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Production of electricity from the treatment of urban waste water using a microbial fuel cell☆

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Abstract

In this work, is studied the oxidation of the pollutants contained in an actual urban wastewater using a two-chamber microbial fuel cell (MFC). By using an anaerobic pre-treatment of the activated sludge of an urban wastewater treatment plant, the electricity generation in a MFC was obtained after a short acclimatization period of less than 10 days. The power density generated was found to depend mainly on the organic matter contain (COD) but not on the wastewater flow-rate. Maximum power densities of 25 mW m^{-2} (at a cell potential of 0.23 V) were obtained. The rate of consumption of oxygen in the cathodic chamber was very low. As the oxygen reduction is coupled with the COD oxidation in the anodic chamber, the COD removed by the electricity-generating process is very small. Thus, taking into account the oxygen consumption, it was concluded that only 0.25% of the removed COD was used for the electricity-generation processes. The remaining COD should be removed by anaerobic processes. The presence of oxygen in the anodic chamber leads to a deterioration of the MFC performance. This deterioration of the MFC process occurs rapidly after the appearance of non-negligible concentrations of oxygen. Hence, to assure a good performance of this type of MFC, the growth of algae should be avoided.

Keywords: Waste water treatment; Microbial fuel cell; Electricity generation

1. Introduction

In recent years, research activity in fuel cell technology has remarkably increased. Great expectations are directed to fuel cells because of the forthcoming depletion of Earth's fossil fuel resources [1,2]. Fuel cells offer an environmentally friendly alternative to fossil fuels. Nevertheless, the fuel cell technologies have some disadvantages. For example, in order to be effective, the reaction conditions in traditional fuel cells are usually harsh. Most of the fuel cells use platinum as catalyst, as it is expensive, the resources are limited, and it is easily poisoned by CO, which can be formed if the used fuel is not pure hydrogen.

The biological fuel cell development is an interesting and promising innovation to already existing fuel cell types. In contrast to conventional fuel cells, the biological fuel cells have mild reaction conditions (ambient temperature, normal pressure, and neutral pH) and, overall, platinum is not required. Instead of platinum, the catalyst is either a micro-organism or an enzyme. The biological fuel cell can then convert the chemical energy of organic matter directly into electric energy.

There are a number of biological-based fuel cell types that at the time of writing are object of active research, and include [3,4]:

(i) Processes using a primary fuel (usually an organic waste such as corn husks, whey, urban wastewater, etc.) to generate species such as hydrogen or ethanol, which later are used as a secondary fuel within a conventional fuel cell.
(ii) Cells which generate electricity directly from an organic fuel such us glucose, using either enzymes or complete micro-organisms. Electron mediators are often required to transfer electrons from the micro-organisms to an electrode [5,6] or from enzymes to the electrode [7–9], but in some cases the electrons are directly transferred [10–13].
(iii) Cells which combine the utilisation of photochemically active systems and biological moieties to harvest the energy from sunlight and convert this into electrical energy.

This work is going to be focussed on a particular variety of the second type of cells: the microbial fuel cells (MFC). This

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consists of fuel cells in which bacteria are directly used to catalyze the conversion of organic matter into electricity without the addition of mediators (or artificial electron shuttles) [14]. Both, one-chamber and two-chamber MFCs are studied in literature [15–18], although the latter are reported to obtain higher efficiencies. The power density produced by this type of cell is low and normally it is below 50 mW m^{-2} [14]. However, they are considered to have more commercial application potential than other kinds of biofuel cells due to their simplicity. Furthermore, they do not require the use of artificial electron shuttles, which normally are expensive and toxic to micro-organisms [11,19]. Different kind of fuels can be fed to this type of cells. Among them, the urban wastewater is receiving a growing attention. In fact, this is a prospectively important subject, not for present applications but for future ones. Nowadays, the costs associated to the treatment of urban wastewaters are very high and the development of a technology that allows to simultaneously treat a wastewater and produce energy would have a very high significance. Unfortunately, the efficiencies obtained presently are far away from those required for commercial applications, and a lot of fundamental work has to be done during the next years in order to develop a ready-to-use technology.

In this context, the aim of this work has been to study the performance of a MFC fed with actual urban wastewater as a fuel. Special attention has been paid to clarify the effect of the chemical oxygen demand (COD) concentration on the power generation and the role of the oxygen concentration (in both the anodic and the cathodic chamber) on the cell performance. Likewise, the acclimatization period is also studied and a simple method is proposed to rapidly generate a micro-organisms' culture capable of producing electricity from wastewater.

2. Experimental

Domestic wastewater was collected from the primary clarifier of the Ciudad Real Wastewater Treatment Plant (WWTP). Fig. 1 shows a scheme of the setup used in this work. The main element of the system is the biological reactor (or anolyte chamber), where the micro-organisms remove the organic material and help to produce electricity. This biological reactor consisted of a glass cylindrical chamber (Alamo, Spain) of an empty bed volume of 1000 cm^3. The anode was placed in the reactor and consisted of a graphite cylinder with a total surface of 20 cm^2. The cathodic chamber (100 cm^3) was connected with the anodic chamber through a salt bridge. The cathode also consisted of a porous graphite bar with a total surface of 20 cm^2. The setup worked in continuous mode. A peristaltic pump continuously fed a flow-rate of 0.34 dm^3 h^{-1} of an actual urban wastewater (effluent of the primary decanters of the municipal WWTP of Ciudad Real) to the anodic chamber. A fisheries compressor (maximum flow-rate of 2.5 dm^3 min^{-1} and maximum pressure of 1.2 m of water-column) was connected to the porous cathode to supply oxygen to the cathodic chamber. During normal operation, the anode and the cathode were connected by means of wires and a resistance. A Keithley 2000 Digital Multimeter was connected to the system to monitor continuously the value of the cell potential. Polarization curves were recorded using an Autolab PGSTAT30 potentiostat/galvanostat (Ecochemie, The Netherlands). Impedance spectra were recorded from the operating MFC using the frequency response analyser (FRA) module of the Autolab PGSTAT30.

Chemical oxygen demand was determined using a HACH DR2000 analyser and pH, conductivity and dissolved oxygen

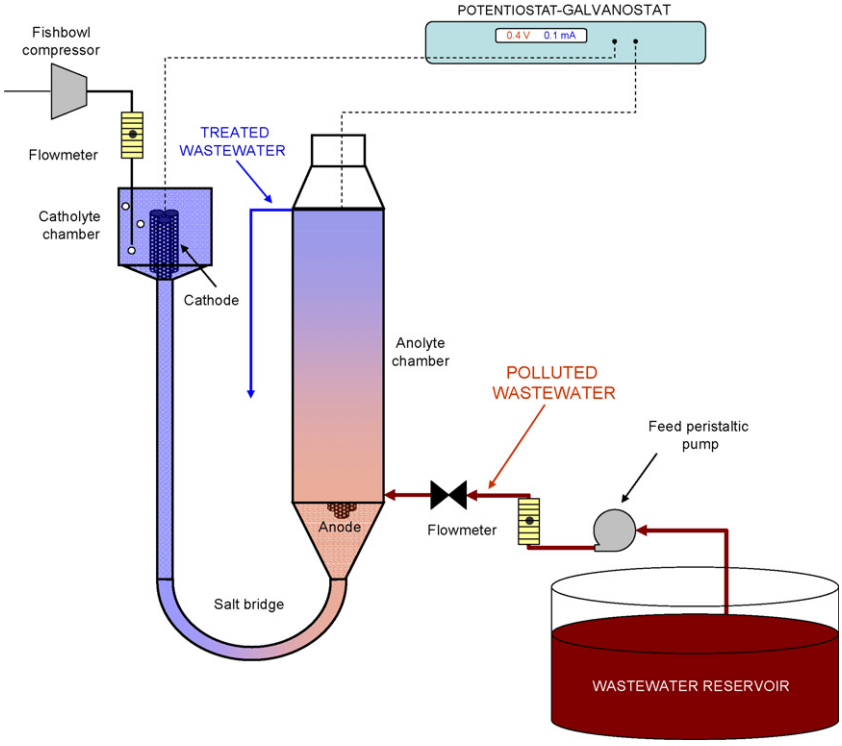

Fig. 1. Microbial fuel cell setup.

were measured by means of a GLP22 Crison pH-meter, LF538 WTW conductivity-meter, Oxi538 WTW oxy-meter, respectively.

3. Results and discussion

3.1. Conditioning stage

To start up the process, activated sludge obtained in the biological reactors of the municipal wastewater treatment plant of Ciudad Real (Spain) was placed in a closed-tank without aeration during 5 days to favour the formation of a mixed culture of aerobic and anaerobic micro-organisms. No wastewater was fed to the system during this conditioning period, so the only substrate available for micro-organisms was that coming from the endogenous metabolism.

After that, the sludge was placed in the microbial fuel cell and the anodic chamber was fed with actual urban wastewater obtained in the WWTP of Ciudad Real (collected after primary decanters), at the same time that air was left to flow through the cathode. Oxygen concentration was measured in both the anodic and the cathodic chambers. These measurements enabled us to confirm that the concentration of oxygen in the anolyte was zero, so the anodic chamber can be considered as anaerobic. Concentrations of oxygen in the cathodic chamber were close to saturation.

The wastewater feed contains all the soluble pollutants of the raw wastewater and small quantities of suspended solids (the primary decanter achieves average efficiencies of 70% in the removal of these species). A resistance of 125 Ω was placed between the anode and the cathode (external circuit). Fig. 2 shows the changes in the power density (part a) and in the inflow and effluent COD (part b) during the following days. It can be clearly observed that power increases with time until attaining steady-state conditions, and that the acclimatization period is shorter than 10 days. The operation steady-state power density is around 5 mW m^{-2} (125 Ω resistance), which is inside the typical range of values published in literature. Hence, the development of a biological culture capable of generating electricity from wastewater is not a very time-consuming process, especially taking into account the long time-constants of the biological processes. Fig. 2b shows the changes in the COD (time-courses) obtained during this conditioning stage. It can be observed that the efficiency of the treatment improved during the conditioning process and that a steady-state in the effluent COD was reached (for the used operation conditions) for values closed to 150 mg dm^{-3}. It is important to note that this value could be decreased (as it will be shown below) by changing the operation conditions (hydraulic and solid retention times) and it is not a limitation in the operation of the biological culture formed, but on the concentration of micro-organisms. Likewise, and as it will be pointed out later, the change in the COD is not only caused by electricity-generating bacteria, but by the whole biological culture. In fact, only a small percentage of the COD is going to be removed by the electricity-generating process.

Fig. 3 shows the polarization curves obtained in different days of the conditioning process. It can be observed an abrupt change

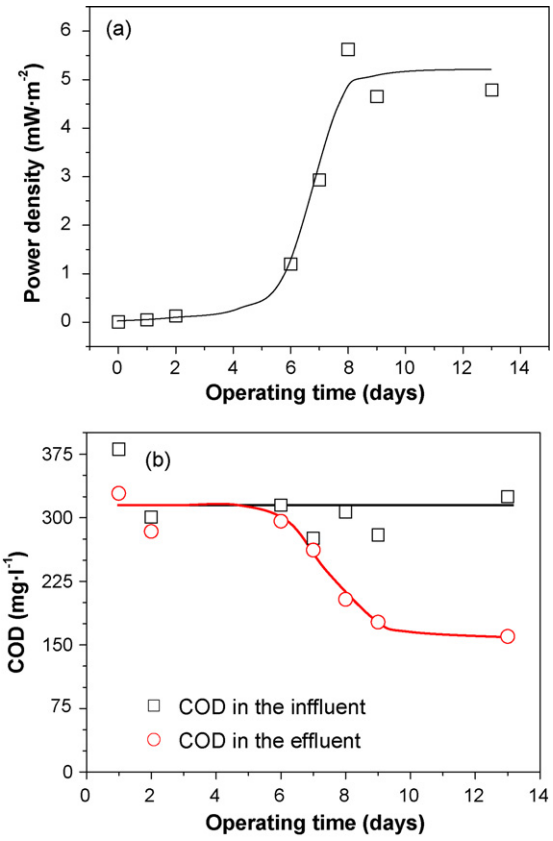

Fig. 2. Time-course of the power density (a) and of the influent and effluent COD (b) during the acclimation period.

between the results obtained in the days before and after the conditioning process, and it can be confirmed that the steady-state conditions are achieved in a short period. At the steady-state conditions, the maximum power density obtained is around 24 mW m^{-2}. This value is obtained at a cell potential of 0.23 V. The open circuit potential also increased with time. The steady-state value of this parameter was 0.42 V.

Fig. 4a shows EIS of the system during the conditioning process. No significant changes in the shape of the spectra are obtained, although the curves move towards the right with time. The polarization resistance was obtained by mathematical fitting and the equivalent circuit modelled consisted of an uncompensated resistance (R_u) coupled to a parallel circuit formed by the polarization resistance (R_p), a Warburg element (Z_W) accounting for mass-transfer limitations and a constant phase element (CPE) as it can be seen in Fig. 4b. Fig. 4c shows that, as expected, the polarization resistance is strongly related to the maximum power density generated. This clearly indicates the electrochemical nature of the biological electricity-generating processes.

3.2. Influence of the organic load

Once the microbial fuel cell was conditioned, the influence of the influent COD and the flow-rate on the performance of the MFC was studied. Fig. 5 shows the results of polarization curves obtained at different initial COD concentrations. It can be clearly observed that the performance of the MFC is influenced by the

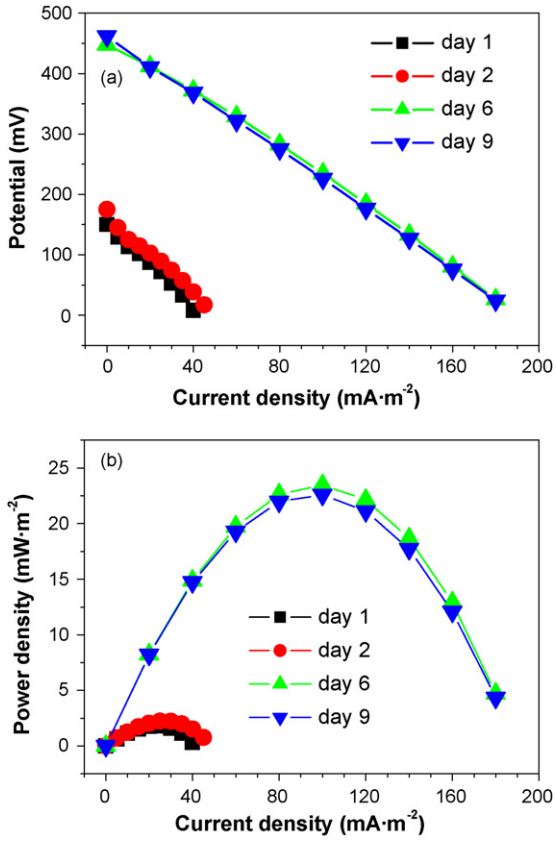

Fig. 3. Polarization curves obtained during different days of the acclimation period. (a) Potential; (b) power output.

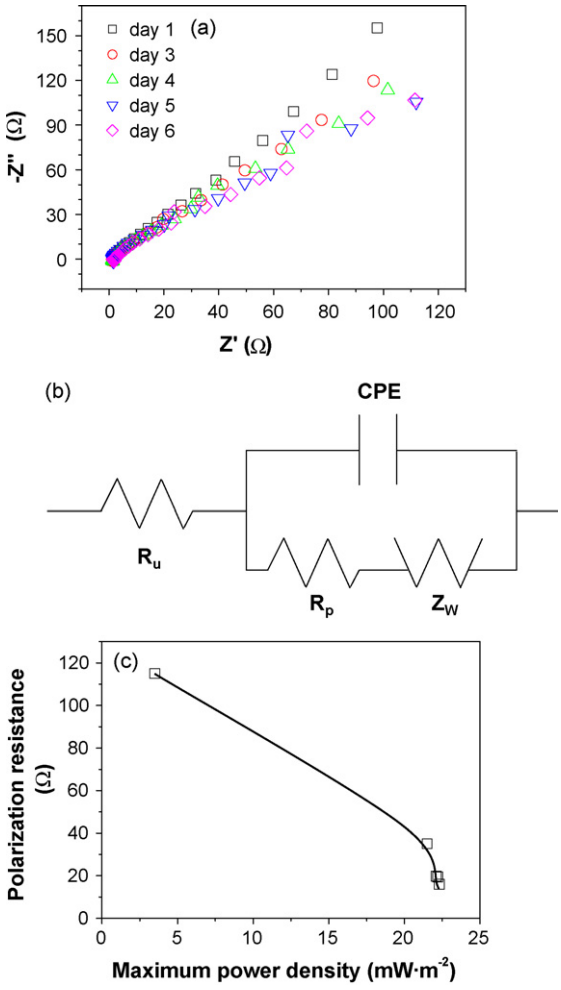

Fig. 4. (a) Impedance spectra of the electrochemical cell obtained during different days of the acclimation period; (b) equivalent circuit used to fit the experimental data; (c) maximum power density generated by the cell vs. the polarization resistance of the system.

COD, and that the higher the COD the better the performance of the cell is. Maximum power densities close to 25 mW m^{-2} were obtained. As it can be observed in Table 1, the obtained values are very close to that of other authors in the treatment of domestic wastewaters using MFC.

Fig. 5 shows the maximum power densities and the organic load removed as a function of the influent COD. As it can be observed the maximum power density is strongly related to the COD concentration but not to the flow-rate (points corresponding to very different flow-rates lay over the same curve). This confirms that the COD limits the rate of the electricity-generating process and that, simultaneously, the mass-transfer processes are not important in this study (as a change of three-times in the flow-rate does not improve the results). This observation can be related to the formation of mediators from the COD of the wastewater. The concentration of mediators should depend directly on the concentration of COD and hence the higher the concentration of COD the better the efficiency of the electrochemical process. However, as the micro-organisms are in contact or very close to the anode surface, changes in the flow-rate do not improved the mass-transfer coefficient (mass transfer is not limiting the process).

On the contrary, it can be affirmed that inside the range of influent COD studied, the rate of COD removal (obtained by mass balance taking into account the influent and effluent COD values and the operation parameters) is almost not affected by the influent COD (Fig. 5b). This can be explained taking into account that the degradation process is not limited by the COD but by the active micro-organisms concentration. Biological wastewater treatment processes are heterogeneous processes and, consequently, the higher the concentration of micro-organisms the higher the degradation rate. The influence of the COD is usually modelled with a Monod-type kinetic equation, where the half-rate constant is usually small. This means

Table 1
Maximum power densities reported in literature for the treatment of actual wastewater with MFC

Substrate	Power (mW m^{-2})	Reference
Anaerobic sediments	16	[21]
Anaerobic sediments	20	[22]
Wastewater with starch	19	[23]
Wastewater with starch	20	[24]
Urban wastewater (with a PEM as separator)	24	[25]
Urban wastewater (with a PEM as separator)	28	[14]
Urban wastewater (with a salt bridge)	25	This work

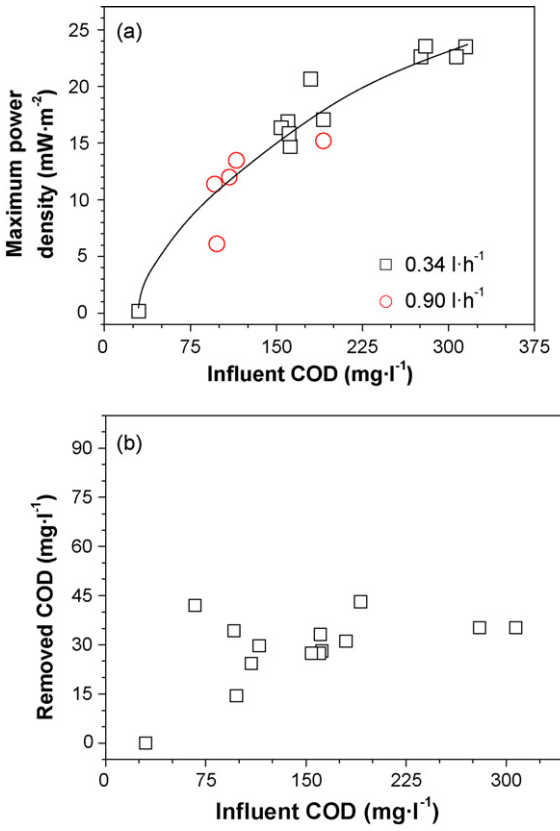

Fig. 5. Influence of the COD on the maximum power density (a) and on the COD removal rate (b).

that the COD limits the process only for very small concentrations of COD. As the range of concentration of COD studied in this work is over these small concentrations, the influent COD seems not to influence the process.

The different limiting mechanisms observed for COD removal and for electricity generation processes suggest that electricity-generating processes yield only a small contribution to the COD removal. This will be confirmed in the next section in which the oxygen concentration decay rate will be used to quantify the percentage of the COD used by electricity-generating processes.

3.3. Effect of the oxygen fed to the cathode

To test the influence of the oxygen fed to the cathode, the air supply was stopped during an experiment. Fig. 6 shows the time-course of the operation cell potential (with a resistance of 125 Ω between the anode and the cathode) and oxygen concentration in the catholyte chamber. It can be observed that both parameters decrease with time and that both are strongly related to each other (see the onset). The rate of the process seems to be very small (it took several days to decrease the concentration of oxygen from 5.0 to nearly 0.5). This means that the reduction of oxygen is a very slow process. As the oxygen reduction is coupled with the COD oxidation in the anodic chamber, this suggests that the COD removed by the electricity-generating process is very small and that research to improve results should also be focussed

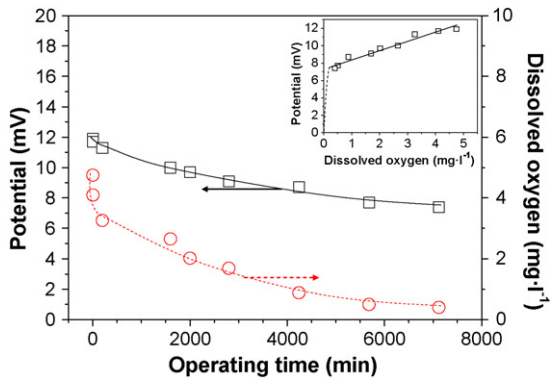

Fig. 6. Time-course of the operation cell potential (with a resistance of 125 Ω between the anode and the cathode) and of the oxygen concentration in the catholyte chamber during an oxygen-depletion experiment. (□) Potential (mV); (◯) dissolved oxygen (mg l^{-1}).

on the cathodic reduction of oxygen as it can limit the overall process rate.

To quantify this COD removal (the percentage of the COD removed by the electricity-generating process) a simple model is proposed. In this model, it is assumed that the rates of oxygen consumption and COD degradation ($(-r)_{O_2}$ and $(-r)_{COD}$, respectively) by direct electrochemical processes are the same, and they can be modelled according to Eq. (1), where I is the current flowing through the external circuit, 4 the number of electrons exchanged in the oxygen reduction process (or in the COD oxidation process) and F is the Faraday constant.

$$(-r)_{COD} = (-r)_{O_2} = \frac{I}{4F} \quad (1)$$

These rate-equations where used in the mass balances to quantify the COD removal due to the electricity-generation processes. Fig. 7 shows, according to the results of the model, the percentage of the COD removed by these processes. As it can be observed, the percentage is very low and almost constant (around 0.25%). If we expressed them as percentage, it does not depend on the influent COD concentration, but expressed as concentration it directly increases with the influent COD concentration. This is important because this clearly shows that only a very small fraction of the COD is used in the generation of electric-

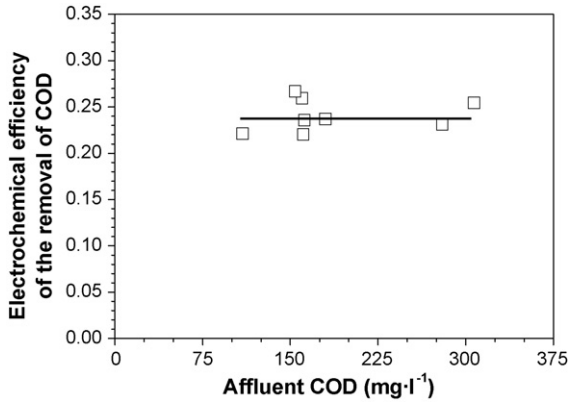

Fig. 7. Percentage of the COD removed by electricity-generating processes.

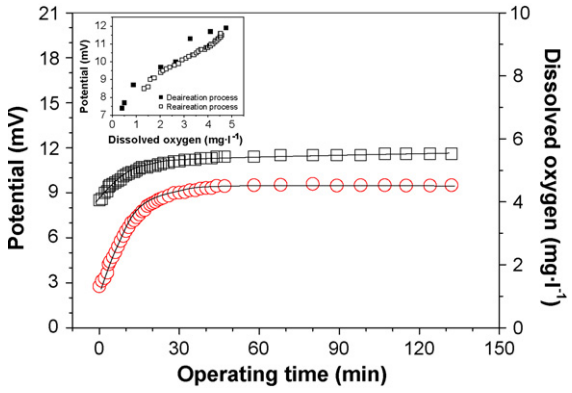

Fig. 8. Time-course of the operation cell potential (with a resistance of 125 Ω between the anode and the cathode) and of the oxygen concentration in the catholyte chamber during an aeration experiment. (□) Potential (mV); (◯) dissolved oxygen (mg l^{-1}).

ity and it confirms our previous observation that the influent COD limits the electricity generation but not the COD removal rate. This also clearly shows that the MFC technology can be widely improved by increasing the percentage of the COD that is available for the electricity generation processes. The remaining COD removal should be consumed by the competing anaerobic degradation processes (formation of carboxylic acids, and of carbon dioxide and methane).

To test the reversibility of the process, the aeration was again re-established after the oxygen-depletion experiment. The oxygen concentration and the power density were monitored. Fig. 8 shows that both parameters increase and returns to their previous values. In this case the steady-state was met in only 50 min. These differences in the dynamics are not related to the electrochemical processes but to the oxygen mass transfer as it can be clearly seen elsewhere [20]. Cell potential versus dissolved oxygen profiles obtained in both experiments (depletion of oxygen and aeration) lay over the same line. This confirms the reversibility of the process and the use of the oxygen in the electrochemical degradation of a portion of the COD.

3.4. Influence of the presence of oxygen on the anodic chamber

Fig. 9a shows the cell potential (with a resistance of 125 Ω placed in the external circuit) monitored during one period in which algae growth was noticed in the anodic chamber. Fig. 9b shows the dissolved oxygen concentrations during these days. As it can be observed, the appearance of oxygen (due to the photosynthetic processes) leads to a deterioration of the MFC performance with a loss of one third of the power. This indicates that the conditions at the anodic chamber should be strictly anaerobic in order to promote the electricity generation processes. The deterioration of the MFC process occurs rapidly after the appearance of non-negligible concentrations of oxygen. It suggests that the intermediates formed during the biological process that occurs on the anodic chamber can be easily oxidized in the presence of oxygen (this process should be favoured with respect to direct electro-oxidation) and obviously, this decreases

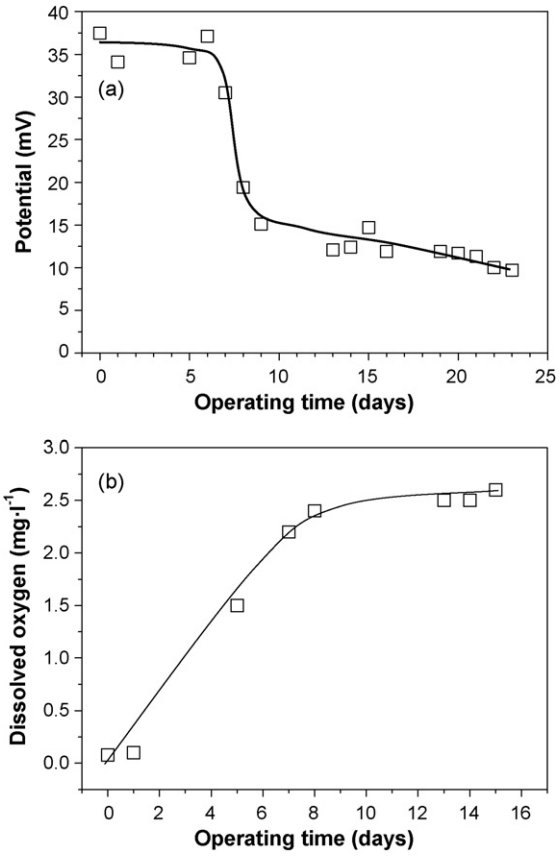

Fig. 9. Effect of algae growth on the performance of the MFC. (a) time-course of the cell potential; (b) time-course of the oxygen concentration on the anodic chamber.

the yield of the direct electrochemical oxidation processes, and hence the generated power.

4. Conclusions

From this work the following conclusions can be drawn.

- The development of a biological culture able to generate electricity from wastewater is not a very time-consuming process, especially taking into account the long time-constants of the biological processes. By using an anaerobic pre-treatment of the activated sludge of an urban WWTP, the electricity generation in a MFC can be obtained after a short acclimatization period shorter than 10 days.
- The power density generated by MFC fed with domestic wastewater depends importantly on the COD but not on the flow-rate. Maximum power densities around 25 mW m^{-2} (at a cell potential of 0.23 V) can obtained for a wastewater with a COD of 330 mg dm^{-3}.
- The COD removal rate does not depend on the influent COD concentration. Taking into account the oxygen consumption it can be concluded that only 0.25% of the influent COD removal is used for the electricity-generation processes. The remaining COD should be removed by anaerobic processes. This suggests that MFC technology can be widely improved

by increasing the percentage of the COD that is available for the electricity generation processes.

- The rate of consumption of oxygen in the cathodic chamber is very low. As the oxygen reduction is coupled with the COD oxidation in the anodic chamber, this indicates that the COD removed by the electricity-generating process is very small. Cell potential and dissolved oxygen concentration, are strongly related.
- The presence of oxygen in the anodic chamber leads to a deterioration of the MFC performance with important power losses. The deterioration of the MFC process occurs rapidly after the appearance of non-negligible concentrations of oxygen.

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