Simultaneous domestic wastewater treatment and renewable energy production using microbial fuel cells (MFCs)

S. Puig, M. Serra, M. Coma, M. D. Balaguer and J. Colprim

ABSTRACT

Microbial fuel cells (MFCs) can be used in wastewater treatment and to simultaneously produce electricity (renewable energy). MFC technology has already been applied successfully in lab-scale studies to treat domestic wastewater, focussing on organic matter removal and energy production. However, domestic wastewater also contains nitrogen that needs to be treated before being discharged. The goal of this paper is to assess simultaneous domestic wastewater treatment and energy production using an air-cathode MFC, paying special attention to nitrogen compound transformations. An air-cathode MFC was designed and run treating 1.39 L d\(^{-1}\) of wastewater with an organic load rate of 7.2 kg COD m\(^{-3}\) d\(^{-1}\) (80% removal efficiency) and producing 1.42 W m\(^{-3}\). In terms of nitrogen transformations, the study demonstrates that two different processes took place in the MFC: physical-chemical and biological. Nitrogen loss was observed increasing in line with the power produced. A low level of oxygen was present in the anodic compartment, and ammonium was oxidised to nitrite and nitrate.

INTRODUCTION

In recent decades, awareness of environmental issues have increased considerably. In the wastewater treatment field, there is now an increasing need to improve effluent quality and minimise the organic matter and nutrients discharged into surface waters. Wastewater treatment plants (WWTPs) have high operational costs mainly associated with aeration systems and sludge production, with energy use for wastewater aeration accounting for up to 50% of operational costs. Aerated treatment processes also produce large amounts of excess sludge, the treatment and disposal of which represents an increasing challenge due to economic, environmental and regulatory factors (Wei et al. 2003; Aelterman et al. 2006). Microbial fuel cell (MFC) technology can deal with wastewater treatment while electricity is simultaneously generated (Liu et al. 2004; Logan et al. 2006).

In an MFC, organic substrates are oxidised by exoelectrogenic bacteria, which produces electrons that are transferred to an anode and then flow to a cathode. The anode and cathode are linked by a conductive material containing a resistor. Protons produced at the anode migrate through the solution across a cation exchange membrane (CEM) to the cathode, where they combine with a reducible compound and electrons. MFCs offer the possibility of harvesting electricity from organic waste and renewable biomass (Rabaey & Verstraete 2005; Lee et al. 2008). These are attractive sources of energy because they are carbon-neutral: the oxidation of the organic matter only releases recently fixed carbon back into the atmosphere (Lovley 2006).

On-site decentralised wastewater treatment can provide a financially attractive alternative to a sewer connection in small WWTPs far from existing sewer networks (Wilderer & Schreff 2000). Domestic wastewater has been treated onsite using different energy-demanding technologies with high efficiency levels (Puig et al. 2005; Abegglen et al. 2008). MFC technology has been used successfully in lab-scale studies to treat domestic wastewater focussing on organic matter removal and energy production (Aelterman et al. 2006; Ahn & Logan 2010). However, domestic wastewater also contains nitrogen that needs to be treated before it is discharged. This is usually done in WWTPs using a conventional
nitrification/denitrification process. This two-step process requires aerobic and anoxic conditions to oxidise ammonium to nitrate (nitrification), and then, using organic matter, to reduce the nitrate (the highly oxidised forms of nitrogen) to gaseous nitrogen, which is far less accessible to life forms but makes up the bulk of our atmosphere. The goal of this paper is the assessment of simultaneous domestic wastewater treatment and electricity production, using an air-cathode MFC and paying special attention to nitrogen compounds transformations.

MATERIALS AND METHODS

Microbial fuel cell setup

The air-cathode MFC consisted of an anode and cathode placed on opposite sides of a methacrylate rectangular chamber as described previously in Puig et al. (2010). The anode frame was filled with 6 mm graphite granules (Alfa Aesar, Germany), which reduced the compartment volume to 242 mL (net anodic compartment). A thinner graphite electrode (28 × 35 mm, Sofacel, Spain) was used to connect to the external electricity circuit. The cathode electrode was C-cloth 0.35 mg cm⁻² of Pt catalyst 30% wet-proofing (Clean Fuel Cell Energy LLC, USA). A cation exchange membrane (CEM, Nafion® 117, Dupont) was treated according to Liu & Logan (2004) and used between the anode and cathode frames. The anode and the cathode were connected through an external resistor to close the circuit.

Urban wastewater was continuously fed to the recirculation loop to (i) maintain well-mixed conditions, (ii) avoid concentration gradients and (iii) avoid clogging of the granular matrix. The system was thermostated at 23 ± 2°C. The MFC was inoculated with effluent from a parent MFC treating synthetic wastewater (mainly composed of sodium acetate and a buffer solution. The MFC operated for 120 days at a mean organic loading rate of 1.02 kg COD m⁻³ d⁻¹ (90% removal efficiency), and produced 8.5 W m⁻³.

Domestic wastewater

The air-cathode MFC treated urban wastewater collected twice a week from the Quart WWTP (Catalonia, N.E. Spain) and transported to the laboratory. Table 1 shows its main characteristics during the experimental period.

The organic matter present in the wastewater was highly biodegradable (74% of the COD). A priori, this composition would facilitate organic matter removal as well as electricity production in the MFC. The nitrogen content was divided into 21% organic nitrogen and 79% ammonium content; the carbon/nitrogen (C/N) ratio was 5.8. At this C/N ratio, the organic matter available may not be enough to completely remove nitrogen using a conventional nitrification/denitrification process (Puig et al. 2007).

Experimental procedure

The operation strategy used was to gradually increase the influent organic loading rate (OLR) when the effluent loading was below 0.60 kg COD m⁻³ d⁻¹. This strategy was followed in order to increase the biodegradable organic matter available for exoelectrogenic bacteria. To cope with that, the hydraulic retention time (HRT) was decreased and the daily flow increased accordingly, from 0.67 to 2.06 L d⁻¹ (Table 1).

Analytical methods and energy measurements

Standard wastewater measurements for organic matter (COD and BOD), nitrogen (TKN, NH₄⁺, NO₂⁻ and NO₃⁻) were taken regularly and analyzed according to Standard Methods for the Examination of Water and Wastewater published
by the American Public Health Association (APHA 2005). The organic and nitrogen loading rates (OLR and NLR, kg COD m\(^{-3}\) d\(^{-1}\) or g N m\(^{-3}\) d\(^{-1}\)) were calculated as the daily influent/effluent organic matter or nitrogen concentrations divided by the HRT. Finally, the organic matter and nitrogen removal rates (ORR and NRR, kg COD m\(^{-3}\) d\(^{-1}\) or g N m\(^{-3}\) d\(^{-1}\)) were calculated as the difference between the influent and effluent loading rates.

Cell potential (V) in the MFC circuit was monitored at 30-min intervals using an on-line multimeter (Alpha-P, Ditel) with a data acquisition system (Memograph\textsuperscript{®} M RSG40, Endress + Hauser). Current (I) and power (P = IV) were calculated according to Ohm’s law. Power density was calculated by dividing the power by net anodic volume (W m\(^{-3}\)). Polarization curves were obtained by varying the external resistance in the circuit and measuring the voltage.

**RESULTS AND DISCUSSION**

**Domestic wastewater treatment and energy production**

Domestic wastewater was treated in the air-cathode MFC. Figure 1 shows the influent and effluent organic loading rates. The MFC started by treating 0.41 kg COD m\(^{-3}\) d\(^{-1}\) of wastewater following an operational strategy which resulted in a maximum treatment rate of 7.20 kg COD m\(^{-3}\) d\(^{-1}\) reached on day 119. In spite of the increase in the influent organic loading rate, the effluent load rate remained constant around 0.57 ± 0.36 kg COD m\(^{-3}\) d\(^{-1}\) (80 ± 10% removal efficiency, on average). Even though organic matter was being treated from the first few days, energy production was not observed until day 15 of operation, when a peak in the power density of 0.15 W m\(^{-3}\) was seen. The fact that organic matter was removed throughout the whole experimental period means that different modes of microbial energy conservation (fermentation and respiration) were taking place in the MFC. From the time power was first produced, the organic loading rate was increased in line with electricity production. Maximum production of around 1.42 W m\(^{-3}\) was achieved on day 133 of operation, when 5.18 kg COD m\(^{-3}\) d\(^{-1}\) were treated (86% removal efficiency). Liu et al. (2004) and Venkata Mohan et al. (2010) reached similar energy production treating domestic and real field dairy based wastewater, respectively. Ahn & Logan (2010) achieved a maximum power production of 12.8 W m\(^{-3}\) when feeding an MFC with 54 kg COD m\(^{-3}\) d\(^{-1}\) of domestic wastewater (25.8% removal efficiency). The highest production level in respect of the air-cathode MFC used in this study came from the highest organic loading rate and the lowest HRT applied.

The evolution of the MFC from an electrical point of view was confirmed by the polarisation curves developed on different operational days. Figure 2 shows the polarisation curves of the MFC treating domestic wastewater. On day 6, it hardly produced any energy (less than 0.001 W m\(^{-3}\)). The open circuit voltage (OCV) was approximately 116 mV in comparison with 642 mV on day 131. The maximum power and current production were 1.23 W m\(^{-3}\) and 9.4 A m\(^{-3}\). This means that the system evolved into an energy production process treating domestic wastewater.

**Nitrogen transformations in an air-cathode MFC treating domestic wastewater**

The air-cathode MFC treated the organic matter in the domestic wastewater efficiently, and at the same time produced renewable energy. However, domestic wastewater also contains nitrogen to be treated before discharge. As can be seen from Table 1, the domestic wastewater used in this study contained on average 87.2 ± 21.0 mg N L\(^{-1}\) (68.8 ± 11.7 mg N-NH\(_4\)\(^+\) L\(^{-1}\)). Figure 3 shows the influent and effluent nitrogen loading rates.

The initial influent NLR applied was 135 g N m\(^{-3}\) d\(^{-1}\). Along with the organic loading rate, this was increased during the experimental period to reach 1176 g N m\(^{-3}\) d\(^{-1}\). The effluent nitrogen loading rate was on average 315 ± 141 g N m\(^{-3}\) d\(^{-1}\). The nitrogen removal rate increased from 8.8 g N m\(^{-3}\) d\(^{-1}\) to around 345 g N m\(^{-3}\) d\(^{-1}\) on day 119, when the system became energetically active (see Figure 2). At that moment, the key issue was to determine which processes were used to remove the nitrogen. From the first days of operation it was seen that some
transformations were taking place in the air-cathode MFC. Figure 4 shows the evolution of TKN concentration in the influent and the ammonium, nitrite and nitrate concentrations in the effluent. On day 12, influent nitrogen was 60.5 mg N L\(^{-1}\) while the ammonium and nitrate concentrations in the effluent were 19.6 mg N-NH\(_4^+\) L\(^{-1}\) and 16.46 mg N-NO\(_3^-\) L\(^{-1}\), which showed that around 25 mg N L\(^{-1}\) had been removed from the wastewater that day. During the whole experimental period, out of a mean value of 87.2 mg N L\(^{-1}\) in the influent, 26.3 mg N-NH\(_4^+\) L\(^{-1}\), 4.12 mg N-NO\(_2^-\) L\(^{-1}\) and 21.31 mg N-NO\(_3^-\) L\(^{-1}\) were present in the effluent. Hence, around 32 mg N L\(^{-1}\) were removed from the wastewater.

On the evidence of these results, some nitrogen transformations (physical–chemical and/or biological) could have taken place. The nitrite and nitrate present in the effluent (Figure 4) suggest that biological processes such as nitrification (an aerobic process that oxidises ammonium to nitrite and nitrate), and maybe then denitrification (reduction of nitrate to nitrogen gas), could have taken place. Oxygen mass transfer tests were carried out and confirmed the permeability of the air-cathode MFC to oxygen (1.76 \(\times\) 10\(^{-5}\) cm s\(^{-1}\)). Apart from that, oxygen would be penetrated via other points. These conditions are suitable for the nitrifying bacteria and 30% of the influent nitrogen...
was oxidised to nitrite or nitrate. It is important to note that at day 105, the nitrate-to-nitrite ratio shifted, probably as a result of oxygen limitation due to an increase of the anodic biomass.

Regarding the nitrogen loss, Kim et al. (2007, 2008) demonstrated that ammonium could be diffused across the membrane in the absence of current. Figure 5 shows the relation between the nitrogen removal rate in respect to the power density produced. It can be seen that the more power is produced, the more nitrogen is removed. The maximal NRR (345 g N m⁻³ d⁻¹) was reached at 0.85 W m⁻³. The results indicate that ammonium, as NH₄⁺, passed through the membrane in order to maintain the electroneutrality of the system. On average, 36% of the nitrogen loading rate was removed via physical–chemical processes. However, it is important to take into account that other nitrogen removal processes, such as denitrification, can also take place in the MFC.

**CONCLUSIONS**

This study demonstrates that MFC technology should be considered for on-site decentralised wastewater treatment and can provide a financially attractive alternative to other technologies. A total of 1.39 L d⁻¹ of domestic wastewater was treated and a carbon loading rate of 7.2 kg COD m⁻³ d⁻¹ achieved, with a removal efficiency of 80%. Almost 1.42 W m⁻³ of renewable energy (electricity) was produced. In terms of nitrogen transformation, the study demonstrates that two different processes took place in the MFCs: (i) physical–chemical and (ii) biological. Nitrogen loss was observed increasing in line with the power produced, while the nitrification/denitrification process took advantage of the oxygen presence in the anodic compartment. Further research is necessary to distinguish and quantify the effect of each process, as well as the microbiological population involved.

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