Hydrogen Generation in a Microbial Electrolysis Cell (MEC) using two configurations: Catalyzed by Platinum and Biocathode

Limberg Alejandro Gómez Roque [a*], Jorge A. Domínguez Maldonado [a], Liliana Alzate Gaviria [a]

[a] Unidad de Energía Renovable del Centro de Investigación Científica de Yucatán (CICY). C.43 No. 130 Col. Chuburná de Hidalgo
97200, Mérida, Yucatán, México.
[*] Tel. (999) 9428330 Ext. 321. mail: limbergberik@cicy.mx

ABSTRACT

Microbial Electrolysis Cells (MEC) are biological devices that offer a new way to produce hydrogen electrolyzing any type of organic matter by the action of electrochemically active microorganisms and an external potential (between 0.22 and 1 V). The MEC require a catalyst to form hydrogen, being platinum the most widely used in these devices. However, platinum is expensive and performance may decrease (poisoning) when it is exposed to compounds such as CO, CO_2 and sulfides. In the present study two types of catalysts were used: platinum (MEC Pt) and a biocathode using a technique that was allowed to reverse the reaction of hydrogenase enzymepresent in the electrochemically active microorganisms, so it was possible to convert a bioanode to biocathode hydrogen generator (MEC b). MEC Pt (0.5 mg/cm^2, 10% Pt / C) generated H_2 0.032 m^3 / m^3 of liquid reactor volume / day at a potential of 0.9 V and MEC b generated H_2 0.010 m^3 / m^3 liquid volume reactor / day at a potential of 1 V.

1. Introduction

The Microbial Electrolysis Cell (MEC) are a novel biological device which is capable of "electrolyser" any biodegradable substrate such as organic matter present in wastewater and convert it directly to hydrogen and CO_2 [1]. The electrolysis of organic matter in a CEM is achieved by a consortium of electrochemically active microorganisms which are capable of transferring electrons across its metabolism to an anode (called bioanode). In this way, electrons can be directed to a cathode through an external circuit, however, the electromotive force is not sufficient for this flow takes place, so it is necessary to apply an auxiliary potential through an power source. While the flow of electrons released from the anode to the cathode occurs, an equal number of protons produced during the metabolism of microorganisms permeate through a proton exchange membrane, reduced at the cathode in the presence of a catalyst to form molecular hydrogen (Figure 1). Thus, the microbial electrolysis can be carried out with potential applied between 0.22 V to 1 V [2].

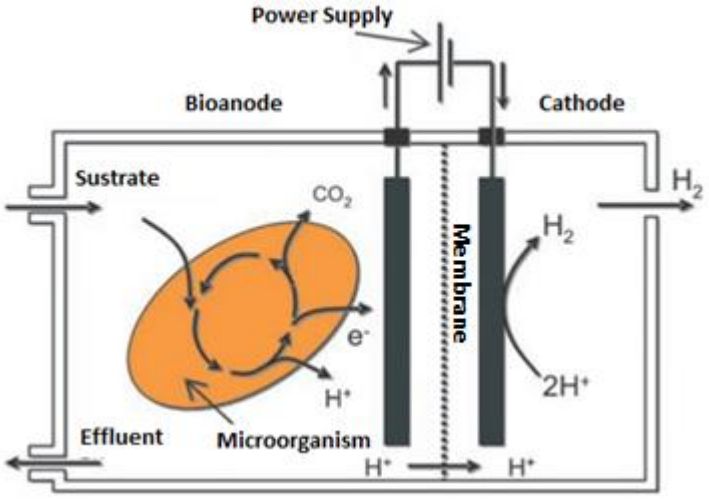

Figure 1. Schematic representation of hydrogen production by Microbial Electrolysis Cell [3].

One of the greatest challenges in the investigation of MEC systems is present in the cathode catalyst. MECs generally operate with platinum as a catalyst, since it has been proved very effective in other systems like the conventional fuel cell. However, the fuel cells operating at current densities around 10^3 to 10^4 A/m^2, which are greater than MEC (between 1 and 10 A/m^2) [4]. So, the production of current is too low to justify the use of expensives catalyst. Within this scenario, biocathodes are a viable option as they promise to be applied in the MECs with relatively inexpensive materials using electrochemically active microorganisms.

The strategy to achieve biologically cathodic reactions is mainly based on the reversibility of the hydrogenase enzyme [5]. The hydrogenase is widely distributed in anaerobic microorganisms. It produces hydrogen both irreversible and reversibly, depending on environmental conditions, being reversible only under strict anaerobiosis [6]. It is known that the reaction catalyzed by the hydrogenase is:

$$H_2 \leftrightarrow 2H^+ + 2e^- \quad (1)$$

In 2008, Rozendal et al. [4] developed a biocathode obtaining it from the electrochemical conversion of a graphite cloth bioanode with electrochemically active microorganisms (not identified yet). The procedure to form the biocathode was to change the polarity of bioanode, manipulating substrate conditions in the MEC to force microorganisms to generate cathodic currents.

The aim of this study is to develop a CEM system with anodic and cathodic reactions catalyzed by electrochemically active microorganisms and compare its performance with a platinum cathode MEC.

2. Experimental procedures.

The MECs were constructed of two polymethylmethacrylate chamber with a working volume of 0.57 L each, separated by a Nafion ® 117 membrane with an area of 22.2 cm^2 (Figure 2). The anode and cathode were made of graphite cloth with an area of 32 cm^2 (Figure 3) [7, 8, 9]. The cathode was prepared with 0.5 mg/cm^2 of platinum (10% Pt / C) and biocathode was obtained by reversing the polarity of an active bioanode [4].

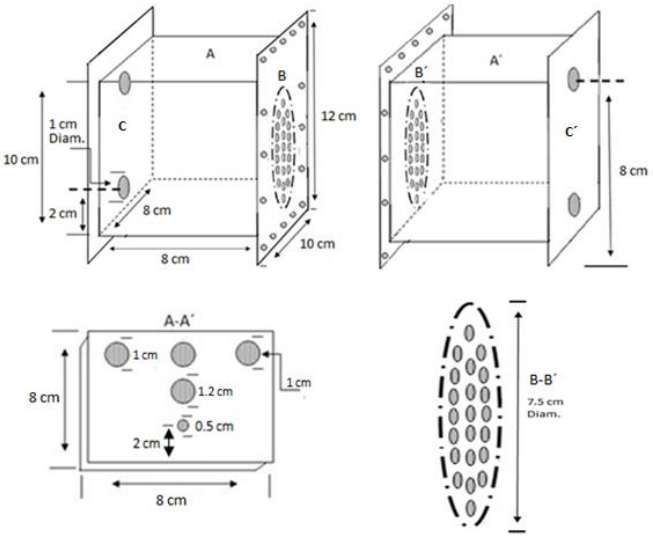

Figure 2. MEC scheme used in this study. (A-A ') Covers with 3 holes of 1 cm diameter each for sampling and gas output, 1 hole of 1.2 cm diameter to place the reference electrode and a 0.5 cm hole for the cable electrode outlet. (B-B ') Membrane support with an O-ring of 7.5 cm diameter. (C-C ') 2 holes of 1 cm diameter for input and output of nutrients.

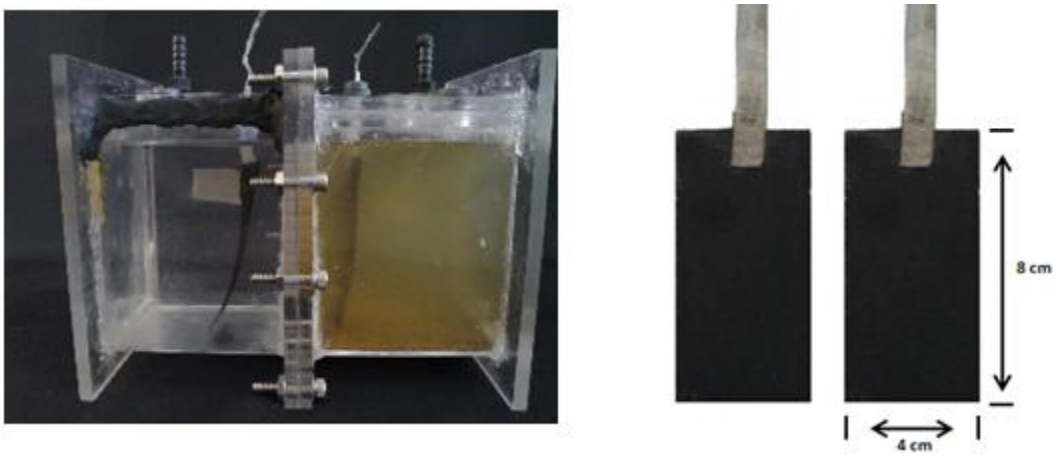

Figure 3. Photograph of the prototype of this study (left) and carbon cloth electrodes held by stainless steel mesh as wire (right).

The MECs had the following nomenclature and function. **CEM b:** Used for the formation of biocathode. It began with a conventional cathode (0.5 mg Pt/cm^2) and then was replaced by an active bioanode from CEM Reserve.**CEM Pt:** MEC formed with a Pt cathode (0.5 mg Pt / cm ^{2}) for comparative purposes to CEM b. **Control:** MEC

uninoculated and without catalyst**. CEM Reserva:** It was used to get a bioanode for CEM b during biocathode formation process.

2.1 Substrate and inoculum

The following nutrient medium was prepared for the anode chamber: 0.74 g / L KCl, 0.58 g / L NaCl, 0.68 g / L KH_2PO_4, 0.87 g / L K_2HPO_4, 0.28 g / L NH_4Cl, 0.1 g / L $MgSO_4 \cdot 7H_2O$ and 0.1g / L $CaCl_2 \cdot 2H_2O$. 12.14 mM of $NaCH_3COO$ was added as carbon source in CEM Pt anode chamber [4, 10], while in the cathode chamber was phosphate buffer at a concentration of 50mM. During the biocathode formation process in CEM b, $NaCH_3COO$ was replaced by 10 mM $NaHCO_3$. The inoculum used in the anode was 100 mL of a mixed microbial consortium described by Alzate et al. (2010) [11]. The pH in all MECs was maintained at 7.

2.2 Characterization and measurement of the gas generated

To measure the gas generated was used a flow meter (Ritter MilligasCounter ® MGC-1) (Figure 4).

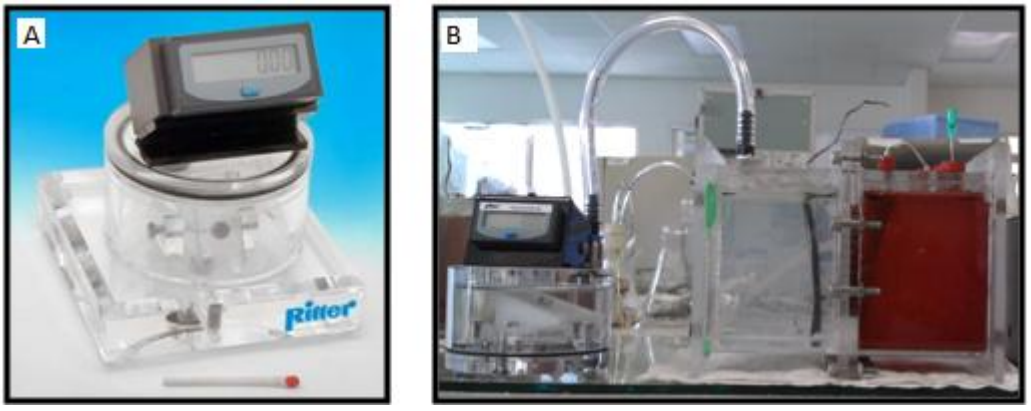

Figure 4. (A) MilligasCounter ® MGC-1 and (B) MilligasCounter ® coupled with CEM Pt.

For the gas characterization the samples were analyzed on a gas chromatograph Perkin Elmer Clarus 500 ® equipped with a thermal conductivity detector (TCD) using a Molsieve column (30 mx 0.53 mm packed) and nitrogen as carrier gas. The volume of H_2 in all the gas (Vt) was determined from [12]:

—— (2)

Where "$V_{E,t}$" (mL) is the expected volume of H_2 based on the load (C), "F" is the Faraday constant (96.485 C / mol), "C_t" is the Coulombs generated and V_M is the molar volume of gas (25.000 mL / mol at 28 ° C).

Cathodic hydrogen recovery (r_{Cat}) was calculated based on the volume ratio of hydrogen obtained experimentally (Vt) between the expected volume of hydrogen ($V_{E,t}$)

The hydrogen production rate (Q) was expressed in m^3 of H_2 generated / m^3 of liquid reactor volume / day ($m^3/m^3/d$) according to Logan et al. (2008) [13]:

(3)

Where "I_V" is the volumetric current density (A/m^3) based on the volume of reactor operation, "T" is the temperature (K) and "r_{Cat}" cathodic hydrogen recovery.

2.3 Electrochemical Analysis

The applied potential was carried out with a adjustable power supply from 0 to 5 V with intervals of 0.01 V (Instrumentation Department CICY, Merida, Yucatan, Mexico) and a potentiostat BioLogic ® SAS VSP 400.
Cyclic voltammetry and cronoamperometry was performed, also were obtained polarization curves and measurements of anodic potential. In all tests were used calomel reference electrode (+0.244 V vs SHE) and a platinum wire Premion ® 8 cm long and 0.5 mm thickness with a purity of 99.997% as auxiliary electrode. All potentials were expressed against the standard hydrogen electrode (SHE).

2.4 Startup and Operation

The MECs were fed every 24 hours with 100 ml of nutrient and carbon source, for CEM Pt was sodium acetate and for the CEM b sodium bicarbonate. Furthermore 0.9 V was applied in CEM Pt and 0.9 and 1 V in CEM b. The applied potentials of MECs were based on the polarization curves, by selecting those with higher current densities. The operating temperature for all MECs were 28 ± 2 ° C.

CEM Pt started with 12.14 mM of sodium acetate every 24 h and a potential of 0.9 V for 4 months. The air was displaced from the entire MEC with N_2 (Praxair, 99.999%) over 20 minutes and was completely sealed to maintain anaerobic conditions [14, 15, 16].

The CEM b started from 100 mL from the anode chamber of CEM Pt after 4 months of operation. CEM b operated for 3 months, 1 month for the biocathode formation and 2 months for operation as catalyzed by biocathode at 0.9 and 1 V. The H_2 supply was made by a metal hydride tank 20L (Udomi Fuel Cells ®) [4].

Reversing the polarity of bioanode in CEM b was as follows: **Stage 1**. Hydrogen was supplied to the chamber of bioanode (bioelectrode) at 40 mL / min for the adaptation of microorganisms to H_2 oxidation [17]. During this stage preliminary tests were performed by applying a potential of +0.34 V to the bioanode (vs. SHE) for one week and then changed to +0.1 V [4]. The carbon source was 12.14 mM sodium acetate every 24 h. **Stage 2**: When the current density was maintained constant, -0.2 V (vs. SHE) was applied on the bioelectrode and subsequently sodium acetate was removed from nutrient medium and replaced with 10 mM sodium bicarbonate every 24 h as inorganic carbon source [4.]. **Stage 3**: H_2 feeding was discontinued and then a linear sweep of -0.2 to - 0.8 volts at a rate of 0.025 mV /s was performed in order to observe the specific potential where the cathodic currents are generated. Finally, we applied the potential obtained from línear sweep to obtain the biocathode. At this point the original CEM b cathode was replaced by a bioanode from CEM Reserva. The feeding was 10 mM of sodium bicarbonate every 24 h [4]. A representative figure of the process is shown in Figure 5.

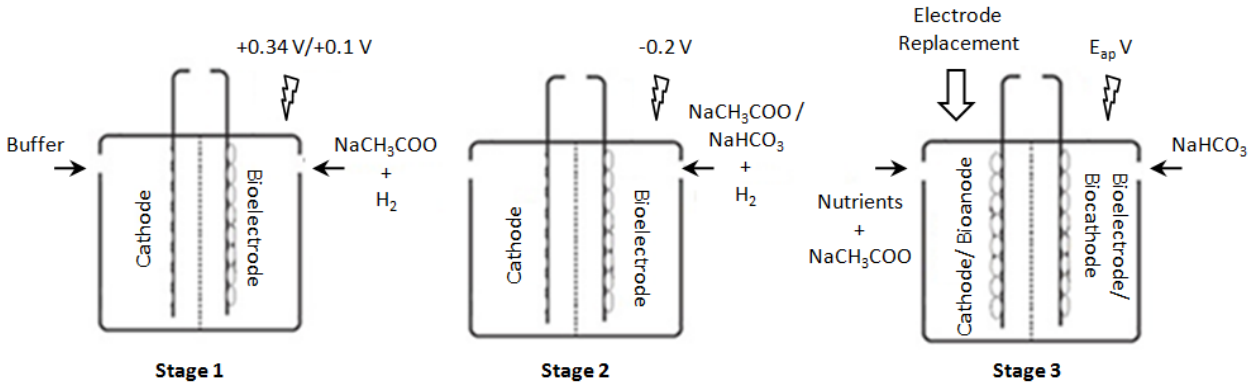

Figure 5. Process of biocathode creation in CEM b.

Once the CEM b catalyzed by biocathode was obtained, 0.9 V was applied to the whole MEC for one month and then increased to 1 V for another month. After that, we compared the current densities and volumes of hydrogen generated against to CEM Pt [10].

3. Results and discussion

The generation of H_2 in the CEM Pt at a potential of 0.9 V started at 24 hours, noticing the typical H_2 bubbling at the cathode. CEM Pt generated a current density of 2 A/m^2, yielding 27 mL H_2 / day (0032 m^3/m^3/d). The concentration of H_2 at the cathode was 38%, while the methane represented less than 1%.

The hydrogen generated experimentally accounted 52% of the total that may form in MEC per day (cathodic hydrogen recovery), while the rest (48%) was probably lost due to leaks in the system or by diffusion towards the anode through the membrane [2].

CEM Pt production was low compared with other platinum catalyzed MEC, like Cheng et al. (2007) with 1.1 m^3/m^3/d at 0.6 V [9] or Tartakovsky et al. (2009) with 6.32 m^3/m^3/d at 1 V [18]. This probably was due to leakage of gas or converting it to other undesirable gases such as CH_4 by methanogenic microorganisms [2]. This is reflected in the percentage recovery of hydrogen in the MEC cathode.

CEM b generated a current density of 0,032 A/m^2 producing 0.07 mL H_2/day, with concentration equal to CEM Pt, 38%. The CEM b performance was improved when the potential was increased to 1 V, the results are shown in Table 1.

Table 1. Results obteined in CEM b and CEM Pt.

MEC	Applied Potential (V)	Current Density (A/m^2)	V_t (mL/d)	$V_{E,t}$ (mL/d)	r_{Cat} (%)	Q (m^3/m^3/d)
CEM b	0.9	0.032	0.07	10.1	0.7	0
CEM b	1	0.53	11.05	18.4	60	0.010
CEM Pt	0.9	2	27	52	52	0.032

Table 1 shows that at a potential of 0.9 V applied for 24 h the current density in CEM b was 0.032 A/m^2. Compared with CEM Pt, the amount is 90% lower, as CEM Pt developed 2 A/m^2 at the end of the 24 h. Moreover, the current density obtained in CEM b at a potential of 1 V was 0.53 A/m^2, improving the density with respect to 0.9 V applied (0.032 A/m^2), but remained below of CEM Pt.

The CEM b at 1 V generated 11.05 mL H_2/day , corresponds to approximately 50% generated in CEM Pt that received 27 mL of H_2/day with similar cathodic hydrogen recovery (r_{Cat}), contrary to what happened in CEM b at 0.9V, that only generated 0.07 mL H_2/day, having a cathodic hydrogen recovery less than 1%.

CEM b compared with other studies, Jeremiasse et al. [10] generated 50 mL H_2/day (0.163 m^3/m^3/day) at 0.5 V in a MEC catalyzed by biocathode obtained from Rozendal et al. (2008) [4]. This value represents 94% higher compared with that produced in the CEM b at 1 V (based on Q, m^3 / m^3 / d). However, there were some differences in the way of starting MECs. In our study a MEC was initiated (CEM Reserve) especially to extract the bioanode and be able to use it on CEM b, while Jeremiasse et al. (2010) [10] inoculated the anode expecting 600 hours for stabilization, and subsequently inoculated the cathode with the MEC used by Rozendal et al. (2008) [4]. This methodology attributed improved stability of microorganisms in their study, generating higher current densities. However, in our study the decision to take a stable bioanode from another MEC became faster the CEM b startup.

About the Rozendal study[4], it´s important to mention that the anolyte was replaced by ferrocyanide to act as artificial electron donor, so in this way he could get more hydrogen production, 0.63 m^3/m^3/d at -0.7 V.
In Figure 6 shows a summary of the hydrogen generated in this study based on the production rate (Q), compared with the results obtained in CEM Pt and CEM b.

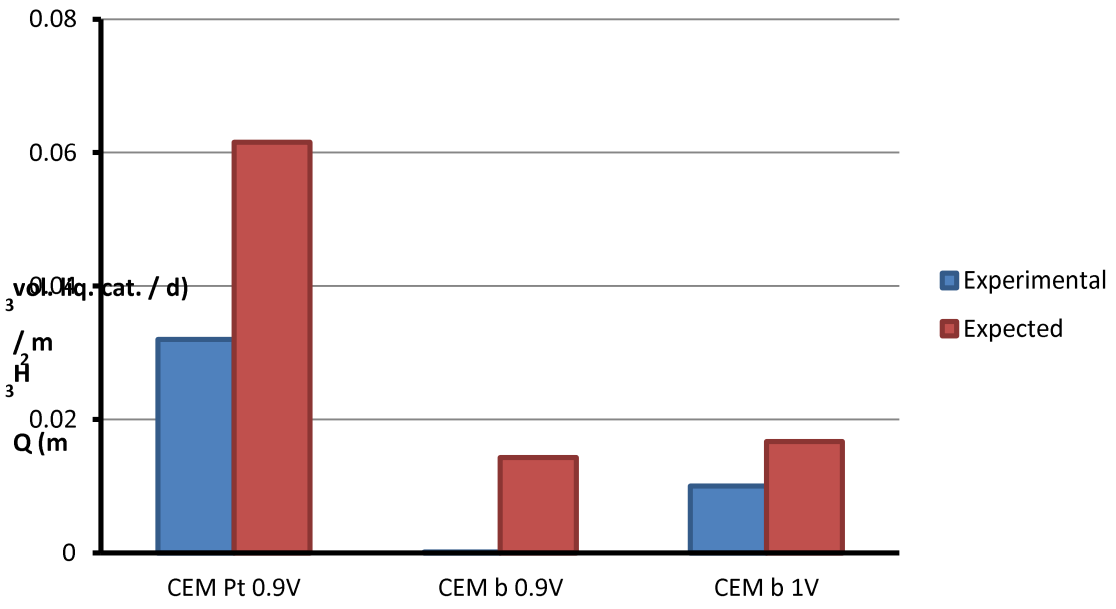

Figure 6. Results obtained in CEM Pt and CEM b.

4. Conclusions.

CEM Pt generated up to 0.032 m^3 H_2 / m^3 of reactor liquid volume / day at an applied potential of 0.9 V with a cathodic recovery rate of 52% due to leaks in the cathode chamber. The generation of H_2 in CEM Pt was low compared to other published works due to platinum poisoning by CO_2 and hydrogen sulfide.

CEM b produced 0.010 m^3 H_2 / m^3 of reactor liquid volume / day at 1 V with a cathodic recovery percentage of 60%. The low performance of CEM b was due to biocathode formation process. During the sweep for the reversal of bioelectrodo polarity, current densities were 50 times lower than that reported in the literature. Therefore, CEM b produced low hydrogen compared with CEM Pt.

5. Acknowledgements

This work was performed in the Scientific Research Center of Yucatan , centre of excellence for sustainable energy research in the southern of Mexico, with the support of the CONACYT studentship No. 236006.

6. References

[1] C. Song. Overview of Hydrogen Production Options for Hydrogen Energy Development, Fuel-Cell Fuel Processing and Mitigation of CO_2 Emissions. in Proc. 20th International Pittsburgh Coal Conference, (2003).

[2] R. Rozendal; H. V. M. Hamelers; G. J. W. Euverink; S. J. Metz and C. J. N. Buisman, Principle and perspectives of hydrogen production through biocatalyzed electrolysis *International Journal of Hydrogen Energy* 1632-1640, (2006).

[3] U. Schröder, From Wastewater to Hydrogen: Biorefineries Based on Microbial Fuel-Cell Technology, *ChemSusChem*, 4, 281-282, (2008).

[4] 5. R. Rozendal; A. W. Jeremiasse; H. V. M. Hamelers and C. J. N. Buisman, Hydrogen production with a microbial biocathode, *Environ. Sci. Technol.*, 629-634, (2008).

[5] P. M. Vignais and A. Colbeau, Molecular biology of microbial hydrogenases, *Curr. Issues Mol. Biol.*, 2, 159-188, (2004).

[6] P. M. Vignais; J.-P. Magnin and J. C. Willison, Increasing biohydrogen production by metabolic engineering, *International Journal of Hydrogen Energy*, 11, 1478-1483, (2006).

[7] J. Ditzig; H. Liu and B. E. Logan, Production of hydrogen from domestic wastewater using a bioelectrochemically assisted microbial reactor (BEAMR), *Int. J. Hydrogen Energy*, 13, 2296-2304, (2007).

[8] K.-J. Chae; M.-J. Choi; J. Lee; F. F. Ajayi and I. S. Kim, Biohydrogen production via biocatalyzed electrolysis in acetate-fed bioelectrochemical cells and microbial community analysis, *International Journal of Hydrogen Energy*, 19, 5184-5192, (2008).

[9] S. Cheng and B. E. Logan, Sustainable and efficient biohydrogen production via electrohydrogenesis, *Proceedings of the National Academy of Sciences*, 47, 18871-18873, (2007).

[10] A. W. Jeremiasse; H. V. M. Hamelers and C. J. N. Buisman, Microbial electrolysis cell with a microbial biocathode, *Bioelectrochemistry*, 1, 39-43, (2010).

[11] L. Alzate; K. González; I. Peraza; O. García; J. Domínguez; J. Vázquez; M. Tzec and B. Canto, Evaluación del desempeño e identificación de exoelectrógenos en dos tipos de celdas de combustible microbianas con diferente configuración en el ánodo, *Interciencia*, 1, 19-25, (2010).

[12] H. Hu; Y. Fan and H. Liu, Hydrogen production using single-chamber membrane-free microbial electrolysis cells, *Water Research*, 15, 4172-4178, (2008).

[13] B. E. Logan, *Microbial Fuel Cells*. 1 ed. 2008: Wiley-Interscience. 216.

[14] D. F. Call and B. E. Logan, Hydrogen production in a single chamber Microbial Electrolysis Cell lacking a membrane, *Environ. Sci. Technol*, 9, 3401–3406, (2008).

[15] R. C. Wagner; J. M. Regan; S.-E. Oh; Y. Zuo and B. E. Logan, Hydrogen and methane production from swine wastewater using microbial electrolysis cells, *Water Research*, 5, 1480-1488, (2009).

[16] A. Wang; W. Liu; N. Ren; J. Zhou and S. Cheng, Key factors affecting microbial anode potential in a microbial electrolysis cell for H2 production, *International Journal of Hydrogen Energy*, 24, 13481-13487, (2010).

[17] P. Parameswaran; C. I. Torres; H.-S. Lee; B. E. Rittmann and R. Krajmalnik-Brown, Hydrogen consumption in microbial electrochemical systems (MXCs): The role of homo-acetogenic bacteria, *Bioresource Technology*, 1, 263-271, (2011).

[18] B. Tartakovsky; M. F. Manuel; H. Wang and S. R. Guiot, High rate membrane-less microbial electrolysis cell for continuous hydrogen production, *International Journal of Hydrogen Energy*, 2, 672-677, (2009).