Microbial Fuel Cells

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Abstract

We compared the performance of two microbial fuel cell (MFC): a cathodic electrode without biomass (abiotic cathode) and another electrode coated with a biofilm (biocátodo) for ≈200 days of operation in batch with cyclical feeds. In these experiments, we used carbon felt electrodes and a Nafion membrane separating the compartments (with 360ml of volume). The mixed microbial consortium used came from a waste water treatment plant and were powered by synthetic effluents.
Control tests allowed to evaluate the influence of the material used and the effect of hydrodynamic stress in the anodic chamber.
For the abiotic cathode the current density (CD) was 122mA/m^2, the power density (PD) 54mW/m^2 and the voltage 440mV. For the biocathode CD was 116mA/m^2, PD was 48MW/m^2 and the voltage 417mV. In the abiotic cathode the wastewater treatment efficiency (removal of COD) was 91% and coulombic efficiency 31% and in the biocathode 93% and 34%, respectively.
In order to improve the performance of MFC's we used an abiotic cathode with potassium permanganate [400µmol/L] witch obtained a CD of 242mA/m^2, PD of 210MW/m^2 and a voltage of 870mV.
It also evaluated two MFC's with a cathode in direct contact with air, one with an electrode impregnated with Ion Jelly and the other with a mixture of Ion Jelly and Laccase, were in the first one the CD was 104mA/m^2, PD was 39mW/m^2 and 375mV of voltage and the second respectively, 47mA/m2, 8mW/m2 and 168mV.
These are promising results, especially for Ion Jelly MFC. More studies are needed.

Keywords: Energy, Microbial Fuel Cells, Biocathode, potassium permanganate, Ion Jelly, Laccase.

1. Introduction

Currently, the electricity produced worldwide comes essencialy from coal, gas, oil and nuclear energy, due to the easy access to these resources (International Energy Agency, 2009). However, they are all associated with environmental problems and are limited by their scarcity. As a possible solution to the great problem of energy sustainability, among the new renewable energy sources, in recent years Fuel Cells (FC) have emerged with greater emphasis.
A FC is an electrochemical device capable of converting chemical energy into electrical energy with good efficiency and low emissions. Among FC's there are the Microbial Fuel Cells (MFC) that consist in a reactor (similar to an electrochemical cell), where the electric energy production occurs in a simple way: the microorganisms are placed in a chamber with organic matter and its metabolism generates electron and protons that are transported to the electrode where electrochemical transformations occur.
The major importance in the study of MFCs is the possibility to transform industrial, domestic and urban waste, with high quantities of organic matter into electrical energy with a high use of electrons extracted from the organic compounds. These reactors can be self-sustainable and renewable, when inoculated with microorganisms that make use of organic compounds by dregadating them (Reddy et al, 2010; Lovley, 2006).
The applications for this technology are the use of effluents from waste water treatment plants, which is an almost infinite supply of human and industrial wastes that may allow a high degree of sustainability, reducing the environmental impact, while simultaneously produces energy.

2. Materials and Methods

2.1 MFC Design

In this project, we constructed the two chambers in "H" form, where they communicated with each other but were separated by a membrane, Figure 1.
The key to the "H" form design is selecting a membrane which allows exchange proton between the chambers and prevents oxygen in the anode chamber.
The bioreactor of this study had two compartments, with a volume of 360ml each and were constructed with polymethyl methacrylate, because it´s the easier material for laboratory handling and also because of its corrosion resistance.

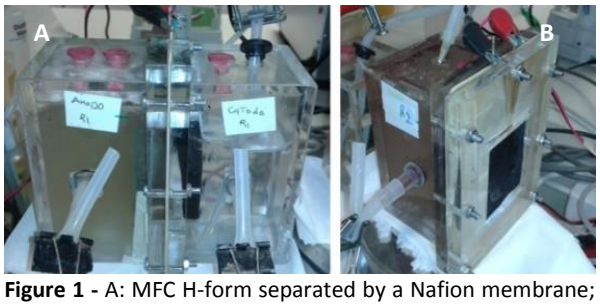

Figure 1 - A: MFC H-form separated by a Nafion membrane; B: MFC with an anode chamber and cathode in direct contact with air.

The existence of two compartments was decisive to the operation of the anode and cathode in separate aqueous media. These two compartments were separated by a selective membrane H^+, a Nafion membrane with a thickness of 0,180mm (produced by Alfa Aesar, A Johnson Matthey company).

The interior of each compartment had a carbon felt electrode (produced by the same company), with an area of 36cm^2 (6cm x 6cm) having a thickness of 5mm. We used copper wire to contact the electrodes, connected to a fixed resistance of 1kΩ, which was located in an intermediate position between the cathode and the anode. The electrodes were placed as close as possible to the membrane.
Initially in the experimental test the cathode compartment was fed continuously with air, through a small air compressor ELITE mark - 801 C. Holf Nagen, UK Ltd., to keep the environment under aerobic conditions. The aqueous solution was bubbled continuously to facilitate the dissolution of oxygen, making constant the quantity of electron acceptors.
In the second part of the laboratory work we created an MFC without a cathode chamber, as shown in Figure 1, were the electrode was in direct contact with air.
The anode compartment, during the tests, was on anaerobic conditions, with rotation (≈1000rpm) and contained an aqueous solution of the synthetic sewage and the inoculum biomass, from a wastewater treatment plant.
Other experiments were also conducted with different synthetic wastewater and an oxidizing agent to test the increased efficiency of MFC.

2.2 Description of the inoculum

The inoculum used in this study to colonize the MFC, came from a wastewater treatment plant (in Chelas city). We used the primary sedimentation of the waste water because, according to the literature, it is not concentrated in organic matter and microorganisms, ideal for testing in the laboratory. If the sample was derived from the sludge tank, it could contain pathogenic microorganisms and on the other hand, a larger MFC would be needed due to the quickly consumption of synthetic effluent.

2.3 Description of synthetic wastewater

The synthetic effluent used as organic source and mean for biomass growth, consisted in a specific chemical composition as described in Table 1. Theses effluents were tested and evaluated previously in order to meet the metabolic needs of the consortium microorganisms capable of producing energy, developed by Venkata Ramanaiah (co-supervisor of this work). The pH of the aqueous solutions was constantly analyzed and buffers were used to maintain pH stable in pH 7.

Table 1 - Chemical composition used in the anode and cathode chambers.

Chemical compounds	Anode	Biocathode	Abiotic cathode	*Whey* anode
CH_3COONa (Sodium acetate)	0,82g/L	---	---	---
KH_2PO_4 (dihydrogen phosphate)	5,751g/L	5,751g/L	5,751g/L	---
K_2HPO_4 (dipotassium phosphate)	10,04g/L	10,04g/L	10,04g/L	---
NH_4Cl (ammonium chloride)	1,06g/L	---	---	---
Na_2CO_3 (Sodium carbonate)	---	1,05g/L	---	---
H_2O (Distilled water)	270ml	270ml	270ml	---
Milk serum	---	---	---	270ml
Inoculum	90ml	90ml	---	90ml

Another synthetic effluent used was milk serum derived from milk day. This product did not suffer dilution and was autoclaved at 121°C for 15 minutes and after cooling to room temperature, centrifuged at 11.000rpm in sterilized tubes for 15 minutes to remove solid aggregates. The supernatant milk was cooled for 12 hours and before being used as a growth medium for microorganisms, it´s pH was adjusted to neutral because it was acid (pH 4,8). The carbon source contained in milk treated serum and used for the microorganism's growth was lactose.

2.4 Determination of energy production

Data were collected by a data acquisition system (digital multimeter), in order to monitor the generation of energy and changes/system disorders, from the reading of the potential difference values (voltage) and intensity of electric current.
For the digital multimeter be alble to obtain a more precise value of the current intensity and a higher power density, we used a fixed external resistance of 1000Ω. This process was necessary also because the internal resistance of the multimeter would be insufficient to acquire uniform and stable values.
The current intensity was calculated by Ohm's Law - Equation 1:

$$V_{MFC} = R_{ext} * I \quad \textbf{(1)}$$

In equation 1, R_{ext} is the external electrical resistance system (Ω), V_{MFC} is the electric potential difference of the MFC in volts (V) and I the intensity of electric current in ampere (A). Obtaining energy depends on the potential difference and the electrical current intensity generated by the MFC, it is possible to obtain the system power using both-Equation 2:

$$P = V_{MFC} * I \quad \textbf{(2)}$$

By applying the fundamental laws of electronics it's possible to detect power values produced by the system under study. The current density (CD) expressed in A/m^2 was determined according to the equation 3:

$$CD = \frac{I}{A_{\text{anode}}} \quad \textbf{(3)}$$

Where A_{anode} corresponds to the projected surface area of the anode (m^2) and I the current intensity (A).
The power density (PD) expressed in W/m^2 was calculated by power and projected surface area of the anode (A_{anode}) - equation 4:

$$PD = \frac{P}{A_{\text{anode}}} \quad \textbf{(4)}$$

The maximum power depends on the internal resistance system (R_{int}). Therefore, if an MFC has a very high internal resistance, their potency is low. The maximum power that can be generated is related to the open circuit voltage (Open Circuit Voltage - OCV) according to the equation 5 (Logan, 2008).

$$P_{máx} = \frac{OCV^2 * R_{ext}}{(R_{int} + R_{ext})^2} \quad \textbf{(5)}$$

The coulombic efficiency (CE) is defined as the ratio between the number of coulombs effectively transferred to the anode and the total number of coulombs produced, expressed in percentage (%), considering all oxidized substrate produce electrons - equation 6 - where M is molecular oxygen mass ($32gO_2/molO_2$), I the current intensity, F a constant Farafay, b the number of electrons transferred per mole of oxygen ($4e^-$), q the flow rate (L/s) and ΔCOD (gO_2/L) variation of the chemical oxygen.

$$E_c = \frac{\text{MI}}{FbqΔCOD} \quad \textbf{(6)}$$

2.5 Determination of COD by potassium dichromate method

To calculate the CE is necessary to determine the chemical oxygen demand (Chemical oxygen demand - COD).
The COD is used as a measure of the oxygen equivalent to the organic fraction sample susceptible of oxidization by the action of a chemical compound of strong oxidizing power (Logan, 2008). Thus, it is possible to relate the COD value with the amount of organic matter contained in effluent.
The method of COD analysis, equation 7, correlates with equal precision and proportionality the disappearance of organic matter and the appearance of electric energy in the system without causing any interference (Logan, 2008), by titration with ferrous ammonium sulfate (FAS), under reflux method with potassium dichromate. This method was selected mainly due to the high oxidizing power of the chemical, its applicability to a wide variety of samples and because of the easy handling.

$$COD = \frac{(B-A) * M * 8000}{V_{amostra}} \quad \textbf{(7)}$$

Where A is the volume of gas used in titration of the blank and B in the titration of the sample, M is the FAS concentration (0,10M), 8000 is the molar mass of oxygen ($32000mgO_2/4e^-$) and V is the volume sample (1,5ml). From the COD formula we can calculate its direct proportionality with the organic matter in wastewater, titrated with ferrous ammonium sulfate. The COD values are ideal when they approaches zero, showing that the carbon sources have been totally consumed.

3. Start of Microbial Fuel Cells

Experimental tests were always operated in batch and at ambient temperature (≈25°C). The compartments of MFC were electrically connected through the external circuit between the electrodes of the anode and cathode. All the anode chambers of this study contained biomass and were under anaerobic conditioning.
New effluents were added in the MFC when the potential difference was inferior of 90mV, value that represented the end of a cycle. At this time, the systems of rotation and air compression were paused for 20 minutes, so that the biomass could deposit. After this period, a residual volume of 100ml was perserved in both chambers where then was added 260ml of effluent in both compartments to initiate a new cycle.
In the beginning and the end of each cycle, 10ml samples were removed from the aqueous solution for subsequent analysis and comparison of results. These procedures were identical in all tests performed in this experimental study.

3.1 Control Test

In this experimental study, a controlled test was carried out, in which, a Naflon membrane (7cm x 7cm) was placed in distilled water for 12 hours, in order to increase its elasticity.
After washing the reactors with distilled water, the MFC assembly process was initiated, starting with the isolation of the anode from the cathode with the Nafion membrane. Then, this membrane was glued on the extremities to prevent leakage or contact between both compartments. The quality of the isuflation was verified with the addition of distilled water in one of the chambers.

When the MFC was guaranteed suitable for testing, synthetic effluent was placed in the respective compartments. The copper wire disposed in each chamber was connected to a multimeter, with the purpose of analyzing the interference and oxidation with medium (Control 1).
In the second stage of control test (Control 2) the copper wires were attached inside the carbon felt, at a distance of ≈10cm from each other.
In the third step of the process, the synthetic effluent from both chambers was renewed (Control 3) and then it was added 90ml of biomass in the anodic chamber. The anode was exposed to nitrogen for 30 minutes, with the purpose of replacing the dissolved oxygen (O_2) by nitrogen (N_2), thus transforming in an anaerobic anodic chamber. To verify if the distance was influencing the acquisition of electrons, each electrode was maintained at a distance of ≈5cm from the Nafion membrane. After 10 days it was possible to check the electrode impregnated with the biofilm.
In Control 4, a connection of ≈2,5cm was created between the electrodes and the membrane.
In the penultimate stage of the control experiment (Control 5) the electrodes were approached as much as possible (less than 0.5cm), the effluent was renewed and 90ml of biomass was added.
Finally, the last objective consisted in the establishment of whether the agitation in the anode chamber was relevant to energy production (Control 6), that goal was reached by the analysis of three cycles with and without agitation.
(The stirring speed, that was used during this experiment reached ≈1000rpm.)
To maximize PD in the MFC, the state of the art reccomends the usage of an external resistance of 1000 Ω (Larminie, 2003; Larminie, 2004; Rahimnejad, 2011; Logan, 2008). So, in this experimental study, in order to obtain maximum efficiency in the MFC, it was carried out the study of its polarization, by evaluating the performance of diferent external resistors, as such: 20Ω; 220Ω, 560Ω, 820Ω, 1000Ω and 5000Ω. In every test, after adding a new resistance to the external electrodes, we waited for 30 minutes and then the measurements were carried out. This is the optimal interval of time required to reach equilibrium in the internal MFC system (Logan 2008).

3.2 Different Cathode used

In the analysis with biocathod, the cathodic compartment contained 90ml of biomass, in which the carbon source was the sodium carbonate efluente 3mM and the buffer solution at 50mM.
The essay with the abiotic cathode was not seeded with biomass but it was added 360ml of a phosphate buffer solution at 50mM and also a oxidising agent in order to increase the performance of the MFC. Therefore, was selected potassium permanganate at a concentration of 400µmol/L.
In order to create the most economical bioreactor possible, we performed an MFC with airy cathode. For that it was removed the cathode chamber, leaving the cathode electrode (surface area 30cm^2) in direct contact with air and with the Nafion membrane. This experiment was performed with three different cathodes: cathode without impregnation; impregnated with Ion Jelly; cathod impregnated with Ion Jelly and Lacase.
The Ion Jelly is a conductive, transparent and flexible polymer material, which combines the chemical versatility of organic salt - ionic liquid (IL); with the morphological versatility of a natural and inexpensive biopolymer - gelatin (Pedro Vidinha, 2008; Rui Carvalho, 2012). This compound targets the use of thin-film batteries and has a good ionic conductivity (10^{-4} Scm^{-1}); high stability to 180°C; establishing stable hydrogen bonds between the IL and ionic gelatin; large electrochemical window and biocompatibility. IL employed to prepare the hydrogel was the [bmim][$N(CN)_2$], 1-butyl-3-methylimidazolium dicyanamide [bmim][$N(CN)_2$] provided by IoLiTec. It was selected since this IL preserving its shape and gelatinous structure in contact with the air and was not too viscous, thus facilitating its handling (Rui Carvalho, 2012).
The laccase (type oxidase enzyme containing copper) was added to ion Jelly, in another experiment, taking into account the properties and advantages thereof, the creation of a favorable and stable environment for enzymes. The redox enzyme was employed with the aim of studying the catalysis in the direct transfer of electrons in the reduction of O_2.

3.3 Anode with milk serum

The milk serum is an agricultural residue which can be used as alternative substrates for preparation of low cost culture environment, more ecofriendly. It was created a MFC with milk serum in the anode chamber, used as na indiluted efluent without resourcing to mediators, in an anaerobic environment. In the abiotic cathod it was added 360ml of a phosphate buffer solution at 50mM and was bubbled continuously.

4. Results and Discussion

4.1 Test control

Control tests were designed to detect the influence of the materials used in the construction of MFCs. Figure 2 shows the energy graph obtained in control tests over time, according to the experiments carried out in particular in the placement of the electrodes, use of biomass, presence or absence of stirring, described in A (Control 1 and 2), B (Control 3), C (Control 4) and D (Control 5).

Section A is the first 10 days of data and reveals that the materials used, such as copper wire (Control 1) and carbon felt electrodes with copper wire, 10cm from each other (Control 2) , do not promote any kind of electricity production in the presence of synthetic effluent. However, the copper wires used in the anode and cathode compartment had a slight corrosion detected by a blue-green layer more evident at the cathode. This was due to copper slowly reaction, not with water but with atmospheric O_2. In the anode, copper wire corrosion was almost negligible, because the medium was anaerobical.

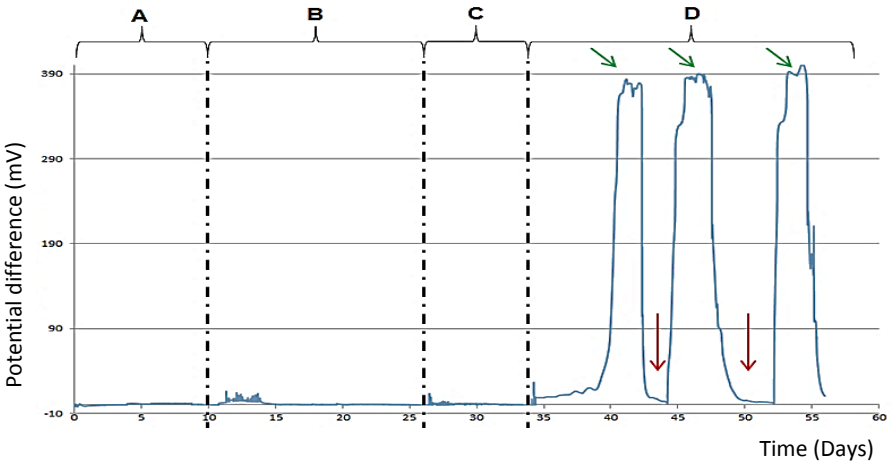

Figure 2 - MFC behavior control without agitation in the anode chamber, thru potential difference over time, A: copper + synthetic effluent + carbon felts (distance 10cm between cathode electrode and the anode); B: same as A + biomass; C: same as B (with a distance of 5cm); D: same as C (with the eletrodes approached as much as possible).

Figure 2B represents the biofilm formation on the electrode, which occurred not very uniformally and had a duration of ≈10 days (Control 3). By analyzing the graph, we can detect from day 11 to day 15, a voltage of 10mV, probably due to the microbial activity adjustment to the environmental conditions. From the 15th to the 25th day, it is not detected any energy production. The small voltage changes detected on day 26, were due to electrodes approachement to a distance of 5cm (Control 4), but were not significant and stabilized on day 27th.

By assessing the figure it possible to verify that from day 34, (Control 5, section D), there is an instant increase in potential difference with 382mV voltage values in the first six days, because of closest approach of electrodes. The green arrows show the beginning of each cycle and the red the end of the cycles.

With this analysis we concluded that the approximation of the electrodes as much as possible facilitates the transport of electrons when there is no agitation in the anodic chamber and this method should be the preferred in the construction of a MFC. These results are according with those obtained by tests performed by Logan in 2008, on an identical MFC design with activated carbon electrodes.

4.1.1 Effect of the agitation on the anode chamber

Two tests were performed, shown in Figure 3 (Control 6), three cycles with agitation conditions in the anode compartment (blue line) and one cycle for the test without agitation (red line).

In the test without agitation, each cycle had a stable phase of electricity production averaging 3 days and were voltage reached ≈385mV. In the test using agitation (≈1000rpm), the obtained cycle had a stable phase of ≈20 days of electricity production and the tension reached ≈428mV.

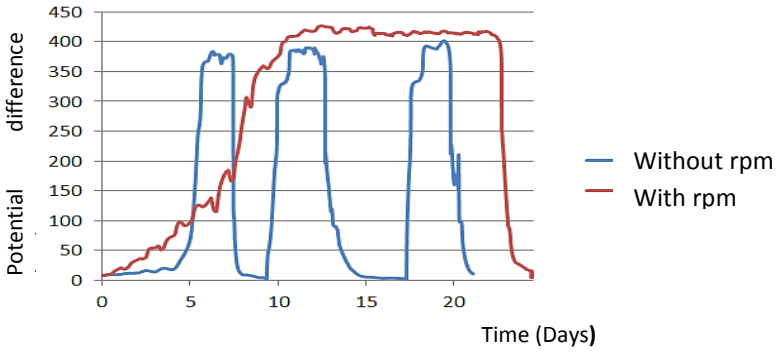

Figure 3 - Comparison of MFCs with and without agitation of the aqueous medium of the anode chamber.

These results show that the agitation better distributes the organic matter present in the anodic chamber causing it to reach a greatest number of microorganisms (biomass increase), generating electricity almost constant for 15 days (≈400mV).

An efficient homogenization of the synthetic substrate in the effluent causes an adapt and grow of the microorganisms, promoting a more rapid formation of the biofilm, extremely critical in the renovation of organic matter and therefore leads to increased production of electrons by the MFCs system. In the test without agitation, in the same amont of time, the bioreactor had to be fedback 3 times, due to the break of organic matter flow.

That is, while in a 15-day period we had one cycle of energy production in the MFC with agitation, in the MFC without agitation we had 3 cycles (Figure 3). The probable cause is related we the difficulty of distribution of the organic matter and also with the probable consumption of this organic matter by microorganisms deposited on the bottom of the reactor that didn't reached the biofilm because of the absent of agitation.

Nevertheless, the wastewater treatment efficiency was not affected in the tests without agitation, removal of COD was almost always higher than 87%.

We obtained a DP (equation 4) of 51 and 41mW/m^2 for the experiment with and without agitation, respectively. Briefly, the agitation has an electric power generation efficiency of 85% (comparing energy production to cycle times) versus absence of agitation and a DP 19% higher.

4.1.2 Effect of the external resistance

As stated earlier, we did a control test for the study of polarization, which evaluated the performance of different external resistors (20Ω, 220Ω, 560Ω, 820Ω, 1000Ω, 5000Ω) integrated in the external circuit of the MFC.

With the MFC in the maximum efficiency we measured open circuit voltage (OCV), that is, the maximum voltage that can be obtained in a system with infinite resistance. And as can be seen in Table 2, the voltage was evaluated by the CO and DP for each tested external resistors. It was detected a decrease in voltage in the MFC with the reduction of external resistors.

Thus, it was concluded that the maximum DP was achieved with external resistance of 1000Ω, as shown by other studies (Rahimnejad 2011 Logan 2008). And for that reason, this was the resistance selected to carry out the laboratory experiments.

Tabela 2 - Values obtained (voltage, DC, and DP) for each of the tested.

	OCV	5000Ω	1000Ω	820Ω	560Ω	220Ω	20Ω
Voltage (mV)	498	422	374	272	212	114	8
DC (mA/m²)	0	28	125	111	127	174	129
DP (mW/m²)	0	12	47	30	27	20	1

4.2 Biocathode

The MFC with the biocathode was operated over approximately 195 days, corresponding to a total of 11 cycles fed-batch, figure 4. The green and red arrows show respectively the beginning and end of each cycle. A new cycle always began when the MFC reached a constant voltage and ended when down to a minimum voltage (red arrows), an event that occurred naturally due to the consumption of the substrate.

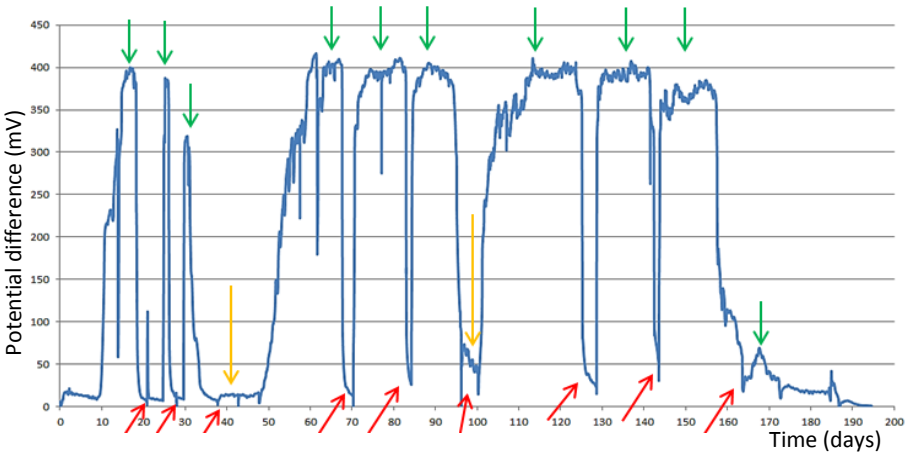

Figure 4 - Voltage ratio and time in MFC with the biocathode, where the green and red arrows represent the beginning and end of a cycle, respectively and yellow arrows the injecting biomass.

When this occurred the synthetic effluent were renewed from each compartment for a next cycle being.

The yellow arrows indicate the injection of biomass in both compartments. This procedure was performed when the synthetic effluent by itself was not sufficient to recover the production of electricity by the MFC. The last green arrow in Figure 4 represents the last cycle done in this laboratory experiment. The maximum voltage of this cycle was 76mV, the lower value of the process, which justifies the importance and need for biomass injection into the MFC. Wiht Figure 4 we can examine an excellent performance of the MFC in the production of bioelectricity, with a mixed microbial community. It obtained a maximum voltage of 417mV, having reached the maximum DP of 48mW/m^2, a DC of 116mA/m^2 and an OCV of 534mV. The stable phases of electricity production corresponded to an average of 13 days and the larger cycle reached 25 days (between day 100 and day 125).

4.3 Cathode abiotic

The MFC with an abiotic cathode was operated over approximately 230 days, corresponding to a total of 12 cycles fed-batch, shown in Figure 5. The green and red arrows show the beginning and end of each cycle, respectively. As in the MFC presented above, a new cycle always starts when the MFC reaches a constant voltage and ends when down to minimal pressure.

The yellow arrows in Figure 4 indicate the biomass injection into the anode compartment and the orange arrow points to the absence of an expected peak of electrical production due to the cathode abiotic lack of feedback from synthetic wastewater (it occored an academic pause). The feedback was performed only on day 122 and as can be seen in Figure 5, the microorganisms proliferated, even in conditions of stress and without adding new inoculum biomass.

There was an excellent performance of the MFC in the production of electricity, with a mixed microbial community, obtaining a maximum voltage of 440mV, a DP reached a maximum of 54mW/m^2, the DC of 122mA/m^2 and OCV was 561mV. The cycles had a bioelectricity production stability, on an average of 15 days and the larger cycle reached 20 days (between day 77 and 97).

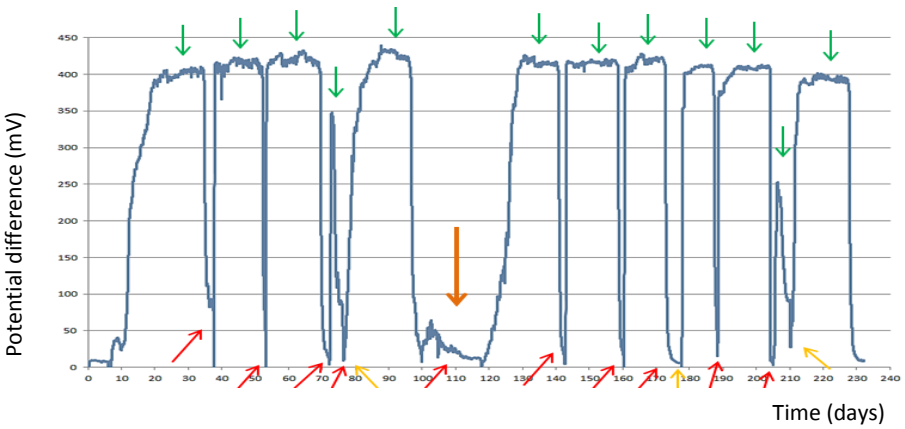

Figure 5 - Voltage ratio and time in MFC with abiotic cathode, where the green and red arrows represent the beginning and end of a cycle and yellow injecting biomass.

4.3.1 Cyclic voltammetry of abiotic cathode

The cyclic voltammetry (CV) is a tool to determine the operating points of an electrode or a machine. This technique allowed us to know the redox behavior of the electrode, through the number of observation and reversibility of oxidations and reductions that occurred during each cycle (Rachinski, 2010; Peixoto, 2013; Logan, 2008).

Two CVs were carried out in the first assay (CV1) were anode was used as working electrode, the counter electrode as the cathode and the silver electrode as a reference electrode, Figure 6A. In the second assay (CV2), the counter electrode was replaced by a platinum electrode, keeping the rest of the configuration, Figure 6B. As shown in Figure 6, the voltammogram of the mixed bacterial culture exhibits a maximum potential of 800mV for the various counter electrodes; 0,07A of current intensity for the counter electrode of platinum and 0,13A for the cathode electrode against the abiotic. This behavior occurs due to the spontaneous oxidation of some constituents of the mineral culture.

The green arrows indicate the oxidation peaks and the blue arrows the reduction peaks. The oxidation peaks correspond to electron transfer by diverse mechanisms, responsible for direct and indirect transfer electrons to electrodes (Logan, 2008; Peixoto, 2013).

Whit the results of this voltammogram it's possible to prove the importance of direct electron transfer in the production of current intensity. And on the other hand, the relevance of biofilm formation on the surface of the electrode, which significantly increases the intensity of the oxidation peak, as it grows.

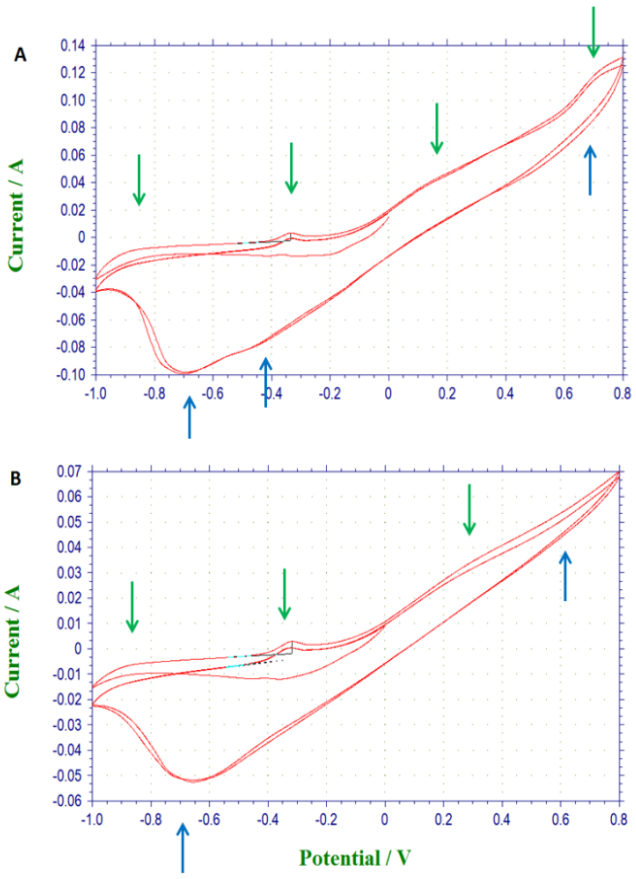

Figure 6 – CV of the MFC with abiotic cathode current and potential relationship. A: CV1, abiotic cathode electrode as a counter electrode; B: CV2, platinum as a counter electrode.

4.4 Biocathode versus abiotic cathode

The Figure 7 shows an overlay of the potential difference obtained for the biocathode and abiotic cathode, in which it is possible to see a greater energy production in the abiotic cathode (blue), with higher voltage values. Clearly, the biocathode (red) had a slower and gradual starting, demonstrating the need for biofilm growth in both compartments as an essential factor for the ionic exchange of H^+ cations.

According to the literature, the anode chamber under anaerobic conditions selects the microbial consortium, comprising mostly restricted and facultative anaerobes (Rabaey, 2005; Logan, 2008; Rachinski, 2010). And the biocathode chamber in agitation conditions, selects the restricted aerobic and some facultative anaerobic (Logan, 2008; Sharma, 2010). Since it didn't occur a biofilm formation on the the abiotic cathode, because it had no biomass, this MFC was faster in generating electrons.

From the analysis of Figure 7, it can be established that the MFC's in the study were able to generate electricity for three cycles with 90ml of biomass, only needing to replace the synthetic effluent. In the first cycle just after the

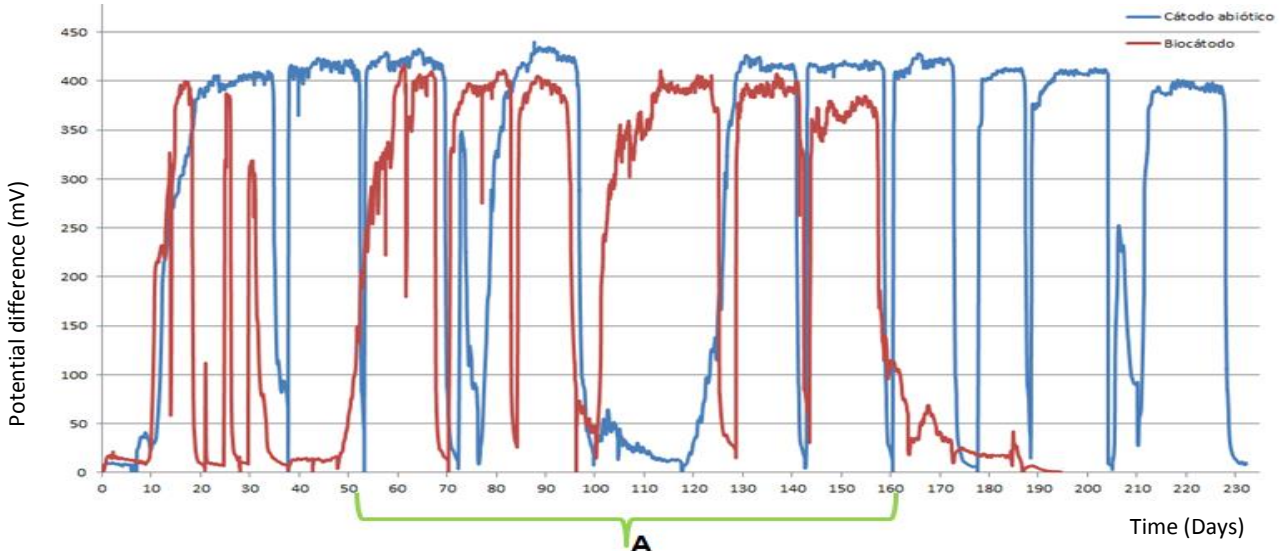

Figure 7 - Voltage vs. time in days, in the two MFC's created (abiotic and biocathode), in a cycle of approximately 200 days.

addition of biomass it is found that the electric energy production was always higher in both MFCs.v

The A zone identified in Figure 7 indicates the day on which occurred higher production of electricity with higher potential differences for both MFC and cycles with greater stability and duration of bioelectricity production. This occurrence due to the increase in the laboratory room temperature. This incident allowed to determine that the temperature has an influence on microbial behavior, as described in other studies. (Logan, 2008)

The COD removal efficiency and coulombic efficiency (CE%) of the system for both MFC was calculated. The wastewater treatment in the abiotic cathode efficiency was 91% and CE% was 31%. For the biocathode COD was 93% and CE% was 34%. With this information we confirmed that both MFCs had a similar wastewater treatment efficiency, but biocathode proved slightly more efficient than the abiotic cathode, as also shown by several authors (Guodong Zhanga, 2012; Liu, Jing Wei, 2012). The COD removal efficiency was greater than 90% for both MFCs, promising results compared to other studies (Guodong Zhanga, 2012; Liu Jing-Wei, 2012; Logan, 2008). As for the coulombic efficiency that was around 30%, it was quite satisfactory, considering that is similar to many other studies (Guodong Zhanga, 2012; Rachinski, 2010; Peixoto, 2013).

We concluded that on one hand, if the objective of the MFC created is the degradation of organic matter by microorganisms of the consortium, the biocathode should be the method of choice (93% vs 91%), and on the other hand, if the aim is exclusively electrical energy (most common), abiotic cathode should be prefered, since the stable production of energy occurs early (day 11 vs. day 52) and medium voltage produced is higher (398mV vs. 346mV considering energy production as stable in the range of 200mV).

4.5 Abiotic cathode with potassium permanganate

In order to improve the reduction reaction and therefore MFC performance with abiotic cathode, it was added potassium permanganate with 0,4mM concentration to the cathode compartment.

Figure 8 discloses a 19 day cycle for the MFC with potassium permanganate, with only one addition of biomass and synthetic effluent. The results presented show a remarkable improvement in electricity generation in relation to the MFC without the addition of oxidizing agent, with a voltage almost 50% higher.

The maximum potential difference in this MFC was 870mV and OCV was 970mV. Figure 9 shows DP and DC vs. tension, with values of 210mW/m^2 and 242mA/m^2, respectively.

Using the same conditions as the author Mostafa Rahimnejad (2011), in this experimental work it was possible to obtain over 37% PD (210mW/m^2 vs. 133mW/m^2) in the MFC with potassium permanganate.

We concluded that the cathodic reaction is a major factor limiting the production of energy in MFCs (Mostafa Rahimnejad, 2011; Logan 2008) and despite the use of mediating agents endear the process, these enhance better results and their use should be considered.

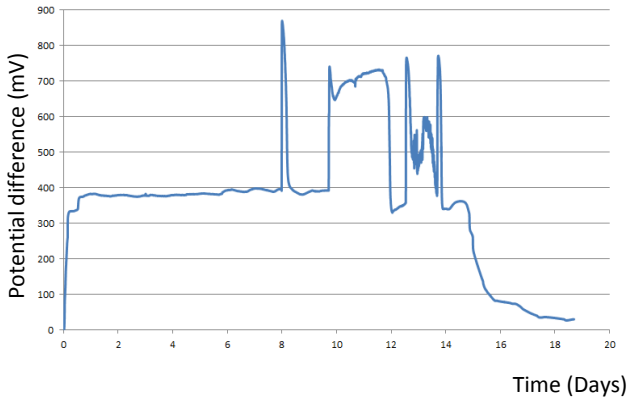

Figure 8 - MFC voltage vs. time in the abiotic cathode with potassium permanganate.

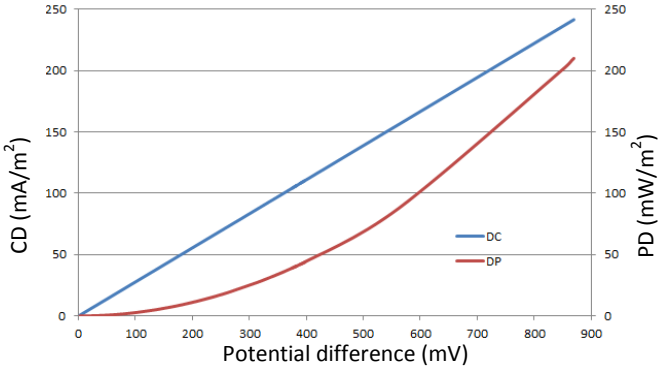

Figure 9 - Polarization curve: current density and power density function vs. potential difference in the MFC with potassium permanganate.

4.6 Cathode in direct contact with the air

A. Cathode carbon felt electrode without impregnation

The MFC with carbon felt cathode electrode in direct contact with air, without impregnation, did not obtain positive results from energy production due to the electrode incompletely dry.

The physical and chemical properties of the carbon felt depend on its hydrophilic character and so this requires an aqueous medium to complete the circuit. With the electrode in direct contact with air, although there was a production of cations in the anode chamber, there is no transfer for the cathode. This experience has never been produced or reported by other studies. The objective of this laboratory work was merely control.

B. Cathode-impregnated carbon felt electrode with Ion Jelly

With the assessment of Figure 10, we can detect an excellent performance of the MFC with the cathode electrode impregnated with Ion Jelly in bioelectricity prodution, with a total of 3 cycles fed-batch.

For this MFC we obtained a maximum voltage of 375mV, a DP of 39mW/m^2, a DC of 104mA/m^2 and an OCV of 498mV. The stable phase of the MFC with constant electricity production amounted to a total of 14 days (from day 7 to day 20). The green and red arrows respectively expose the beginning and end of each cycle. The yellow arrows indicate the biomass injection into the anode compartment.

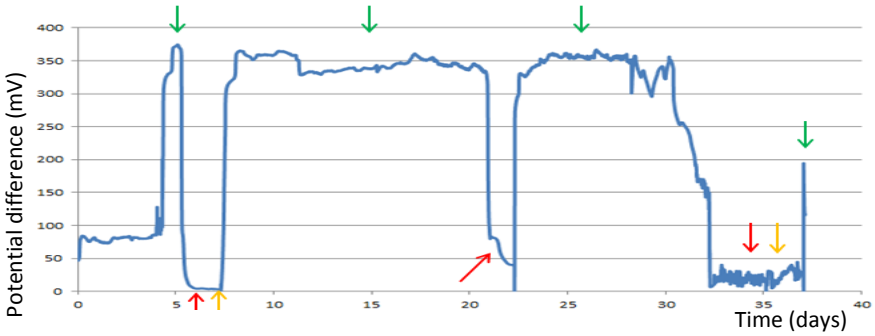

Figure 10 - Voltage ratio vs. time on the MFC-impregnated cathode with Ion Jelly, where the green and red arrows represent the beginning and end of a cycle, respectabily and yellow arrows the injection of biomass.

Because the Ion Jelly is degradeted once it has contact with water (Peter Vidinha, 2008; Rui Carvalho, 2012), for this experiment it was necessary to calculate the water produced by the cathode. It was possible to maintain the integrity of the carbon felt as the production of wastewater was not disrupting or degrading the Ion Jelly film.

This was a new experience in this area, because as mentioned earlier, this material has never been applied in MFC's. The DP results achieved are not far from the values obtained for the abiotic cathode and the biocathode, but it's still necessary to take into account that the electrodes used in the experiment with Ion Jelly was smaller (6cmx5cm MFC Ion Jelly vs. 6cmx6cm MFC cathode abiotic and biocathode).

C. Cathode carbon felt electrode impregnated with Ion Jelly and Laccase

The Figure 11 shows the results obtained for bioelectricity productionin the MFC with Ion Jelly and laccase. For this experiment we obtained a maximum voltage of 168mV, a DP of 8mW/m^2 and a DC of 47mA/m^2.

The green arrow indicates the maximum voltage acquired when it was put the electrode in the MFC, which almost immediately dropped dramatically. During the period of 9 days, we waited for the increasing voltage, however, this did not occurred and it was necessary to add biomass to the MFC, but it still could not provide electrical output results. It was expected that the use of laccase in the MFC would oxidize the oxygen environment and therefore accelerate the electron transfer to the anode surface, so the expected voltage values were much higher than those that were obtained.

These results may arise from various factors, such as impregnation; the reutilization of an electrode; or even incompatibility of the Ion Jelly. The impregnation of Ion Jelly and laccase on the surface of the electrode, requires a certain viscosity and when it's not perfect, may reduced adhesion to the membrane of Nafion and turn ion exchange difficult.

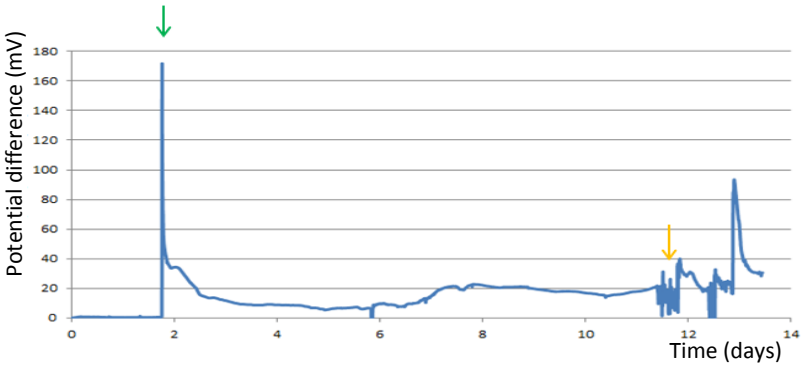

Figure 11 - Voltage ratio and time on the MFC-impregnated cathode with Ion Jelly and Lacase where the green arrow represents the start cycle and yellow injecting biomass.

4.7 Anode with milk serum

The MFC with milk serum in the anode compartment was operated for approximately 22 days, with only one addition of biomass and synthetic effluent. The microorganisms were able to utilizate a carbohydrate, especially lactose, for the generation of bioelectricity.

In the analysis of Figure 12 there is a weak performance of the MFC in the production of electricity, with a mixed microbial community. We obtained a maximum voltage of 53mV, a DP of 1mW/m^2 and a DC of 14mA/m^2.

This study was based on other authors works, including Aishwarya DD., Nasirahmadi 2011 and S. 2011.

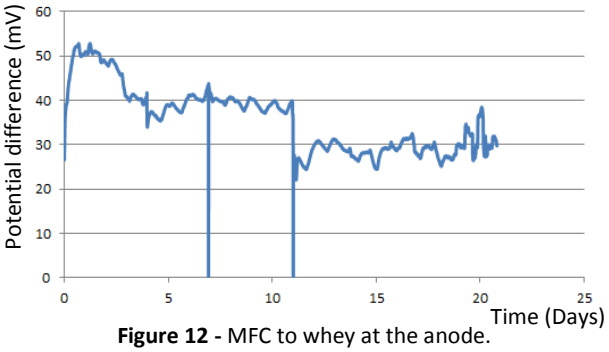

Figure 12 - MFC to whey at the anode.

Both studies used an identical design for the MFC, an equally mixed microbial consortium and milk serum. In this woks, all the material they used were sterilized. The main difference in this laboratory experiment, was that only milk serum was sterilized, since this step is expensive and one of the goals was to create a MFC with the lowest possible cost. For this reason, the microbial consortium contaminated the anode compartment and the MFC was necessarily autoclaved to avoid the risk of toxicity. This occurrence explains the low voltage values (53mV vs. 360mV for Aishwarya DD, 2011;. Vs. 400mV to Nasirahmadi S., 2011).

5. Conclusion and future work

This experimental study had as an objective the creation of different types of MFCs at the lowest possible cost, with the highest possible energy production through the degradation of organic matter. To achieve that, the MFCs were created with different cathodes: abiotic; biocathode; in contact with air; using potassium permanganate, milk serum and, also with a novelty in this field, the development of new eletrodes, the Ion Jelly and the Jelly with laccase.

Control tests were carried out to evaluate the influence of the material used and the effect of hydrodynamic stress.

It was shown in this experimental study that agitation produces greater generation of energy, due to its effecient distribution of the substrate.

It was also investigated the ideal external resistance to the MFCs under study, in order to increase the maximum output power, and the resistance of 1kΩ was shown as the most appropriate, since it reached the higher PD during tests

When the MFCs with abiotic cathod or biocathode were used in the experiment, it was found that they are able to generate electricity for three cycles with 90ml biomass, requiring only the feedback process with effluent. For the cathode abiotic obtained a PD 54mW/m^2 and a voltage of 440mV and the biocathod 48MW/m^2 and 417mV, respectively.

The wastewater treatment efficiency in the abiotic cathod and bio-cathod performed within expected parameters, revealing promising results compared to other studies. Although the MFC with biocathode had a slower start, which proved the need for growth of the biofilm, it nevertheless, obtained an higher COD.

It is relevant to point out that the usage of potassium permanganate as oxidizing agente, showed na improvement in the performance of the MFC with abiotic Cathod, revealing a PD of 210MW/m^2 a 870mV tension and a tension nearly 50% higher than the abiotic cathode without mediators. It was therefore concluded that the cathodic reaction is a major factor that limits the production of energy in MFCs and that despite that the usage of mediating agents endear the process, these enhancers potentiate better results.

In both cathod in direct contact with air MFCs (the electrode impregnated with Ion Jelly and the mixture of Ion Jelly and laccase) it was obtained a CD of 104mA/m^2, 47mA/m^2, a tension of 375mV and 168 mV and a PD of 39mW/m^2 and 8mW/m^2, respectively.

The PD results with the Ion Jelly sample are not too distant from the values obtained for the abiotic cathod and bio-cathod, it is necessary to consider that the probe used in this experiment was indeed smaller. It would be expected that the results of PD, CD and voltage in the MFC Ion Jelly with laccase to be superior of those that were obtained, since the laccase is expected to oxidize the environment wich would cause an acceleration of the electron transfer in the anode surface.

In the case of the MFC with milk serum, the results did not reach the initial expectations, we suppose that the cause behind those results could be related with the absence of a sterilization protocol of the material that was used.

It can be pointed out some limitations in this study such as the size of the cathod, which is refered in some references as an important influence factor of the PD. Studies have demonstrated that using a cathode 14 times the anode, it is possible to obtain higher PD (Fan, 2008). The very length of the study can be considered a limiting factor, as is the case of MFC with Ion Jelly, where there have been promising values, but the duration of which failed to achieve their full potential.

In the future it would be important to understand and detect which specific strain is predominant in MFCs created in this laboratory experiment, in order to control this variable and counter the variability in comparative studies.

There is the need to develope this area, since the MFC technology has a vast potential regarding the production of electricity through the degradation of organic material in domestic or industrial effluents and applicability to various small and large scale.

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