Bioresource Technology 105 (2012) 81–87

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Evaluation of potato-processing wastewater treatment in a microbial fuel cell

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ARTICLE INFO

Article history:
Received 18 August 2011
Received in revised form 16 November 2011
Accepted 24 November 2011
Available online 1 December 2011

Keywords:
Microbial fuel cell
Wastewater treatment
Methanogenesis
Energetic conversion
Microbial electricity

ABSTRACT

Wastewaters from potato-processing industries have been traditionally treated by a sequence of steps that include the production of methane as the anaerobic one. This work explores the feasibility of replacing or supplementing methanogenesis with the emerging technology of microbial fuel cells (MFCs). Electricity producing biofilms have been enriched from a real anaerobic sludge, and the conversion of potato-processing wastewater into electricity has been studied. When tested as a single treatment step, MFCs were able to process the wastewater with high COD removal but with low energetic conversion efficiency. On the other hand, as a complimentary step for methanogenesis, they improved conversion efficiency and significantly reduced the organic matter load of the final effluent. These results point at the combination of the energetic yield of methanogenesis and the improved COD removal of the electricity producing treatment as the implementation choice.

1. Introduction

Annually 300–400 thousand tons of potatoes are industrially processed in the most active agricultural region of Argentina, generating large amounts of wastewater composed mainly by debris and chippings of potato peeling. In order to reduce the organic load of the waste, both aerobic (Lasik et al., 2010) and anaerobic (Linke, 2006) biological processes are implemented. Anaerobic treatments recover chemical energy from the effluent in the form of methane or hydrogen, but are inefficient when working at room temperature or under moderate organic carbon loads (Pham et al., 2006). Thus, to further reduce the organic load of the effluent, a downstream aerobic step is required, increasing the energy investment of the treatment scheme (Chan et al., 2009).

Microbial fuel cells (MFCs) appear as a new possibility for the treatment of organic wastes (Logan et al., 2006; Rabaey and Verstraete, 2005). They are similar to conventional fuel cells but make use of electro-active microorganisms as catalysts for the oxidation and/or reduction reactions. In the typical case, a biofilm of these microorganisms oxidizes organic matter in the wastewater, obtaining carbon and electrons. After consuming part of their energy for growth, bacterial cells transfer the electrons to the conductive biofilm matrix, or eventually to an external electron shuttle. Finally, during the electrochemical oxidation (anodic reaction) of redox molecules located at the biofilm/electrode interface, electrons are transferred to the electrode (Busalmen et al., 2008). After traveling through an external circuit electrons are consumed in the cathodic compartment to reduce oxygen (in the typical cathodic reaction), thus closing the electric circuit for electricity production (Rabaey and Verstraete, 2005).

MFCs are considered an attractive alternative for wastewater treatment because they offer the possibility of generating electrical energy directly from the oxidation of organic matter. They have been studied either as the unique energy recovering process (Du et al., 2007; Huang et al., 2011; Liu et al., 2004; Min et al., 2005; Rodrigo et al., 2007; Venkata Mohan et al., 2008) or as an additional treatment to be included after an anaerobic digestion step (Aelterman et al., 2006; Pham et al., 2006).

Some studies have demonstrated that the indigenous microbial population of many industrial wastewaters can be used as the source inoculum of electricity producing microorganisms (Aelterman et al., 2006; Kim et al., 2005; Rabaey et al., 2004). The strategy aims at exploiting the catabolic capabilities of autochthonous communities (Pham et al., 2006; Rabaey and Verstraete, 2005; Torres et al., 2007) and results more practical for industrial applications as compared to using pure cultures of model organisms. The present work explores the possibility of enriching an electricity producing biofilm from methanogenic activated sludge, obtained from a potato-processing plant. Then the feasibility of either replacing or complementing the classical methanogenic process by an electrogenic one is analyzed. The influence of current harvesting on methane production is also examined.

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0960-8524/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.biortech.2011.11.095

2. Methods

All the experiments were performed on simulated wastewater prepared by grinding 0.1 kg of fresh potatoes in 1 L of distilled water using a commercial blender. The resulting suspension was vacuum filtered through a 20 μm sieve. The retained cake was washed and the resulting suspension was added to the filtrate. Finally, peptone was added to reach a COD/N/P ratio of 200/5/1.

The inoculum for the biological treatments consisted on sludge obtained from a methanogenic digester operating at a local potato-processing plant. It served as the source of both the microorganisms for control experiments in which methane production took place and the electricity producing microorganisms for experiments in which the conversion of chemical to electric energy was tested.

2.1. Microbial fuel cell setup and experimental procedure

The experimental setup consisted of a three compartment tubular microbial fuel cell (Fig. S1 in the Supplementary material) composed by two anodic chambers located at both sides of a central cathodic chamber, separated by Nafion® 117 cation exchange membranes. Anodic chambers were filled with graphite particles of 3–4 mm in diameter and a BET area of 1.2 $m^2 g^{-1}$. The resulting fixed bed electrodes had a surface of about 35 m^2. One of the anodes was electrically connected to the cathode (closed-circuit) through a variable resistor with a range of 0–1 KΩ. The other was kept at open circuit to serve as the control for the electricity producing treatment. The cathode was made of graphite felt and completely filled the central chamber to minimize cathodic limitations. Electric contacts were made using graphite rods (diameter:6 mm).

A volume of 0.4 L of simulated wastewater buffered at pH 7 by addition of Na_2HPO_4/KH_2PO_4 were circulated through each anodic chamber in a closed loop from auxiliary reservoirs by means of peristaltic pumps. The catholyte was a concentrated phosphate buffer saline solution (pH 7.2) saturated with air by permanent bubbling in an auxiliary reservoir. The flow rate in all the chambers was 10 ml min^{-1}. The potential of all the electrodes was measured all over the experiments against an Ag/AgCl–KCl sat. Reference electrode located in the central cathodic chamber.

Non-absorbable gases (mainly methane) evolving from both anodic chambers were independently quantified by pressure difference after bubbling in NaOH 1 M to remove CO_2. All treatments were performed in an incubator at 36 °C.

Different tests were performed in order to gain information about the biofilm enrichment and performance:

Test A was aimed at stimulating biofilm formation by the indigenous microorganisms. Runs were performed inoculating 0.36 L of wastewater with 0.04 L of the activated sludge. The circuit was closed to enable current flow and the evolution of the system was monitored over time. The resistor value was fixed at 1000 Ω. In some of the experiments the resistor value was sequentially reduced in order to provide the appropriate potential for bacterial growth.

Once the biofilm had been grown in Test A, several sequential batch treatments were performed by replacing the depleted wastewater. The operating conditions were those implemented in Test A, with the exception of the resistor value that in this case was fixed at 325 Ω. Upon obtaining the same performance in two successive cycles, the results were considered as representative for a mature biofilm already adapted to produce current (Test B).

After Test B, the capability of the MFC for treating the effluent from a conventional anaerobic methane producing reactor was evaluated in Test C.

The anaerobic methane producing reactor was a 1.5 L Pirex glass reservoir. It was fed with the same wastewater used in test B and operated during 80 days at 36 °C with continuous stirring at 200 rpm. Methane production and COD degradation were measured in order to compare the energetic efficiencies with the values obtained in MFC treatments. A volume of 0.4 L of the effluent from this reactor was circulated through the anodic chamber of the MFC under Test B conditions.

During each test, effluent samples were taken at regular intervals from anodic chambers to perform analytical measurements as described below.

Control tests were simultaneously performed in identical conditions but keeping the anode at the open circuit potential throughout the experiments.

2.2. Analytical methods

Total and soluble COD were determined according to the APHA method 5520 (Closed Reflux Method) (APHA, 1998). Samples of 4 mL were taken at regular times. Two milliliter were centrifuged during 10 min at 14,000 rpm (IEC Micro-MB). For the determination of soluble COD 1 mL of the supernatant was taken. The remaining 2 mL of the original sample were homogenized in a Wheaton homogenizer and diluted in distilled water for determination of total COD.

2.3. Scanning electron microscopy (SEM) of adsorbed bacteria

Sample graphite granules were collected from the anodic compartments at the end of the experiments. The biofilms were fixed by immersion in 2.5% glutaraldehyde during 15 min, dehydrated by immersion in an alcoholic series (40%, 60%, 80%, and 100% ethanol in ultrapure water), air-dried, and sputtered with gold for the observation by SEM. Samples were observed in a JEOL JSM-6460LV scanning electron microscope.

2.4. Efficiency calculations

In order to compare the performance of treatments, the coulombic efficiency (CE) for the MFC treatment was calculated as proposed by Logan (2007) (Eq. (1)), where F is the Faraday constant, I is the harvested current, V is the volume of wastewater treated, ΔCOD is the COD decay and 8 are the grams per electron in oxygen. The equivalent CE for the methanogenic treatment (Eq. (2)) was calculated as the moles of electrons recovered as methane (N_{CH4}) divided by the electrons consumed during wastewater treatment (V. ΔCOD/8), considering 8 electrons per mol of methane:

$$CE_{\mathrm{MFC}} = \frac{8 \cdot \int_0^t I \cdot dt}{F \cdot V \cdot \Delta\mathrm{COD}} \tag{1}$$

$$CE_{\mathrm{CH_4}} = \frac{8 \cdot \mathrm{N_{CH4}}}{V \cdot \Delta\mathrm{COD}/8} \tag{2}$$

The treatment efficiency (TE) represents the fraction of the original COD that was removed in the process. It was calculated as shown in Eq (3), where ΔCOD is the COD removed in the process and $COD_{t=0}$ represents the initial COD of the wastewater:

$$TE = 100 \cdot \frac{\mathrm{COD}_{t=0} - \mathrm{COD}_{t=tf}}{\mathrm{COD}_{t=0}} = 100 \cdot \frac{\Delta\mathrm{COD}}{\mathrm{COD}_{t=0}} \tag{3}$$

Finally, the percentage of energy released in a usable form from that available in the original wastewater (%ER) was calculated. For the MFC treatment it was estimated as the integral of power over the time of the test (Eq. (4)). For methane production it was calculated taking the moles of methane produced (N_{CH4}) and the combustion heat of methane ($\Delta H = 890\ \mathrm{kJ\ mol^{-1}}$). After cleaning-up a gas stream, CH_4 can be burned in a thermoelectric plant with an efficiency of 35% (typical efficiency of the Rankine steam cycle); the electric energy released can be calculated as shown in Eq. (5).

$$ER_{\mathrm{MFC}} = \int_0^t E_{\mathrm{cell}} \cdot I \cdot dt \tag{4}$$

$$ER_{\mathrm{CH_4}} = 0.35 \cdot \Delta H \cdot \mathrm{N_{CH_4}} \tag{5}$$

Stewart et al. (1984), determined the energy available in potato wastewater as 16.4 MJ per kilogram of total solid. The total solids content (TS) of wastewater in $\mathrm{kg\ L^{-1}}$ was estimated according to (APHA, 1998) and the total energy available in the original wastewater (EA_T) was calculated as:

$$\mathrm{EA}_T = 16.4 \cdot TS \cdot V \tag{6}$$

the %ER thus results,

$$\%\mathrm{ER} = \frac{\mathrm{ER}_X}{\mathrm{EA}_T} \tag{7}$$

where X is MFC or CH_4 of Eq. (4) or Eq. (5), respectively.

3. Results and discussion

3.1. Enrichment of electricity producing biofilm from a methanogenic consortium

Upon polarization of the supporting electrode by connecting it to the oxygen cathode the enrichment and growth of an electricity producing biofilm is expected to be induced (Torres et al., 2009). The evolution of the process was followed by considering the current output as an indicator of biofilm growth, while the potential of each individual electrode was determined as an evidence of the occurrence of anodic or cathodic kinetic limitations. Results are presented in Fig. 1. The cell potential was initially very low, but increased steadily during the first 24 h of treatment to about 0.3 V. As a consequence, the current output increased from almost zero to about 250 μA. The cell potential remained stable for the following 130 h, but after 200 h increased to about 0.4 V. Consequently, the current reached a steady state value of about 400 μA. The potential of the cathode remained stable at about 0.0–0.1 V during the whole experiment, evidencing the absence of a cathodic limitation in the selected experimental conditions. The potential of the connected anode showed two decreasing periods, the first one to about −0.2 V during the initial 30 h and the second one to about −0.4 V after 200 h of treatment (Fig. 1a).

Fig. 1b shows the progress of the waste treatment process in terms of soluble and solid COD. As it can be seen, during the first 100 h the solid COD decreased while the soluble COD increased, which might be the result of the action of hydrolytic bacteria (Gerardi, 2003). Although it is not a direct electricity-producing step, the typical accumulation of reduced intermediate compounds, including acetate and other volatile fatty acids (VFA) (Gerardi, 2003), can drive the observed potential change. Thus, the accumulation of reduced compounds in the anodic chamber might be one of the reasons for the first increase in the reducing power of the anodic half cell. In addition, this compounds can yield a low current through direct electrochemical oxidation (Martinez-Huitle and Ferro, 2006). The shift of the potential to negative values was also observed for the non-connected anodes, which reached a potential of about −0.6 V (data not shown).

Provided the polarization conditions at the electrode interface (Torres et al., 2009). Volatile fatty acids (VFA) serve as fuel for electricity producing bacteria which grow preferentially forming a biofilm on the anode (Marsili et al., 2008; Schrott et al., 2011). The

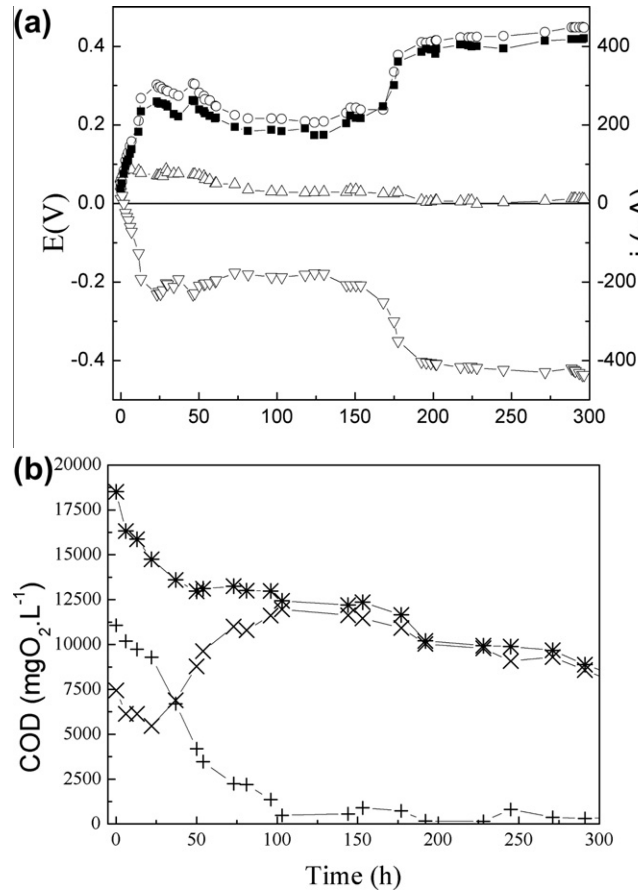

Fig. 1. (a) Evolution of current output (fill squares), potential difference (open circles) and cathode (up triangles) and anode (down triangles) potential during the enrichment of an electricity producing biofilm in a typical Test A (see M&M section for details). (b) Evolution of total (∗), soluble (X) and solid (+) COD during the same experiment.

growth of these bacteria is evidenced by the increase in current output observed during the first 200 h (Fig. 1). From that time on the soluble COD decreased at constant rate, in accordance with the observed constant current production (Fig. 1). This suggests a close relationship between COD decrease and the production of current through the activity of electricity producing microorganisms.

To corroborate the presence of a biofilm on the granular graphite anode, some granules were sampled from reactors at steady state current output (i.e. after 300 h) to be inspected by Scanning Electron Microscopy. A well developed biofilm composed mainly by rod-like and coccoid bacteria covered virtually all the electrode surface (Fig. S2 in the Supplementary material). The biofilm seemed to be closely attached to the electrode covering both planes and edges of the graphite surface.

3.2. Influence of current harvesting on methane production

It is important to note that electricity production started just after the accumulation of VFAs. As these acids also serve as fuel for methanogenic bacteria, their bio-electrochemical consumption has been proposed to inhibit methanogenesis. This inhibition has been previously reported by Ishii et al. (2008), but in the light of data emerged so far it cannot be generalized. In fact, active methanogenesis has been observed in several MFC reactors harboring mixed microbial communities (He et al., 2005; Kim et al., 2005), while it was not substantial in other reported cases (Rabaey et al., 2004).

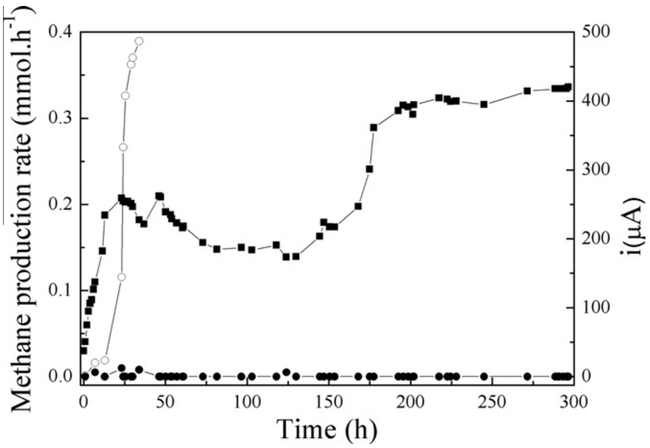

Fig. 2. Comparison of current generation (solid squares) and methane production rate in the connected anode (solid circles) vs. methane production in non-connected control anode (open circles) during the enrichment of an electricity producing biofilm in a typical Test A.

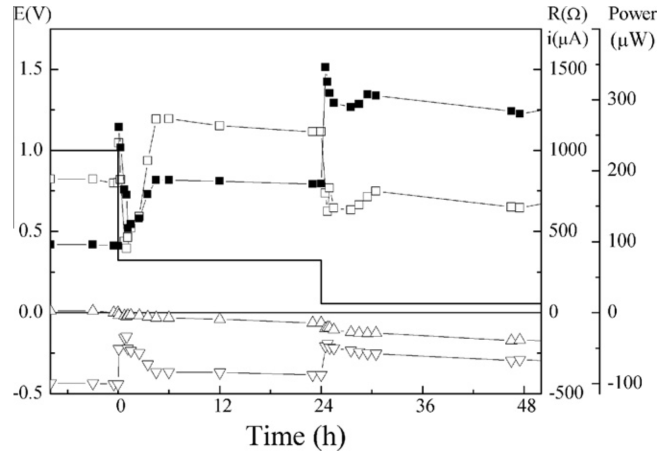

Fig. 3. Evolution of current output (fill squares), cathode potential (up triangles), anode potential (down triangles) and power output (open squares) under different external loads. See text for details.

Differences in the production of methane were observed here between the control and the connected-anode experiments. After a lag period of about 10 h a rapid increase in the evolution of methane was observed in control experiments (not connected anode), which exceeded the detection limit of the measuring device (Fig. 2). On the other hand, under electricity producing conditions, methane production was negligible throughout the test, suggesting that current harvesting in some way inhibits this process (Fig. 2). He et al.(2005) have proposed that methane can be produced in a microbial fuel cell if the organic load exceeds the oxidative capacity of electricity producing organisms, thus allowing the accumulation of reduced compounds that generate the strong reducing environment required for methanogens to proliferate. In this direction, acquiring the potential data for every individual electrode opens the possibility of verifying this postulate. A potential of about −0.6 V was measured for the non-connected anode during the active methane production phase (data not shown) evidencing the occurrence of a reducing environment. Under current harvesting on the other hand, the anode was strongly depolarized to potential values of about −0.2 V. A potential as negative as −0.3 V vs. the standard hydrogen electrode (SHE) (i.e. −0.5 V vs. Ag/AgCl) is required for methanogenesis to occur (Gerardi, 2003). Thus, the complete inhibition of methane production shown in Fig. 2 can be the consequence of the inadequate redox environment forced by current harvesting.

3.3. Influence of the external load

In order to favor the growth of electricity producing biofilms one of the most important variables is the anode polarization potential (Torres et al., 2009). Although general rules cannot be yet established, the half-wave potential of molecules wiring electricity producing biofilms to electrodes has been found to be at about −0.2 V (SHE) (−0.4 V (Ag/AgCl)) (Marsili et al., 2010; Richter et al., 2009; Schrott et al., 2011). Voltammetric studies have indeed shown that current harvesting is limited by the gating action of wiring cytochromes and results to be maximal once all cytochromes are in the oxidized state, at potentials beyond −0.2 V (Ag/AgCl) (Schrott et al., 2011). Taking the above arguments into account, after Test A the external resistance was reduced in two steps aiming at keeping the anode polarization at −0.2 V (Fig. 3). The resulting resistor values at each step were 325 and 50 Ω. After each resistor change the current show an initial peak, evidencing charge accumulation under the previous load. Latterly the current increased to values of about 750 and 1300 μA for each resistance (Fig. 3). The stabilization of the current took over 4–5 h after each reduction of the external resistance. This is thought to be the consequence of a biological adaptation to the new anodic conditions. It is important to note that each increment in current was accompanied by the return of the anode potential to more negative values. It evidenced once again the accumulation of charge at the biofilm–electrode interface (Schrott et al., 2011) and indicated that the anodic counterpart of microbial fuel cells may support an additional reduction of the external resistance for improving current yield. Unfortunately, this could not be corroborated due to the weakness of the cathodic counterpart, shown by the polarization of the cathode to negative potentials (Fig. 3). In agreement with previous reports (Rismani-Yazdi et al., 2008) the cathodic reaction appears here as limiting power output under high current regime.

Table 1
Maximal stable current and power output values (as referred to actual COD) and COD removal rates for different external loads.

External resistor values	1000 (Ω)	325 (Ω)	50 (Ω)
Current/COD (μA L/mgO_2)	0.049	0.108	1.808
Power/COD (μW L/mgO_2)	0.022	0.035	0.023
COD removal rate (mgO_2/L h)	17.34 ± 3.42	12.66 ± 2.17	22.54 ± 1.86

Stabilization values for current and power outputs as referred to the actual COD content and the soluble COD degradation rates for every external resistance are presented in Table 1. Current obtained per COD unit progressively increased in each step, while the power output showed a maximum at the intermediate load. It opens at least two options for the operation of the cell: at high current, for speeding up the treatment of the wastewater, or at high power output which may improve energy production.

3.4. MFC wastewater treatment

After obtaining a well developed biofilm the system was operated in sequential batch to get the maximal energy conversion rate by adapting the microbial population to produce current (Kim et al., 2005; Min et al., 2005). It required typically three cycles. The results of the last one are here presented (Test B) to compare the performance of the MFC with a mature biofilm, with that previously observed in Test A.

The potential of the electrodes, the obtained current and the wastewater treatment indicators for Test B are shown in Fig. 4a

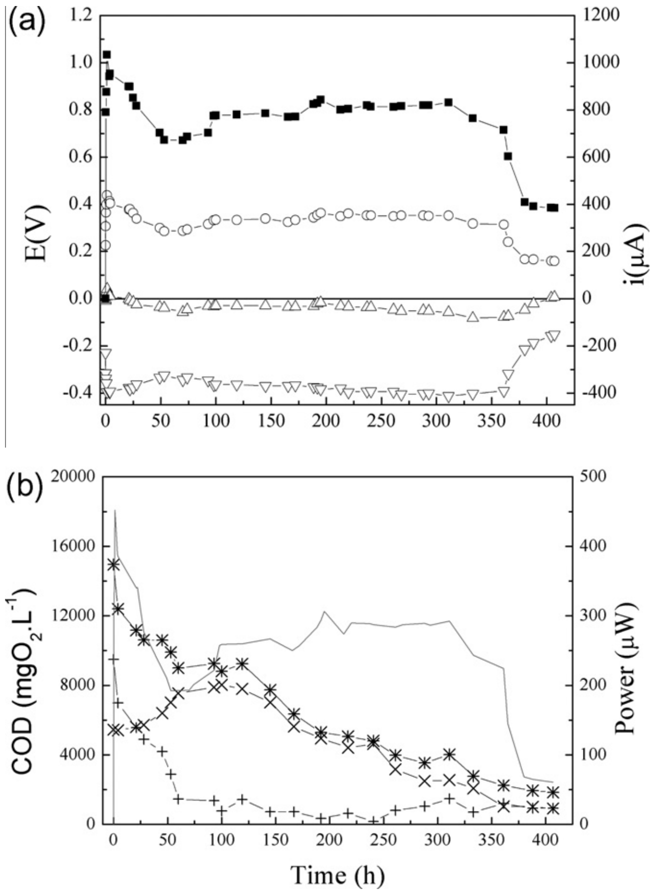

Fig. 4. (a) Evolution of current output (fill squares), cell potential (open circles), cathode potential (up triangles) and anode potential (down triangles) along a typical Test B. (b) Evolution of total (∗), soluble (X) and solid (+) COD and power output (line) during the same test.

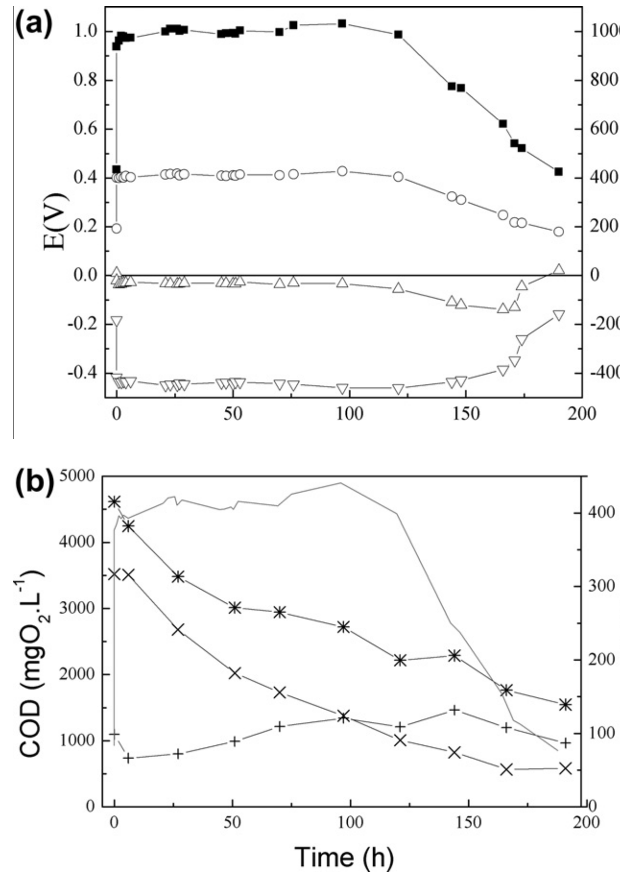

Fig. 5. (a) Evolution of current output (fill squares), cell potential (open circles), cathode potential (up triangles) and anode potential (down triangles) along a typical Test C. (b) Evolution of total (∗), soluble (X) and solid (+) COD and power output (line) during the same test.

and b, respectively. The anode potential immediately shifted to very negative values rendering a cell potential of about 0.4 V (Fig. 4a), differing with the behavior observed during Test A. Owing to the large potential difference the current output was high from the very beginning of the test and doubled that obtained in Test A after the same time of treatment (Figs. 1a and 4a). The conversion of solid to soluble COD evolved as in Test A confirming that this process does not depend on electricity generation. The overall treatment required only 400 h (Fig. 4b), in contrast to the 1000 h required for COD consumption in Test A. Once soluble COD reached the maximum, the anode potential remained stable at about −0.4 V and current production was constant. The reduction of soluble COD was also constant at a rate of 26.23 ± 1.71 $mgO_2\,L^{-1}\,h^{-1}$ until the waste was completely depleted (Fig. 4b). The above results suggest that the performance of biofilms in cleaning wastewaters can be optimized in real application through sequential batch cycling.

3.5. Electrogenic post-treatment

After conventional anaerobic digestion subsequent post treatment is required to meet the effluent discharge standards (Chan et al., 2009). MFCs technology has been proposed to be a good choice to complement treatment schemes (Aelterman et al., 2006; Pham et al., 2006). This is mainly based on the possibility of operating the microbial fuel cells at room temperature and on low COD wastewaters, which are not favorable conditions for methanogenic treatments. Tests C were here developed to evaluate the applicability of an MFC post-treatment for the processing of effluents coming from a methanogenic reactor. The results of electrical measurements obtained during Test C as well as relevant parameters indicating the evolution of the treatment, are shown in Fig. 5. As previously shown for Tests B, the current output immediately reached a stable value of about 1000 μA at a cell potential of nearly 0.4 V (Fig. 5a). Current and potential remained constant for about 150 h of treatment before exhaustion of the waste. The solid COD load was initially low in this case and remained constant at about 1000 $mg\,L^{-1}$ all over the current generation process (Fig. 5b), suggesting that it cannot be further reduced in the MFC post-treatment. The possibilities for additional reduction of the organic load thus rely on the consumption of soluble COD that was observed to decrease at almost constant rate to a final value that was well below 700 $mg\,L^{-1}$ (Fig. 5b), representing a reduction of almost 80%. The MFC step thus allowed the conversion of 62% of the incoming total COD.

3.6. Comparison of alternative treatment schemes

Table 2 summarizes the results of three alternative schemes studied in this work for the treatment of potato-processing wastewater: (a) the electricity producing treatment in a MFC, (b) the conventional treatment in a methanogenic reactor, and (c) a methanogenic treatment followed by a MFC post-treatment, to illustrate the potential utility of MFC technology in industrial applications.

As shown in Fig. 4 and Table 2 the MFC treatment (Test B) required about 400 h to consume 87% of the initial COD falling within

Table 2
Efficiencies related parameters for the tested treatments.

Treatment	MFC treatment	Conventional anaerobic treatment	Conventional + MFC treatment
Operation time (h)	400	1800	2000
TE	87%	75%	91% (62%[a])
CE	1.73%	33.6%	28.2% (4.12%[a])
% ER	0.3%	7.4%	7.6% (0.2%[a])

[a] In MFC post-treatment stage.

previously reported performances (Aelterman et al., 2006; Du et al., 2007; Liu et al., 2004; Min et al., 2005; Venkata Mohan et al., 2008). It clearly outperformed the degradation in the typical methanogenic treatment that required about 1800 h for consuming only 75% of the initial COD. The values of final particulate material were in the same range for both treatments with 930 and 1100 $mgO_2\,L^{-1}$ for the electricity producing and the methane producing treatments, respectively. Soluble particulate material was notably lower in the MFC effluent with 950 against 3520 $mgO_2\,L^{-1}$ in the methanogenic reactor. This clearly indicates that organic load that cannot be consumed in a conventional anaerobic treatment is able to be degraded in the MFC.

In spite of the shorter operation time and the higher COD removal, the energy recovery in the MFC treatment was extremely low, with only 0.3% of the chemical energy available in the wastewater recovered as electrical energy. This contrasts with the 7.4% of the methanogenic treatment (Table 2).

The low energetic yield of the electricity producing treatment is clearly related to the low coulombic efficiency of the conversion process. Less than 2% of the electrons available in the wastewater were recovered as current in the presented case (Table 2), contrasting with the 33% of recovery calculated for the methanogenic treatment. While CE values higher than 75% were reported for non-fermentable molecules as acetate (Aelterman et al., 2006; Kim et al., 2007; Torres et al., 2007), they were in the range of 40–70% for fermentable pure substrate as propionate or ethanol (Lee et al., 2008; Parameswaran et al., 2009; Torres et al., 2007). Values were even lower at around 25–30% for artificial or chemically simple wastewaters (Aelterman et al., 2006; Min et al., 2005) to fall down to 0.8–13% for complex wastewaters (Aelterman et al., 2006; Cercado-Quezada et al., 2010; He et al., 2005; Liu et al., 2004).

Since no methane production was observed during the electricity producing tests, the poor energetic performance can be attributed to some of the following factors: biomass production, presence of alternative electron acceptors, production of molecular hydrogen and presence of molecular oxygen that might permeate from the cathodic compartment across the separating membrane. Provided that the reported electron investment in producing attached biomass is 14–16% for fermentable substrates (Lee et al., 2008; Parameswaran et al., 2009) and considering the complexity of the influent material, biomass in the biofilm can be expected to retain not less than this percentage of electrons in the influent wastewater in the present case. Although the detailed chemical composition of the wastewater is unknown, contents of nitrogen and sulfur species as well as that of metal ions are generally low (less than 5%) in these kind of wastewaters (Gerardi, 2003; Liu et al., 2004), not representing therefore a significant electron sink. Hydrogen production was not measured in our experiments, but estimations based on a general mass balance for the production of hydrogen by fermentation indicates that a maximum of almost 30% of the electrons available in the wastewater could be consumed in the production of H_2 (Parameswaran et al., 2009). This gas could be lost through the effluent stream and absorbed in the NaOH solution. Finally, considering the oxygen mass transfer coefficient through the Nafion 117 membrane (1.3×10^{-4} cm/s) (Kim et al., 2007) a net oxygen flow to the anodic chamber of $4.7 \times 10^{-2}\,mgO_2\,h^{-1}$ can be calculated, yielding 47.05 $mgO_2\,L^{-1}$ during all the test, which suggests that only about 0.5% of the electrons available in wastewater might be directed to contaminating oxygen.

Presented results reinforce the idea of a combined scheme as the most convenient option for the treatment of potato-processing wastewater. As shown in Table 2 the MFC treatment consumed 62% of the incoming total COD for this step, which added to the consumption reached during the methanogenic step accounted for a 91% decrease of the total COD in the original wastewater. The CE of the MFC post treatment step was 4.12% falling within the values reported in the literature for real wastewaters (Aelterman et al., 2006; Du et al., 2007; Liu et al., 2004). The improvement indicates that the effluent from an anaerobic reactor is a more suitable influent for the MFC than the original wastewater. This observation is also supported by the stabilization of the effluent at a lower soluble COD of 580 $mgO_2\,L^{-1}$ at the end of the treatment. It is important to note that the overall energy recovery of the combined scheme was 7.6% (Table 2) not representing a great improvement as compared to that of the methanogenic step. Nevertheless, presented results clearly show that the downstream application of a MFC after a methanogenic treatment of potato-processing wastewater can reduce further the final COD of the effluent in a relatively short additional time. In agreement with Aelterman et al. (2006) and Pham et al. (2006), our results demonstrate that anaerobic digestion and MFC technologies are most probably better to complement than to compete to each other. In this direction, it has to be noted that the present work was not aimed at obtaining the most efficient MFC for replacing traditional aerobic steps. Several modifications can still be implemented on the reactor in order to either enhance the energy recovered from the electrogenic step or to lower the energetic requirements of the treatment. For example, the use of an air cathode would avoid the need of circulating the cathodic solution and bubbling air to the cathode, improving the overall energetic efficiency of the process.

4. Conclusions

An electricity producing biofilm can be directly enriched on the anode of a MFC from a methanogenic activated sludge. Although a MFC can reduce the COD of the waste relatively fast, its energetic efficiency is not yet high enough to postulate it as a direct alternative to the classic methanogenic treatment. In spite of this, when placed downstream of an anaerobic step, the MFC can further reduce the COD of the methanogenic effluent. With this configuration, the main advantages of both processes are exploited, making it an attractive possibility for multi-step effluent treatment schemes.

Acknowledgements

This research was supported by the European Union through the BacWire project (contract # NPM4-SL-2009-229337). JPB is a member of the scientific staff from CONICET, Argentina. ID and PSB are Doctoral fellows from CONICET, Argentina. The technical assistance of Juan Asarou and Hector Asencio is greatly acknowledged.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.biortech.2011.11.095.

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