end) indicating medium strength wastewaters could contain sufficient amounts of organics and that MFCs could attain high enough performance under these conditions to achieve energy-neutral treatment.

Taking the same approach as above but for the low strength wastewater ($\Delta COD = 150$ mg/L), achieving energy neutral treatment would require that the product of the E_{MFC} and CE equaled 0.80. At an average E_{MFC} of 0.35 V, achieving energy neutral treatment (at 0.40 kWh/m³) is not possible, even at 100% CE . Similarly, at an E_{MFC} of 1 V (a value not typically seen even with synthetic wastewater), the CE would need to be at least 80%, which is beyond the range of CE s observed when treating real wastewater. Researchers have obtained CE s greater than 70% [37,38] but experiments were performed with acetate.

It is important to note that we assume each of the variables is independent of each other, however, it may be the case that altering one parameter (the voltage, for example) may influence the CE , and could shift the biofilm and/or the substrate biodegradation rate (thus, the COD removed at steady-state). The interplay phenomenon reported by Stoll et al. [21] highlights the concept that the MFCs tend towards an equilibrium given the environmental conditions at the anode and cathode electrodes: increasing the MFC's performance in one aspect (i.e., improving the anode potential), adversely affects a separate aspect of the MFC at the same time (i.e., decreases the cathode potential). One study by Sluetels et al. found that increasing the anode potential and decreasing the substrate concentration when feeding acetate improved the CE [39], however, to our knowledge, the interconnectivity of these parameters has not been quantified and, therefore, requires further investigation.

3.4. COD Removal Requirements for Energy-Neutral Wastewater Treatment

The previous section evaluated energy-neutral requirements at fixed ΔCOD values using Equation (8). In this section, we use Equation (9) to solve for an array of ΔCOD values and the corresponding E_{MFC} and CE values that would be needed to achieve energy neutral treatment at 0.40 kWh/m³. This exercise can be useful for trying to determine if a given wastewater stream

has sufficient organics to achieve energy-neutral treatment while assuming reasonable E_{MFC} and CE values. In this analysis, we assume E_{MFC} and CE values range 0.2 V–0.7 V and 10%–50%, respectively. The results are plotted in Figure 2.

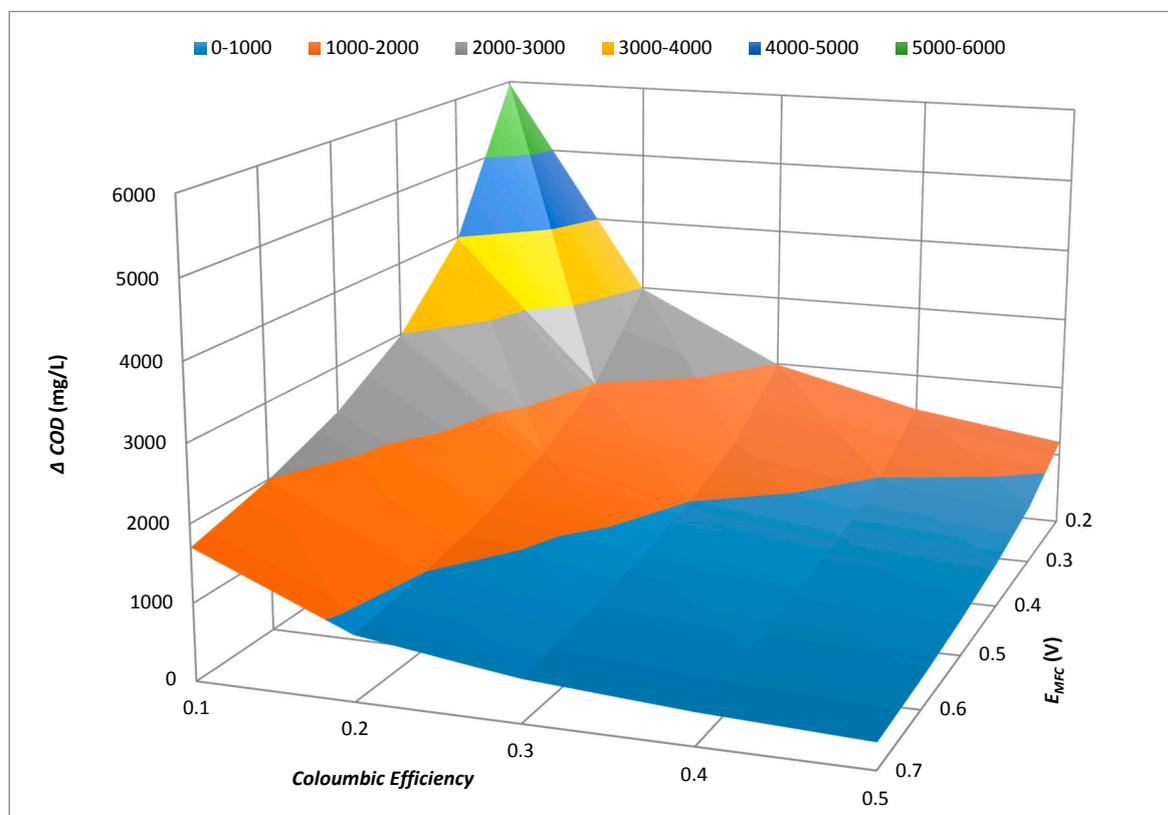


Figure 2. Contour map depicting the COD removal needed for energy-neutral treatment (ΔCOD), MFC voltage (E_{MFC}) and Coulombic Efficiency (CE) required for an MFC to be energy-neutral. Colors indicate ranges of ΔCOD , according to the legend.

As expected, MFCs with high E_{MFC} and CE s will require less COD removal to achieve energy neutral treatment and MFCs with low E_{MFC} and CE s will require more COD removal to achieve energy neutral treatment. Possibly less intuitive is that, because the E_{MFC} and CE terms are in the denominator of Equation (9), the equation takes the form of $y = \frac{1}{x} \cdot \frac{1}{y}$. Therefore, a linear decrease in either parameter (E_{MFC} or CE) while holding the other constant results in an exponential increase in ΔCOD required for energy neutral treatment. For example, if it is assumed that an MFC can achieve energy neutral treatment at $N_{WWTP} = 0.40 \text{ kWh/m}^3$ by removing 750 mg/L COD at steady-state and has an E_{MFC} of 0.4 V and a CE of 0.4, a 25% decrease in E_{MFC} performance would result in an $E_{MFC} = 0.3 \text{ V}$ (holding CE constant) and would require that 1000 mg/L be removed, a 33% increase in the required COD removal. If both E_{MFC} and CE decrease linearly from their initial values, the result is an even larger increase in the COD removal required. For example, under the same scenario of $\Delta COD = 750 \text{ mg/L}$, $E_{MFC} = 0.4 \text{ V}$ and $CE = 0.4$ initially, a 25% decrease in both parameters corresponding to an $E_{MFC} = 0.3 \text{ V}$ and $CE = 0.3$ would require a ΔCOD of 1325 mg/L to achieve the same energy output, a 77% increase. Conversely, linear changes in ΔCOD required for energy-neutral treatment would require relatively small changes in E_{MFC} and CE .

3.5. Future Opportunities and Considerations

The purpose of these examples is to demonstrate the utility of Equation (8), and to show that it is possible to calculate performance requirements for energy-neutral wastewater treatment under a given wastewater composition and a target energy generation per unit volume.

Thus far we have assumed steady-state conditions and constrained the model to calculate what the ΔCOD , E_{MFC} and CE values are required for energy-neutral treatment. It is not likely that a full-scale MFC installed at a WWTP will experience steady-state conditions for a prolonged period of time. Diurnal variations and normal daily COD loading fluctuations at a WWTP will result in non-steady state behavior, and E_{MFC} and I_{SS} (CE) will most likely vary as well. Therefore, even if an MFC is able to achieve energy-neutral treatment at steady-state conditions as per Equation (8) or (9), fluctuations in COD loading will most likely cause E_{MFC} and CE to vary such that more or less energy is generated than required for energy neutral treatment, something that the equations were not originally intended to calculate. Of course, the energy generated by the MFC can be calculated using the right-hand side of Equation (8) and compared to the target energy utilization of the WWTP (N_{WWTP}), but this process is cumbersome and is no longer takes a predictive approach that made Equations (8) and (9) useful.

In this paper we have assumed hypothetical MFCs that were operated independently of each other. This approach was used for simplicity in the modeling calculations but does not account for series/parallel operation and it is unknown what implications operating in these configurations have on CE and biofilm properties.

We have also assumed that it is acceptable to comparing real world WWTP energy consumptions to lab and pilot-scale energy productions of an MFC. Although it is known that smaller scale systems typically generate more energy than larger scale systems, to our knowledge there are no data on performance metrics of full-scale MFCs at WWTPs. As such, a direct comparison was not possible. Regardless, if MFCs are to become viable systems, then their performance at larger scales will need to improve to offset the energy densities generated at real WWTPs.

If MFCs are to achieve energy-neutral or -positive treatment, all variables on the right-hand side in Equation (8) must be optimized. However, the extent in which the CE and E_{MFC} can be manipulated is still unknown. In the above discussion, we treated the parameters E_{MFC} and CE as variables; however, this suggests these parameters could intentionally be altered. This may not be the case though, and the user may not have control over when or how much these variables change. E_{MFC} is the difference between the cathode (E_{cathode}) and anode potentials (E_{anode}). Environmental conditions, such as pH at the cathode surface and substrate concentration at the anodic biofilm surface, can influence the electrode potentials according to their respective Nernst Equation. Stoll et al. have demonstrated increasing E_{MFC} by either adding acid to the cathode or using a more biodegradable substrate (acetate vs. wastewater) in the anode [21]. However, it was discovered that when wastewater was used as the substrate, interplay between the electrodes exists, whereby E_{cathode} and E_{anode} change as a function of the other: decreasing voltage losses at the cathode (decreased pH) resulted in increased voltage losses at the anode, and vice versa. Although electrode conditions can be altered to generate more favorable electrode potentials, the system as a whole resists changes when the wastewater composition is altered in order to maintain equilibrium [21]. Because the pH of wastewater is circumneutral (between pH 6 and 8) and interplay exists, it may be more accurate to consider E_{MFC} as a constant for a given system that is dependent on the wastewater characteristics and fuel cell architecture/materials, and not as a variable that can be manipulated.

The CE is the percent of electrons that are removed by the exoelectrogens and converted into electricity. It has been demonstrated that simple substrates lead to higher CE than when domestic wastewater is used [31]. Additionally, studies have shown that the use of active energy harvesting devices instead of passive charge pumps can increase the CE . For example, when Wang et al. used a maximum power point controller (MPPC) instead of a charge pump, the CE increased from 0.7% to 15.6% [40]. This was attributed to the MPPC allowing the MFC to operate at an optimum external resistance. Beyond this, however, little is known and no methods or explanations exist that

would inform a user how to manipulated the *CE*. More work is needed to better understand the extent in which the *CE* can be altered to improve the system performance.

Although this paper focuses on organic matter removal, COD is not always the crucial parameter for the treatment of civil or industrial wastewater. The biological stage of a WWTP is often designed to accomplish the nitrogen cycle. Nitrogen rich effluents can be successfully treated by MFC, but this may imply a more complex system and additional costs, and, in any case, an electron consumption, thus determining a lowering of the *CE*. For example, Virdis et al. demonstrated MFCs could use nitrate as a cathodic electron acceptor, allowing for simultaneous removal of carbon (at the anode) and nitrogen (at the cathode) [41,42]. The process involves feeding the ammonium-containing effluent from the carbon-utilizing anode to an external biofilm-based aerobic reactor for nitrification, and then feeding the nitrified liquor to the MFC cathode for nitrate reduction using nitrite as cathodic electron acceptor.

In this paper, we assumed conservative ammonia concentrations for medium strength wastewater and the mass of oxygen required for oxidizing ammonia (4.6 kg O₂/kg NH₃) and calculated that approximately 37% of a WWTP's aeration requirements are for nitrogen removal. However, new nutrients management methods have been developed that can avoid or reduce the need for nitrogen removal [43], or recover nitrogen from wastewater using source separated treatment [44,45]. An alternative to complete nutrient removal is to retain nutrients in wastewater and use reclaimed water as a medium to convey valuable dissolved nutrients (i.e., nitrogen and phosphorous) for purposes such as agricultural and urban landscape irrigation. Farmers typically use fresh water and fertilizer to grow crops, but the downside of this approach is that producing fresh water and fertilizer are energy intensive processes. Altering or "tailoring" WWTPs to retaining desired concentrations of nutrients in the effluent (e.g., ammonia) allows for energy intensive processes, such as nitrification/denitrification, to be minimized, reducing the overall energy utilization rate. Given MFCs' ability to remove nitrogen is modest, the system may be well suited to generate tailored water.

4. Conclusions

The main motivation of this study was to develop a tool to quantify the minimum performance an MFC must achieve to be energy-neutral. By developing a simple model that accounts for the biofilm performance and efficiency (as *CE*), the wastewater characteristics (Δ COD), the fuel cell performance (as E_{MFC}) and the electrical energy requirements at a WWTP (N_{WWTP}), the feasibility of MFCs achieving energy-neutral wastewater treatment can be determined. Furthermore, this work provides qualitative and quantitative insights as to which parameters are important for maximizing power and energy outputs. Testing the model with values from the literature showed that MFCs are more capable of energy-neutral wastewater treatment at high influent CODs. Energy-neutral treatment is not likely possible when using low-strength wastewater because of the high E_{MFC} and *CE* required. Research that explores how the E_{MFC} and *CE* parameters can be manipulated to improve performance will be challenging but highly beneficial to improving overall performance. The framework described here will serve as a fundamental platform for realizing MFCs as a viable wastewater treatment technology, allowing users to reconcile energy-positive treatment with capital costs and effluent quality.

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