



Influence of the fuel and dosage on the performance of double-compartment microbial fuel cells



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ABSTRACT

This manuscript focuses on the evaluation of the use of different types and dosages of fuels in the performance of double-compartment microbial fuel cell equipped with carbon felt electrodes and cationic membrane. Five types of fuels (ethanol, glycerol, acetate, propionate and fructose) have been tested for the same organic load (5,000 mg L⁻¹ measured as COD) and for one of them (acetate), the range of dosages between 500 and 20,000 mg L⁻¹ of COD was also studied. Results demonstrate that production of electricity depends strongly on the fuel used. Carboxylic acids are much more efficient than alcohols or fructose for the same organic load and within the range 500–5,000 mg L⁻¹ of acetate the production of electricity increases linearly with the amount of acetate fed but over these concentrations a change in the population composition may explain a worse performance.

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1. Introduction

For a very long time, microbial fuel cells (MFC) have been studied as promising substitutive technologies for the biological reactor of conventional municipal wastewater treatment plants (Logan et al., 2006; Rodrigo et al., 2007). In a parallel application, they have also been considered for the treatment of highly-loaded industrial effluents (Logan et al., 2006; Huang et al., 2009; Cusick et al., 2010). Results were promising at the lowest scale, but unfortunately, the scale-up of this bio-electrochemical technology is a huge handicap nowadays and much work has to be carried out in the next years in order to overcome it successfully (Virdis et al., 2008).

This bio-electrochemical technology is not easy and researchers are now realizing it. This point can be explained taking into account that, in fact, it consists of the combination of two very different technologies: fuel cells based on the electrochemistry and organic biodegradation based on biotechnology. The difficult coupling of these two different disciplines can help to explain the necessity of further research and the need for great efforts in order to find a ready-to-use technology. There is a great deal of papers focused on

trying to improve the performance of microbial fuel cell and, particularly, their efficiency (Rabaey et al., 2003). Topics of interest include the electrode materials, fuel cell mechanical design and use of different types of synthetic solutions or real wastewater as fuel (Kim et al., 2015; Lee et al., 2015).

This last topic is of a great relevance because, perhaps, the environmental application looked for in the last years is not the best choice for this type of energy conversion devices. In turn, the power supply to systems with a low energy requirement in remote applications could have greater real opportunities. Within this context, the perspective of feeding the MFC with a synthetic fuel, manufactured only to harvest energy from organic matter can be a way to optimize these devices. Obviously, due to the metabolic requirements, the fuel used should be a solution containing not only a carbon source but also nutrients in ratios enough to do not become the limiting reagents of the process, such as happens naturally with the wastewater types typically fed to these systems (Rodrigo et al., 2009).

There are many types of potential fuels for MFC (Oh and Logan, 2005; Virdis et al., 2010). Obviously, the simpler the molecule the easier and more effective is the resulting process, because complex molecules should be hydrolyzed before they can be oxidized by microorganisms. Metabolism of sugars, alcohols and carboxylic acids proceeds through very different pathways, for which the redox transfer enzymes and/or redox mediators involved can be

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very different and these differences should reflect on the performance of a MFC. It is important to know which of this carbon sources provides a higher efficiency, in the search for new applications of the technology. Hence, although typically, MFC have been studied as alternative for wastewater treatment processes, this application, although promising, is perhaps not the best choice because of the low power yielded by these devices. In the search for new applications of the technology, it is interesting to evaluate their performance with different synthetic fuels and in different concentrations, trying to determine the fuel that produces the highest efficiency.

The substrate also plays another important role in MFC (Lobato et al., 2012) helping to select population and hence to the development of optimal biofilms (Chae et al., 2009; Liu et al., 2009). A great variety of substrates can be used in MFCs for electricity production ranging from pure compounds such as glucose, acetate, butyrate, lactate, ethanol (Rabaey and Verstraete, 2005) to complex mixtures of organic matter present in wastewater (Rodrigo et al., 2009; Pant et al., 2010). The electrogenic bacteria are only capable of completely oxidizing non-fermentable substrates such as acetate by electricity production, while the fermentative bacteria convert carbohydrates into short-chain fatty acids such as acetate (Lovley, 2008).

Careful control of the substrate feed can thus be used to optimize the biofilm and in turn the electricity generation. These substrates include pure and non-fermentable ones such as acetate and lactate (Bond and Lovley, 2003; Rabaey et al., 2003) in addition to fermentable ones such as glucoses and xylose (Huang and Angelidaki, 2008; Ishii et al., 2008; Rezaei et al., 2009; Mäkinen et al., 2013). Mixed substrates present in mixed inoculum feeds such as domestic and industrial wastewater, which contain fatty acids, protein, and carbohydrates, have also been studied (Feng et al., 2008).

With this background, the goal of this work has been to evaluate the best organic load, within the range 500–5,000 ppm of acetate, and the best type of fuel, within a set that includes carboxylic acids, alcohols and sugars, in order to get information for the application of the technology in different fields, not only wastewater treatment but also in sensors and other devices.

2. Materials and methods

2.1. Microbial fuel cell

The set-up used in this work consisted of a MFC with two chambers (4 cm³ volume each one) separated by a proton exchange membrane, PEM (Sterion[®]), which has a high ionic conductivity (0.9–0.02 meq g⁻¹) and low electronic conductivity (8 × 10⁻² S cm⁻¹). MFC is formed by two HDL (high pressure laminate) plates and two silicon plates to improve the mechanical properties and avoid liquid losses. Carbon felts (KFA10, SGL Carbon Group[®]) were used as electrodes in both chambers (3 cm² each). The electrode spacing between the anode and the cathode was minimized in order to reduce as much as possible the internal electrical losses from the system. The two electrodes were connected by an external resistance (R_{ext}) of 120 Ω; this low value was chosen to prevent activation losses and facilitate electron transfer during the acclimation period (Rodrigo et al., 2009). The MFCs were operated simultaneously in semi-continuous mode and at room temperature (25 ± 3 °C). The cathode compartment of the MFC was connected to a water reservoir of 100 cm³ and a peristaltic pump was used to circulate an HCl solution (pH 3.5) from the reservoir through the cathode chamber of the MFC at 25 cm³ min⁻¹. A fishery compressor that can provide a flow rate of 1.6 L min⁻¹ and a maximum pressure of 1.2 m of water-column was connected to the

cathode to supply oxygen to the cathodic chamber (Penteado et al., 2016).

2.2. Inoculum and synthetic wastewater

Activated sludge from a wastewater treatment plant (Ciudad Real, Spain) was used as the inoculum for the anodic compartment. The activated sludge of the biological reactors was placed in the anodic chamber for three days in a 1:2 ratio without aeration to favor the formation of a mixed culture of anaerobic microorganisms. In this period, no synthetic wastewater was supplied to feed the culture. After this period, different carbon based fuels were studied to evaluate the performance of the MFC. In all cases, inorganic compounds of the synthetic wastewaters were the same (see Table 1).

Three types of carbon based fuels were studied: alcohols (ethanol and glycerol), a volatile fatty acid (acetic and propionic acid) and a monosaccharide sugar (fructose) (see Table 2).

It is worth to remind that although the MFC was fed only once a day, its operation mode can be considered as semi-continuous within long periods of time. HTR was 3.16 days in the different experiments. In all case no changes were made in the rest of parameters that may affect the performance of the cell, and even the nutrient solution was kept the same in the five test (concentrations of nutrients were checked to be high enough to not become limiting reagents).

2.3. Electrochemical and chemical measurements

A digital multimeter (Keithley 2,000 multimeter) was connected to the system to monitor continuously the value of the cell voltage at the value of the external load (120 Ω). Chemical oxygen demand (COD) was determined using a Velp ECO-16 digester and a Pharo 100 Merck spectrophotometer analyzer and pH, conductivity and dissolved oxygen were measured with a GLP22 Crison pH meter, a Crison Cm 35 conductivity meter and an Oxi538 WTW oxy meter, respectively. Polarization curves have been done in MFC. Three important parameters were evaluated: the open circuit voltage (OCV) or the maximum allowable MFC voltage, the maximum intensity and the maximum power density of the MFC. In addition, the shape of curves gives important information about the limiting processes, which control the performance of the cell. Polarization curves can be divided into three zones: a decrease of the current due to the activation losses, a linear decrease due to ohmic losses, and a third zone that corresponds to the region controlled by mass-transfer (concentration losses).

3. Results and discussion

Fig. 1 shows the changes in the COD monitored in the anode chamber of a divided MFC during 2.5-month tests in which different fuels, made up with acetate at different concentration, are fed in order to check the effect of the organic load on the performance of the cell. Over the tests, the other inputs are kept constant, including hydraulic retention time, temperature and external electric load of the cell. Likewise, the nutrient solution was the same and it was checked that concentrations of all nutrient were high enough to not become the limiting reagent in the performance of the MFCs. Hence, changes in these experiments are expected to be only consequence of the organic load of the influent fed to the MFCs.

This is confirmed by results obtained in this work. Thus, the Fig. 1 shows how the COD remaining in the anode compartment changes up to a steady-state value that it is related to the concentration fed, in agreement to what it could be expected for a semi-

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