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Cathodic Optimization of a MFC for Energy Recovery from Industrial Wastewater

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In a photosynthetic MFC with algae at cathodic compartment, algae use inorganic carbon source, carbon dioxide, and sunlight and produce oxygen by photosynthesis. The oxygen produced is used at cathode as electron acceptor. In this way, the use of algae at the cathode of a MFC has interesting advantages: carbon dioxide fixation and oxygen supply. In order to study if algae form a biofilm on cathodic electrode of a photosynthetic microbial fuel cell and how this biofilm affects on performance of this photosynthetic MFC and on electricity production, cathodic electrode of a photosynthetic MFC at steady state was changed by another identical electrode. When cathode was changed, the cell voltage fell down from 14 mV to 0 mV (light phase). After 10 days, the cell voltage increased and steady state was reached after 22 days, with values of 9 mV (light phase). When electricity starts to increase after changing cathode, algae concentration in suspension decreased from 600 until 250 mg/L. The decrement of algae concentration and the increment of cell voltage indicated that algae in suspension could form a biofilm on cathodic electrode positively influencing on electricity production. The cathode polarization resistance increased after changing cathode due to the elimination of algae biofilm from electrode. Once biofilm was formed, this resistance decreased from 80800 until 23060 Ω.

1. Introduction

A microbial fuel cell is a bioelectrochemical device where electricity is produced from organic matter by biocatalytic reactions. In a MFC, the substrate (organic matter) is oxidized in a type of biological process in which microorganisms deliver electrons to the anode surface. The electrons flow through an external load and they are released at the cathode, where they reduce an oxidant such as oxygen (Logan, 2008) (electrical current). This technology can be used to treat wastewater. In this way, microorganisms degrade organic matter from wastewater and simultaneously electricity is generated. This type of wastewater treatment has interesting advantages versus traditional, activated sluge, wastewater treatment (): less sludge production and energy input and aeration is reduced or is not needed, which will help to minimize the overall operating cost of treatment plant by decreasing the cost of sludge management and aeration.
There are many types of MFC's. In conventional MFCs, the anode is biological and cathode is abiotic. However, more recently, full-biologicals MFC has emerged. In this system, microorganisms are used at the cathode, so-called biocathode. On the other hand, when sunlight is converted into electricity within the metabolic reaction scheme of a MFC, this system is described as a photosynthetic MFC (Rosenbaum et al., 2010). In this system, photosynthetic microorganisms are used at the anode, at the cathode (biocathode) or at both. On the other hand, oxygen is the most conventional terminal electron acceptor in MFC's. However, the supply of oxygen as a final electron acceptor for cathodes reduced the net energy output of MFC as aeration is energy demanding (He and Angenent, 2006; Logan, 2009). Taking into account that, recently, a type of photosynthetic MFC with a biocathode containing algae has emerged. In

this system, algae use inorganic carbon source, normally carbon dioxide, and sunlight and produce oxygen by photosynthesis. In this way, the oxygen produced by algae is used as electron acceptor in cathode. Thereby, the use of algae at the cathode of a MFC have interesting advantages: carbon dioxide is a greenhouse gas and algae contribute to eliminate carbon dioxide; oxygen supply is not required, in this way, the mechanical aeration is eliminated and energy costs are reduced (which in the case of the industrial wastewater is a significant saving of money); and algae can also act as a biological electron acceptor while simultaneously reducing carbon dioxide to biomass under illumination (Powell et al., 2009). Mechanisms for microbe-electrode electron transfer in the anodic compartment have been subject of study in many publications (Busalmen et al., 2008; Lovey and Nevin, 2008; Wrana et al., 2010), as well as the influence of electrode-attached microorganisms (biofilm) on electricity production (Venkata et al., 2008; Sharma et al., 2010; Wu et al., 2014). However, it is not known if algae grow on cathodic electrode forming a biofilm and if the biofilm has a positive impact on electricity production.
Therefore, the aim of this work is to study if algae form a biofilm on cathodic electrode of a photosynthetic microbial fuel cell and to study of its effect on the performance with the final objective of determine the optimum situation when treating industrial wastewater in the anodic compartment.

2. Materials and methods

In this work, a photosynthetic microbial fuel cell with two compartments was used (Lobato et al., 2013; Gonzalez del Campo et al., 2013). The useful volume of each compartment is 800 mL. A proton exchange membrane (Sterion®) with high ion exchange capacity (0.9-0.02 meq/g), high ionic conductivity ($8·10^{-2}$ S/cm) and low electronic conductivity ($<10^{-10}$ S/cm) is used to separate the electrode. The electrodes with an active area of 8 cm^2 were built of Toray carbon cloths with 10 % of Teflon in order to improve the mechanical properties of the carbon (Lobato et al., 2008). The electrodes were connected by an external resistance of 120 Ω.
A Keithley 2000 Digital Multimeter was connected to the system to monitor continuously the cell potential. The cell is placed over a multipoint magnetic stirrer in order to keep the anodic and cathodic compartment in suspension and improve the matter transfer.
The anodic compartment was initially inoculated with an activated sludge from biological reactor of wastewater treatment plant (Ciudad Real, Spain) and it was continuously fed with 1.2 mL/min of a wastewater containing a DQO of 343 mg/L (González del Campo, 2013).
The cathodic compartment was initially inoculated with a culture of Chlorella vulgaris. Algae were illuminated for 12 h a day (from 8:00 h to 20:00 h) with an 11 W Fluorescent lamp (Philips). Every day, carbon dioxide was bubbled during 30 minutes and water evaporated from the cathodic chamber was replenished with Bold’s basal medium (Bold, 1949). The temperature in both compartments was 26 ± 1 ºC. Dissolved oxygen in the cathodic compartment was continuously monitored with an Oxi538 WTW oxymeter.
In both compartments, pH were measured with a PCE-228 pH meter. Volatile suspended solids in both compartments were measured according to APHA (1998). Inorganic carbon (IC) concentration was monitored using a Multi N/C 3100 Analytik Jena analyzer.
On the other hand, electrochemical impedances spectroscopy (EIS) were recorded with an Autolab PGSTAT 30 potentiostat/galvanostat (Ecochemie, The Netherlands). These measurements were carried out using the frequency response analyzer (FRA) module under open circuit conditions, with an ac signal of 10 % of OCV and in a frequency range of 10 kHz to 1 mHz. The EIS were run on the complete cell. The cathode was used as the working electrode and the anode as the counter and reference electrode. The full cell EIS data were fitted to an equivalent circuit (Figure 1) in order to obtain the ohmic (or diffusion) resistance and the polarization (or charge transfer) resistance of each electrode. The equivalent circuit model consists of two electrodes (anode and cathode), each comprised of a parallel resistor and a constant phase element (CPE), and separated by a resistor (membrane + solution resistance) (Borole et al., 2010; Gonzalez del Campo, 2013).

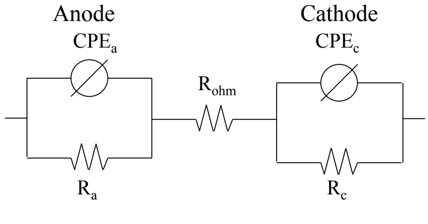

Figure 1: Equivalent circuit.

3. Results and Discussion

In order to determine if algae form a biofilm on cathodic electrode and if it contributes positively to electricity production, cathodic electrode of a photosynthetic MFC which operates in steady state was replaced by another identical and new electrode. In this way, the effect of changing cathodic electrode on enhancement of photosynthetic MFC was studied.

In Figure 2, it can be seen the evolution of dissolved oxygen in the cathodic compartment and cell voltage during the experiment. Cathodic electrode was changed the 5th day. Although dissolved oxygen and cell voltage were continuously monitored, the data of two hours during steady state of dark and light phase, 5:00 h and 17:00 h, were chosen to represente daily evolution, respectively. Dissolved oxygen (Figure 2a) was kept constant after changing cathode in dark phase (4 mg/L) and in light phase (14 mg/L). Therefore, the change of cathode does not affect oxygen production by algae, that is, algae in suspension in the cathodic compartment carried out photosynthesis and produce oxygen in the same way with or without biofilm. On the other hand, dissolved oxygen was higher during light phase than during dark phase, this is because during light phase algae carry out photosynthesis and produce oxygen and during dark phase algae consume oxygen in respiration.

However, when cathode was changed (5th day) the cell voltage (Figure 2b) fell down from 14 mV in light phase and 9 mV in dark phase to 0 mV in both phases. After 10 days (day 15), the cell voltage starts to increase and steady state was reached the day 27 with values of 9 mV in light phase and 3 mV in dark phase. It indicates that in order to carry out reduction reaction and to produce electricity in a photosynthetic MFC, the formation of a biofilm on cathodic electrode is required. In this way, when cathode was changed, cell voltage was not produced until after 10 days when other new biofilm was formed on new electrode. When electricity production reaches the steady state, a reductionin oxygen dissolved in the cathodic compartment during light phase was observed, which could be related to an increase in the oxygen consumption for the reduction reaction.

a) b)

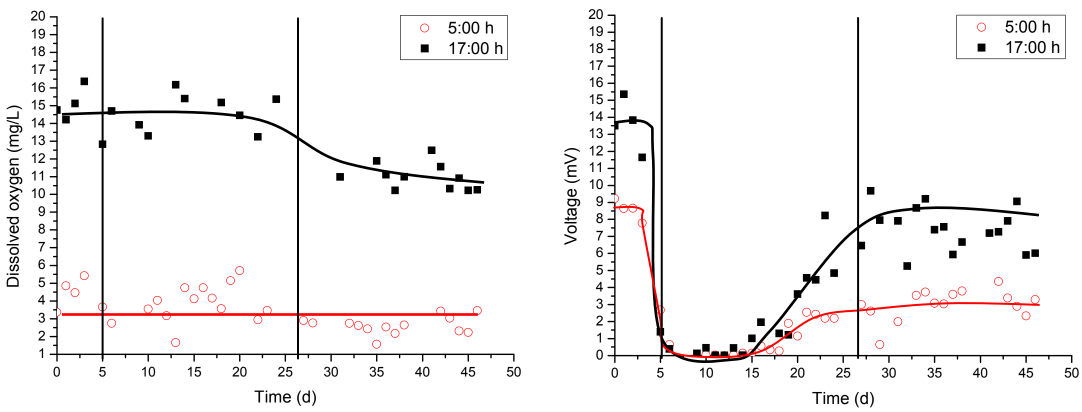

Figure 2: Evolution of: a) dissolved oxygen and b) cell voltage in light and dark phase during the experiment. The cathodic electrode was changed the 5th day.

An important parameter in a photosynthetic MFC is pH. Microorganisms and algae need a pH close to neutral in order to carry out their vital functions (González del Campo, 2013). In order to determine the effect of changing cathode on pH of cathodic and anodic compartment, this parameter was registered every day (Figure 3). The Figure 3 shows as cathodic pH decreased from 6 until 4.5 when cathode is changed (day 5). It is because protons produced in oxidation reaction pass through PEM and they are not consumed in reduction reaction and protons are accumulated in the cathodic compartment, therefore, pH decreases. After, at the day 20, pH starts to increase because protons are consumed in reduction reaction and at the day 27 (when electricity production reached steady state), pH of cathodic compartment reached steady state with a value of 8. On the other hand, pH of anodic compartment is kept constant around 6.5. The observed differences between anodic and cathodic pH after steady state is reached are because the PEM causes transport barrier to the cross membrane diffusion of the protons, and proton transport through the membrane is slower than its production rate in the anode and its consumption rate in the cathode chambers at initial stage of MFC operation, thus brings a pH difference (Gil et al., 2003).

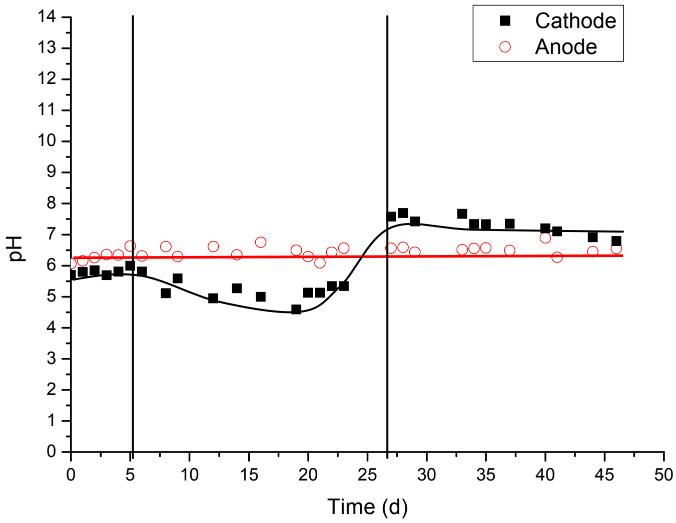

Figure 3: Evolution of pH in anodic and cathodic compartment during the experiment. The cathodic electrode was changed the 5th day.

Anodic and cathodic compartment contained microorganism and algae in suspension, respectively. In the Figure 4, microorganisms and algae concentration during the experiment is shown. Microorganisms concentration in the anodic compartment was constant during the experiment around 125 mg/L. However, at the day 15, a decrement of algae concentration was observed. At this moment, electricity started to increase after changing cathode. In this way, algae concentration in suspension decreased from 600 until 250 mg/L at the day 27, when electricity production reached steady state. A drop of algae concentration in suspension during biofilm formation on anodic electrode was also observed in others studies during the start-up of MFC (Lobato et al., 2013; González del Campo et al., 2013). Therefore, the decrement of algae concentration indicated that algae in suspension could form a biofilm on cathodic electrode decreasing the concentration in suspension.

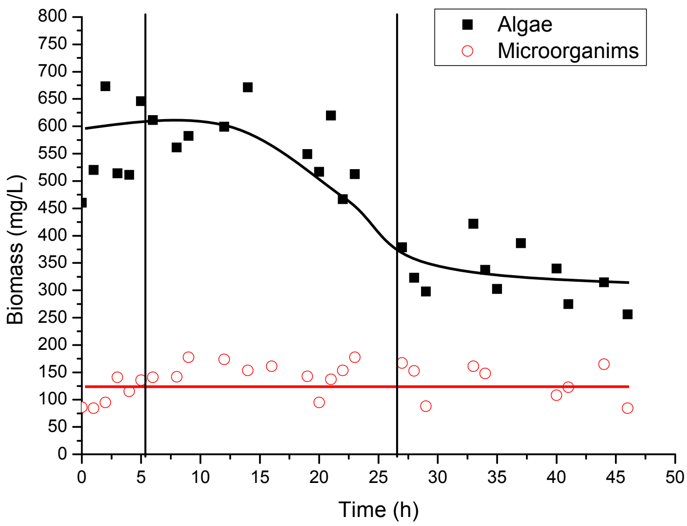

Figure 4: Evolution of microorganisms and algae concentration in anodic and cathodic compartment, respectively, during the experiment. The cathodic electrode was changed the 5th day.

Electrochemical impedance spectroscopies were carried out before changing cathode, during biofilm formation and after biofilm formation in order to determine the influence of change of cathode and algae biofilm formation on the resistances (ohmic or diffusion, and polarization or charge transfer) of each part of the cell separately. In the Figure 5, Nyquist plots and fitting of the equivalent circuit to EIS data obtained during this experiment can be observed. Those plots show a high polarization resistance represented by an unclosed semicircle, especially after changing cathode and before algae biofilm formation, while the lowest polarization resistance was obtained before changing cathode.

In Table 1, the parameters from the equivalent circuit fitting of EIS data are shown. In all cases, the correlation coefficient was 0.99. It indicated that the fit is very good. The ohmic resistance is kept constant along the experiment, that is, proton exchange membrane is not affected by changing cathode. However, the cathode polarization resistance is increased tenfold after changing cathode due to the elimination of algae biofilm from electrode. Once biofilm was formed, this resistance decrease from 80800 until 23060 Ω. So that, algae biofilm on cathodic electrode reduced the cathodic polarization resistance. On the other hand, it can be seen that the anodic polarization resistance increased from 2393 to 26830 Ω when cathode was changed and, after algae biofilm formation, the anodic polarization resistance continued being high. This fact indicates that the change of cathodic electrode affects negatively the enhancement of anodic electrode, not being possible its recovery after 30 days, when algae biofilm was developed.

On the other hand, it is important highlight that the cathodic polarization resistance is much higher than the polarization resistance of the anodic electrode, that is because a precious catalyst was not used in the cathode. In general, biocathodes have higher electrical resistances (Clauwaert et al., 2008; He et al., 2006; Ronzendal et al., 2008).

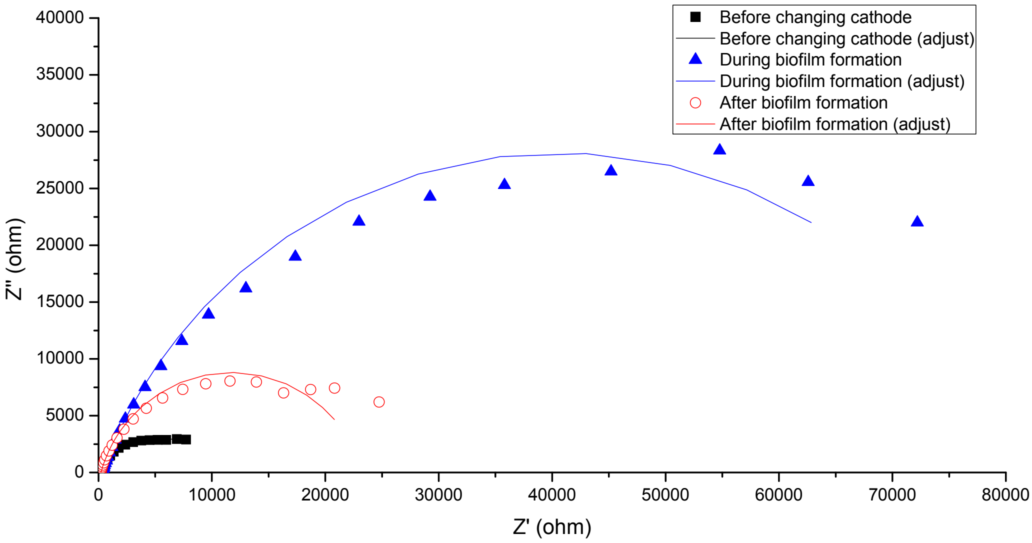

Figure 5: Nyquist plots showing fitting of the equivalent circuit to EIS data obtained before changing cathode, during biofilm formation and after biofilm formation.

Table 1: Parameters from equivalent circuit fitting of the complete cell impedance data before changing cathode, during biofilm formation and after biofilm formation.

	R_{anode} (Ω)	R_{ohm} (Ω)	$R_{cathode}$ (Ω)	r^2
Before changing cathode	2393	198.2	8810	0.994
Before biofilm formation	26830	276	80800	0.994
After biofilm formation	28560	192.8	23060	0.989

4. Conclusions

From this study, the following conclusions were obtained:

- When there is no biofilm of algae on cathodic electrode, reduction reaction is not carried out and, therefore, electricity is not produced, although oxygen is producted, because the cathodic polarization resistance is very high.
- The formation of a biofilm of algae on cathodic electrode influences positively on electricity production, the cathodic polarization resistance decreases and cell voltage increases. In this way, in order to carry out reduction reaction and to produce electricity, the formation of a biofilm of algae on the cathodic electrode is needed.

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