

# Tubular Microbial Fuel Cells for Efficient Electricity Generation

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A tubular, single-chambered, continuous microbial fuel cell (MFC) that generates high power outputs using a granular graphite matrix as the anode and a ferricyanide solution as the cathode is described. The maximal power outputs obtained were 90 and 66 W m<sup>-3</sup> net anodic compartment (NAC) (48 and 38 W m<sup>-3</sup> total anodic compartment (TAC)) for feed streams based on acetate and glucose, respectively, and 59 and 48 W m<sup>-3</sup> NAC for digester effluent and domestic wastewater, respectively. For acetate and glucose, the total Coulombic conversion efficiencies were 75 ± 5% and 59 ± 4%, respectively, at loading rates of 1.1 kg chemical oxygen demand m<sup>-3</sup> NAC volume day<sup>-1</sup>. When wastewater was used, of the organic matter effectively removed (i.e., 22% at a loading of 2 kg organic matter m<sup>-3</sup> NAC day<sup>-1</sup>), up to 96% was converted to electricity on a Coulombic basis. The lower overall efficiency of the wastewater-treating reactors is related to the presence of nonreadily biodegradable organics and the interference of alternative electron acceptors such as sulfate present in the wastewater. To further improve MFCs, focus has to be placed on the enhanced conversion of nonrapidly biodegradable material and the better directing of the anode flow toward the electrode instead of to alternative electron acceptors. Also the use of sustainable, open-air cathodes is a critical issue for practical implementation.

## Introduction

Microbial fuel cells (MFCs) are of interest as a technology for the conversion of carbohydrates to electricity (1–3). In these reactors, bacteria transfer the electrons gained from their electron donor toward an anode. These electrons are subsequently conducted over a resistance or power user toward a cathode, where oxygen or an alternative electron acceptor is being reduced (4, 5). The applications range from offshore sediment-based electricity generation toward small-scale batteries and larger-scale bio-converters (6).

The output of a MFC is determined by the bacterial turnover rate, the internal resistance, and the activation overpotential at the electrodes (8). The bacterial turnover rate is in turn determined by biological parameters such as bacterial density, substrate adaptation, temperature, and pH (6, 9). The other two bottlenecks are of an electrochemical nature. The internal resistance of the MFC can be lowered by decreasing the distance between the anode and the cathode and selecting the appropriate materials (6). The activation overpotential is determined by the electrode surface and the nature of the electron transport process from

the bacteria to the electrode (8). Electron transfer can occur either directly at the bacterial cell surface (10) or by mobile, shuttling compounds that are produced by bacteria (11) or added to the medium. The latter addition is economically not viable in many cases. Also providing catalysts within the electrode matrix may decrease the activation overpotential. Park and Zeikus (12) obtained a power density of 788 mW m<sup>-2</sup> by supplementing a graphite electrode with MnO<sub>2</sub>, while the nonmediated electrode allowed power densities of only 0.65 mW m<sup>-2</sup>. This result was obtained using a mixed culture; the power output results for axenic cultures are generally lower (4, 12, 13). Using a mixed culture fed with glucose, Rabaey et al. (7, 14) obtained densities of up to 4310 mW m<sup>-2</sup> using an adapted consortium. This adapted consortium was capable of producing redox mediators in situ; hence the system was mediated (11).

One of the most promising applications of MFCs is the energy-efficient treatment of wastewater. Wastewater treatment by conventional aeration now represents substantial energy expenditure. Alternatives have been developed, such as upflow anaerobic sludge blanket reactors (15). This technology enables energy recuperation by the digestion of organic matter toward biogas, which can be utilized in a combustion engine. However, the diluted nature of the domestic wastewater and the need for elevated temperatures hamper the direct anaerobic digestion of sewage (16). MFCs operating on real wastewater were proposed as early as 1991 (17). An improved design was recently proposed by Liu et al. (2), obtaining power densities of 1.6 W m<sup>-3</sup> total anode compartment (TAC). This output was increased to 3.7 W m<sup>-3</sup> TAC using a reactor design without a proton exchange membrane (18). However, the omission of the membrane decreased the Coulombic efficiency to 20%. The majority of the systems described thus far were operated in batch mode, while the treatment of wastewater requires a flow-through mode (19).

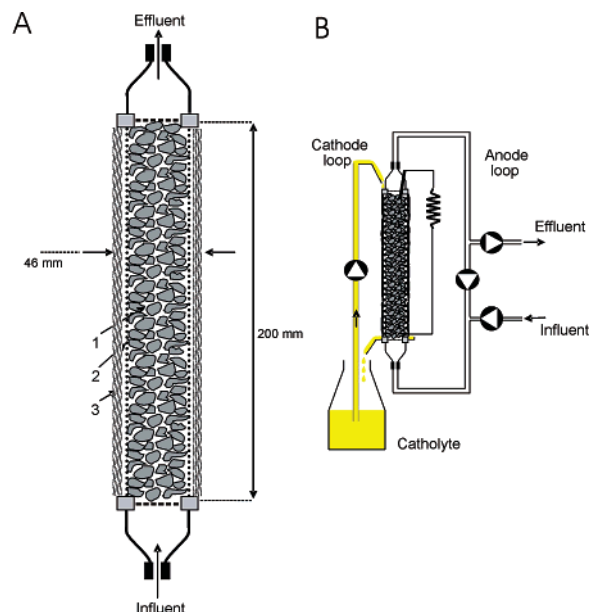
Rabaey et al. (20) constructed continuous reactors, operated on oligomeric carbohydrates, which were capable of removing up to 50% of the substrate COD as current, with a concomitant power generation of 49 W m<sup>-3</sup> net anodic compartment (NAC). In view of the fact that the anode compartment contained graphite carbon granules for 52% of its volume, the former value corresponds with a power generation of 32.5 W m<sup>-3</sup> TAC. He et al. (21) designed an upflow MFC based on artificial wastewater, which was operated in continuous mode. The power output of this system was limited due to the internal resistance of 84 Ω. The internal resistance of the upflow, membraneless reactor used by Jang et al. (22) was considerably higher, notably 3.9 MΩ, which even more limited the attainable power output.

To alleviate the above-mentioned bottlenecks and in particular to decrease the internal resistance, we redesigned a MFC that takes into account both the electrochemical and the biological requirements to obtain a higher power output. All our systems described use ferricyanide as an artificial catholyte, which enables comparison with previously used systems. The reactors operated on diverse substrates, and several operating parameters were investigated to achieve higher power output in continuous flow mode.

## Materials and Methods

**Microbial Fuel Cells.** The reactors were comprised of a robust cation exchange membrane (Ultrex CMI7000, Membranes International, Inc.), which was folded and sealed through soldering to provide a cylindrical structure (Figure 1). Two glass stoppers, each with two inlets/outlets were inserted on

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**FIGURE 1.** View of the tubular microbial fuel cell used for the experiments. (A) Scheme (1, granular anode; 2, membrane; 3 cathode electrode); (B) overall setup.

both sides of this cylinder. Generally, the total inside volume of the anode compartment (TAC) was 390 mL, with the exception of a prolonged acetate-fed reactor having a volume of 560 mL. The reactor was filled with graphite granules (type 00514, diameters between 1.5 and 5 mm, estimated surface areas between 817 and 2720 m<sup>2</sup> m<sup>-3</sup>, Le Carbone, Belgium), functioning as the anodic electrode matrix. The granules have a porosity of 0.53. This decreased the reactor liquid volume (NAC) to 210 mL. The external contact was provided through a graphite rod (Morgan, Belgium, 5 mm diameter). The anode compartment was inoculated with a bacterial culture obtained from an active microbial fuel cell (20). An anode recirculation at 6 L h<sup>-1</sup> was applied, using a peristaltic pump (Watson Marlow, Belgium). The cathode consisted of a high surface area woven graphite mat (Alfa Aesar, Belgium) tightly matched around the membrane. The cathodic electrolyte, prepared according to Park and Zeikus (12), was a 50 mM K<sub>3</sub>Fe(CN)<sub>6</sub> solution in 100 mM KH<sub>2</sub>PO<sub>4</sub> (adjusted to pH 7 with 1 N NaOH) buffer (Merck, Belgium). The catholyte was dripped over the cathode at a rate of 6 L h<sup>-1</sup> and replaced before or upon depletion.

**Influent.** The synthetic influent was prepared as previously described (20) and fed at a rate of 720 mL per day to the anode compartment. Glucose and acetate were supplied to reach reactor loading rates of 0.5, 1.1, 1.6, and 2.7 kg m<sup>-3</sup> NAC day<sup>-1</sup> (0.27, 0.59, 0.86, and 1.45 kg m<sup>-3</sup> TAC day<sup>-1</sup>). Two types of wastewaters were tested (i.e., domestic wastewater (Ossemeersen, Ghent, Belgium) and a hospital wastewater (Maria Middelaers, Ghent, Belgium)). The wastewaters were prefiltered over a woven cloth to remove suspended solids before addition to the reactor. The chemical oxygen demand (COD) concentrations of the prefiltered wastewaters used were, respectively, 429 ± 292 and 332 ± 73 mg COD L<sup>-1</sup>. The biological oxygen demand (BOD<sub>20</sub>) values were 160 ± 95 and 340 mg BOD L<sup>-1</sup>. For the additional tests, acetate (400 and 100 mg L<sup>-1</sup>) and peptone (100 mg L<sup>-1</sup>) were spiked to the influent wastewater. In experiments where the influence of sulfate reduction was assessed, 10 mM NaMoO<sub>4</sub> was used as a sulfate reduction inhibitor. Digester effluent from a potato processing plant (Primeur, Waregem, Belgium) was used as the MFC influent after 2 days of incubation, during which fermentation increased the acetate content to 1269 ± 105 mg L<sup>-1</sup>.

**Electrochemical Monitoring.** Measurements of the power output were performed using an Agilent HP 34970 data acquisition unit. Every 60 s, a full channel scan was performed, and the data were stored. The external system resistance  $R$  was at its maximum at 100 Ω, and the current was deducible as

$$I = VR^{-1} = Qt^{-1} \quad (1)$$

with  $I$  the current (A),  $V$  the voltage (V),  $Q$  the charge (C), and  $t$  time (s). The power outputs of the cells were calculated as

$$P \text{ (W)} = IV \quad (2)$$

Energy production can then be expressed as

$$E \text{ (J)} = Pt \quad (3)$$

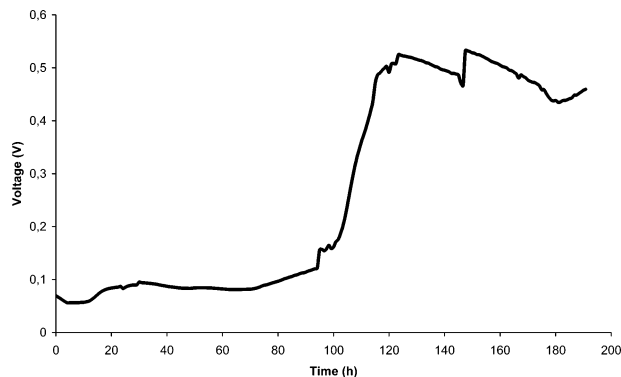
Potentiostatic measurements were performed using a PAR Bi-Stat potentiostat (Princeton Applied Research), and an Ag/AgCl reference electrode (0.197 mV vs standard hydrogen electrode) (BAS) was used as a reference within the anode compartment. The internal resistances of the reactors were determined according to the current interrupt method (21).

**Data Representation.** All values given are expressed as daily averages, except the maximum power results, which are hour-based. Unless indicated otherwise, the calculations concerning loading and power output per unit volume refer to the NAC, i.e., the anode liquid volume. This enables comparison with other MFC systems described thus far. The TAC refers to the total anodic volume, including the volume of the liquid and the volume occupied by the solid anode. The Coulombic efficiency expresses the efficiency of transferring electrons available in the substrate to an electrode, while the energetic efficiency describes the energy recovery from the substrate (3). These efficiencies can be calculated as

$$\epsilon_{\text{Coulombic}} = \frac{It_{\text{exp}}M}{Fn(\text{COD}_{\text{added}})} \quad \epsilon_{\text{energetic}} = \frac{VI t_{\text{exp}}}{E_{\text{added}}}$$

where  $F$  is Faraday's constant (96 485 C mol<sup>-1</sup>),  $t_{\text{exp}}$  the experiment time (s),  $\text{COD}_{\text{added}}$  the amount of COD added (g) with energetic content  $E_{\text{added}}$  (J),  $n$  the number of electrons exchanged per mole of oxygen (4), and  $M$  the molar mass of oxygen (32 g mol<sup>-1</sup>)

**Chemical Analysis.** For analysis of the volatile fatty acids, an extraction in diethyl ether was performed (23). The samples were analyzed with a capillary flame ionization detector (FID) gas chromatograph, GC 8000 Carlo Erba Instruments (Wigan, U. K.), connected to a computer. The column used was an Alltech (Deerfield, IL) EC-1000 (30 m, 0.32 mm i.d.,  $d_f$  0.25 μm). The temperature was controlled at 135 °C for the isotherm oven and 200 °C for the detector and the injector. Nitrogen gas was used as the carrier gas at 3 mL min<sup>-1</sup>. Gas chromatography (Intersmat IGC 120 MB) was used for determination of CO<sub>2</sub> and CH<sub>4</sub> in the headspace (24). H<sub>2</sub> was measured using an OPUS H<sub>2</sub> sensor (Zellweger Analytics Ltd., Dorset, U. K.). Chemical oxygen demand measurements were made according to the dichromate method (23). Total suspended solids and volatile suspended solids of the biomass trapped in the graphite matrix were determined by drying and incineration (23), after which the weight and the COD of the material were determined. Samples were filtered through a syringe 0.22-μm filter unit (Millex), and SO<sub>4</sub><sup>2-</sup> was determined using a Dionex ion chromatograph with an AS9HC column (Dionex); a 9 mM Na<sub>2</sub>CO<sub>3</sub> solution was used as eluent, at a flow of 1 mL min<sup>-1</sup>. A sample loop of 100 μL was used; the detector was an electrochemical conductivity detector.



**FIGURE 2. Power output over time of a microbial fuel cell fed with acetate (external resistance of 100  $\Omega$ ). A long lag phase precedes the period in which high power output levels are attained.**

## Results

**Acetate-Fed Microbial Fuel Cells.** Acetate-based current generation increased sharply after a 100-h lag phase, demonstrating a need for biomass buildup and adaptation (Figure 2).

The maximum power output was  $90 \text{ W m}^{-3} \text{ NAC}$  ( $48 \text{ W m}^{-3} \text{ TAC}$ ,  $31 \text{ mA}$ ,  $20 \Omega$ ), obtained after 26 days of operation with an organic loading rate of  $1.1 \text{ kg COD m}^{-3} \text{ NAC day}^{-1}$ . The average power output at this loading rate was  $52 \pm 10 \text{ W m}^{-3} \text{ NAC}$ , implying an average Coulombic efficiency of  $75 \pm 7\%$  (Table 1). At a higher loading rate of  $2.1 \text{ kg m}^{-3} \text{ NAC day}^{-1}$ , the average Coulombic efficiency was  $36 \pm 2\%$ , with a maximum power output of  $58 \text{ W m}^{-3} \text{ NAC}$ . This reactor type was able to convert up to  $1.12 \text{ kg COD m}^{-3} \text{ NAC day}^{-1}$  to electricity on a daily basis. Upon variation of the organic loading rate and the external resistance, changes in the overall power output and the substrate to current conversion efficiency were obtained (Figure 3). The lower the external resistance, the higher the Coulombic efficiency generally is, while this does not imply a higher energetic efficiency.

The sulfate that was entering the reactor was not reduced during the test runs (data not shown). The bacteria degrading acetate preferred the anode as the electron acceptor over sulfate, even while the redox potential of the anode remained below  $-220 \text{ mV}$  versus the standard hydrogen electrode, which is normally the potential at which bacteria perform sulfate reduction (25). No hydrogen gas production was detectable, although this cannot be excluded because of the fact that the cation exchange membrane allows for gas exchange with the cathode compartment (18). Upon increase of the reactor volume from 210 to 300 mL, an increased current output of up to 59 mA ( $32 \pm 5 \text{ mA}$  on average at  $10 \Omega$ ) could be obtained, amounting to a substrate to current conversion of  $1.41 \text{ kg COD m}^{-3}$  anodic volume  $\text{day}^{-1}$ . The average power output per unit volume was  $51 \pm 17 \text{ W m}^{-3} \text{ NAC}$  ( $27 \text{ W m}^{-3} \text{ TAC}$ ,  $1.1 \text{ kg COD m}^{-3} \text{ NAC day}^{-1}$ ,  $15 \Omega$  resistor,  $32 \text{ mA}$ ). Apparently, no gain in additional power density was obtained through larger sizing.

**Glucose-Fed Microbial Fuel Cells.** The power output of the glucose-fed MFCs was generally lower than that of the acetate-fed reactors (Table 1). The maximum power output obtained on a daily basis was  $66 \text{ W m}^{-3} \text{ NAC}$ , at a loading rate of  $1.6 \text{ kg COD m}^{-3} \text{ NAC day}^{-1}$  ( $35 \text{ W m}^{-3} \text{ TAC}$ ,  $20 \Omega$  resistor,  $27 \text{ mA}$ ). On average, the power output was  $49 \pm 8 \text{ W m}^{-3} \text{ NAC}$  ( $1.6 \text{ kg COD m}^{-3} \text{ NAC day}^{-1}$ ,  $26 \text{ W m}^{-3} \text{ TAC}$ ). At a loading rate of  $1.1 \text{ kg COD m}^{-3} \text{ NAC day}^{-1}$ , an average COD to current efficiency of  $59 \pm 4\%$  was obtained. The current of  $27 \text{ mA}$  obtained corresponded to a  $0.92 \text{ kg COD m}^{-3} \text{ NAC day}^{-1}$  removal as current. The concentration of fermentation products such as acetate, propionate, and butyrate was generally low; only acetate could be measured in considerable

quantities (above 1 ppm) at concentrations of  $26 \pm 15 \text{ mg L}^{-1}$ . Sulfate was to a major extent reduced; the average concentrations dropped from  $37.3 \pm 0.4 \text{ mg L}^{-1}$  in the influent to  $6.4 \pm 1.1 \text{ mg L}^{-1} \text{ SO}_4^{2-}\text{-S}$  in the effluent.  $\text{H}_2\text{S}$  can permeate through the membrane toward the cathode; hence an estimation of the concentration of  $\text{H}_2\text{S}$  in the gas phase was not possible. Taking into account the fact that upon reduction of 1 mol of  $\text{SO}_4^{2-}$  to  $\text{S}^{2-}$  a maximum 8 mol of electrons are diverted from the electrode, the sulfate reduction accounts for a COD as sulfide removal of a maximum of  $0.243 \pm 0.009 \text{ kg COD m}^{-3} \text{ NAC day}^{-1}$ . However, because sulfide can be reoxidized and hence participate in the current generation, the amount of electrons diverted from the electrode can be notably smaller (26, 27). As previously observed for acetate, variation of the loading rate changed the overall power output and the Coulombic efficiency (Figure 4).

**Wastewater- and Digester-Effluent-Fed Microbial Fuel Cells.** The output provided by the MFC fed with wastewater was generally lower than the output of the synthetic influents. The maximum power output in the first 60-day period was  $18 \text{ W m}^{-3} \text{ NAC}$  ( $10 \text{ W m}^{-3} \text{ TAC}$ ,  $75 \Omega$ ,  $7 \text{ mA}$ ), while on average  $5 \pm 2 \text{ W m}^{-3} \text{ NAC}$  was obtained. This corresponded to a daily COD as current removal of  $0.14 \pm 0.08 \text{ kg COD m}^{-3} \text{ NAC day}^{-1}$ . The COD removal of the reactors was highly variable due to the fluctuations of the influent COD concentration; on average the removal was  $0.71 \pm 0.06 \text{ kg COD m}^{-3} \text{ NAC day}^{-1}$ . This implies that only 20% of the removed COD was actually related to current. Hence, a significant portion of the COD in the wastewater was probably removed through the use of either alternative electron acceptors or accumulation in the reactors. After a 60-day run, the biomass dry weight accumulated in the reactors accounted for  $70 \pm 4\%$  of the removed COD. This fraction consisted both of trapped, recalcitrant material and active microbial biomass.

During the test run, sulfate removal was observed; on average  $11 \pm 3 \text{ mg SO}_4^{2-}\text{-S L}^{-1}$  influent was unaccounted for on a daily basis. The sulfate reduction represents a maximum COD removal of  $0.086 \pm 0.024 \text{ kg COD m}^{-3} \text{ NAC day}^{-1}$ . Part of the formed sulfide was possibly measured as COD in the effluent during COD analysis. Inhibition of sulfate reducers by  $\text{NaMoO}_4$  addition decreased the sulfate reduction from  $47 \pm 15\%$  to  $-4 \pm 11\%$  but did not entail a higher Coulombic efficiency; only in the short term an increase could be noted (data not represented). Overall, of the  $0.71 \pm 0.06 \text{ kg COD m}^{-3} \text{ NAC day}^{-1}$  removed from the filtrate (possibly higher due to some  $\text{S}^{2-}$  oxidation that disrupts the COD measurement of the effluent),  $0.086 \pm 0.024 \text{ kg COD m}^{-3} \text{ NAC day}^{-1}$  was removed through sulfate reduction,  $0.14 \pm 0.08 \text{ kg COD m}^{-3} \text{ NAC day}^{-1}$  as current, and  $0.49 \pm 0.03 \text{ kg COD m}^{-3} \text{ NAC day}^{-1}$  as trapped material and formed biomass.

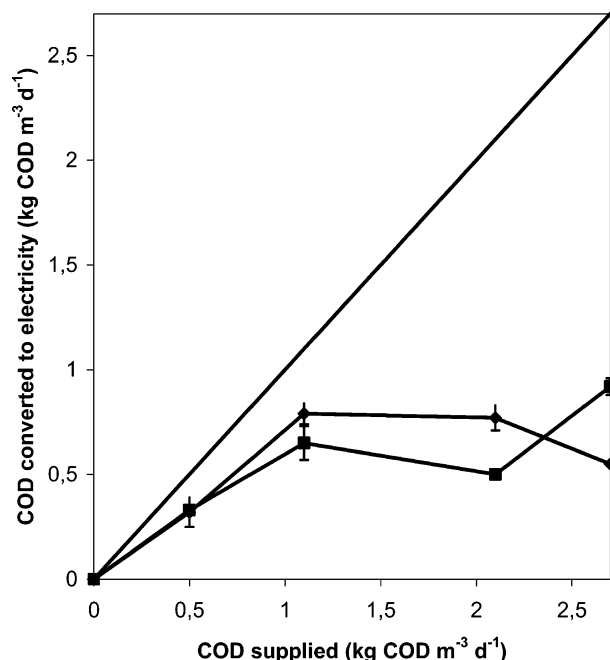
To further decrease the reduction of alternative electron acceptors and increase the biodegradation, the resistance of the external circuit was lowered in a subsequent test run, in which a different, more concentrated wastewater (i.e., hospital wastewater) was fed to the reactor. The lower external resistance causes a smaller voltage over the MFC for the same current and hence a higher (or less negative) anode potential (3). The decrease of the resistance caused an increase in MFC power output to  $8 \pm 5 \text{ W m}^{-3} \text{ NAC}$  ( $4 \text{ W m}^{-3} \text{ TAC}$ ) on average, with a maximal power output of  $48 \text{ W m}^{-3} \text{ NAC}$  ( $25 \text{ W m}^{-3} \text{ TAC}$ ). The average current output was  $13 \pm 4 \text{ mA}$  ( $21 \text{ mA}$  maximum). Hence, the reactor removed  $0.43 \pm 0.10 \text{ kg COD m}^{-3} \text{ NAC day}^{-1}$  as current. In total, the reactor removed  $0.45 \pm 0.44 \text{ kg COD m}^{-3} \text{ NAC day}^{-1}$  ( $23 \pm 22\%$  of the COD input), of which on average 96% was current. The sulfate reduction was not affected, corresponding to a COD removal of  $0.14 \pm 0.04 \text{ kg COD m}^{-3} \text{ NAC day}^{-1}$ .

Upon replacement of the wastewater with digester effluent, an increase of the power output to  $59 \text{ W m}^{-3} \text{ NAC}$  was noted, with an average power output of  $39 \pm 9 \text{ W m}^{-3}$  during

**TABLE 1. Results Obtained on Diverse Substrates, Using a Tubular MFC and Hexacyanoferrate as the Catholyte ( $n = 2$ , Based on Daily Averages)<sup>a</sup>**

substrate (kg COD m <sup>-3</sup> )	average (maximum) power (W m <sup>-3</sup> )	average (maximum) Coulombic efficiency (%)	average (maximum) substrate to electricity (kg COD m <sup>-3</sup> day <sup>-1</sup> ) <sup>b</sup>	losses to sulfate (kg COD m <sup>-3</sup> day <sup>-1</sup> ) <sup>b</sup>
acetate (0.321)	52 ± 10 (90)	75 ± 7 (98)	0.79 ± 0.08 (1.12)	0.002 ± 0.005
glucose (0.467)	49 ± 8 (66)	43 ± 9 (74)	0.69 ± 0.06 (0.92)	0.243 ± 0.009
hospital wastewater (0.332 ± 0.073)	8 ± 5 (48)	22 ± 5 (36)	0.43 ± 0.10 (0.69)	0.086 ± 0.024

<sup>a</sup> The results are based on the indicated substrate concentration, except the maximum results for substrate to electricity, which are at higher concentrations. <sup>b</sup> Expressed as NAC

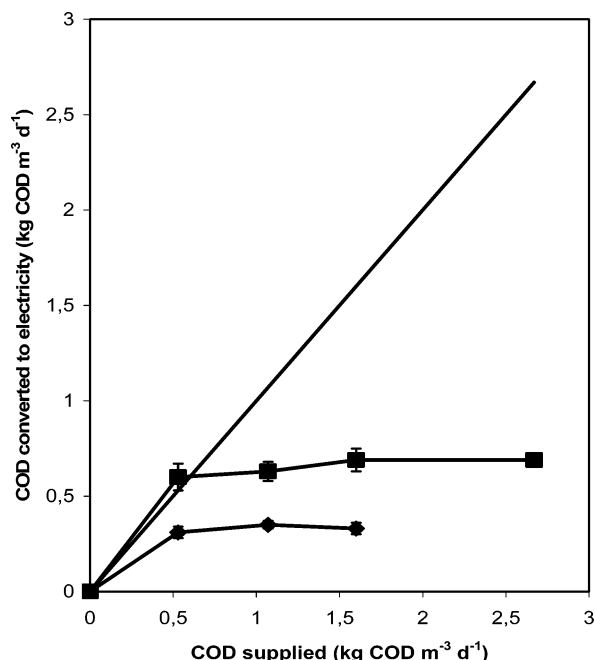


**FIGURE 3. Evolution of the amount of COD removed as electricity as a function of the COD loading rate for an acetate-fed tubular reactor. The external resistances applied were 20 Ω (◆) and 10 Ω (■).**

the experimental period. This corresponds to a COD as current removal of  $0.75 \pm 0.09$  kg COD m<sup>-3</sup> day<sup>-1</sup>. However, due to the low buffer capacity of the digestate, the pH in the reactor decreased to approximately 5.3 after 8 h, which caused a reactor failure.

**Reactor Spiking.** When 400 mg L<sup>-1</sup> influent acetate was spiked to wastewater poor in biodegradable COD (bCOD), the power increased from  $4.3 \pm 0.4$  to  $14.3 \pm 0.7$  W m<sup>-3</sup> NAC, demonstrating that the reactor mainly produces power through degradation of readily biodegradable organics (for 100 mg L<sup>-1</sup> influent the power increased from  $0.7 \pm 0.3$  to  $7.4 \pm 2.1$  W m<sup>-3</sup> NAC). The same holds for peptone; the power output increased from  $3.6 \pm 3.3$  to  $14.2 \pm 5.7$  W m<sup>-3</sup> NAC.

**Influence of the Cathode Performance.** As catholyte, a 50 mM K<sub>3</sub>Fe(CN)<sub>6</sub> solution was used. While the reductive reaction of this compound at the graphite electrode occurs at high rate, the reoxidation at the ambient air is not of significant proportion. The potential evolution of MFCs was monitored for both anode and cathode potential (Figure 5). Figure 5A demonstrates that the cathode potential remained rather constant through time, even in case the wastewater degenerates within the influent vessel. Upon renewal of the influent vessel, the anode potential rapidly resumes its original voltage, while the cathode is only slightly affected. This demonstrates the substantial stability of the K<sub>3</sub>Fe(CN)<sub>6</sub> catholyte. The decrease in the cathode potential is due to the

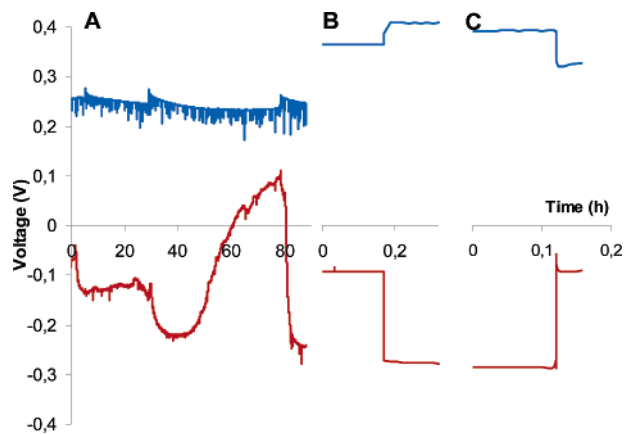


**FIGURE 4. Evolution of the amount of COD removed as electricity as a function of the COD loading rate for a glucose-fed tubular reactor. The external resistances applied were 50 Ω (◆) and 25 Ω (■). Upon a further decrease of the external resistance to 10 Ω, the amount of COD converted to current increased to 0.92 kg COD m<sup>-3</sup> day<sup>-1</sup>.**

limited regeneration of the catholyte by oxygen, causing a decrease in the ratio Fe(III)/Fe(II) in the K<sub>3</sub>Fe(CN)<sub>6</sub> catholyte. Upon replenishment of the catholyte, a rapid return of the cathode potential to the original value was observed. Disconnection of the electrical circuit of an acetate-fed MFC to determine the open-circuit potential caused a large potential drop at the anode (Figure 5B). This indicates that the potential losses during operation are mainly present at the anode side. The reverse evolution can be observed upon a decrease of the external resistance from 20 to 10 Ω; mainly the anode potential was affected (Figure 5C).

## Discussion

**Overall Process Balance.** Depending on the provided substrate, the Coulombic efficiency and the nature of the conversion process differ significantly. Acetate can be converted at a rate of  $0.79 \pm 0.08$  kg COD m<sup>-3</sup> NAC day<sup>-1</sup> and an efficiency of 75 ± 7%. Clearly, the fact that the degradation occurs through a generally oxidative metabolism by adapted bacteria has a major influence on the performance. The glucose and wastewater experiments demonstrate the impact of alternative electron acceptors present and the relevance of fermentative processes on the electron recovery. Methane generation has often been observed by other researchers (1, 28). Upon inhibition of methanogens, Kim et al. (1) obtained



**FIGURE 5.** Evolution of the potential of both anode (red) and cathode (blue) through time. (A) During a test run with wastewater, the anode potential can vary substantially due to breakdown of the influent in the feed vessel (between 45 and 75 h); after replenishment (75 h) the anode rapidly resumes activity; the cathode remains rather constant (the variation of the signal is caused by electrochemical noise in the surroundings). (B) Switching an MFC on acetate toward an open circuit causes mainly a drop in the anode potential. (C) Decreasing the resistance of an MFC on acetate from 20 to 10  $\Omega$  affects both anode and cathode potentials.

an increase in Coulombic efficiency from 40% to 70%. Yet, the conditions in our setup were not optimal for methanogens (moderate temperatures, pH levels below 7, putative oxygen intrusion through the membrane). Moreover, in previous studies it has been shown that at low external resistances, as used here, no methanogenesis occurs (14). However, at higher loading rates, methanogenesis was possibly one of the factors determining the reduced efficiency, aside from increased potential losses and a decreased overall removal. However, the possible oxygen influx through the membrane did not appear to entail substantial losses in the used setup.

Sulfate reduction appears to be the main alternative route used by the bacteria. The output of electrical current of reactors fed with wastewater did not increase after addition of sodium molybdate, although the sulfate reduction of sulfate to sulfide was effectively inhibited. One would expect the possibilities for electron diversion to sulfate to be seriously hampered upon addition of this inhibitor. Indeed, the addition effectively stopped the reduction of the sulfate. According to a recent study by Straub and Schink (27), sulfide can be reoxidized at metal surfaces and hence act as an electron shuttle, as previously suggested for sediment MFCs (26). The amount of electrons lost to sulfate reduction could thus be (partially) recovered through the reoxidation of sulfide. Hence, the addition of the molybdate in our case caused (i) the loss of an electron shuttle and (ii) a putative electron recovery that is higher than that attainable when sulfate reduction is possible, but not as high as 8 mol of electrons per 1 mol of sulfate reduced. Both antagonist factors may eliminate each other.

**Adaptation and Accumulation.** All reactors that were newly started showed a significant lag phase of 100 hours or more. This suggests the need for biomass buildup in the reactor. This buildup may be necessary for several reasons. First, oxygen enters through the cation exchange membrane in quantities that cannot be neglected. Taking into account calculations by Liu et al. (2) on the putative intrusion of oxygen through Nafion, this diffusion could account for a substantial COD removal of the influent fed to the tubular reactors. Initially, this oxygen influx will impede a lowering of the anode potential. As biomass builds up, this oxygen can be depleted, and the redox potential lowered. Moreover, formation of a biofilm onto the membrane can decrease the oxygen

influx. Second, sufficient substrate turnover rates are needed to reach the desired power outputs. If 1 kW power output per total 1 m<sup>3</sup> of the reactor is the objective (3) and assuming a theoretical energy content of 3 kWh per 1 kg of organics, then one needs to convert about 24 kg of organics per 1 m<sup>3</sup> NAC per day, at an energetic efficiency of 30%. Consider a microbial biomass operating at the level of highly loaded activated sludge; i.e., at 1.0 kg COD per 1 kg biomass dry weight (DW) per day (29), this corresponds with 24 kg of active biomass DW present per 1 m<sup>3</sup> reactor. Because about 50% of the reactor space is taken by the electrode, this implies a biomass density of about 50 kg m<sup>-3</sup> NAC. Such biomass densities are reported for anaerobic digesters (30). Evidently, higher energetic efficiencies and higher sludge loading rates can decrease this biomass amount by half or more. Moreover, the design of electrodes that have a similar or larger specific surface without large volume losses in the reactor can lead to a factor of 2 increase in the power per 1 m<sup>3</sup> of complete reactor. Finally, it must be stressed that adaptation of the bacterial association is needed (14); the species adapted to the substrate and the anode need to become performant.

**Factors Limiting Overall Conversion Efficiency.** The colloidal and particulate nature of part of the COD present in the filtrate can create obstructions within the anode compartment, where bacteria are not contacting the anode, in both the physical and the electrical sense. Hence, these bacteria can biodegrade some of the COD present through fermentation or the use of alternative electron acceptors as observed for sulfate. The biodegradation of the nonsoluble and more recalcitrant matter will also be hampered due to the fact that anaerobic degradation of these components is considerably slower than the aerobic, oxygen-driven degradation. Indeed, oxygen does not only function as an electron acceptor but also as a reactant to initiate biodegradation (25). Higher residence times could on one hand entail a higher Coulombic efficiency, while on the other hand this would increase the reactor dimensions.

The internal resistance was approximately 4  $\Omega$ , which is substantially lower than the resistances reported by He et al. (21) and Gil et al. (9). This positively influenced the performance by decreasing the losses.

**Sustainable and Efficient Electrodes.** While stable and robust, the cathode used in these experiments was not sustainable. The K<sub>3</sub>Fe(CN)<sub>6</sub> reoxidizes poorly with oxygen and needs to be replaced regularly. Catalyzed open-air cathodes need to be developed (31). At the moment, Pt is widely used as a catalyst in open-air cathodes. However, this catalyst is extremely sensitive to poisoning (32) and expensive. Alternative materials with high stability are needed. The data have been represented per unit NAC volume. Hence, the inner volume of the granules is not taken into account. Future electrode design will possibly allow a decrease of the volume of the anodic material. Because the volume of the liquid phase will increase in relation to the total reactor volume, this will lead to a higher power density of the overall reactor.

**Perspectives.** The tubular, upflow fuel cell presented here is simple in terms of construction and operation. Material costs amount to about \$16 per MFC of 0.21 L NAC used for the study; this does not include the costs for the pumps and for the catholyte. The simplicity of the system and the satisfactory results obtained provide perspective for treatment of liquid waste streams. Effluents of anaerobic reactors, containing substantial residual concentrations of volatile fatty acids (33), could be suited for conversion in the described setup.

At the current cost and the obtained power levels, the technology is not viable to produce electricity as a sole objective. As the maximum power obtained was 90 ± 11 W m<sup>-3</sup> NAC, the cost per 1 W of installed capacity would be on the order of \$900, which is roughly a factor 1000 higher than

the cost for other sources of renewable electricity such as, for example, wind mills (34). However, MFCs offer the opportunity for energy-efficient wastewater treatment. The issues to focus on are the accumulation of nonsoluble organic matter in the reactor and the diversion of electrons toward alternative electron acceptors. Controlling the anode potential and adapting the anode characteristics may decrease the sulfate reduction. If the particular organic material can be removed prior to entry to the MFC or can be removed at acceptable rates within the MFC, then the two problems may be solved and the Coulombic efficiency increased.

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