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Wastewater Treatment and Online Chemical Oxygen Demand Estimation in a Cascade of Microbial Fuel Cells

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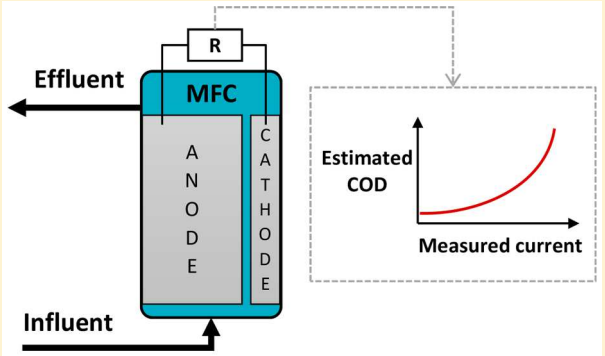
ABSTRACT: This study demonstrates degradation of synthetic wastewater in two MFCs hydraulically connected in series. To maximize chemical oxygen demand (COD) removal, external resistance of each MFC is optimized using a perturbation−observation maximum power point algorithm. Under optimal operating conditions a removal efficiency over 90% is achieved at an influent acetate concentration of 750 mg L^{-1} and organic loading rates ranging from 0.75 to 3.0 g L^{-1} day^{-1}. Furthermore, regression analysis is used to correlate current and power output of each MFC with the analytically measured COD concentrations, thus providing a means for online COD estimations. The accuracy of online COD estimations is further improved by developing a model-based soft-sensor.



1. INTRODUCTION

Microbial fuel cells (MFCs) are bioelectrochemical devices designed for direct electricity production from organic matter.[1,2] MFCs are primarily studied for energy generation from renewable organic wastes, such as wastewater. Although a number of obstacles, including a relatively low power density, need to be resolved, significant progress has been recently achieved in the development of practical MFC-based wastewater treatment systems.[3,4] In particular, wastewater treatment in a cascade of MFCs (hydraulically connected in series) was shown to improve effluent quality.[5−7] Indeed, such a "reactor-in-series" approach is often used in biological wastewater treatment, where low effluent concentration is required to satisfy treatment norms.

MFC application for measuring chemical oxygen demand (COD) or biochemical oxygen demand (BOD) concentrations is another emerging area of MFC applications.[8−15] Also, MFC application for measuring dissolved oxygen was recently demonstrated.[16] Conventional laboratory procedures for COD and BOD determination carried out off-line are time-consuming, labor intensive, and costly. Furthermore, these measurements are prone to inaccuracies due to sample inhomogeneity, complexity of analytical procedures, and errors in data analysis.[13] Several online sensors were recently developed, for example, spectroscopy-based sensors;[17] however, most of these sensors require chemicals for operation and are relatively expensive.[18] Thus, development of an MFC-based biosensor might provide a practical low-cost approach for online COD as well as BOD measurements.

Real-time MFC-based COD measurement using electrical performance monitoring has been already demonstrated.[8−12,14,15] In these works MFCs were operated at a fixed (preset) external resistance. Meanwhile, MFC performance can be optimized by matching the external resistance (electrical load) with the internal resistance estimated through a polarization test, for example, manually. Furthermore, in recent years several online approaches for maximizing MFC power output were proposed including the perturbation and observation (P/O)[19] and pulse-width modulated (PWM) algorithms.[20] In these and other studies an increase in COD concentration has been shown to lead to an increase in the current produced by the MFC as well as to a decrease in MFC total internal resistance.

This study demonstrates COD removal in a cascade of two MFCs with optimally controlled external resistances. Moreover, we hypothesize that optimal resistance selection in each MFC enables online COD estimations. Accordingly, regression dependencies are derived based on a comparison of analytical COD measurements and electrical parameters (current, power output, and total internal resistance) of each MFC. Also, improved accuracy of COD estimations is achieved by using a simple dynamic model as a soft-sensor.

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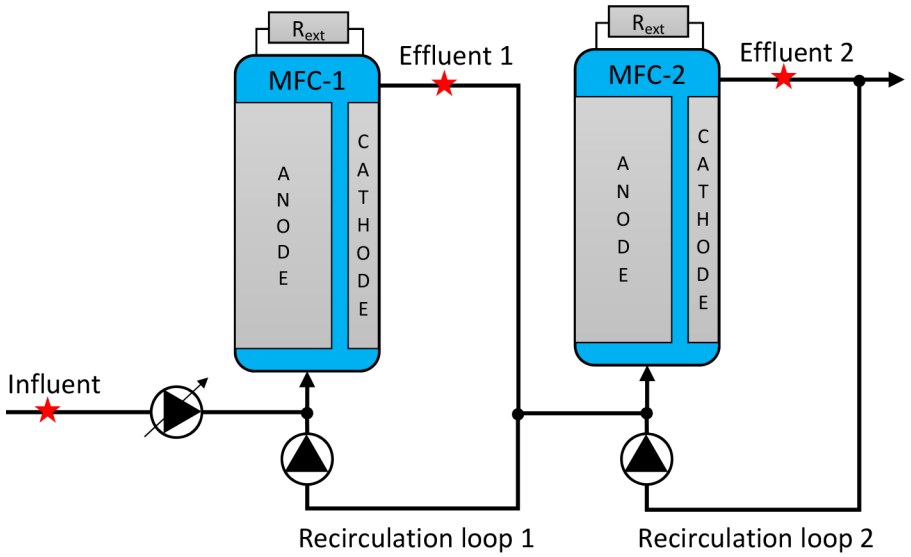

Figure 1. Schematic diagram of the two MFCs connected in series. Asterisks represent the influent and effluent COD sampling ports.

2. MATERIALS AND METHODS

2.1. MFC Design, Operation, And Monitoring. Experiments were conducted in two continuous flow membrane-less air-cathode MFCs. Each MFC had an anodic compartment volume of 50 mL. Electrodes consisted of a 10 × 5 cm carbon felt anode with a total thickness of 5 mm (SGL Canada, Kitchener, ON, Canada) and an air cathode made of a 10 × 5 cm manganese-based catalyzed carbon E4 electrode (Electric Fuel Ltd., Bet Shemesh, Israel). The two MFCs were hydraulically connected in series; that is, the effluent of the first MFC (MFC-1) was connected to the influent of the second MFC (MFC-2) as shown in Figure 1. Mixing in each anode compartment was provided by an external recirculation loop. Temperature was maintained at 23 °C using a flow through heater and a thermocouple connected to a temperature controller (model JCR-33A, Shinko Technos Co. Ltd., Osaka, Japan).

Each MFC was inoculated with 5 mL of homogenized anaerobic sludge (Lassonde Industries, Inc., Rougemont, QC, Canada) with a volatile suspended solids (VSS) content of approximately 40−50 g L^{-1} and 20 mL of effluent from an actively operating MFC. MFC-1 was fed with a synthetic wastewater consisting of acetate as described in Woodward et al.[19]

The acetate stock solution was combined with dilution water and maintained at a target influent COD concentration of 750 mg L^{-1}. Acetate and dilution water streams were delivered to MFC-1 using peristaltic pumps (model L/S, Masterflex, Cole-Parmer Instrument Company LLC., Chicago, IL, USA). Dilution water flow varied from 100 to 600 mL d^{-1} providing a hydraulic retention time from 12 to 2 h in each MFC. Acetate concentration in the anodic liquid was analyzed on an Agilent 6890 gas chromatograph (Wilmington, DE, USA) equipped with a flame ionization detector. Method details are provided in Tartakovsky et al.[21]

2.2. Numerical Methods. To maximize power production, external resistance (R_{ext}) of each MFC was optimized in real time using a P/O algorithm with a sampling period of 20 s. A detailed algorithm description of the algorithm can be found elsewhere.[19] A Labjack U3-LV data acquisition board (LabJack Corp., Lakewood, CO, USA) was used to control a digital potentiometer (model X9C102 from Intersil, Milpitas, CA, USA), which provided a resistance variation from 4 to 133 Ω with a step of 1.3 Ω. The P/O algorithm was implemented in Matlab R2014a (Mathworks, Natick, MA, USA).

JMP statistical software (SAS, Cary, NC, USA) was used to carry out regression analysis. The soft-sensor model equation was solved using finite (backward) difference method in Excel (Microsoft Corporation, Redmond, WA, USA).

3. RESULTS AND DISCUSSION

3.1. Acetate Removal in a Cascade of Two MFCs. Reactor connection in series (cascade connection) is often used to maximize the overall rate of biodegradation in biological wastewater treatment. For instance, aerobic wastewater treatment can be accomplished in a series of aerated reactors or in a single reactor divided into several compartments operated at different aeration rates.[22] Here, the first reactor in series receives the highest organic load and, accordingly, is operated at the highest aeration rate. The following reactors receive lower organic loads and are less aerated. This approach provides sufficient oxygen supply to each reactor, while reducing overall energy consumption for aeration. Similarly, the overall power production and COD removal can be maximized by optimally controlling R_{ext} of each MFC.

Importantly, MFC performance was demonstrated to strongly depend on the value of R_{ext} at which it operates.[23,24] Optimal performance can only be achieved if R_{ext} matches the MFC's internal resistance (R_{int}).[23] Also, optimal selection of R_{ext} is instrumental in maintaining long-term MFC stability, as increased Coulombic efficiency associated with the proliferation of anodophilic microorganisms was demonstrated in an MFC operated at optimal R_{ext}.[19] Furthermore, voltage reversal was observed in MFCs operated at $R_{ext} < R_{int}$,[25] while operation at $R_{ext} < R_{int}$ led to proliferation of methanogenic populations.[7] Considering that during wastewater treatment R_{int} depends on multiple uncontrollable factors, such as carbon source composition, concentration, and temperature, which vary over time, a real-time optimization of R_{ext}, for example, using a P/O,[19] might be required. In a cascade of two MFCs the P/O algorithm can be used to dynamically select (optimize) R_{ext}

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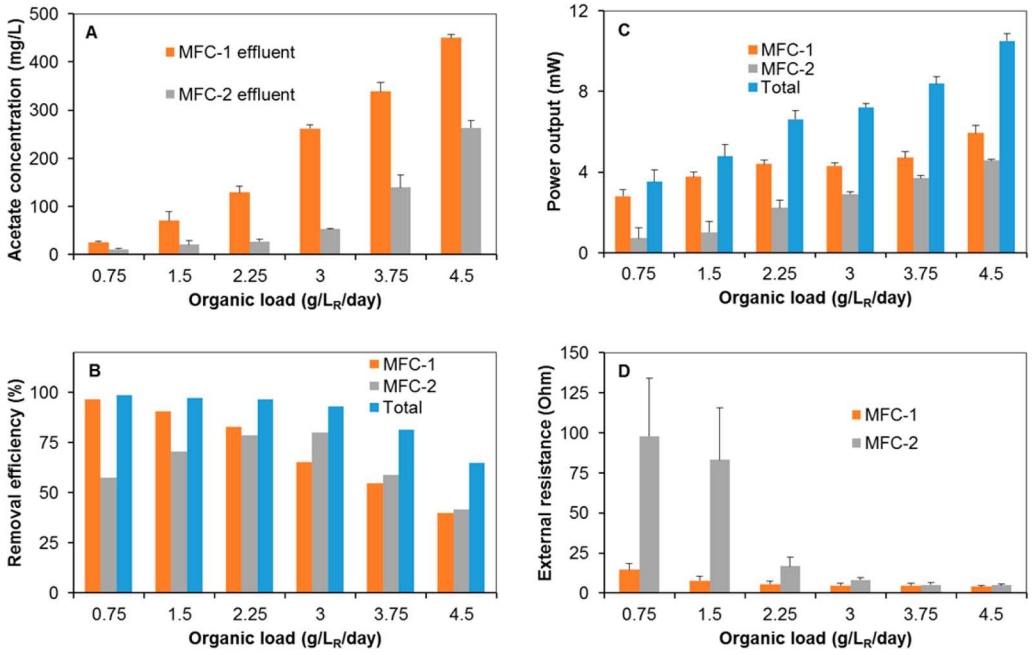

Figure 2. (A) Effluent acetate concentrations; (B) COD removal efficiencies; (C) power outputs; and (D) optimal external resistances determined by the P/O algorithm during MFC-1 and MFC-2 operation at several organic loads. Influent acetate concentration was maintained at 750 mg L^{-1}.

values at high (first MFC) and low (second MFC) COD concentrations.

The experimental setup shown in Figure 1 was used to demonstrate the approach of wastewater treatment in a cascade of two MFCs. This reactor system was operated at several total organic loading rates (OLRs) ranging from 0.75 to 4.5 g L_R^{-1} d^{-1} (here, OLR was calculated based on a total volume of two MFCs, that is, 100 mL). Figure 2 shows performance of each MFC in terms of acetate removal and power production. As it can be seen from these graphs, at the lowest organic load acetate was mostly degraded in MFC-1, while MFC-2 was used for effluent polishing (Figure 2A,B). As a result, the acetate removal efficiency of MFC-2 was low. Accordingly, power production in MFC-1 was significantly higher than in MFC-2 (Figure 2C). Importantly, R_{ext} values of both MFC-1 and MFC-2 were dynamically adjusted using the P/O algorithm. The resulting values were significantly different, with R_{ext} of MFC-1 significantly lower than that of MFC-2 (Figure 2D). As the flow rate to MFC-1 increased (leading to higher total OLR), MFC-1 reached its maximal removal rate at an OLR of 2.25 g L_R^{-1} d^{-1}. Above this organic load the effluent acetate concentration of MFC-1 started to increase, while its power output remained nearly constant. The increase in acetate concentration entering MFC-2 led to higher power output and lower R_{ext} of this MFC (Figure 2C,D). At organic loads between 0.75−2.25 g L_R^{-1} d^{-1} the overall removal efficiency remained high with MFC-2 effluent acetate concentrations in a range of 11.2 to 27.5 mg L^{-1} (Figure 2 A). Finally, at the highest tested organic load of 4.5 g L_R^{-1} d^{-1} the effluent acetate concentration of MFC-2 increased to 263 mg L^{-1}, while the power output remained nearly constant. This behavior indicated organic overload of the treatment system.

Overall, the cascade treatment system provided robust acetate removal and demonstrated near constant power production in a broad range of organic loads, while also providing low effluent acetate concentration.

3.2. COD Correlation with MFC Current and Power Output. A comparison of effluent COD concentrations shown in Figure 2A with the corresponding power outputs in Figure 2C suggests that the MFC electrical performance depends on the carbon source concentration. If a regression dependence between the MFC power output (or electrical current) and carbon source concentration can be inferred, the MFC can be used as an online COD sensor. Indeed, the concept of an MFC-based COD/BOD sensor has been already proposed.[9−12,14,15] However, in these studies MFCs were used to develop rapid off-line assays in which carbon source degradation was observed over a relatively short period of time (e.g., several hours). It would be beneficial to use the MFC electrical performance for online COD estimations. To enable such estimations, all available analytical COD measurements (collected during the 17-day test described in the previous section) were regressed with the corresponding power outputs and currents of each MFC. Considering that in both MFCs R_{ext} was optimized in real time using the P/O algorithm, the optimal external resistance values (R^*_{ext}) were also included in the regression analysis.

Several linear and nonlinear regression models were developed and compared (Table 1). Figure 3A, B, and C compares COD measurements and best-fitting regression dependencies obtained using current (Figure 3A), power (Figure 3B), and R^*_{ext} (Figure 3C). This comparison confirms that COD concentrations can be estimated in real time using either current or power output measurements of an MFC operated at a maximal power output with dynamically adjusted R_{ext}. As shown in Table 1, the highest R^2 values of COD estimations using current and power output are 0.90 and 0.82, respectively. The COD estimations using R_{ext} values were less accurate (R^2 = 0.75, Table 1). It might be noted that R^*_{ext} values determined by the P/O algorithm oscillated around the actual optimal resistance[19] thus contributing to the inaccuracy of the estimation.

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Table 1. Regression Dependencies. Some Experimental Values Were Discarded When Estimating the Best Set of Regression Model Parameters

regression equation	measurement (X)	R^2	number of data points	model parameters
$COD = a + bX$	I	0.81	21	a = 2.08, b = 9.39
	P	0.65	21	a = 10.8, b = 8.62
$COD = a + bX + cX^2$	I	0.89	45	a = 29.5, b = −5.08, c = 0.38
	P	0.69	45	a = 0, b = −5.36, c = 11.3
$COD = a\ e^{bX}$	I	0.90	45	a = 10.9, b = 0.09
	P	0.82	45	a = 8.51, b = 0.66
$COD = aX^b$	I	0.75	45	a = 4.32, b = 1.04
	P	0.62	45	a = 27.6, b = 1.03
	R^*_{ext}	0.75	45	a = 662, b= −0.90
$OLR = a + bX$	I	0.82	34	a = 0, b = 0.14
	P	0.73	34	a = 0, b = 0.83
$OLR = a + bX + cX^2$	I	0.85	41	a = 0, b = 0.06, c = 0.004
	P	0.85	41	a = 0, b = 0.43, c= −0.62
$OLR = a\ e^{\ bX}$	I	0.70	41	a = 0.15, b = 0.12
	P	0.85	41	a = 0.07, b = 0.99
$OLR = aX^b$	I	0.78	41	a = 0.04, b = 1.34
	P	0.74	41	a = 0.42, b = 1.46
	R^*_{ext}	0.77	41	a = 33.1, b = −1.21

As can be seen from the comparison shown in Table 1 and Figure 3, the following exponential regression model provided the best fit:

$$S = a\ e^{bI} \tag{1}$$

where a and b are the regression coefficients, S is the COD concentration, and I is the MFC current. The estimated regression coefficients are a = 10.9 mg L^{-1} and b = 0.09 mA^{-1}. Notably, eq 1 implies a COD concentration of 11.1 mg L^{-1} at zero current. This COD concentration can be considered to be the low boundary of MFC-based measurements. A linear regression equation can be also used at low COD concentrations (e.g., less than 100 mg L^{-1}). However, the linear dependence results in a lower R^2 value (Table 1).

Both influent COD concentration and liquid flow through anaerobic compartment are expected to influence MFC performance.[26] Accordingly, the regression analysis was repeated using organic loading rates calculated for each MFC, which provide a combination of these parameters (here, OLR = FS_{in}/V, where F is the flow rate, S_{in} is the influent COD concentration, and V is the MFC anodic compartment volume). The regression analysis showed results similar to COD concentration approximations (Table 1). Figure 3D–F shows experimental and approximated OLR values obtained using best-fitting regression equations. Once again, a linear regression equation can be only used at low OLR values, while the exponential regression dependence provided a better overall fit for the estimations based on the MFC power outputs. A second order polynomial provided a slightly better fit for OLR estimations (Table 1); however, the difference was statistically insignificant. The R^2 of these OLR estimations using current (Figure 3D), and power (Figure 3E) are 0.849 and 0.850, respectively. Online OLR estimations can be useful for developing real-time control strategies aimed at timely avoidance of reactor overloads, due to hydraulic or organic overloads.[9]

Overall, it was shown that MFC power output and current observed during wastewater treatment can be conveniently used to provide online estimations of organic loads and effluent COD concentrations. Although acetate was used throughout the tests as a carbon source, a linear dependence of MFC current on COD concentration was demonstrated in several studies carried out using a variety of complex organic substrates, including volatile fatty acids,[27] and municipal and industrial wastewaters.[28−30] Importantly, the COD estimations were made possible due to MFC operation using the P/O algorithm, which dynamically selected R_{ext}, thus maximizing power production at all times. The regression eq 1 does not consider the influence of temperature, pH, nitrogen species, dissolved oxygen,[16,31] and other operating parameters on MFC current. A more complex regression equation could be developed if significant variations of these parameters are expected. Also, the impact of hydraulic retention time on the MFC current can be accounted for by including organic load rather than COD concentration in eq 1 (Table 1). Also, an MFC sensor can be built and operated at a fixed flow rate. Finally, MFC sensing accuracy and sensitivity can be further improved through advanced MFC design.[32]

3.3. MFC Dynamic Model as Soft-Sensor for Enhanced COD Estimations. In addition to regression dependencies enabling COD and OLR estimations based on MFC current and power output, a soft-sensor approach for COD estimations was also tested. Here, a simple dynamic model was used to estimate effluent COD concentrations. The soft-sensor was expected to provide improved estimation accuracy.[33]

The dynamic model used to develop the soft-sensor was based on the anodic compartment material balance. Modeling assumptions included ideal mixing within the compartment and negligible carbon source consumption by microbial populations other than anodophilic microorganisms (e.g., contribution of methanogenic microorganisms to COD removal was assumed to be negligible). Under these simplifying assumptions a dynamic mass balance of the carbon source concentration in the anodic compartment can be written as

$$\frac{dS}{dt} = -qX + D(S_{in} - S) \tag{2}$$

where S is the effluent carbon source concentration (mg L^{-1}), q is the carbon source consumption rate (d^{-1}), X is the concentration of anodophilic microorganisms (mg L^{-1}), D is the dilution rate (d^{-1}) calculated as $D = F/V$, S_{in} is the influent carbon source concentration (mg L^{-1}).

Carbon source consumption by the anodophilic microorganisms in eq 2 is described by the negative term ($-qX$). For a mature biofilm with near constant biomass concentration, it

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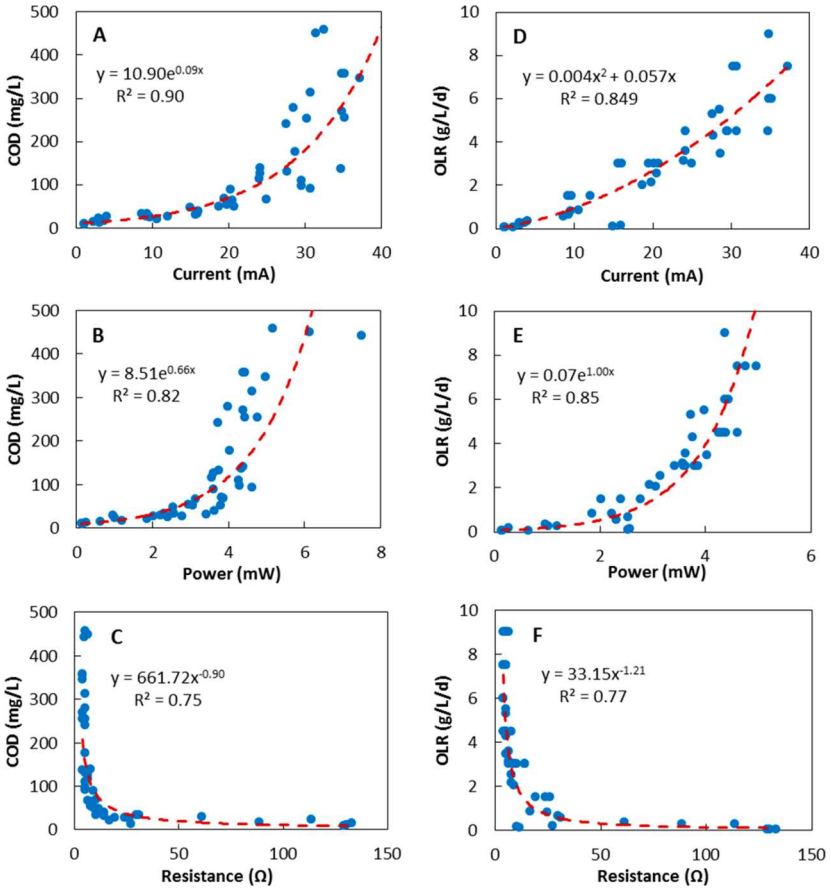

Figure 3. Statistical correlation fitting the experimental COD concentrations and organic loading rates against the electrical current (A,D), the optimal external resistance (B,E), and power (C,F).

can be assumed that the current produced by the MFC does not depend on the biomass concentration; therefore, the term qX in eq 2 can be replaced with the MFC current:

$$\frac{dS}{dt} = -\beta I + D(S_{in} - S) \tag{3}$$

where I is the MFC current (mA), and β is the coefficient defined as a ratio of carbon source consumption to current production (mg L^{-1} d^{-1} mA^{-1}). Notably, β can be shown to be inversely proportional to Coulombic efficiency.

A value of β in eq 3 can be estimated under steady state conditions, so that $\beta = D(S_{in} - S)/I$. Once β is estimated, the online measurements of the electric current can be used for COD estimations, providing that both the flow rate and the influent COD concentration are known. The latter requirement can be challenging at wastewater treatment plants, where influent COD concentration can significantly vary. Yet, in many instances an average influent COD concentration is known. Notably, the accuracy of the estimated effluent COD will depend on the accuracy of β estimations, which can be improved by using several COD and the corresponding current values.

The soft-sensor approach was applied to the experimental results described in the previous section as follows. First, parameter β was estimated for each MFC during steady state operation corresponding to $t = 0$. Effluents of each MFC were sampled, and triplicate COD analysis was carried out. The average COD values were divided by the corresponding current values averaged over a 3 h period. The following values were estimated: $\beta_1 = 118$ and $\beta_2 = 85.5$ mg L^{-1} d^{-1} mA^{-1}, for MFC-1 and MFC-2, respectively. Once β values were estimated, COD values were predicted using eq 3.

Figure 4 compares the accuracy of the soft-sensor (eq 3) and regression model (eq 1) COD estimations. The figure also shows the flow rate profile and the experimentally measured COD concentrations at the exit of MFC-1 and MFC-2. Also, current produced by each MFC and R^*_{ext} values are shown in Figure 4B and C, respectively. Note that a technical problem between days 4 and 6 of the test resulted in a corrupted data log file (marked as a gray area). Nevertheless, the R_{ext} control was carried out normally during this period. Oscillations in R^*_{ext} values determined by the P/O algorithm during MFC-2 operation after day 8 can be noticed. These oscillations can be attributed to MFC-1 operation at a lower influent COD concentration, which led to low COD concentration in MFC-1 effluent. Accordingly, COD concentration in MFC-2 was even lower, thus causing the P/O algorithm to adjust the optimal value of R_{ext} bringing it to the upper limit of the digital resistor (133 Ω). At the same time, MFC-1, which received higher organic loads, was operated at relatively low R_{ext} values. Also, the Coulombic efficiency estimations based on all available acetate measurements were 83 and 96% for MFC-1 and MFC-2, respectively. Also, Coulombic efficiency estimations using β values estimated at $t = 0$ yielded similar values (75 and 103% for MFC-1 and MFC-2, respectively). These Coulombic efficiency estimations confirm the efficiency of optimal R_{ext} control, which promoted growth of the anodophilic micro-

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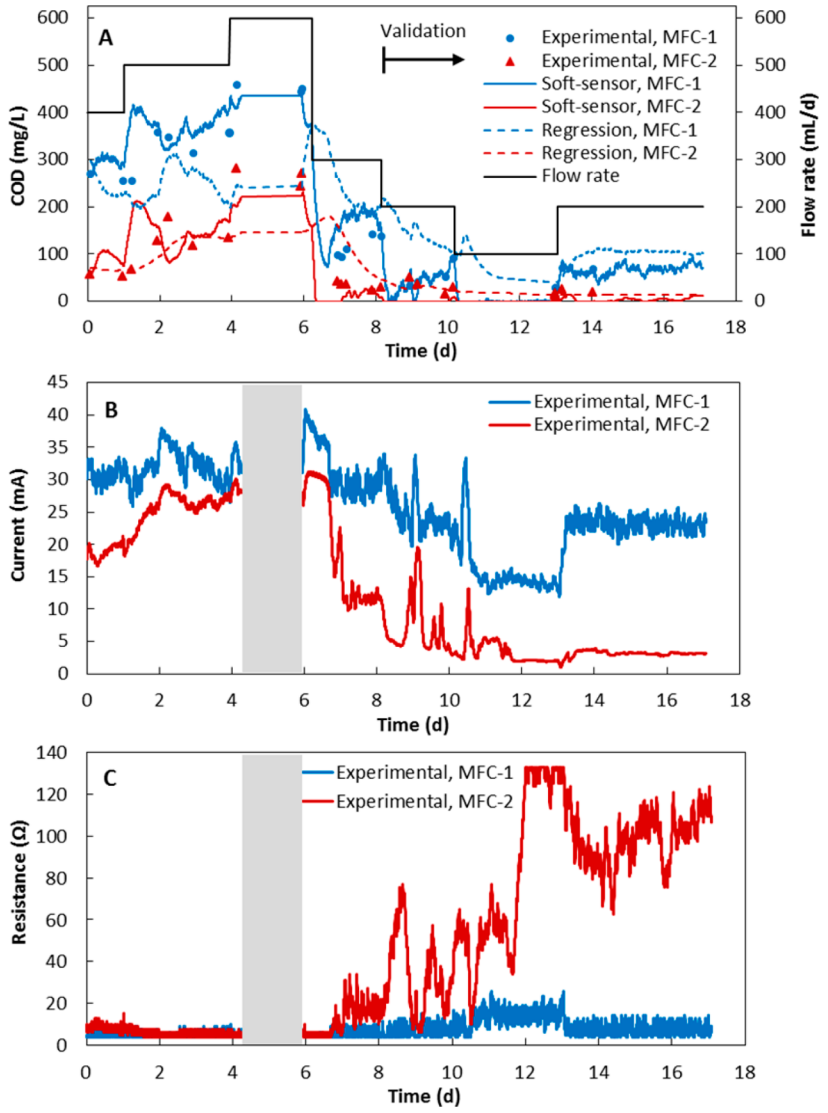

Figure 4. COD degradation performance for the two MFCs in series and online effluent substrate concentration estimation using the simplified mass balance (eq 2). Applied flow rate, measured and estimated effluent COD concentrations (A), current (B), and applied external resistance (C). Current values were filtered using an exponential filter.

organisms both at low and high COD (acetate) concentrations and minimized methanogenic activity.

Overall, the soft-sensor approach allowed for improved estimation accuracy, as can be seen from the correlation curves shown in Figure 5. For this analysis the first 15 experimental values (days 0 to 8) were used to estimate regression coefficients in eq 1, while current measurements between days 9 and 17 were used to validate the regression model (Figure 4). Importantly, effluent COD concentrations were considerably higher during the first 8 days of operation as compared to the rest of the test, due to a high influent COD concentration. Thus, by estimating regression coefficients during this high COD period and applying eq 1 to predict CODs at lower influent COD concentrations (days 9−17), the regression model was validated with the data outside of the calibration range, which confirms its predictive capacity.

Not only is the R^2 value corresponding to the soft-sensor prediction higher (0.9 vs 0.7), but also the slope of the curve in Figure 5B is closer to 1 as compared to the slope in Figure 5A, which points to a better estimation accuracy. The COD (acetate) values predicted by the two methods were also compared to the measured values using the Bland-Altman analysis. This comparison showed a bias (mean of the difference) of 0.1 and 6.3 mg L^{-1} for the regression and the soft-sensor methods, respectively. Since the differences are normally distributed (not shown) the standard deviation is used to determine the limits of agreement. A standard deviation of 33 mg L^{-1} was obtained for both techniques with the agreement ranges shown in Figure 5C and Figure 5D for the regression and the soft-sensor models, respectively.

It should be noted that although the soft-sensor approach required the knowledge of flow rates and influent COD concentrations, a practical implementation of this approach can involve operation of a miniature MFC (essentially a biosensor) at a high flow rate. Accordingly, a constant dilution term in eq 3 can be assumed thus extending the applicability of the soft-sensor approach.

4. CONCLUSION

The existing off-line techniques for effluent quality monitoring in wastewater treatment make it difficult to use advanced

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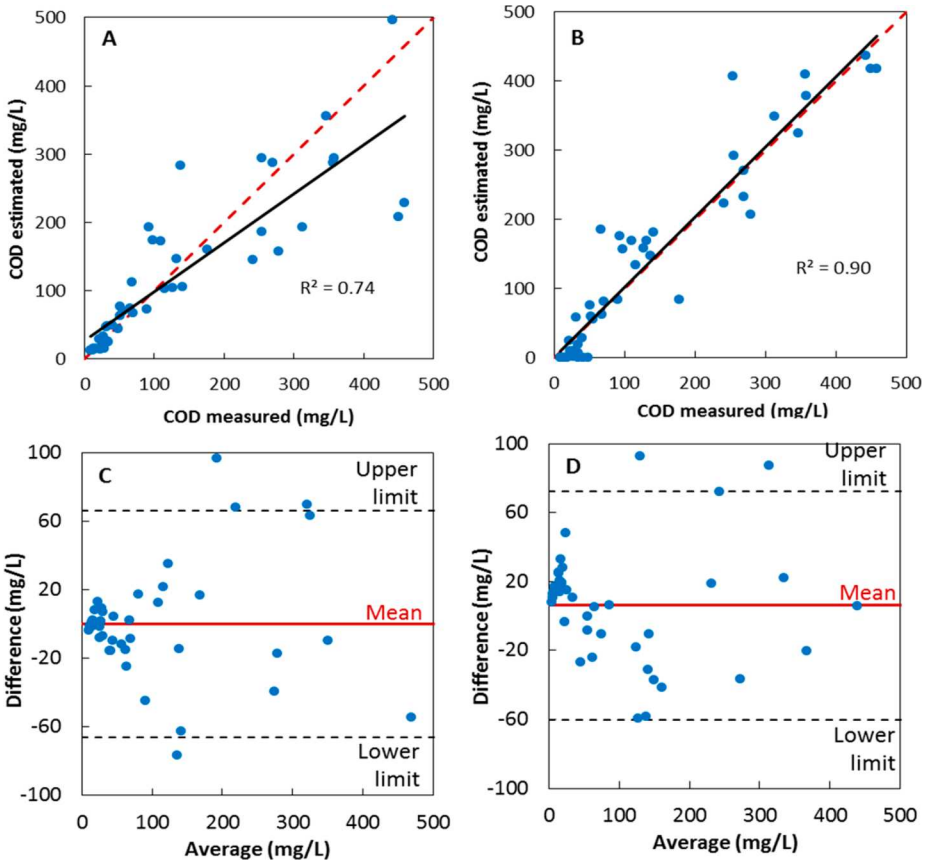

Figure 5. Regression analysis of the exponential model with output current as measurement (A) and the dynamic model as a softsensor (B) for the online estimation of the effluent acetate concentration. Solid and dashed lines show linear regression and line of agreement ($y = x$) trendlines, respectively. Bland and Altman plots for the exponential (C) and softsensor (D) models show the difference between the measured and estimated values and limits of agreement.

control strategies, which rely on real-time measurements. Wastewater treatment in a cascade of two MFCs offers a dual advantage of energy-positive COD removal and online estimation of effluent COD concentration. Importantly, the approach of MFC-based online COD measurements can be extended to a single MFC installed in the effluent stream of a conventional wastewater treatment process.

Our work presents two distinct approaches for COD estimation using the electrical performance of an MFC. In one approach, a simple regression model can be used to infer current produced in the MFC with the COD concentration. Alternatively, a simple COD mass balance-based dynamic model representing a soft-sensor can also be used. While online COD estimations demonstrated in this study are based on acetate-fed MFCs, a similar approach could be used with more complex wastewaters, since a linear dependence of MFC current on COD and BOD wastewater concentrations has been previously demonstrated in batch tests.[27−30] Furthermore, while this study was focused on current and power correlations with COD measurements, the MFC-based sensor can also be used for BOD estimations due to the near constant COD/BOD ratio of wastewaters. Furthermore, removal of ammonia and sulfate in an MFC was recently demonstrated[34,35] suggesting the possibility of developing respective MFC sensors.

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Notes

The authors declare no competing financial interest.

REFERENCES

(1) Chaudhuri, S. K.; Lovley, D. R. Electricity generation by direct oxidation of glucose in mediatorless microbial fuel cells. *Nat. Biotechnol.* **2003**, *21* (10), 1229−32.

(2) Rabaey, K.; Verstraete, W. Microbial fuel cells: novel biotechnology for energy generation. *Trends Biotechnol.* **2005**, *23* (6), 291−8.

(3) Li, W. W.; Yu, H. Q.; He, Z. Towards sustainable wastewater treatment by using microbial fuel cells-centered technologies. *Energy Environ. Sci.* **2014**, *7* (3), 911−924.

(4) Du, Z.; Li, H.; Gu, T. A state of the art review on microbial fuel cells: A promising technology for wastewater treatment and bioenergy. *Biotechnol. Adv.* **2007**, *25* (5), 464−82.

(5) Ledezma, P.; Greenman, J.; Ieropoulos, I. MFC-cascade stacks maximise COD reduction and avoid voltage reversal under adverse conditions. *Bioresour. Technol.* **2013**, *134*, 158−65.

(6) Hodgson, D. M.; Smith, A.; Dahale, S.; Stratford, J. P.; Li, J. V.; Gruning, A.; Bushell, M. E.; Marchesi, J. R.; Avignone Rossa, C. Segregation of the Anodic Microbial Communities in a Microbial Fuel Cell Cascade. *Front. Microbiol.* **2016**, *7*, 699.

DOI: 10.1021/acs.iecr.7b02586
Ind. Eng. Chem. Res. 2017, 56, 12471−12478

(7) Pinto, R. P.; Tartakovsky, B.; Perrier, M.; Srinivasan, B. Optimizing treatment performance of microbial fuel cells by reactor staging. *Ind. Eng. Chem. Res.* **2010**, *49* (19), 9222−9229.
(8) Jin, X.; Angelidaki, I.; Zhang, Y. Microbial Electrochemical Monitoring of Volatile Fatty Acids during Anaerobic Digestion. *Environ. Sci. Technol.* **2016**, *50* (8), 4422−9.
(9) Chang, I. S.; Jang, J. K.; Gil, G. C.; Kim, M.; Kim, H. J.; Cho, B. W.; Kim, B. H. Continuous determination of biochemical oxygen demand using microbial fuel cell type biosensor. *Biosens. Bioelectron.* **2004**, *19* (6), 607−613.
(10) Chouler, J.; Di Lorenzo, M. Water Quality Monitoring in Developing Countries; Can Microbial Fuel Cells be the Answer? *Biosensors* **2015**, *5* (3), 450−70.
(11) Di Lorenzo, M.; Curtis, T. P.; Head, I. M.; Scott, K. A single-chamber microbial fuel cell as a biosensor for wastewaters. *Water Res.* **2009**, *43* (13), 3145−3154.
(12) Kim, B. H.; Chang, I. S.; Cheol Gil, G.; Park, H. S.; Kim, H. J. Novel BOD (biological oxygen demand) sensor using mediator-less microbial fuel cell. *Biotechnol. Lett.* **2003**, *25* (7), 541−545.
(13) Geerdink, R. B.; van den Hurk, R. S.; Epema, O. J. Chemical oxygen demand: Historical perspectives and future challenges. *Analytica Chimica Acta.* **2017**, *961* (18), 1−11.
(14) Pasternak, G.; Greenman, J.; Ieropoulos, I. Self-powered, autonomous Biological Oxygen Demand biosensor for online water quality monitoring. *Sens. Actuators, B* **2017**, *244*, 815−822.
(15) Sun, J. Z.; Kingori, G. P.; Si, R. W.; Zhai, D. D.; Liao, Z. H.; Sun, D. Z.; Zheng, T.; Yong, Y. C. Microbial fuel cell-based biosensors for environmental monitoring: a review. *Water Sci. Technol.* **2015**, *71* (6), 801−9.
(16) Zhang, Y.; Angelidaki, I. A simple and rapid method for monitoring dissolved oxygen in water with a submersible microbial fuel cell (SBMFC). *Biosens. Bioelectron.* **2012**, *38*, 189−194.
(17) Carstea, E. M.; Bridgeman, J.; Baker, A.; Reynolds, D. M. Fluorescence spectroscopy for wastewater monitoring: A review. *Water Res.* **2016**, *95*, 205−19.
(18) Geerdink, R. B.; Sebastiaan van den Hurk, R.; Epema, O. J. Chemical oxygen demand: Historical perspectives and future challenges. *Anal. Chim. Acta* **2017**, *961*, 1−11.
(19) Woodward, L.; Perrier, M.; Srinivasan, B.; Pinto, R. P.; Tartakovsky, B. Comparison of real-time methods for maximizing power output in microbial fuel cells. *AIChE J.* **2010**, *56* (10), 2742−2750.
(20) Coronado, J.; Perrier, M.; Tartakovsky, B. Pulse-width modulated external resistance increases the microbial fuel cell power output. *Bioresour. Technol.* **2013**, *147*, 65−70.
(21) Tartakovsky, B.; Manuel, M. F.; Neburchilov, V.; Wang, H.; Guiot, S. R. Biocatalyzed hydrogen production in a continuous flow microbial fuel cell with a gas phase cathode. *J. Power Sources* **2008**, *182* (1), 291−297.
(22) Åmand, L.; Olsson, G.; Carlsson, B. Aeration control - a review. *Water Sci. Technol.* **2013**, *67*, 2374−2398.
(23) Pinto, R. P.; Srinivasan, B.; Guiot, S. R.; Tartakovsky, B. The effect of real-time external resistance optimization on microbial fuel cell performance. *Water Res.* **2011**, *45* (4), 1571−8.
(24) Zhang, L.; Li, J. V.; Zhu, X.; Ye, D.; Fu, Q.; Liao, Q. Startup Performance and Anodic Biofilm Distribution in Continuous-Flow Microbial Fuel Cells with Serpentine Flow Fields: Effects of External Resistance. *Ind. Eng. Chem. Res.* **2017**, *56* (14), 3767−3774.
(25) Sugnaux, M.; Savy, C.; Cachelin, C. P.; Hugenin, G.; Fischer, F. Simulation and resolution of voltage reversal in microbial fuel cell stack. *Bioresour. Technol.* **2017**, *238*, 519−527.
(26) Liu, B.; Lei, Y.; Li, B. A batch-mode cube microbial fuel cell based "shock" biosensor for wastewater quality monitoring. *Biosens. Bioelectron.* **2014**, *62*, 308−14.
(27) Jin, X.; Angelidaki, I.; Zhang, Y. Microbial Electrochemical Monitoring of Volatile Fatty Acids during Anaerobic Digestion. *Environ. Sci. Technol.* **2016**, *50*, 4422−4429.
(28) Di Lorenzo, M.; Curtis, T. P.; Head, I. M.; Scott, K. A single-chamber microbial fuel cell as a biosensor for wastewaters. *Water Res.* **2009**, *43*, 3145−3154.
(29) Kim, B. H.; Chang, I. S.; Gil, G. C.; Park, H. S.; Kim, H. J. A novel bioelectrochemical BOD sensor operating with voltage input. *Biotechnol. Lett.* **2003**, *25*, 541−545.
(30) Chang, I. S.; Jang, J. K.; Gil, G. C.; Kim, M.; Kim, H. J.; Cho, B. W.; Kim, B. H. Continuous determination of biochemical oxygen demand using microbial fuel cell type biosensor. *Biosens. Bioelectron.* **2004**, *19*, 607−613.
(31) Martin, E.; Savadogo, O.; Guiot, S. R.; Tartakovsky, B. The influence of operational conditions on the performance of a microbial fuel cell seeded with mesophilic sludge. *Biochem. Eng. J.* **2010**, *51*, 132−139.
(32) Zhang, Y.; Olias, L. G.; Kongjan, P.; Angelidaki, I. Submersible microbial fuel cell for electricity production from sewage sludge. *Water Sci. Technol.* **2011**, *64*, 50−55.
(33) Luo, S.; Sun, H.; Ping, Q.; Jin, R.; He, Z. A review of modeling bioelectrochemical systems: engineering and statistical aspects. *Energies* **2016**, *9* (2), 111.
(34) Zhang, Y.; Angelidaki, I. Recovery of ammonia and sulfate from waste streams and bioenergy production via bipolar bioelectrodialysis. *Water Res.* **2015**, *85*, 177−184.
(35) Zhang, Y.; Angelidaki, I. Submersible microbial desalination cell for simultaneous ammonia recovery and electricity production from anaerobic reactors containing high levels of ammonia. *Bioresour. Technol.* **2015**, *177*, 233−239.

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