A quantitative method to evaluate microbial electrolysis cell effectiveness for energy recovery and wastewater treatment

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ABSTRACT

Microbial electrolysis cells (MECs) are potential candidates for sustainable wastewater treatment as they allow for recovery of the energy input by producing valuable chemicals such as hydrogen gas. Evaluating the effectiveness of MEC treatment for different wastewaters requires new approaches to quantify performance, and the establishment of specific procedures and parameters to characterize the outcome of fed-batch treatability tests. It is shown here that Coulombic efficiency can be used to directly calculate energy consumption relative to wastewater treatment in terms of COD removal, and that the average current, not maximum current, is a better metric to evaluate the rate of the bioelectrochemical reactions. The utility of these methods was demonstrated using simulated current profiles and actual wastewater tests. Industrial and domestic wastewaters were evaluated using small volume MECs, and different inoculation strategies. The energy needed for treatment was $2.17 \text{ kW h kg}^{-1} \text{COD}$ for industrial wastewater and $2.59 \text{ kW h kg}^{-1} \text{COD}$ for domestic wastewater. When these wastewaters were combined in equal amounts, the energy required was reduced to $0.63 \text{ kW h kg}^{-1} \text{COD}$. Acclimation of the MEC to domestic wastewater, prior to tests with industrial wastewaters, was the easiest and most direct method to optimize MEC performance for industrial wastewater treatment. A pre-acclimated MEC accomplished the same removal ($1847 \pm 53 \text{ mg L}^{-1}$) as reactor acclimated to only the industrial wastewater ($1839 \pm 57 \text{ mg L}^{-1}$), but treatment was achieved in significantly less time (70 h versus 238 h).

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1. Introduction

A microbial electrolysis cell (MEC) is a type of bioelectrochemical system that uses exoelectrogenic microbes to oxidize organic matter at the anode and produce a chemical of interest at the cathode [1]. Using MECs for wastewater treatment allows for conversion of the chemical energy in the organic compounds in wastewaters into a useful fuel such as hydrogen gas. Producing hydrogen requires the addition of a relatively small voltage compared to that needed for water electrolysis. The theoretical voltage needed for the MEC based on acetate is ~0.14 V, compared to 1.2 V for water electrolysis [2], but in practice voltage >0.2 V is needed for the MEC, with >0.5 V typically applied [3–5]. The production of other chemicals at the cathode, such as hydrogen peroxide [6] and methane has been also demonstrated [7].
MECs are usually operated in fed-batch mode in the laboratory, where the liquid is replaced following a decrease in current or voltage below some set minimum, although continuous flow operation would be used for practical applications. Fed-batch tests provide a rapid and effective method for initial testing and characterization of MEC reactor designs [8–11], electrode materials [12], and treatability of wastewaters [13,14]. However, the current profiles produced over a fed-batch cycle are often quite variable, making it difficult to determine how to translate the results of batch tests into useful information for reactors run under continuous flow conditions. MEC tests conducted over a fed-batch cycle can be operated in potentiostatic (constant voltage) or galvanostatic (constant current) mode. Operation under galvanostatic conditions enables constant current and hydrogen generation rates at the cathode, but problems can occur at the anode. When the substrate is depleted in the anode at the end of a fed-batch cycle, the potentiostat or the power supply will continue to draw current from the anode by forcing another less thermodynamically favorable reaction there, such as oxygen evolution or oxidation of the electrode (dissolution), which will result in an increase of voltage and destruction of biofilm activity. To avoid such unfavorable reactions, a potentiostatic mode is preferred for batch-fed MECs, where the end of a batch cycle is determined by the drop of current. Thus, the criterion for defining the end of a cycle is a predetermined current threshold, which can lead to different current profiles over the course of the fed-batch cycle.

Although the current produced using constant polarization can be quite variable over time, the overall characteristics of the batch cycle (initial and final) are more essential for evaluation of wastewater treatability. Thus, the instantaneous or maximum current production is not as useful as the final result in terms of total Coulombs or volume of hydrogen gas recovered. Unlike microbial fuel cells (MFCs), where the maximum power is a useful parameter for characterizing the performance of the system, we assert here that the main performance characteristics for MECs should be accumulated product and charge over a set period of time. While the maximum current may give an early indication of treatability and performance, we argue that this value is not a good representative characteristic for the performance of the MEC over the full cycle (equivalent to a set hydraulic retention time in continuous flow mode).

In this paper we present simple quantitative methods for comparing the performance of different wastewaters in MECs operated under fed-batch conditions. This approach is based on using the current profile for evaluating chemical energy production, and chemical oxygen demand (COD) measurements for treatment efficiency. To assess the overall electrochemical characteristics during a fed-batch cycle, we introduce a new measure of the performance: the average current, which is based on the total charge and the time needed to achieve 90% of the total charge. In addition, we discuss the Coulombic efficiency relative to electrical energy input to treat a certain mass of organics, and define it as the most important merit of the process along with the average current. We demonstrate the utility of these metrics through theoretical evaluation of hydrogen gas production using typical current profiles, and through laboratory tests using industrial and domestic wastewaters. As a part of this wastewater evaluation, we examined the effects of different inoculation strategies on startup time and performance. Tests were conducted using inexpensive, small volume, membraneless MECs to allow for easy handling of a large number of samples and replicates, and also avoiding the need to ship large volumes of wastewater from a wastewater treatment plant to our laboratory [10].

2. Methods

2.1. Reactors and inoculation

Single-chambered MECs were constructed using 5 mL clear glass serum bottles (Wheaton) as previously described [10]. Anodes were graphite plates, cut to dimensions of 1.5 cm × 1 cm, with Ti wire used for electrical connections. Cathodes were cut from stainless steel (SS) mesh (Type 304, mesh size 60 × 60; McMaster-Carr) to the same projected area as the graphite plates. Voltage was applied to the circuit using an external programmable power supply (model 3645A; Circuit Specialists, Inc.) by connecting the positive lead in series to a 10 Ω resistor (to measure current) and the anode, and the negative lead to the cathode. A multimeter (model 2700; Keithley Instruments Inc.) was used to record the current at 20 min intervals based on the voltage across the resistor. All reactors were operated at applied voltage of $U_{ap} = 0.7$ V since previous experiments have shown that this voltage is enough to sustain a reasonable rate of hydrogen production [15], while avoiding high voltages that could result in water electrolysis. A current decrease to $< 0.02$ mA was chosen as the threshold for the end of a fed-batch cycle. The MECs were sparged with nitrogen gas every time after the wastewater sample was replaced in order to remove the dissolved oxygen.

Reactors were inoculated in several different ways to assess the most useful approach for achieving wastewater treatment. The following wastewater samples were tested: industrial wastewater (IW); domestic wastewater (DW) as a positive control that is known to be treatable in a MEC [4,16]; 1:1 mixture of IW and DW (IW + DW) to provide a microbe-rich inoculum for the IW; and a 1:1 mixture of DW and IW operated under open circuit conditions (IW + DW OC) as a negative control for evaluating organics removal without current generation. DW was obtained from the primary clarifier effluent from the Penn State University Wastewater Treatment Plant. COD of the starting and ending solutions was measured using standard methods (TNT plus, COD Reagent; HACH Company) after the performance of the MECs was stabilized. All experiments were performed using triplicate reactors.

Following these tests, additional experiments were conducted to determine whether initial inoculation of the MEC with DW would enhance subsequent treatability of the IW alone. Therefore, for MECs that were operated with DW and the 1:1 mixture IW + DW, the reactors were subsequently switched to a feed of only the IW sample and no DW. This feeding approach was referred to as “cross-feeding” (CF) and the respective MECs have been denoted as DW/CF and IW + DW/CF. These experiments were performed using duplicate reactors.
2.2 Evaluation method and calculations

Two characteristics of the current profile in a batch cycle, essential for the evaluation of MEC performance, are the total charge Q (number of Coulombs transferred) and the time t. The charge is important because it is the primary factor in the calculation of the Coulombic efficiency (Ce), which is calculated as:

\[ Ce = \frac{8Q}{FV_{an} \Delta COD} \]  

(1)

where F is the Faraday constant, \( V_{an} \) is the liquid volume, \( \Delta COD \) is the COD removed, and 8 is used to convert COD to moles of electrons. The cycle time is usually used to calculate the removal rate \( r \) (mg L\(^{-1}\) day\(^{-1}\)) as:

\[ r = \frac{\Delta COD}{t} \]  

(2)

The cycle time is an essential characteristic of the treatment process and it should be minimized in order to increase productivity and reduce the potential for hydrogen losses. The COD concentration measured before and after a fed-batch cycle allows for calculation of COD removal, removal efficiency, and removal rate. The Ce indicates how many of the electrons theoretically available in the organic matter were actually used for generation of current, and therefore it is defined as a ratio between the charge Q and the COD removal \( (\Delta COD) \). In general, the Ce should be maximized for better utilization of the chemical energy stored in the wastewater.

The average current \( (I_{AVG}) \) over a batch cycle is a measure of the average bioelectrochemical reaction rate. This rate is a useful characteristic parameter for the evaluation of the performance of MECs, and it is calculated from the charge transferred and time as:

\[ I_{AVG} = \frac{Q}{t} \]  

(3)

The average current is also a good approximation of the current that could be produced under continuous flow conditions. We further argue that a better metric for evaluation of the bioelectrochemical oxidation rate is the average current calculated over the time for accumulation of 90% of the charge, or \( I_{AVG,90} \), because this value focuses on the most useful part of the current generation cycle and eliminates issues associated with small current densities at the end of the cycle as demonstrated below.

The energy used for wastewater treatment \( (W_{EL}, \text{ kWH kg}^{-1} \text{COD}) \) is an important parameter for evaluating process performance [17–19]. For MECs, the energy used is linked to the Ce by:

\[ W_{EL} = \frac{QU}{m_{COD}} = \frac{CeFU_{ap}}{8} \]  

(4)

where \( U_{ap} \) is the applied voltage and \( m_{COD} = V_{an} \Delta COD \) is the mass of removed COD.

The two variables, \( W_{EL} \) and \( I_{AVG,90} \), are proposed here as the two primary quantitative indicators of the wastewater treatability in an MEC process. The consumed electrical energy to remove COD, and the average current, together determine the average rate of hydrogen production. To evaluate the combined significance of these two parameters (low energy consumption versus high rate of hydrogen production), we introduce a third parameter, the treatability rate \( (r_{w}, \text{ mg day}^{-1} \text{ V}^{-1}) \), which is:

\[ r_{w} = \frac{I_{AVG}}{W_{EL}} = \frac{m_{COD}}{U_{ap} t} = \frac{v_{an} r}{U_{ap}} \]  

(5)

This rate is a ratio of the amount of energy needed to produce the measured electrochemical rate, and it is proportional to an already known parameter, the removal rate \( r \). The utility of \( r_{w} \) is that it can be used to normalize observed rates to the applied voltage. Thus, while the evaluation of MEC performance and efficiency is primarily based on \( W_{EL} \) and \( I_{AVG,90} \), here, treatability based on \( r_{w} \) is also useful as a measure of the average rate of bioelectrochemical oxidation of organic matter (and indirectly hydrogen generation) at a specific applied voltage. In this study, all experiments were performed at the same applied voltage with the same reactor volume, and therefore either \( r \) or \( r_{w} \) serve the same function. Therefore, rates were based on \( r_{w} \) since it is easily calculated from the COD measurements before and after the cycle.

The energy balance for an MEC includes the input of chemical energy \( (W_{COD}) \) and electrical energy \( (W_{EL}) \), and the output chemical energy in the form of the recovered hydrogen gas \( (W_{H2}) \) [1]. Ideally, the evaluation of MEC performance should be based on constant monitoring of all energies. The time when the sum of \( W_{COD} \) and \( W_{EL} \) is equal to the produced \( W_{H2} \) could be a useful parameter to evaluate performance [20]. \( W_{H2} \) is easily calculated from the charge according to the Faraday’s law, based on either the free Gibbs energy or the heat of combustion of hydrogen [1]. The energy based on COD, however, is only an estimate of the chemical energy available. Actual energy measurements must be made using calorimetry [20] and the results for wastewaters are quite variable. For instance, 14.7 \text{kJ g}^{-1} \text{COD} was reported for a raw municipal wastewater [21], but a more inclusive method that captured volatile organics produced values ranging from 17.7 to 28.7 \text{kJ g}^{-1} \text{COD}. Therefore even a detailed energy analysis is just an approximation due to unknowns in the energy in the wastewater components.

Since \( W_{COD} \) is difficult to determine, it is convenient to define the theoretical energy efficiency \( (\eta_{EL}) \) of the process only based on the electrical energy input \( W_{EL} = QU_{ap} \). For this calculation we use the absolute electrical energy \( (W_{EL}) \) and not the electrical energy normalized to the mass of removed COD \( (W_{EL}) \) as in Eq. (4). Hydrogen energy is calculated as \( W_{H2} = \Delta H_{H2} Q_{cat} F_{z} \), using the enthalpy of gaseous hydrogen \( (\Delta H_{H2} = 285.83 \text{kJ mol}^{-1}) \), \( z = 2 \) as the number of transferred electrons, and assuming a cathodic recovery of \( r_{cat} = 100\% \). This maximum efficiency can then be simply defined as

\[ \eta_{EL} = \frac{W_{H2}}{W_{EL}} = \frac{1.48}{U_{ap}} \]  

(6)

Since the amount of hydrogen gas that can be produced is dependent on the current, the charge terms cancel out, resulting in a maximum energy efficiency that depends only on the applied voltage. For the case here, where \( U_{ap} = 0.7 \text{V} \), we calculate \( \eta_{EL} = 2.11 \), or a maximum of 211% more energy recovered than applied. The applied voltage was not varied.
here, and hydrogen gas production was not measured because the goal of these mini-MEC tests was evaluation of the treatability, and not hydrogen gas recovery. Thus, energy efficiency is not used as a process evaluation parameter here.

The three characteristic parameters, $I_{AVG,90}$, $W_{EL}$, and $r_{W}$, used for the analysis of small-scale MECs, comprise a method for rapid screening and evaluation of wastewater samples without measurement of the hydrogen production. The resulting values of these parameters provide the basis for comparison of data in these tests with results on other wastewaters through measurement of total hydrogen production and an energy balance.

3. Results and discussion

3.1. Interpretation of an idealized current profile

The utility of the $I_{AVG} = Q/t$ approach can be assessed by examination of the hypothetical cases shown in Fig. 1. In all cases, there is the typical initial rise in the current to a value reflective of the degradation rates achieved with a high concentration of organics. This is followed by a steep (Profile 1) or more moderate (Profile 2) decrease in current. If we assume $t$ is expressed in seconds and $I$ in amperes, evaluation of Profiles 1 and 2 reveals that $Q$ in both cases equals 6 C and the $I_{AVG}$ is 1.5 A for Profile 1 and 2 A for Profile 2. Therefore, Profile 2 has better performance than Profile 1 because treatment is accomplished with less time, for the same $Q$, and $I_{AVG}$ is higher for Profile 2 than Profile 1. This outcome cannot be deduced simply by comparison of the respective Coulombic efficiencies for these two situations, but Profile 2 however would be judged superior to Profile 1 on the basis of the maximum current (4 A versus 3 A). For Profile 3, the maximum current is lower (3 A) than that shown for Profile 2, and the cycle time is longer (5 s versus 3 s) but the total charge is higher (11.5 C versus 6 C), which results in higher $I_{AVG}$ (2.3 A) and therefore better performance for Profile 3 than the other two cases. Thus, when compared over the length of a fed-batch cycle (which can vary), the total charge is more essential to product recovery and treatment than maximum current.

Current measured from MECs in the laboratory usually decreases exponentially, as shown in Fig. 2. In this case, most of the charge is accumulated in the first half of the cycle. The current generated toward the end of the cycle does not contribute significantly to the total charge, and it substantially increases the cycle time and thus leads to underestimation of the average current. Low current can be due to slow degradation of some organics, but it also could result from hydrogen recycling (hydrogen used at the anode that was released into solution at the cathode), which does not contribute to the wastewater treatment or net hydrogen production. To avoid including these low current densities in our analysis, a better measure of the time used for calculating the average current, is that needed for recovery of 90% of the charge, defined as $I_{AVG,90}$ (or $Q/t_{90\%}$). This current is more useful than $I_{AVG}$ for process evaluation as it reflects the time needed to accumulate most of the charge from the organic matter in the wastewater, and it minimizes the impact of hydrogen recycling on the average current (Fig. 2).

In addition to a "long tail", the current profile of an MEC can exhibit various other characteristics. In some cases, the maximum current is not observed at the very beginning of the cycle, and in others more than one single peak is present. The use of $I_{AVG,90}$, rather than $I_{AVG}$, therefore captures the performance in terms of recovered charge over a reasonable portion of the cycle. Consider a constant current or a stepwise profile as shown in Fig. 3. The stepwise profile (black solid line) is characterized by higher currents in the beginning of the fed-batch cycle, while the other (red solid line) sustains a constant current; however, both reach the same $Q$ at the end. If $I_{AVG}$ is used as a measure, both profiles would have the same performance. The higher value of $I_{AVG,90}$ for the stepwise profile indicates that charge is accumulated at a faster rate in the first part of the cycle. In addition, if the goal of treatment is to achieve a certain level of COD removal, then the MEC with a

Fig. 1 – Idealized current profiles that could be generated by batch-fed cycles of MECs.

Fig. 2 – A typical current profile (black line) and a normalized charge accumulation (red line) of a batch-fed MEC. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
higher $I_{AVG,90}$ would be preferred as this could achieve the desired COD removal at some earlier time than the end of the cycle. (For interpretation of the references to color in this paragraph, the reader is referred to the web version of this article.)

### 3.2. Evaluation of MEC electrochemical performance using wastewater samples

MECs were acclimated over several cycles to achieve reproducible current profiles with the different wastewater samples. Based on the different current profiles, it can be seen that $I_{AVG,90}$ was a better indicator of electrochemical performance than average or maximum current (Fig. 4a). The DW sample produced the highest maximum current (0.36 mA) almost immediately after the beginning of the cycle, but current rapidly decreased. In this case, the maximum current was a poor measure of overall performance as this maximum did not reflect overall treatment or the total input or output of energy. When the DW and IW samples were combined (IW + DW), there was a slightly lower maximum current, but a shorter cycle time and a broader current peak, which resulted in larger $I_{AVG,90}$ (0.18 mA) than that produced by DW alone (0.09 mA). The IW sample produced an even lower maximum current (0.2 mA), but the current profile had a very broad peak, which likely reflected slow oxidation of the organics present in the sample. As a result, the $I_{AVG,90}$ for the IW sample was 0.16 mA, which was comparable but still lower than that obtained for the IW + DW sample. These results show that there was little correlation between the maximum current and the overall characteristics of the batch cycle, and that $I_{AVG,90}$ better characterizes performance over a fed-batch cycle than maximum or average current.

The charge profile was also useful for characterizing overall wastewater treatability (Fig. 4b). All the charge profiles were steeper at the beginning of the tests. Afterward, there was a more moderate rate of charge accumulation, corresponding with a drop in current after the peak. Charge accumulation for the IW + DW sample was the fastest, reaching 16.2 C in 46 h.

The IW sample had the highest charge of all reactors (103 C), but it took the longest time (240 h) for the complete cycle (Fig. 4b). The charge accumulation rate in the first 48 h for the IW sample was much lower than the other samples.

These wastewater results show that the charge profile is an effective method to visualize essential information about the product of the process (current and indirectly hydrogen), and how fast it is generated. As discussed in Section 2.2, the overall characteristics of the charge profile in time are measured by the average current. On the basis of the $I_{AVG,90}$, it can be seen that the IW + DW had the highest electrochemical performance among all tested samples. The IW sample generated high charge for a long time, while the IW + DW samples produced a lower charge over a shorter time. As a result the $I_{AVG,90}$ for the IW + DW was 0.177 mA for the IW + DW sample, and 0.160 mA for the IW sample. This better result for the combined sample was likely due to the presence of more and/or more efficient exoelectrogenic microbes in this wastewater, compared to the IW only, which enhanced the bioelectrochemical oxidation rate.
3.3. Evaluation of COD removal and energy input

COD removal is the main goal of wastewater treatment, and therefore the change in COD during current generation is important to MEC performance. Comparison of the IW + DW and IW + DW/CF (treatment) and IW + DW OC and IW + DW/CF OC (open circuit controls) shows that there were higher COD removals with current generation (Table 1). This demonstrated the positive effect of current generation on wastewater treatment.

Measurement of COD removal and current during the batch-fed cycle allows calculation of the electrical energy consumption relative to the mass of removed organics, and is proportional to the C_E as discussed in Section 2.2. W_EL of the IW sample was 2.17 kW h kg\(^{-1}\)COD due to the very long cycle time (i.e. high accumulated charge) despite of the high removal of COD for the IW sample achieved (1839 ± 57 mg L\(^{-1}\)). The total charge of the DW sample was much lower than the IW (22.4 vs. 102.8 C) but the energy input of the DW sample was even higher (2.59 kW h kg\(^{-1}\)COD). This was a result of the lower starting COD and consequently the lower COD removal (337 ± 46 mg L\(^{-1}\)). When DW and IW samples were combined, the COD removal was 998 ± 74 mg L\(^{-1}\) which resulted in a similar removal efficiency (0.67 vs. 0.72 and 0.74 for IW and DW samples, respectively). However, the charge was 16.2 C, which resulted in much lower energy input (0.63 kW h kg\(^{-1}\)COD) for the combined sample.

C_E is an established parameter to evaluate how efficient the chemical energy stored in the wastewater was converted into electrical energy, or in other words, how much of the removed COD was converted into electrons. However, the main function of the MECs for wastewater treatment is COD removal [25,26] and minimizing overall energy usage for the process. Therefore, it makes sense to evaluate the process on the basis of the electrical energy input per kg of removed COD (W_EL). When COD removal is the same for two different wastewaters an increase of Q increases C_E and the amount of produced hydrogen. However, since the electrical energy input W_EL is directly proportional to Q and the applied voltage U (constant), a higher recovery of charge must result in directly proportional increased input of electrical energy. As a result, a low electrical energy input (W_EL) is more beneficial than high utilization of the chemical energy (i.e. high C_E). Indeed, it was recently reported in hydrogen-producing MECs that the net energy recovery (expressed as: W_EL – W_EL) per kg of removed COD was positive for samples with low C_E (7–12%) and negative for samples with higher C_E (26–35%) [22].

These results demonstrate the importance of low energy consumption compared to a goal of a high C_E. However, to ensure a high rate of hydrogen production, it is preferable that the low energy consumption is due to high COD removal than to low currents (i.e. charge), as observed in the case of the IW + DW sample.

3.4. Effect of cross-feeding on performance

The acclimation of the MECs with a microbe-rich substrate such as DW (cross-feeding) had a beneficial influence on the treatability of the IW sample. The two cross-feeding samples achieved virtually the same removal as the IW sample alone (Table 1) but in significantly less time. Therefore, the input of energy W_EL decreased to values as low as 0.52 kW h kg\(^{-1}\)COD for the DW/CF and 0.50 kW h kg\(^{-1}\)COD for the IW + DW/CF for the cross-feeding experiments. The average currents of 0.15 mA for DW/CF, and 0.14 mA for IW + DW/CF, were slightly lower but still comparable to the current produced by the IW sample (0.16 mA). Thus, the inoculation of MECs with the microbes present in DW allowed for the same rate of charge accumulation and the same COD removal for significantly less time.

3.5. Overall assessment of MEC performance using wastewater samples

Data for the five different samples are shown in Fig. 5 and summarized in Table 2 along with some other parameters such as Q, C_E, and cycle time. The two terms, average current

<table>
<thead>
<tr>
<th>Sample</th>
<th>Influent COD [mg L(^{-1})]</th>
<th>Effluent COD [mg L(^{-1})]</th>
<th>Removal [mg L(^{-1})]</th>
<th>Removal efficiency [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>IW</td>
<td>2546 ± 48</td>
<td>707 ± 31</td>
<td>1839</td>
<td>0.72</td>
</tr>
<tr>
<td>IW + DW</td>
<td>1501 ± 47</td>
<td>503 ± 57</td>
<td>998</td>
<td>0.67</td>
</tr>
<tr>
<td>DW</td>
<td>456 ± 46</td>
<td>119 ± 6</td>
<td>337</td>
<td>0.74</td>
</tr>
<tr>
<td>IW + DW OC</td>
<td>1501 ± 47</td>
<td>865 ± 134</td>
<td>636</td>
<td>0.42</td>
</tr>
<tr>
<td>DW/CF</td>
<td>2546 ± 48</td>
<td>699 ± 22</td>
<td>1847</td>
<td>0.73</td>
</tr>
<tr>
<td>IW + DW/CF</td>
<td>2546 ± 48</td>
<td>751 ± 33</td>
<td>1795</td>
<td>0.71</td>
</tr>
<tr>
<td>IW + DW/CF OC</td>
<td>2546 ± 48</td>
<td>1624 ± 142</td>
<td>922</td>
<td>0.36</td>
</tr>
</tbody>
</table>
Different parameters used to evaluate MEC performance relative to treatment and energy.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Charge [C]</th>
<th>Time [h]</th>
<th>Average current 90 [mA]</th>
<th>Coulombic efficiency [%]</th>
<th>Energy input [kW h kg⁻¹ COD]</th>
<th>Removal rate [mg L⁻¹ day⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>DW</td>
<td>22.41</td>
<td>94</td>
<td>0.09</td>
<td>110</td>
<td>2.59</td>
<td>86</td>
</tr>
<tr>
<td>IW + DW</td>
<td>16.17</td>
<td>46</td>
<td>0.18</td>
<td>27</td>
<td>0.63</td>
<td>521</td>
</tr>
<tr>
<td>IW</td>
<td>102.78</td>
<td>238</td>
<td>0.16</td>
<td>93</td>
<td>2.17</td>
<td>185</td>
</tr>
<tr>
<td>DW/CF</td>
<td>24.67</td>
<td>70</td>
<td>0.15</td>
<td>22</td>
<td>0.52</td>
<td>636</td>
</tr>
<tr>
<td>IW + DW/CF</td>
<td>23.12</td>
<td>70</td>
<td>0.14</td>
<td>21</td>
<td>0.50</td>
<td>618</td>
</tr>
</tbody>
</table>

$I_{\text{AVG,90}}$ and energy input per kilogram of removed COD $W_{\text{EL}}$ ($\text{kW h kg}^{-1}\text{COD}$), together allow for more effective evaluation of MEC performance than other parameters such as maximum current. The IW + DW and the two cross-feeding samples had comparable energy requirements and the average current decreased in the following order: IW + DW > DW/CF > IW + DW/CF. The DW sample had the highest energy input (2.59 kW h kg⁻¹ COD), and lowest average current of all five samples. The energy input for the IW sample was also high (2.17 kW h kg⁻¹ COD), but this was compensated for by the high average current. The higher $W_{\text{EL}}$ for the pure DW and IW samples, plus the long cycle in the case of the IW, showed that they were not as effectively treated using MECs as the other three samples.

The comparison between the DW and IW + DW samples is straightforward: the IW + DW exhibited higher average current (0.18 mA) and lower energy consumption (0.63 kW h kg⁻¹ COD). Comparison between the IW + DW and DW/CF samples reveals that the DW/CF has lower average current (0.15 mA) but also lower energy input (0.52 versus 0.63 kW h kg⁻¹ COD). As discussed in Section 2.2, the removal rate $r$ (an analogous metric to the treatability rate $r_{\text{AVG,90}}$ with constant $U_{\text{up}}$ and $v_{\text{an}}$) can be further used to assess the significance of both $I_{\text{AVG,90}}$ and $W_{\text{EL}}$. Based on this criterion, we conclude that the DW/CF sample (636 mg L⁻¹ day⁻¹) outperformed the IW + DW sample (521 mg L⁻¹ day⁻¹) since it had lower energy consumption and higher removal rate, opposed to the lower average current. In addition, it is more feasible from a technological point of view that the reactor is inoculated with a microbe-rich DW periodically rather than constantly operated with a mixture of IW and DW (DW might not be conveniently available at the industrial site).

Similar comparison can be made between the cross-feeding samples inoculated with DW only (DW/CF) and a mixture of IW and DW (IW + DW/CF), which also show divergent behavior with respect to $I_{\text{AVG,90}}$ and $W_{\text{EL}}$. The MEC inoculated with the two wastewaters exhibited lower energy consumption (0.50 kW h kg⁻¹ COD) but also lower average current (0.14 mA). Based on the removal rate, the DW/CF ($r = 636$ mg L⁻¹ day⁻¹) had slightly better performance than the IW + DW/CF (618 mg L⁻¹ day⁻¹).

Although the removal and treatability rates are proportional to a very characteristic parameter, namely the energy consumed to treat a certain amount of organics and to generate a given current (and produce hydrogen), they cannot serve as the ultimate descriptor of MEC performance, since they only indirectly involve the generated charge $Q$. To properly evaluate the MEC process the removal and treatability rates should be used in conjunction with the other two parameters, $I_{\text{AVG,90}}$ and $W_{\text{EL}}$ in addition to consideration of the specific engineering requirements.

4. Conclusions

The proposed quantitative method to evaluate MEC effectiveness in fed-batch reactors is based on measurements of the current and the COD concentrations before and after the batch cycle. These measurements allow for calculation of a characteristic parameter for wastewater treatment, the specific energy consumption per kg of removed COD $W_{\text{EL}}$. $I_{\text{AVG,90}}$ is more useful to evaluate various current profiles that occur in laboratory tests. Quantitative assessment of the respective performances is based on comparison of $W_{\text{EL}}$ and $I_{\text{AVG,90}}$ for the different samples. In case where two samples exhibit divergent behavior (low energy input and low currents versus high energy input and high currents), the treatability or removal rate can be used as an additional parameter for evaluation.

Cross-feeding (inoculation with a microbe-rich substrate) was a feasible approach for treating industrial wastewater samples. The reactors, inoculated with DW, achieved the same removal for significantly less time compared than MECs acclimated only to the IW, thus having a lower $W_{\text{EL}}$. DW proved to be a more suitable inoculum for enrichment of the electrodes than the IW + DW with respect to the treatment of IW sample, despite the initial hypothesis that inoculation with both industrial and domestic wastewater would be more favorable since the biofilm would acclimate to the organics present in the IW. This phenomenon might be ascribed to the formation of a more robust biofilm when using only DW, compared to IW + DW.

The quantitative method for evaluation shown here compares the performance of different wastewater samples and inoculation strategies but it can be extended to other test conditions, such as different reactors, electrode materials, and studies with pure cultures. This method is convenient for initial screening of MEC performance without actual measurement of the recovered hydrogen, especially in conjunction with the use of small-scale reactors and provides a basis for further more detailed tests, which involve complete energy balance.

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