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Low temperature performance of microbial fuel cells

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Single and double chamber microbial fuel cells (MFCs) were tested in batch mode at seven different temperatures ranging from 4 to 35 ºC and results were analyzed in terms of efficiency in soluble organic matter removal and capability of energy generation. The reactors were feed with brewery wastewater diluted in domestic wastewater. This mix (initial soluble chemical oxygen demand of 1200 mg L^{-1} and 492 mg L^{-1} of volatile suspended solids) was the source of carbon and inoculum for the experiments. Control reactors (sealed container with support for biofilm formation) as well as baseline reactors (sealed container with no support) were run in parallel to the MFCs at each temperature in order to assess the possible differences between water treatment in the MFCs including electrochemical process and conventional anaerobic digestion (either in the presence of a biofilm, or planktonic cells). Anaerobic digestion in MFCs showed improvements regarding rate and extent of COD removal in comparison to control and baseline reactors at low temperatures (4, 8 and 15 ºC), whilst differences became negligible at higher temperatures (20, 25, 30 and 35 ºC). Temperature was found to be a crucial factor in the yield of MFCs both, for COD removal and electricity production, with results that ranged from 58% final COD removal and maximum power of 15.1 mW m^{-3} reactor (8.1 mW m^{-2} cathode) during polarization at 4ºC, to 94 % final COD removal and maximum power of 174.0 mW m^{-3} reactor (92.8 mW m^{-2} cathode) at 35ºC for single chamber MFCs with carbon cloth based cathodes. Bioelectrochemical processes in these MFCs were found to have a temperature coefficient, Q_{10} of 1.6.

1. Introduction

Fuel Cells convert the energy stored in chemical bonds of organic compounds into electrical energy by electrochemical reactions. In Microbial Fuel Cells, this is achieved through the catalytic effect of certain microorganisms that are attached onto the surface of the cell's anodes. One of the potential applications of these systems is the treatment of wastewater effluents due to their capacity to process a wide range of organic matter types. In this sense, MFCs technology is a novel technology that may have to compete with the mature methanogenic anaerobic digestion, which has a wide commercial

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application, since they use the same biomass in many cases for energy production (biogas).

Municipal waste waters contain a multitude of organic compounds and microorganisms that can fuel a MFC. Being water scarcity and renewable energies of primary concern in our region, MFCs were considered for the treatment of waste waters from the South East of Spain. Waste water used was from primary clarifier of the Municipal Wastewater Treatment Plant Murcia-Este (Murcia, Spain). For each experiment, COD content was adjusted to the desired COD starting level by mixing with it water from a local biofuel industry. The cathodic chamber was filled with phosphate buffer (pH = 7) made out from monobasic and dibasic potassium phosphates.

Temperature is one of the most important parameters in anaerobic digestion and methane production is strongly dependent on it. Most of anaerobic digesters operate at the mesophilic range and the characteristics of this process have been widely studied and documented (Gavala et al., 2003) (Gavala et al., 2003). Most of the studies report a marked decrease in methane production as a function of temperature decrease; optimum temperature for mesophilic bacteria is known to be around 35-40ºC (Bohn et al., 2007). When the reactor temperature is lower, the mesophilic bacterial consortia goes through a long selection and adaptation process during which their activity slows down drastically, explaining the behaviour of digesters installed in areas characterized by large seasonal temperature differences, where each winter biogas production sometimes even stops. The result of this process is a group of mesophilic psycotrophic bacteria. Differently there is a group of bacteria called psycrophilic bacteria that naturally prefer low temperature environments; they have become more recently object of study. A microbial community capable to provide acceptable biogas production yields at low temperatures would promote a great advance in wastewater treatment for cold areas where average annual temperature is between 8 and 10ºC or even lower, with no big seasonal changes (Bohn et al., 2002, Kashyap et al., 2003, Lettinga et al., 2001). Biogas production at these temperatures is currently possible but in a very low productivity with typical values of 0.02-0.04 m^3biogas (m^3 sludge)$^{-1}$ day^{-1} (Alvarez et al., 2006).

The most frequent solution to raise methane production in cold areas had been to use different technologies (i.e. variety of heat exchangers, plastic covers to obtain greenhouse effect) to set a high operational temperature (Axaopoulos et al., 2001) However, there is a growing interest in the study of psycrophilic species as well as anaerobic bioprocesses alternative to methanogenesis that can work properly at low temperatures (Lettinga et al., 1997, McKeown et al., 2009). The spectrum of bioprocesses screened for wastewater treatment alternative to methanogenesis include the anaerobic respiration called electrogenesis which occur in microbial fuel cell (MFC) reactors and uses a solid conductive electrode as final electron acceptor (Narihiro and Sekiguchi, 2007) Research in MFC field have enormously increased during the last years and studies at different temperatures ranging from 4ºC to 35ºC have been carried out.

However, results from the various authors were obtained under different conditions and systems, leading to a huge variation in parameters reported for each temperature; this makes difficult to establish the effect of this factor on the performance by comparing the outputs from the different works available.

Hence, it was considered of interest for microbial fuel cell research to systematically analyse the influence of the operational temperature on the behaviour of these devices and specially to investigate their sensitivity to low temperatures in relation to that happening in methanogenesis. A temperature range of 4 ºC to 35 ºC was screened in a series of experiments executed under identical conditions, counting with the appropriated number of replicas in each case.

2. Materials and methods

Data reported were obtained from two different types of microbial fuel cell: two chambered MFCs with cathodes of platinised titanium mesh and one chamber MFCs with cathodes of platinum sprayed on carbon cloth (0.3 mg Pt cm^{-2}). In both cases, reactors were constructed with jacketed 250 mL glass bottles (Schott Duran ®, Germany) modified with a cylindrical flange. The external jackets had a capacity of 150 mL and were designed to accommodate the flow of thermostatic liquid for temperature control. Temperature was fixed using a thermostatic bath (P Selecta, Spain) connected to a circuit linked to all reactors operated at a given temperature. Thermostatic fluid was commercial cooling liquid. Fuel added to anode chambers consisted of barley processing wastewater from a brewery diluted in domestic wastewater to give a chemical oxygen demand (COD) of 1200 mg L^{-1}. Volatile suspended solids (VSS) and pH were measured for the mixes prepared for each experiment, giving an average value for VSS of 492.3 $\pm$ 85.7 mg L^{-1} and an average value for pH of 7.04 $\pm$ 0.51. Together with the MFCs, control and baseline reactors were run for each experiment. Control reactors consisted of a sealed chamber with 100 mL of graphite granules and 100 mL of wastewater (biofilm assisted anaerobic digestion); baseline reactors consisted of a sealed reactor with 100 mL of wastewater (anaerobic digestion strictly by planktonic cells). According to previous studies using two chambered MFCs (Larrosa-Guerrero et al., 2009) working with a 1 kΩ external resistor, with 4 replicates, for observed differences to be considered statistically significant, with a confidence level of 95% and statistical power of 0.8, differences between measurements would need to be at least 3.6 % for COD removal, 30.2 mV for cell voltage and 45 mg L^{-1} for VFAs. For every experiment, four MFCs were run under identical operational conditions; as well as two control reactors and two baseline reactors. In the case of control and baseline reactors, where the number of replicates was reduced to two, according to Larrosa-Guerrero et al. (Larrosa-Guerrero et al., 2009), differences of 4.8 % in COD removal and 60 mg L^{-1} in VFAs are needed to show an effect of the external variables applied. Data shown for MFCs are an average of the four reactors run for each system type and each temperature; data shown for controls and baselines are averages of two replicates. Standard deviation was below the values cited above for the significance of the differences in all cases. For every type of system a different experiment, including four MFCs, two control and two baseline reactors, was run for each temperature studied. Experiments started always with a clean anode, so a period of biofilm attachment, development and stabilisation is included in the data presented. On the cathode side, for two chamber MFCs and for one chamber MFCs with the catalyst on carbon cloth, the same four platinized titanium meshes and four cloth cathodes were used for all temperatures, and the Nafion membranes were changed for each experiment. For one chamber MFCs with the catalyst sprayed on the membrane, the same four membrane-cathodes were used for all temperatures. Wastewater was added and measurements started at 0 h. Samples for COD and VFA analysis were withdrawn every 24 h. pH was measured at the beginning and the end of each test. Voltage was continuously monitored. The duration of the test was 144 h for one-chamber MFC experiments and 200 h for two-chamber MFC experiments. Polarization was carried out at around 72 h after the beginning of each experiment. Voltage was continuously monitored by a data acquisition system (PCI 6010, National Instruments, USA) at 1 data point per minute scan rate. Intermittently, it was also read off-line using a DVM891 digital multimeter (HQ Power, Germany). pH was determined using a digital pH meter (Crison Instruments, Spain). Chemical oxygen demand (COD) and volatile suspended solids (VSS) were conducted according to APHA (Andrew D. Eaton 2005). A Spectroquant Nova 30 spectrophotometer (Merck, Germany) was used for COD measurements. Volatile fatty acids were analysed by gas chromatography. The gas chromatograph (Agilent, 6890N, USA) was fitted with a flame ionization detector and a 30m x 0.25mm x 0.25µm DB-Wax column (Agilent, USA). Samples of 0.9 mL were acidified using 0.1 mL of 10 % formic acid solution before GC analysis. The temperature of the GC column was started at 70 ºC for 2 min, then increased at 15 ºC/min to 85 ºC (kept for 2 min), then at 20 ºC/min to a temperature of 120 ºC (kept for 1 min) and finally at 20ºC/min to a final temperature of 170ºC (kept for 0.5 min). The temperature of the injector was 250 ºC and the temperature of the detector was 300 ºC. Helium was used as a carrier gas at a flow rate of 1 mL/min, a constant pressure of 103 kPa and split ratio of 20:1. A self-made (workshop) variable resistor box (11 MΩ-1Ω) was used for polarization test.

3. Results and discussion

Regarding temperature effect, microbial fuel cell performance regarding both, removal of organic matter and electricity production is greatly affected by operational temperature. Performance is enhanced at higher temperatures in the range tested (Table 1). However, MFCs have proved in this study not to be more sensitive to the decrease of temperature from 15 to 4 ºC (Table 2) than conventional anaerobic digesters (Tao et al., 2008); moreover, conventional anaerobic digestion processes (i.e. methanogenesis) are a mature technology whilst the MFCs technology is still in a relatively early stage development. Hence, MFCs are a promising option for low strength wastewater treatment at low temperatures and to deploy MFC wastewater treatment as a potential complement or alternative to conventional anaerobic systems seems promising in remote areas where temperatures are constantly low or in large centres of population in temperate zones which experience low winter temperatures for a considerable proportion of the year wastewater treatment systems. It has been demonstrated that electroactive anodic consortia in a MFCs are able to develop and to carry out effectively both, COD removal and energy generation at temperatures as low as 4 ºC.

***Table 1**: Comparison of values obtained for voltage, current density (i), accumulated charge (Q) and chemical oxygen demand removal (COD_R) from one chambered MFCs*

with cathodes of carbon cloth and two chambered MFCs during sustained operation under load of 1 kΩ.

T (ºC)	MFC type	Max voltage (V)	Max i (mA m^{-2})	Max Q (C)	Max COD_{rem} %
4	Double	0.003	2.35	0.94	42.29
	Single	0.029	23.11	9.07	58.03
8	Double	0.002	1.30	0.54	66.02
	Single	0.041	32.87	15.17	57.60
15	Double	0.002	1.71	0.50	73.12
	Single	0.074	58.72	27.73	88.24
20	Double	0.036	28.77	9.90	77.23
	Single	0.075	59.64	27.97	90.56
25	Double	0.045	35.97	17.73	82.08
	Single	0.093	73.99	49.36	91.01
30	Double	0.052	41.73	24.77	74.76
	Single	0.109	86.71	41.84	95.11
35	Double	0.096	76.15	40.40	74.94
	Single	0.118	93.87	57.65	94.50

Table 2: *Final %COD removal at each temperature for MFCs with carbon cloth cathodes, controls and baseline reactors. Data set includes standard deviation for each average.*

	Final %COD removal						
	4ºC	8ºC	15ºC	20ºC	25ºC	30ºC	35ºC
MFCs	58.0 ± 6.1	57.6 ± 4.7	88.2 ± 4.6	90.6 ± 0.6	91.0 ± 2.1	95.1 ± 1.4	93.9 ± 1.1
Controls	32.2 ± 2.5	53.6 ± 4.2	88.7 ± 3.3	86.1 ± 3.0	92.0 ± 1.2	95.8 ± 0.3	89.6 ± 6.4
Baselines	30.4 ± 1.7	47.5 ± 7.5	76.7 ± 0.8	78.7 ± 0.4	91.3 ± 1.4	87.9 ± 2.0	87.6 ± 1.1

Overall, in the appraisal of reactor configuration it demonstrated to be crucial on the performance of MFCs (Table 1). From two chambers with carbon cloth anodes to single chamber with graphite granules, the electrode spacing was reduced and the ratio anode surface area to volume was increased; also when carbon cloth based were changed to membrane based cathodes, the contact membrane-catalyst was improved and the transport of protons to the reduction reaction place was facilitated. All these factors contributed to lower the internal resistance. In agreement to published works (Manohar and Mansfeld, 2009, Liang et al., 2007) the reduction of the internal resistance resulted in enhancing the efficiency of the reactors both, in terms of COD removal and electricity generation. The enhancement of the results was significant in terms of power output at all temperatures; however the improvement regarding COD removal was significant only at the low temperature range (4-15 ºC).

4. Conclusions

In this work, it has been demonstrated that electroactive anodic consortia in a MFCs are able to develop and to carry out effectively both, COD removal and energy generation at temperatures as low as 4 ºC. Furthermore, the use of single chamber MFCs contributed to lower the internal resistance of the system.

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