



Influence of the initial sludge characteristics and acclimation on the long-term performance of double-compartment acetate-fed microbial fuel cells



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ABSTRACT

In this work, three double-compartment MFCs (DC-MFC) were operated for 1 month in order to compare their performances in terms of wastewater treatment capacity and electricity production and to get information about how this performance is influenced by the start-up procedure. To do this, they underwent different start-up procedures. One of them (aerobic-starved MFC) was inoculated with 100% fresh aerobic sludge, another (anaerobic-starved MFC) using 100% fresh anaerobic sludge, and finally a third one (aerobic-fed MFC) was inoculated using a mixture 10% fresh aerobic sludge and 90% synthetic wastewater (based on acetate). Then, from this start-up, the cells were operated exactly under the same feeding and operation conditions and they underwent the same tests. Results demonstrate that after one month of operation, in DC-MFCs, there are no significant differences in the steady state operation conditions reached because the three cells lead to a very similar treatment capacity, quantified in terms of the COD consumption rate, and to a quite similar value of the current produced. A comprehensive electrochemical characterization informed that the small differences cannot be explained in terms of the different start-up period. This means that the DC-MFC technology is robust enough regarding the inoculation and within systems undergoing the same disturbances, outputs obtained are quite the same, which becomes a very important observation for future works.

1. Introduction

In the last decade, research activity on microbial fuel cell (MFC) technology has increased markedly. These devices consist of electrochemical reactors directly generating electricity from an organic fuel using microorganisms [1–5]. Several advantages in developing this technology could be found, as the production of carbon neutral energy in a World concerned by the high pollution levels that are leading to a global warming, and the wastewater treatment capacity of these bioelectrochemical reactors using wastewater as biofuel [6–10]. However, not enough output energy has been obtained for practical applications and a lot of fundamental work must be done to solve this important issue [11,12]. Many inputs have been found to affect the obtained energy by MFCs, being the electrode material one of the most important [13–16]. Among them, carbon based electrodes are the most widely used due to its high conductivity, chemical stability and biocompatibility, which make them suitable for microorganism growth on the electrode surfaces [17–19]. On the other hand, acclimation stage should

not be underestimated, because this fundamental stage affects the development of electroactive bacteria that leads to high output power that are necessary to improve the electrical capacity of MFCs [20].

In the literature, it can be found that aerobic and anaerobic sewage sludge are used as initial inoculum for MFCs, because they are easy to obtain and also because they contain a wide range of microorganism cultures, in which many of them are able to directly produce energy oxidizing the organic matter contained in a fuel [21]. Nevertheless, to maximize the energy output obtained, the growth of electroactive bacteria should be favored, while fermentative and methanogens must be inhibited, not only in order to increase the electric efficiency of MFCs, but also, and more important, in order to avoid the attachment of non-electroactive bacteria on the electrode surface, which are unable to produce an electric current during the operation time.

To enhance the growth of electroactive bacteria in the anode compartment, different methods have been studied, such as adding an inhibitor of the methanogenic activity [22–24], the replacement of an electrode biofilm inoculated with a pure microorganism culture [24,25]

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or the microorganism acclimation using different chemical mediators [26]. However, these methods, that have greatly enhanced the electric efficiency of MFC, could not be easily implemented when scaling up is needed. The use of chemical mediators could affect the sustainability of the process, while the use of pure cultures of microorganism could greatly increase the operational costs of the technology.

With this background, the aim of this work has been to study wastewater treatment capacity and electric performance during the start-up period and early stages of three reactors inoculated with different acclimation procedures, using 100% fresh aerobic sludge, 100% fresh anaerobic sludge, and 10% fresh aerobic sludge and 90% synthetic wastewater (based on acetate) [27–29]. These strategies were focused to meet necessary requirements of readiness and affordability, in a scale-up perspective.

2. Material and Methods

2.1. Inoculation and acclimation

Scope of this work is to determine the influence of first days of operation on MFC performance. For this purpose two different strategies were established. The first one, here reported as “Starving procedure”, is accomplished filling the anodic reservoir with the sludge of a municipal wastewater treatment plan (Ciudad Real WWTP, Castilla-La Mancha, Spain) without any carbon source for 3 days. This strategy was applied to two cells with different inoculum source: the 1st cell was inoculated with secondary decanter sludge of a conventional activated sludge process, the 3rd with anaerobic digester sludge. For the second strategy, “Fed procedure”, a small amount of sludge (10 mL) was put into the reservoir along with a large amount of carbon: the synthetic wastewater described below (90 mL), for the details see Table 1.

MFCs of this work were started according to three different procedures here explained (Table 1). The first and the third were identical but with a different source of inoculum: sludge from the secondary decanter after the activated sludge unit for the 1st, and from the anaerobic digester for the 3rd. The ‘starving’ procedures are characterized by the absence of an external electron source for the first 3 days, while the ‘Fed’ one received a large amount of carbon yet the first day. In this last procedure, the amount of sludge inoculated is much less than the 1st and 3rd.

The synthetic wastewater used to feed the reactors also contained: NaCH_3COO 12 g L^{-1} , NaHCO_3 2.77 g L^{-1} , $(\text{NH}_4)_2\text{SO}_4$ 1.85 g L^{-1} , KH_2PO_4 1.11 g L^{-1} , MgCl_2 0.92 g L^{-1} , CaCl_2 1.25 g L^{-1} , $(\text{NH}_4)\text{Fe}(\text{SO}_4)_2$ 0.07 g L^{-1} . The complete characterization of the solution fed is reported in Table 2. The catholyte was a pH 3 HCl solution. All reagents were bought from Sigma-Aldrich, and the water used was Milli-Q grade.

2.2. Cell assembly and operation

Three two compartment MFCs were made as described elsewhere [10]. Briefly, two cylindrical chambers of 4 cm^3 were realized into $15 \times 15 \times 3 \text{ cm}$ pieces of high density laminate (HDL). Chambers

Table 2

Complete characterization of the synthetic wastewater used during the whole experiment. Analysis of three different batches along with standard deviation.

Synthetic wastewater characterization	
pH (Anodic)	7.36 ± 0.36
Conductivity [mS]	16.10 ± 0.09
Suspended Solids [g L^{-1}]	1.89 ± 0.08
TC [mg L^{-1}]	2971 ± 112
IC [mg L^{-1}]	192 ± 29
Total N [mg L^{-1}]	1.29 ± 1.82
TOC [mg L^{-1}]	2779 ± 141
COD [mg L^{-1}]	7810 ± 57

housed two identical carbon felt (Sigracell® GFA6EA) of 3 cm^2 of projected surface as cathode and anode. A Sterion® proton exchange membrane (PEM) sandwiched between two silicon gaskets separated these chambers. Assembled cells had less than 1 cm of electrode spacing. Electrodes were connected with stainless-steel wires through a 120Ω external resistance. Every chamber had an inlet and an upper outlet connected to a 100 cm^3 reservoir. Here the flow was forced by a peristaltic pump (PD 5001, Heidolph™) running at about 2 mL min^{-1} . Reservoirs housed a third port for sampling and media exchange. For anolyte, after acclimation procedure described above, this operation was performed daily in a semi-continuous regimen of 3 days hydraulic retention time (HRT). Catholyte instead was changed daily and the reservoir incorporated an air diffuser which delivered atmospheric air provided by a fishery compressor at 1.6 L min^{-1} .

2.3. Chemical characterization

Cathodic oxygen consumption was measured with a senION™ + DO6 (Hatch) dissolved oxygen meter. Conductivity was measured with a GLP 31 (Crison) connected to a 5292 (Crison) probe. A pH 25 (Crison) meter connected to a 5050 (Crison) probe was used to measure the pH. Suspended Solids (SS) were estimated gravimetrically, by evaluating the difference in weight of $0.45 \mu\text{m}$ glass microfiber dried filters (Prat dumas, France), before and after filtering a volume of 10 mL of re-suspended anodic reservoir bulk solution. Filters were dried for 1 day at 105°C in a oven. Total, Inorganic and Organic carbons were measured with a multi N/C 3100 (Alitik Jena) analyzer. Chemical Oxygen Demand (COD) was evaluated with Spectroquant® COD Cell tests (MERCK) (Sulfuric acid, potassium dichromate, mercury(II) sulfate) for COD range from 500 to $10,000 \text{ mg L}^{-1}$. According to manufacturer instructions, filtered samples (1 mL) were injected into the test vials and then heated for 120 min at 150°C with an ECO 25 (Velp scientifica) thermoreactor. COD values were obtained after cooling at room temperature with a Spectroquant® Pharo 100 (MERCK) spectrophotometer regularly calibrated. Sludge Volume Index SVI was evaluated filling a graduated cone with 30 mL of the anodic solution and measuring the volume of the settled solids after 30 min. From this

Table 1

Acclimation procedures applied in this work.

Acclimation procedures			
	1	2	3
Day ↓	Starving aerobic	Aerobic fed	Starving anaerobic
1st	100 mL total reservoir volume. 100 mL fresh aerobic sludge (50 mL decanted + 50 mL supernatant).	100 mL total reservoir volume. 10 mL fresh aerobic sludge (Decanted) + 90 mL synthetic wastewater.	100 mL total reservoir volume. 100 mL fresh anaerobic sludge (50 mL decanted + 50 mL supernatant).
2nd	50 mL withdrawn and replenish with fresh aerobic sludge (25 mL decanted + 25 mL supernatant).	50 mL withdrawn and replenish with synthetic wastewater.	50 mL withdrawn and replenish with fresh anaerobic sludge (25 mL decanted + 25 mL supernatant).
3rd	As the 2nd.	As the 2nd.	As the 2nd.
4th	Start of standard feeding with synthetic wastewater at a Hydraulic Retention Time of 3 days (33 mL changed every day).		

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