

Microbial fuel cells for wastewater treatment

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Abstract Microbial fuel cells (MFCs) are emerging as promising technology for the treatment of wastewaters. The potential energy conversion efficiencies are examined. The rates of energy recovery (W/m^3 reactor) are reviewed and evaluated. Some recent data relating to potato-processing wastewaters and a hospital wastewater effluent are reported. Finally, a set of process configurations in which MFCs could be useful to treat wastewaters is schematized. Overall, the MFC technology still faces major challenges, particularly in terms of chemical oxygen demand (COD) removal efficiency.

Keywords Anaerobic digester; anode; energy efficient; energy recovery; sustainable

Introduction

The conventional aerobic treatment of low-strength wastewaters such as domestic wastewater faces not only high capital expenditure but also considerable operational and energy consumption costs. The aeration of sewage represents an energy demand of about 0.5 kWh/m^3 , amounting to an energy use of the order of 30 kWh per capita per year. Furthermore, large amounts of excess sludge are produced, requiring an appropriate treatment and disposal (Wei *et al.*, 2003).

Microbial fuel cells (MFCs) can provide an answer to several of the problems which traditional wastewater treatment faces. They enable the recovery of energy out of the wastewater, while limiting both the energy input and the excess sludge production (Rabaey and Verstraete, 2005). However, for an extended period after their conception, MFCs remained a scientific curiosity because of their limited efficiency. Today, power outputs of MFCs are increasing and due to the integration of both microbial and electrochemical aspects, important hurdles have been tackled (Park and Zeikus, 2003; Rabaey *et al.*, 2005a). Nevertheless, several bottlenecks still exist, each requiring an appropriate development.

The technological aspects of MFCs are assessed in relation to the theoretical electricity conversion and the power outputs actually obtained. The treatment of wastewaters by MFCs is investigated and the niches of MFCs in the domain of wastewater treatment are explored.

Methods

Microbial fuel cell set-up and operational conditions

The MFCs were constructed of Perspex frames. In the frames, both a sample port and two inlets were constructed and two partitions were installed to obtain a flow-through pattern. A robust cation exchange membrane (Ultrex™ CMI7000, Membranes International Inc., USA) was used between the anode and cathode of the MFCs. Both the anode and cathode electrodes consisted of graphite granules (type 00514, diameter between 1.5 and 5 mm, Le Carbone, Belgium) and a graphite rod (5 mm diameter, Morgan, Belgium) to collect the electrons. Prior to use, the granules were washed three times with water to remove

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the dust. The catholyte was prepared according to Park and Zeikus (2003) and consisted of a 50 mM $K_3Fe(CN)_6$ solution containing a 100 mM phosphate buffer (Merck, Belgium) at pH 7. The catholyte was recirculated through the cathode matrix and its redox potential was controlled by a periodic renewal of the catholyte solution. The empty volume of one frame was 156 ml. After the installation of two partitions and a graphite electrode, the anode void volume amounted to 60 ml. This void volume was used in the calculations of the power density and volumetric loading rate.

Inoculation and operational conditions

The anodic compartment of the MFCs was inoculated with a mixture of anaerobic (Dendermonde, Belgium) and aerobic (Gent, Belgium) sludge. The MFCs were operated on two industrial organic streams: the influent and effluent of an anaerobic digester from a potato-processing factory (Waregem, Belgium). The chemical oxygen demand (COD) values of the latter two waters were respectively, 2.3 and 1.0 g COD per litre. The wastewaters were continuously fed to the MFCs by a peristaltic pump (Watson Marlow, Belgium) at a flow rate of 7–15 ml/h. The anodic liquid was recirculated at a rate of 106 ml/h. The MFCs were operated at a room temperature of 22 ± 3 °C. In a further part of the study, wastewater from a hospital (Gent, Belgium) with a COD of 0.6 g/l was used.

Calculations of the electrical parameters

The electrodes were connected by an external resistance (R). The potential (V) of the MFCs was measured and stored every 60 s with a 34970A Data Acquisition Switch Unit (Agilent, Diegem, Belgium). Using Ohm's law, the current (I) was calculated as $I = V \times R^{-1}$ with R the external resistance, varying from 50 to 100 Ω . The volumetric power density (P_v) was calculated as $P_v = U \times I \times V^{-1}$ with V as the void volume corresponding to 60 ml. The power densities were averaged hourly using the moving average of 60 P_v measurements. The coulombic efficiency (Q_{eff}) was determined by integrating the amount of coulombs produced over time (Q_{out}), divided by the amount of coulombs present in the loaded influent (Q_{in}) or $Q_{eff} = Q_{out} \times Q_{in}^{-1} = \sum(I \times \Delta t) \times (COD_{inf} \times n \times MM^{-1} \times F \times Q_f \times \sum \Delta t)^{-1}$ with Δt the duration of sample interval, COD_{inf} the COD concentration of the influent, n the number of electrons per mole of O_2 (equal to 4), MM the molar mass of O_2 (32 g/mol), F the Faraday constant (96485 C/mol electrons), and Q_f the flow rate of the influent.

Results and discussion

Theoretical conversion efficiencies

In an MFC, the biochemical energy contained in the organic matter is directly converted into electricity in what can be called a microbiologically mediated “combustion” reaction (Figure 1). This implies that the overall conversion efficiencies that can be reached are potentially higher for MFCs compared to other step processes.

Based on the calorific content of glucose, an MFC can theoretically (at 100% efficiency during metabolism) deliver 3 kWh for every kilogram of organic matter (dry weight) in one single step. As a matter of comparison, biomethanization yields 1 kWh of electricity and 2 kWh of heat per kilogram of COD removed. This means that during substrate conversion in MFCs, hardly any energy is released in the form of external heat, and that all biochemical energy in the waste can be potentially converted into electricity.

Substrate to electricity conversion: state of the art

Table 1 summarizes the current state of the art of MFCs operating on different discrete substrates. These reactors use hexacyanoferrate as electron acceptor and are hence not

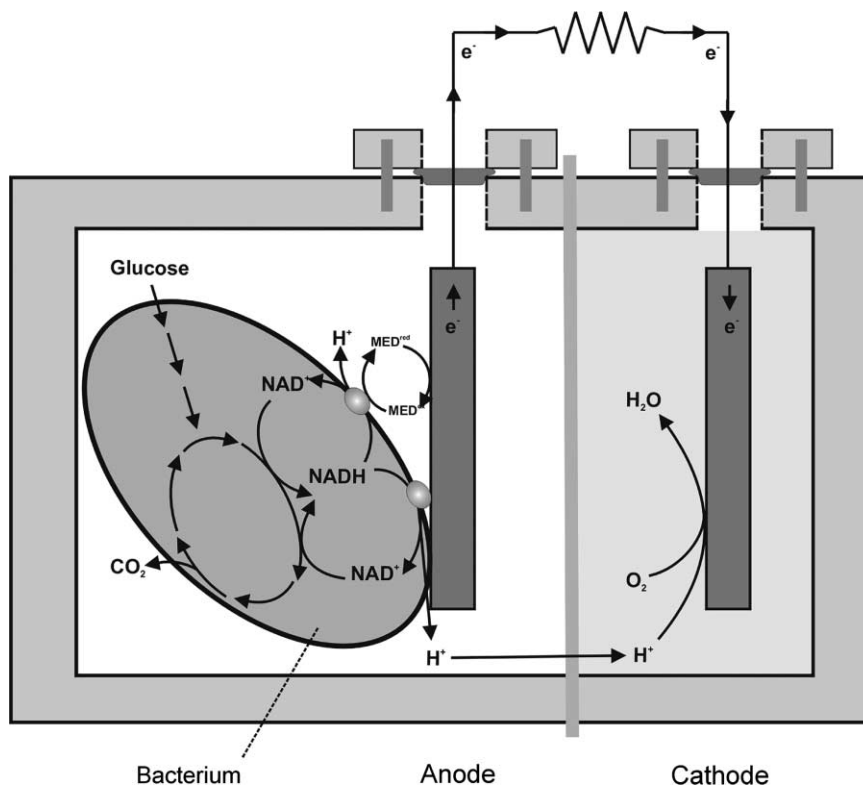


Figure 1 The principle of an MFC. The substrate is metabolized by bacteria, which transfer the gained electrons to the anode. This can occur either directly through the membrane or by means of mobile redox shuttles. The symbol \odot indicates terminal electron shuttle in/on the bacterium (Rabaey and Verstraete, 2005)

considered sustainable. However, the described reactors (two tubular designs and a stack design) worked continuously and produced the highest power densities described thus far. Connecting several stacked MFCs in a series or in parallel enabled the production of power outputs of 228–248 W/m³ at increased voltages (2.02 V in series) or currents (255 mA in parallel), thereby further expanding the potential of MFCs (Aelterman *et al.*, submitted).

Table 2 provides a series of values reported for Pt-based open-air cathodes. In contrast to hexacyanoferrate systems, the Pt catalyst directly reduces oxygen to water, resulting in a clean and sustainable cathode reaction. Currently, the performance of Pt-based cathodes in MFCs is improving and outputs up to 102 W/m³ using an artificial wastewater containing

Table 1 Power outputs in lab-scale MFCs supplied with defined substrates and using hexacyanoferrate as electron acceptor

Substrate	Power density (W/m ³)*	% COD captured as power	Substrate removal (kg COD per m ³ per day)*	CE (%)	Reference
Acetate	90	25	> 1.12**	98	Rabaey <i>et al.</i> (2005b)
Acetate	258	25	> 4.72**	72	Aelterman <i>et al.</i> (submitted)
Glucose	66	25	> 0.92**	74	Rabaey <i>et al.</i> (2005b)
Sucrose	1.67	–	1.2	2	He <i>et al.</i> (2005)
Sucrose	49	–	0.7	54	Rabaey <i>et al.</i> (2005c)

–: Data not available; CE: coulombic efficiency; *Expressed as NAC: netto anode compartment;

**Value based on maximal substrate-to-current conversion

Table 2 Power outputs in lab-scale MFCs supplied with defined substrates and using Pt-based open-air cathodes

Substrate	Power density (W/m ³)*	% COD captured as power	Substrate removal (kg COD per m ³ per day)*	CE (%)	Reference
Acetate	12.7	7.2	–	31	Liu <i>et al.</i> (2005a)
Butyrate	7.6	5	–	15	Liu <i>et al.</i> (2005a)
Glucose	12.5 ± 0.5	–	–	9–12	Liu and Logan (2004)
Artificial wastewater	102	–	8.9	34	Moon <i>et al.</i> (2006)

–: Data not available; CE: coulombic efficiency; *Expressed as NAC: netto anode compartment

glucose and glutamic acid (Moon *et al.*, 2006) have been measured. However, the use of Pt is expensive (Tsuchiya and Kobayashi, 2004), and in the future, cost-effective and efficient open-air cathodes suitable for wastewater treatment need to be developed for direct oxygen reduction.

The data for the discrete substrates indicate that large differences between reported data exist. Generally, the substrate-to-current efficiencies (coulombic efficiencies) are acceptable and even amount to 98%. Nevertheless, it should be observed that the energetic conversion efficiencies of COD to power are still below the maximum theoretical energetic conversion efficiency.

MFCs for the treatment of wastewaters

In this study, three wastewaters (both low and high strength) have been tested in a system using hexacyanoferrate as an electron acceptor. Figure 2 presents the power output while treating the influent and effluent of the anaerobic digester from a potato-processing factory. The highest power output treating the influent of the anaerobic digester amounted to $58 \pm 2 \text{ W/m}^3$. After 12 h, the power declined. In addition, the pH of both the substrates (i.e. the influent of the anaerobic digester) and the effluent of the MFC decreased to a pH of 5.5. When the effluent of the anaerobic digester at pH 7.5 was dosed, the power increased to $42 \pm 8 \text{ W/m}^3$. This indicates the importance of pH as a parameter for the functioning of the MFC. Furthermore, this revealed that the anaerobic digester effluent was a suitable substrate for energy recovery by means of an MFC, even at ambient temperature.

Several authors have used wastewater as an electron donor for MFCs. The wastewater data in Table 3 illustrate that the power outputs for complex wastewaters are factor 5 or lower compared to discrete substrates. While substrate removal rates for real wastewaters range from 0.5 to 2.99 kg COD per m³ reactor per day, the removal rates for artificial wastewater can reach up to 8.9 kg COD per m³ reactor per day, indicating the potential to

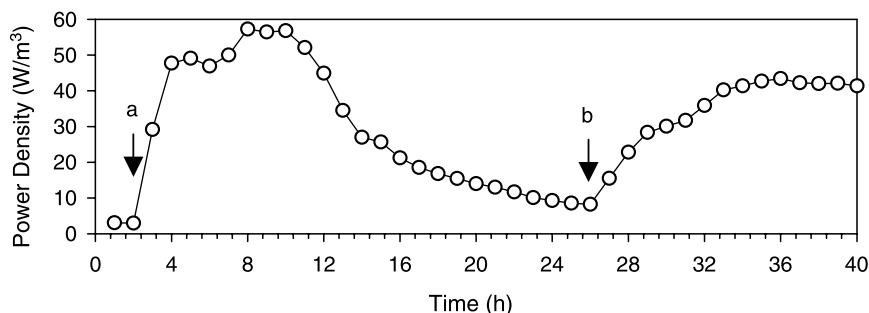


Figure 2 Hourly averaged power output of an MFC with hexacyanoferrate as catholyte and fed with an industrial a) influent and b) effluent of an anaerobic digester from a potato-processing factory

Table 3 Power outputs in lab-scale MFCs during the treatment of several wastewaters using Pt/C and hexacyanoferrate (HCF) as a cathode

Substrate	Power density (W/m ³)*	Substrate removal (kg COD per m ³ per day)*	CE (%)	Cathode	Reference
Domestic wastewater	1.7	0.43–0.60	3–12	Pt/C	Liu <i>et al.</i> (2004)
Domestic wastewater	3.7 ± 0.2	–	20	Pt/C	Liu and Logan (2004)
Hospital wastewater	8 ± 5	0.71 ± 0.06	22	HCF	Rabaey <i>et al.</i> (2005b)
Hospital wastewater	14 ± 1	0.67	13	HCF	This work
Influent from AD	58 ± 2	1.23	20	HCF	This work
Effluent from AD	42 ± 8	2.99	29	HCF	This work

–: Data not available; CE: coulombic efficiency; AD: anaerobic digester; *Expressed as NAC: netto anode compartment

treat high-strength substrates. The COD for the current conversion of wastewater is of the order of 5–40%. In particular, the overall COD removal levels, which are only of the order of 20–60%, need to be improved. Yet, the fact that microbial communities in MFCs are functioning with a diverse metabolic potential (Phung *et al.*, 2004; Rabaey *et al.*, 2004), substantiates the hope that higher clean-up efficiencies will be possible in the future.

Search for MFC niches

Increased voltages, currents and power outputs may enhance the potential of MFCs as a valuable energy recovery technology for a variety of wastewater treatments. In Figure 3, three potential niches of the MFC are presented. The niches illustrate how MFCs can be implemented in existing bioconversion technology, thereby increasing energy recovery.

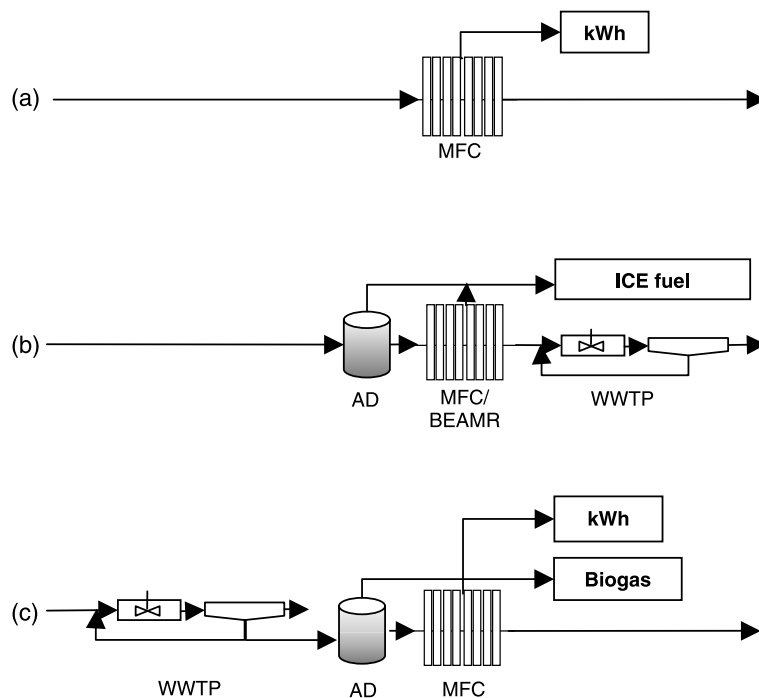


Figure 3 Scheme of the potential niches for MFCs. (a) MFC stacks provide sustainable energy as a stand-alone power source. (b) The production of high-quality ICE (internal combustion engine) fuel by combining an AD and an MFC/BEAMR unit followed by WWTP. (c) The MFC as a polishing step and energy recovery technology during anaerobic sludge fermentation

In the first application (Figure 3(a)), the MFC serves as a stand-alone power source. The MFC is able to deliver power outputs at the desired voltage and current by connecting several MFCs in series or in parallel. Several low-value but energy-rich discrete organic streams can be used as “fuel” in the MFC, thereby transforming waste into a valuable energy source and decreasing the costs for further treatment.

To address the energy recovery of particularly high-strength wastewaters (Figure 3(b)), several anaerobic digestion (AD) technologies have been developed. Most widespread in this context is the upflow anaerobic sludge blanket (UASB) reactor, in which methane is produced from industrial wastewater. UASB reactors typically handle highly digestible wastewaters at a loading rate of 10–20 kg COD per m³ reactor per day, and have, with a combustion engine as converter, overall electrical efficiencies of up to 35%, implying a power output of 0.5–1 kW/m³ reactor. However, the digestate, i.e. the liquid stream that leaves the anaerobic digester, still contains residual levels of volatile fatty acids at a total COD concentration of up to several kg COD per m³. By implementing an MFC/BEAMR (bio-electrochemically assisted microbial reactor) unit, the residual volatile fatty acids can be converted to electricity and subsequently to hydrogen at high efficiency (Liu *et al.*, 2005a,b). Subsequently, the hydrogen produced can be supplemented to the biogas in order to produce an internal combustion engine fuel (ICE-fuel) with improved quality. The latter can enable a decrease of NO_x emissions during combustion.

In order to treat low-strength wastewaters, such as domestic wastewaters, a conventional aerobic wastewater treatment plant (WWTP) is most commonly used (Figure 3(c)). However, large amounts of excess sludge are produced, which can be converted to biogas by means of a conventional anaerobic digester. The digestate still contains residuals of up to several kg COD per m³. This digestate can be treated using an MFC, the latter thereby serving as an additional energy recovery technology and polishing step. By retrofitting the current WWTP and sludge fermentation system, the energy and carbon circle can be further closed.

Conclusions

MFCs undoubtedly have potential in terms of energy recovery during wastewater treatment. They may occupy a market niche in terms of a stand-alone power source and also in the direct treatment of wastewater. They can also post-treat effluents from anaerobic digesters, even at ambient temperatures, as demonstrated by this study. Yet, it must be observed that several hurdles have to be faced, such as the need to implement sustainable cathodes, the fate of particular organics present in sewage and the removal of residual nutrients.

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