Hydrogen production in a microbial electrolysis cell fed with volatile fatty acids

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ABSTRACT

The organic matter consumption and the hydrogen production rate were evaluated in a two chamber microbial electrolysis cells (MEC). Three chemical oxygen demand concentration (COD) levels (400, 600 and 1200 mg/L) were tested. The COD was composed of a mixture of volatile fatty acids (VFAs) present in the effluent of a dark fermentation process containing. Two levels of voltage were studied: 350 mV and 550 mV. The MEC were operated in 120-hours batches. The performance of the MFC was evaluated using either an anionic (AEM) or a cationic exchange membrane (CEM). The robustness of the MEC was tested using a real dark fermentation effluent and another spiked with 1100 mg/L glucose. The highest production rates (81 mL/L/d) were obtained with 550 mV and 85% of COD consumption was attained. No significant differences on hydrogen production rate were observed when the COD was increasing from 400 to 1200 mg/l and using 550 mV. However, maximal hydrogen production rates were obtained with the lower COD concentration using 350 mV. No significant differences in the performance of the MEC were found by using AEM or CEM and also no significant differences of hydrogen production rates were found when real substrate o synthetic substrate was fed to the MFC. The substrate spiked with glucose was more slowly degraded since glucose was first transformed into VFAs (first 48 h) then the VFAs were consumed to produce hydrogen. In this case, methane and carbon dioxide were found after 120 h.

Keywords: microbial electrolysis cells; hydrogen; volatile fatty acids

1. Introduction

Environmental and economic issues related with fossil fuels become the research for alternative fuels into a necessity. Hydrogen has the highest combustion heat of all fuels. It is a good energy carrier, but its current main production processes are thermochemical processes that consume fossil fuels [1]. Biological processes are able to produce hydrogen from wastewater and other residues so they are attractive subjects for research.

Dark fermentation is a favorable biological process for hydrogen production. In comparison to other options, the main advantage of dark fermentation is that the H_2 production rate is orders of magnitude larger than those achieved by other biological means [2]. It is known that dark fermentation effluent contains a high concentration of volatile fatty acids (VFAs) which are considered as organic pollutants and need treatment before been discharged to the environment. There are biological processes that are capable of utilizing VFAs and produce value products.

The bioelectrochemical systems are electrochemical cells where certain microorganisms produce electric current while oxidize organic matter on a biofilm over an electrode called anode. Their organic matter sources are substances such as acetate, cellulose, starch and wastewater [3]. The most studied electrogenic bacteria belong to the families of *Shewanella* and *Geobacteraceae* [4]. There are two kinds of bioelectrochemical systems. The difference between them is the reaction on the cathode:

Microbial fuel cells (MFCs) produce electric current via redox reactions. Electrons travel through an external circuit to the cathode. At the same time, protons travel to the cathode through the electrolyte and through a membrane that divides cathode chamber from anode chamber. Electric current is produced because of oxygen reduction on the cathode [5]. Microbial electrolysis cells (MECs) are modified MFCs that produce hydrogen. Its cathode is anaerobic and without oxygen spontaneous electricity production is not possible since the free Gibbs energy of the reaction is ΔG_r = + 104.6 kJ/mol [6]. To drive electrons from the anode to cathode an external voltage is applied to the circuit. Hydrogen is produced by proton reduction on the cathode [5].

Equations 1 to 3 describe the reactions occurring in the cell when using acetate as a model:

Anode:

$$CH_3COO^-{}_{(ac)} + 4H_2O_{(l)} \rightarrow 2HCO^-{}_{3(ac)} + 9H^+{}_{(ac)} + 8e^- \quad (1)$$

Cathode:

$$8\left(H^+{}_{(ac)} + e^- \rightarrow \frac{1}{2}H_{2(g)}\right) \quad (2)$$

Global reaction:

$$CH_3COO^-{}_{(ac)} + 4H_2O_{(l)} \rightarrow 2HCO^-{}_{3(ac)} + H^+{}_{(ac)} + 4H_{2(g)} \quad (3)$$

At standard conditions of temperature and pressure, the voltage required is 0.14 V using acetate as substrate. However, in reality voltage required is over 0.25 V due to internal system resistances. Nevertheless this voltage is lower than that of the water electrolysis, 1.8-2.0 V [7].

For this paper organic matter consumption and the hydrogen production rate were evaluated in a two chamber microbial electrolysis cells (MEC) using as substrate dark fermentation the effluent containing VFAs. Voltage, COD and substrate composition were evaluated.

2. Experimental

2.1 System operation

Four MECs were constructed using a two-chamber configuration (163 mL/chamber) with a distance between electrodes of 3.7 cm. The anode was made of graphite cloth (Brunsen de Occidente S.A. de C.V., Guad., Jal., Mex.) whereas the cathode was constructed of carbon paper with Pt (5 cm × 5 cm, 0.5 mg Pt/cm2, ElectroChem, Inc., Woburn, MA). Internal connections were made using titanium wire, 10 cm, (Sigma-Aldrich Co., St. Louis, MO). External connections were made of copper wire. Two input voltages (0.35 and 0.55 V) were applied using a power source (GWInstek, model GPS-4303).

The anode was colonized operating the cell in MFC mode with 48-hour batches. Cycles were conducted until the generated voltage reached by the cell was maximum and reproducible during at least three cycles. A mixture (75:25) of municipal wastewater (wastewater treatment plant of Campus Juriquilla, UNAM) and sodium acetate (20 mM) in 100 mM phosphate buffer solution and vitamins and minerals [8] was used as the inoculum source and cell fuel. The chambers were separated by a cationic exchange membrane (CEM) (CMI 7000, Membranes International, Glen Rock, NJ). Temperature was 25° C maintained constant in a water bath with a submersible heater.

For the electrolysis cells, the synthetic substrate was prepared with a mixture of FVAs based in the composition of a dark fermentation effluent. The pH was set at a value of 7 with 1M HCl and 1M NaCl. The purpose of the synthetic mixture was to have only VFAs (which the cell is supposed to consume) in the substrate and exclude other substances from the dark fermentation effluent such as glucose or ethanol, which can interfere with the hydrogen production via electrolysis. VFA percentage in the mixture was 26% acetic, 12% propionic y 63% butyric. Three levels of synthetic substrate COD were used: 1200, 600 y 400 mg/L. The cells were operated in batch during 120h until a stable hydrogen production was observed. The COD consumption was also evaluated at the end of each cycle.

Once the synthetic substrate study was completed, the cell was fed directly with a real dark fermentation effluent, to compare the hydrogen production vs. the synthetic substrate. Next, the robustness of the system was evaluated. For that, a dark fermentation effluent containing a high concentration of glucose (simulating a malfunctioning of the dark fermentation process) was tested in the MEC using first 120 h batches, and then reducing the cycle time to 48 h in order to inhibit the methane formation. The performance of the system with the CEM vs. an anionic exchange membrane, AEM, (AMI-7001, Membranes International, Glen Rock, NJ) was also studied.

The dark fermentation reactor used to obtain the substrate was a continuous 2-liter UASB reactor, operated under the following conditions: pH 4.5, 35° C and 16 h of hydraulic retention time. Glucose was used as a carbon source. The reactor operated with three glucose concentrations: 5 g/L; 0.6 g/L (for real vs. synthetic and membranes comparison) and 10 g/L (for the robustness study).

2.2 Measurements

Voltage was monitored with a DAQ USB 6008 (National Instruments Inc., Austin, TX) and LABVIEW 7 software. pH was measured after every batch with an OAKION pH 510 Series potentiometer with a pH Orion 9156BNWP electrode. COD was measured by using an spectrophotometer (Hach 435 and 430 methods).

VFAs were identified and quantified with a gas chromatograph Varian 3300 equipped with a flame ionization detector according to [9] and gas composition in the cathode chamber was measured with a SRI8610C gas chromatograph equipped with a thermal conductivity detector as described in [10]. All experiments were performed

using duplicate cells and the reported data are the average of at least six values (three cycles for each cell). In all cases, hydrogen volume was measured in an inverted cylinder filled with water.

3. Results and discussion

3.1 Synthetic substrate

No traces of CO_2 or CH_4 were found in the MEC cathode. Figure 1 shows the hydrogen production rate as a function of the applied voltage and the initial COD fed to the reactor. The maximum hydrogen production rate was 81±5 $mLH_2/L/d$ and it has the same order of magnitude as other results reported in the literature as can be seen in table 1.

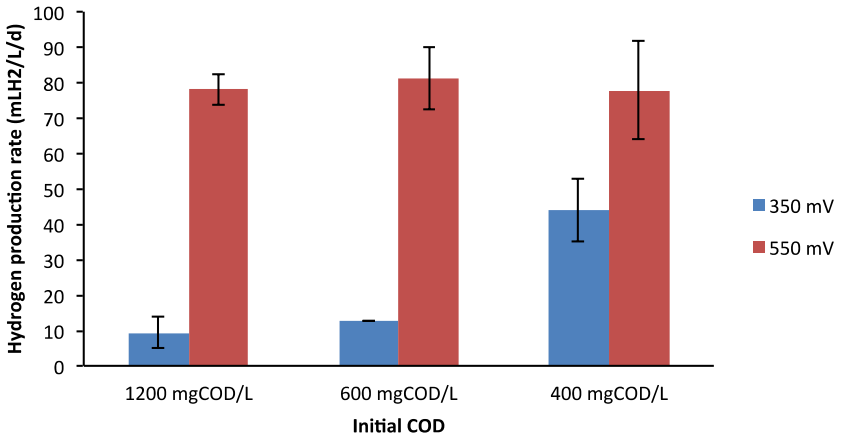

Figure 1. Hydrogen production rate versus the applied voltage and initial COD.

Table 1. Hydrogen production rate in two chamber system using low voltages

Substrate	Anode	Cathode	Membrane	Voltage	Max. H_2 prod. Rate	Reference
Acetate	Carbon paper	Carbon paper with Pt	PEM	0.4 V	18 $mLH_2/L/d$	[11]
Domestic wastewater	Graphite felt	Carbon paper with Ni	Cellulose cloth	0.2-1.4 V	45 $mLH_2/L/d$	[12]
Domestic wastewater	Graphite felt	Stainless steel	Polyethylene membrane	0.6 V	15 $mLH_2/L/d$	[13]
Sodium acetate	Carbon paper	Carbon paper with Pt	CEM	0.418 V	14 $mLH_2/L/d$	[14]
Fermented activated sludge	Graphite fiber brush	Carbon cloth with Pt	CEM	0.6 V	68 $mLH_2/L/d$	[15]
Mixture of acetate, propionate, butyrate	Graphite cloth	Carbon paper with Pt	CEM	0.550 V	81 $mLH_2/L/d$	This study

ANOVA analysis indicated that there exists a significant influence on hydrogen production rate of the applied voltage and the initial COD. When a high input voltage is applied, there not exists a significant influence on the production rate, when the initial COD was increased from 400 to 1200 mg/L, but with the low input voltage, the productivity increases when concentration decreases.

Figure 2 shows the organic matter consumption as a function of the applied voltage and initial COD. COD removal was in the interval of 38 - 85%. Higher COD removals were observed with lower initial COD. In this case, no significant influence of the applied voltage was found. This behavior indicates that the organic matter consumption is not the limiting factor for hydrogen production (Fig. 1). The pH changes were evaluated (table 2). It was found that the higher the substrate concentration, the higher the pH difference between the two chambers and the required voltage for electrolysis increases. With the high voltage there is enough energy to compensate this pH change, so there is a high production rate. At the low voltage, the production rate was higher at low COD concentration; however low COD were observed after the cycle indicating that the MEC is not enough for organic matter removal generating residual organic matter that needs to be further removed.

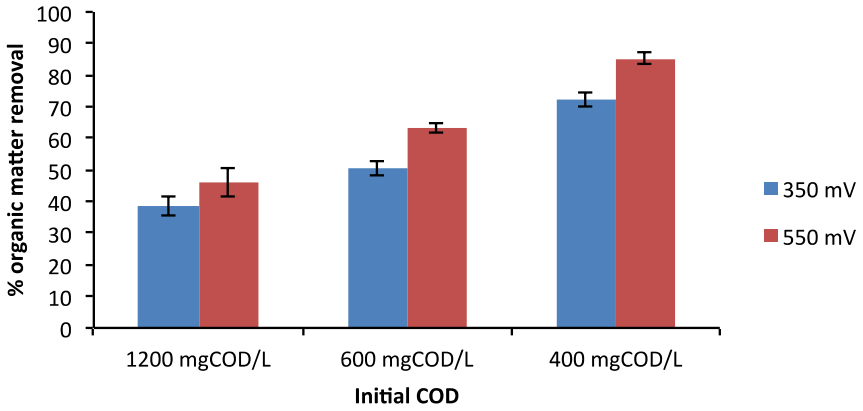

Figure 2. Organic matter removal measured as COD in a 120 hours batch using synthetic substrate.

Table 2. pH values at the end of a 120 hours batch measured in the anodic and cathodic chambers.

	Cathode		Anode		ΔpH	ΔpH
	350 mV	550 mV	350 mV	550 mV	350 mV	550 mV
1200 mg COD	7.43	7.69	6.61	6.07	0.82	1.62
600 mg COD	7.26	7.53	6.60	6.22	0.66	1.31
400 mg COD	7.16	7.24	6.56	6.29	0.6	0.95

3.2 Real substrate

The effluent obtained from the dark fermentation reactor presented the following composition (in mg/L): Glucose (10±2), ethanol (66±8), acetate (100±5), propionate (32±15) butyrate (57±7), COD (420±14). The hydrogen production rate and the organic matter removal obtained with the synthetic substrate and the real effluent are presented in figures 3 and 4. The ANOVA analysis indicates that there were not significant differences, despite 38% of the COD in the real substrate was formed by other compounds different to the VFAs as was the case for the synthetic substrate.

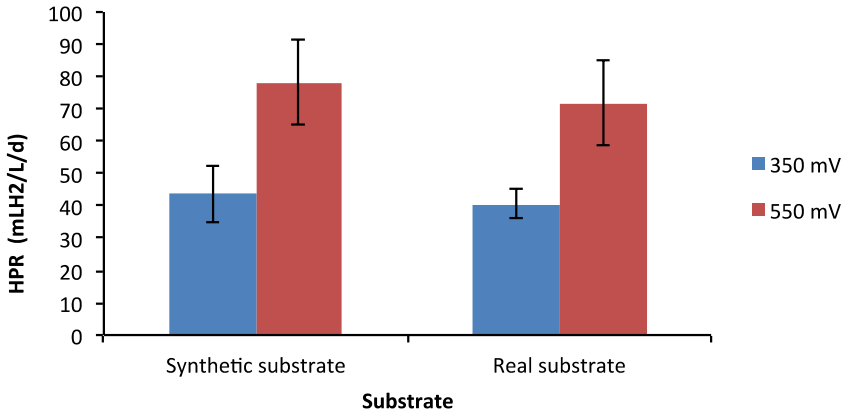

Figure 3. Hydrogen production rate in a MEC fed with synthetic and real substrate.

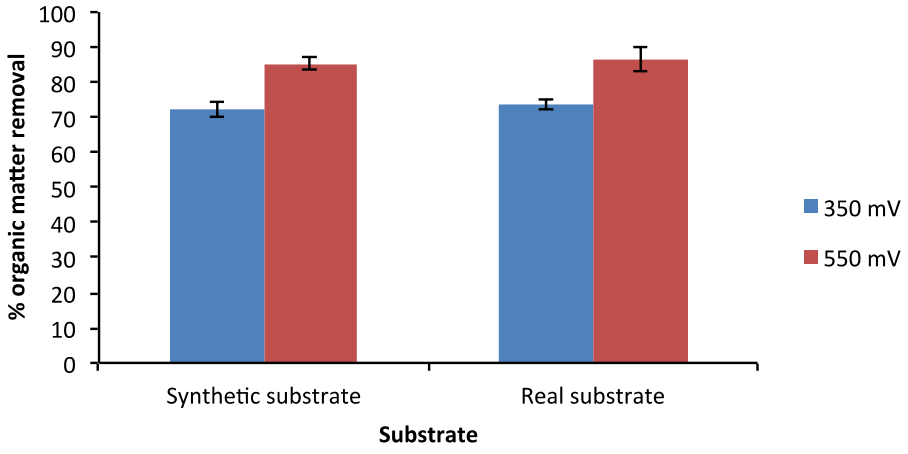

Figure 4. Organic matter consumption in a MEC fed with synthetic and real substrate.

3.2.2 Performance of the MEC using cationic (CEM) and anionic exchange membranes (AEM).

It has been reported [16] that an AEM (Fumasep FAA, FuMa-Tech GmbH, Germany) allows higher production rates than a CEM (Fumasep FKE, FuMa-Tech GmbH, Germany). This increment was attributed to the differences of ionic transport in the membranes [16]. The importance of the phosphate buffer anions diffusion through the AEM membrane has already been explained by Sleutels et al. [16]. The HPO_4^{2-} ion diffuses to the cathode and the PO_4^{-} ion does to the anode. The transport of buffer anions is equivalent to the transport of H^+/OH^-, which are the main charge carriers in the electrolysis system. On the other side with a CEM all the cations travel to the cathode chamber. H^+ exists in a lower concentration than the other cations, so its diffusion to the cathode is lower. Because of this transport and acidity the CEM eventually has a positive charge on the anode side and reflects the cations. Thus, it is more difficult to the protons produced on the anode to reach the cathode.

In order to evaluate the effect of the type of membrane on the hydrogen production rate, the cells were tested using an anionic exchange membrane (AMI-7001). Real substrate was used. As can be seen in figure 5 no significant differences were found by using an AEM or a CEM, independently of the voltage supplied. ANOVA indicates there is no important difference when the control variable is the membrane. The materials used for the membranes can explain the difference with the previous study. The membranes used for this study presented higher electric resistance (40 $\Omega.cm^2$ for the anionic membrane and 30 $\Omega.cm^2$ for the cationic membrane) than the membranes already reported [16] (1.9 $\Omega.cm^2$ for the anionic membrane and 3 $\Omega.cm^2$ for the cationic membrane). Thus, although the ionic transport reported in literature exists, the electric resistance of the membranes of this study dissipates energy instead of favoring hydrogen production. Another important factor is the input voltage since in the present study lower input voltages were applied than the values reported by Sleutels et al. [16], which conducted the experiments using 1000 mV.

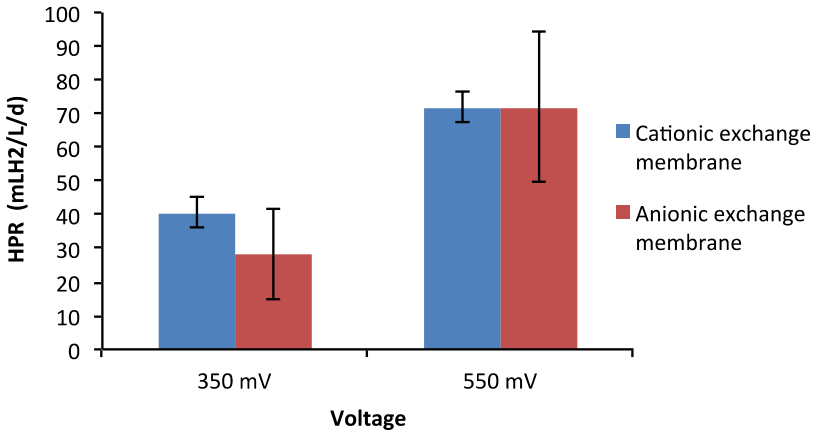

Figure 5. Hydrogen production rate in a MEC with two ionic exchange membranes.

3.3 Robustness of the System

To evaluate the robustness of the MEC a real effluent containing a high glucose concentration was study. The substrate composition was (in mg/L): glucose (1137±25), ethanol (8.1±3), acetate (397±19), propionate (75±7),

butyrate (363±23) and COD (3700±20). When the cells were operated under that condition, the biogas production stopped after 48 h and after 120h, when the cycle was completed methane was detected in the biogas (60% for 550 mV and 70% for 350 mV) the rest was CO_2. No H_2 was found. It is possible that glucose passed through the membrane to the cathodic chamber favoring the growth of Archea. To avoid the methane formation the cycle duration was reduced to 48 h. In this case, no CH_4 was found and H_2 percentage was 80% for 350 mV and 90% for 550 mV. Decreasing the time of the batch was enough to avoid growth of Archea and methane production. The production rate obtained with this substrate was compared to the high COD level in the synthetic substrate. Hydrogen production rate was similar for both substrates at 350 mV, but it was clearly inferior at 550 mV (Figure 6). The maximum production rate with this real substrate containing glucose in excess was 28±3 mL/L/d; almost three times lower than a substrate containing only VFA. The reason for this behavior can be explained considering that microorganisms present in the MEC first transform the glucose into VFAs, and then these are utilized to generate hydrogen.

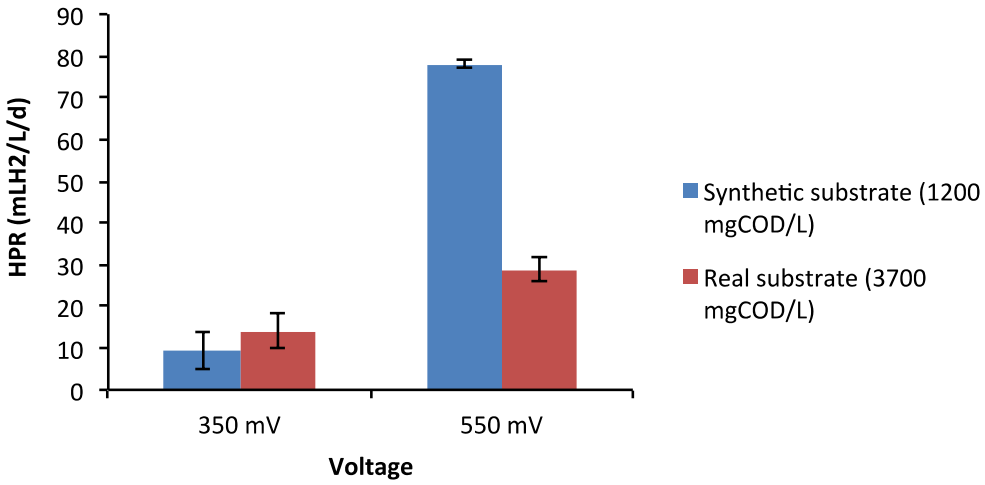

Figure 6. Hydrogen production rate in a MEC fed with synthetic and real substrate with carbohydrates.

Figures 7 and 8 present the evolution of the substrate as a function of time in the anodic chamber when the 120h cycle was operated. It is possible to observe that glucose is degraded as the VFAs are produced. The maximum VFAs production was reached at 24 hours for 550 mV and at 48 hours for 350 mV after this time concentration decreases. It was found an important COD consumption of 59% for 350 mV and 66% for 550 mV. Indicating that some of the fuel was not directly utilized for hydrogen production and explaining the lower hydrogen production rates.

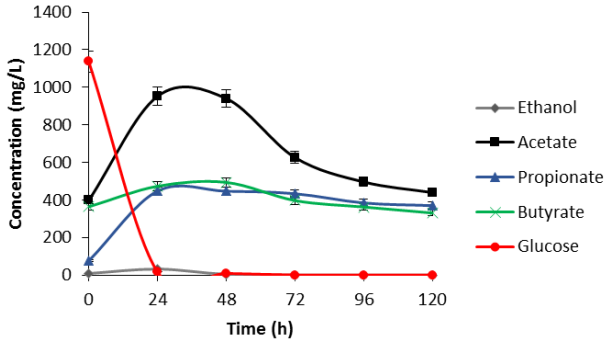

Figure 7. VFAs, ethanol and glucose evolution for 550 mV.

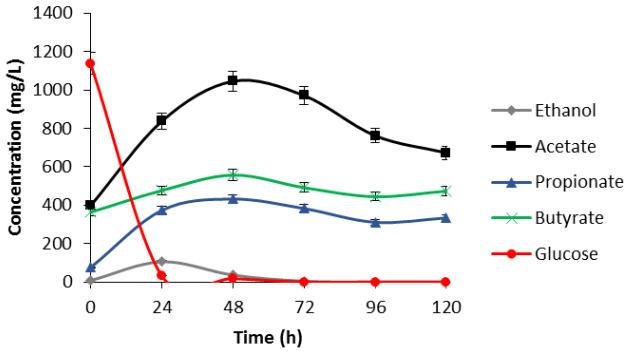

Figure 8. VFAs, ethanol and glucose evolution for 350 mV.

4. Conclusions

Best local conditions for the operation of a microbial electrolysis cell for hydrogen production using volatile fatty acids were obtained using an input voltage of 550 mV, cycles of 96 h, and initial COD from 400 to 1200 mg/L. Under these conditions, maximum hydrogen production rate was 81 mLH_2/L/d and maximum organic matter removal was 85 %. In general, low organic matter levels are recommended for the operation of the system. When a dark fermentation effluent was utilized, similar results to the synthetic substrate were obtained. Under the condition operated with the system no significant differences were found when an anionic exchange membrane or a cationic exchange membrane were used. When the substrate fed to the cell contains carbohydrates, the hydrogen production rate decreases significantly and some methane can be produced. It is important for the correct performance of the microbial electrolysis cell, when coupling to a dark fermentation process, that no carbohydrates are present in the effluent.

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