Bioelectrochemical Organic Matter Conversion into Hydrogen, Comparison of Different Polarization Strategies

Valeria Pierpaoli, Beatrice Notari, Marco Zeppilli, Marianna Villano*

Department of Chemistry University of Rome Sapienza, Piazzale Aldo Moro 5 00185 Rome
marco.zeppilli@uniroma1.it

Hydrogen plays a pivotal role in the decarbonization of the fuel industry as both an energy vector and a chemical, however most of the available technologies still heavily rely on fossil fuels and sustainable processes are still unused due to their higher operational costs. MECs are devices based on the utilization of electroactive microorganisms that can interact with polarized electrodes (usually graphite-based), using them as the final electron acceptor for their metabolism. The use of a bioanode capable of oxidizing the organic substances contained in wastewater makes it possible to utilize part of the chemical energy present in the reduced waste compounds for the generation of green hydrogen, reducing the required (theoretical) potential by 85% compared to conventional electrolysis (+1.23 V vs +0.187 V). This study aims to compare two different polarization strategies of a microbial electrolysis cell aimed at hydrogen production coupled with the oxidation of synthetic wastewater. The study clearly showed the advantage of using potentiostatic polarization over galvanostatic polarization due to lower energy consumption during the potentiostatic polarization mode. Indeed, galvanostatic polarization promoted the loss of biological activity due to kinetic limitations in the biological reactions. Consequently, water oxidation on graphite granules occurred in the anodic chamber, increasing the anodic potential up to 0.95 V vs. SHE.

1. Introduction

The energy source sector, propelled by climate change, has undergone a deep transformation in the recent years. While most of the energy supply still comes from fossil fuels and countries are still investing in more traditional energetic vessels, the annual clean energy investment has risen much faster than investment in fossil fuels (Gao et al., 2017). The European New Deal has recognized the role of hydrogen as a priority in reaching carbon neutrality goal set for 2050 through both the decarbonization of the hydrogen producing sector and its usage as energy carrier. Global hydrogen production stands at around 75 MtH_2/yr as pure hydrogen and an additional 45 MtH_2/yr as part of a mix of gases (Koroneos et al., 2004), however most of the production process still heavily rely on fossil fuels, with only an unaccountable percentage of green hydrogen produced every year (Holladay et al., 2009). In Europe alone the conventional production methods of reforming, partial oxidation, gasification, by-product production from refining operations, and by-product production from ethylene and styrene represent 95.7% of total production capacity. Hydrogen is classified by color accordingly to its production methods and their environmental impact, however only green hydrogen, obtained through water electrolysis using electricity from renewable sources, is considered to be the only truly carbon neutral one. Green hydrogen accounts for a small percentage of overall hydrogen production because of the numerous variables implied in its production such as cost of electricity and electrolyzer efficiency, which affect its operational cost: an alkaline electrolyzer operates with an average energy supply 4.5 kWh/Nm^3H_2 produced. An attractive alternative is offered by bioelectrochemical systems, a bio-based approach that relies on some microorganisms' groups ability to exchange electrons on polarized surface, using electrodes as final electron acceptors for their metabolism.

Particularly, Microbial Electrolysis Cells (MEC) have been long been described as an effective technology for both hydrogen production and wastewater treatment (Logan et al., 2008; Rabaey et al., 2009), Indeed, the possibility to use wastewater as a carbon source for the anodic chamber for partially sustain the energy demand of the process result extremely attractive for the wastewater and green energy sector (Cristiani et al., 2024; Rozendal et al., 2008). Considering only acetate as substrate, the oxidation potential required to oxidate carbon compounds is notably lower compared to the one used while oxidising water alone, using a lower working energy compared to a standard alkaline electrolyser. The thermodynamic cell voltage of an MEC is thus considerably reduced with respect to the + 1.23 V threshold of water electrolysis in standard conditions, indeed, considering the oxidation of a single substrate like acetate, the electromotive force of the cell results in + 0.187 V, an 85% lower value (Logan et al., 2006).

This study focuses on comparing different polarization strategies for a microbial electrolysis cell aimed at hydrogen production coupled with oxidation of synthetic wastewater. The polarization strategies include a potentiostatic mode, achieved by polarizing the anodic chamber with a potential of + 0.2 V vs SHE, meanwhile the galvanostatic operational mode was achieved applying a fixed current of 113 mA between the working electrode and the counterelectrode, anode and cathode respectively.

2. Experimentals

2.1 Methods

The microbial electrolysis cell (MEC) consisted of a two-chamber reactor made of Plexiglas, as previously described (Cristiani et al., 2024). The anodic chamber was filled with graphite granules while in the cathodic chamber, a stainless steel plate inserted in a polypropylene packing bed. Anodic and cathodic chamber were separated by a Nafion proton exchange membrane (PEM). The anodic chamber was inoculated with 0.20 L of activated sludge from the wastewater treatment plant of Roma Nord, while cathodic chamber was not inoculated and filled with a mineral medium as described in (Zeppilli et al., 2016). The anodic chamber was continuously fed by a mixture of organic substrates (peptone, yeast extract, glucose, acetate, in order to simulate the soluble COD in an urban wastewater) at an organic load rate (OLR) of 1508 mgCOD/Ld and at a hydraulic retention time (HRT) of 0.56 d. The cathodic chamber was operated in a batch mode with continuous recirculation of the liquid phase; however, a daily spill of cathodic liquid was necessary to counterbalance the liquid diffusing from the anode to the cathode through the PEM. The MEC was operated both in a potentiostatic mode and in a galvanostatic mode. The potentiostatic mode was operated using a three-electrode configuration, where the anode constituted the working electrode while the cathode was the counter electrode (Zeppilli et al., 2021). During the potentiostatic operation, the anode potential was set at +0.2 V vs SHE (standard hydrogen electrode) by using a Ivium-N-stat potentiostat and an Ag/AgCl reference electrode. The galvanostatic mode was set using a fixed current of 113 mA and continuously monitoring the potential difference between the working electrode and the counter electrode. Liquid and gaseous samples of outflows from both anodic and cathodic chambers were daily analyzed in order to assess the MEC performance.

2.2 Analytics

H_2 was analysed by injecting 50µLof headspace sample into a Dani Master GC (Milan, Italy) gas chromatograph equipped with a thermal conductivity detector (TCD). Chemical oxygen demand (COD) was assessed by using commercial test (Nanocolor ® COD Cell Test, Supelco®) and a UV-visible spectrophotometer (Nanocolor). Ammonium nitrogen was analyzed by Nessler colorimetric method according to standards method (Apha, 1995).

2.3 Calculations

The efficiency of electrodic processes was assessed by calculating the Coulombic efficiency (CE, i.e. the ratio of electron equivalents coming from anodic oxidation of COD that are converted into current), the cathode capture efficiency (CCE, i.e. the ratio of electron equivalents that are used to reduce H^+ to H_2) (Villano et al., 2013). Energetic efficiency (, i.e. the ratio between the energy generated from hydrogen combustion anth the electric energy supplied to the the MEC as expressed as electric). Energy balance was used to assess the energy efficiency, i.e. the ratio between the electrical energy used to run the MEC and the energy content of produced hydrogen (Badia-Fabregat et al., 2019).

3. Results and discussion

3.1 Anode performance under potentiostatic and galvanostatic conditions

The potentiostatic operating period, the feeding solution with an average concentration of 1.09 ± 0.23 gCOD/L was fed at a 1.53 L/d in the anodic chamber of the MEC (Figure 1-A). The corresponding applied organic load rate resulted of 1.9 gCOD/Ld. During the 12 days of potentiostatic operation and an outlet concentration of 0.55 gCOD/L was registered. This resulted in an abatement of 0.90 gCOD/Ld. The COD removal efficiency was found to be 55 ± 2 % (Table 1), while the coulombic efficiency was 50 ± 4%, with a current output of 64 ±3 mA. On the other hand, during the galvanostatic operational period, the anodic chamber was fed with an average flow rate of 1.67 ± 0.11 L/d, the influent COD average concentration resulted 1.19 ± 0.21 gCOD/L (Figure 1-B). During the galvanostatic operation, an average COD concentration of 1.14 gCOD/L was measured in the effluent, corresponding to an abatement of 0.55 gCOD/Ld and a COD removal efficiency of 33 ± 6 %. The set of the galvanostatic condition promoted a significative decrease in anodic biofilm performances, caused by the increase of the anodic potential to +1.53 ± 0.06 V vs SHE, indicating the loss of the biological reaction in the anodic chamber. For the potentiostatic condition, on the other hand, the pH of the anode was 6.6 for the influent and 6.4 for the effluent. During the galvanostatic mode, the pH of the anolyte was found to be of 3.8, while the pH of the feeding solution was 6.5.

Table 1: Summary of the bioanode performances during the potentiostatic and galvanostatic MEC operation

	Potentiostatic	Galvanostatic
COD removal (gCOD/Ld)	0.90 ± 0.11	0.55 ± 0.21
COD removal efficiency (%)	55 ± 2	33 ± 6
Average current (mA)	64 ± 3	113 ± 1
CE (%)	50 ± 4	17 ± 7

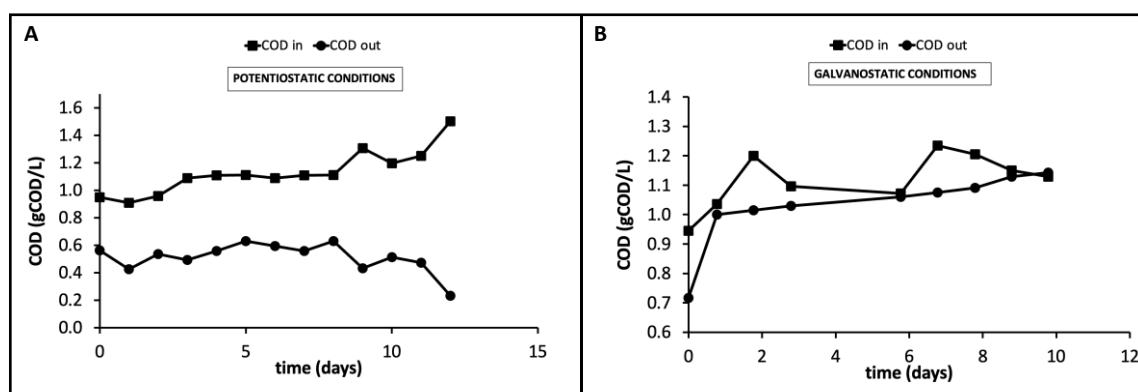*Figure 1. Influent and effluent COD concentration in the anodic chamber during the potentiostatic (A) and galvanostatic (B) operation of the MEC*

3.2 Cathode performance under potentiostatic and galvanostatic conditions

The electrons produced by COD anodic oxidation were transferred to the cathodic chamber in which the hydrogen production occurred on the stainless-steel electrode. Besides the hydrogen production rate, coulombic efficiency for the cathodic reaction was evaluated to assess the fraction of electrons recovered as hydrogen at the cathode. Under potentiostatic condition, in which the anode chamber was the working electrode of the cell, the cathodic performance was directly correlated to the anodic one, i.e. to the ability of the microorganisms at the anode to oxidize the organic matter and thus provide electrons that the cathode. During the potentiostatic conditions, the hydrogen production rate (represented by the slope of the cumulative hydrogen curve) reached an average value of 22 ± meq/d (Figure 2-A) corresponding to 13 mmol/Ld. The cathodic capture efficiency resulted on average 38 ± 8%. Interestingly hydrogen concentration in the cathodic effluent gas increase from 20 to 95 % in almost 6 days. During the potentiostatic conditions, the recorded pH was 12.4±0.2 and had a regular trend: this is a basic- enough value to give the inhibition of the biological pathways of any microorganism in the reactor; it also explains the low organic carbonic value.

Shifting to galvanostatic reactor operation, at a fixed current of 113 mA, an initial lag phase until day 6 was recorded in which a volumetric hydrogen concentration around 0.4 ± 0.2% was recorded. Corresponding to day 6 a sharp increase in hydrogen cumulative production was observed, giving a slightly higher hydrogen production rate of 28 ± 8 meq/d (Figure 2-B) which in any case corresponded to a volumetric concentration of hydrogen around 1.5 %. The resulting cathodic coulombic efficiency observed during the galvanostatic operation was 17 ± 7% (Table 2). During the galvanostatic operation a slightly alkaline pH, i.e. 7.9 ± 0.1 was observed in the cathodic.
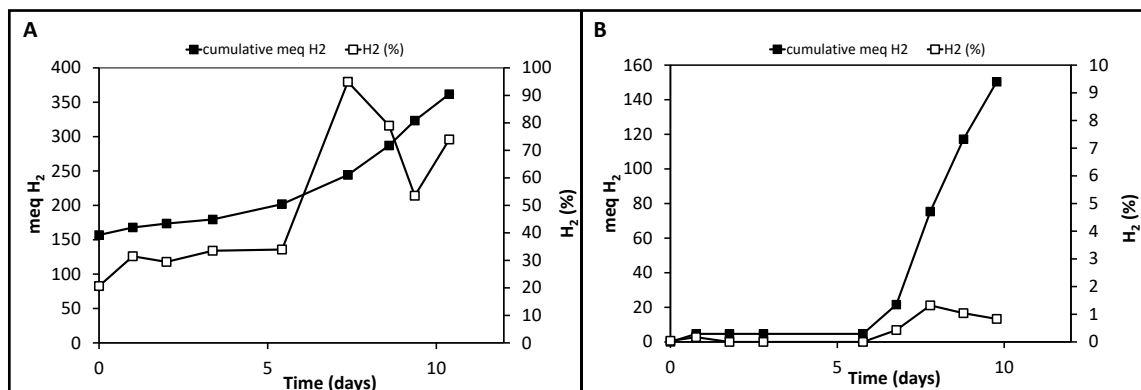

Figure 2. Cumulative hydrogen production and hydrogen volumetric concentration in the outlet of the cathodic chamber during the potentiostatic (A) and galvanostatic (B) operation of the MEC

Table 2: Summary of the cathodic performances during the potentiostatic and galvanostatic MEC operation

	Potentiostatic	Galvanostatic
rH_2 *(meq/d)*	22 ± 8	28 ± 8
CCE (%)	38 ± 8	27±7

3.3 Electrochemical potentials and energy consumption of the process

Under the first potentiostatic condition, the anode potential (i.e. working electrode) was controlled at + 0.21 V vs SHE, during the steady state operation of the MEC, cathodic chamber (i.e. counter electrode) potential resulted on average at -1.15 ± 0.02 V vs SHE while the cell voltage applied resulted on average at -1.56 ± 0.05 V (Figure 3-A). After the shift to galvanostatic condition, with the current controlled at +113 mA, the anodic potential (Figure 3-B) immediately increased to +1.53 ± 0.06 V vs SHE, indicating the establishment of the water oxidation reaction. The explanation of the potential increase relied on the establishment of a kinetic limitation of the anodic reaction, i.e. the bioanode was not sufficient to provide electrons for the new galvanostatic condition, for this reason, the potential increased until reaching a new available oxidation reaction to sustain the imposed condition. The cathodic chamber potential, as showed in Figure 3-B did not change significantly, showing an average value of -1.05 ± 0.03 V vs SHE. As a consequence, the cell voltage applied to the MEC increased to an average value of - 3.03 ± 0.05 V (Table 3).

Table 3: Summary of the cathodic performances during the potentiostatic and galvanostatic MEC operation

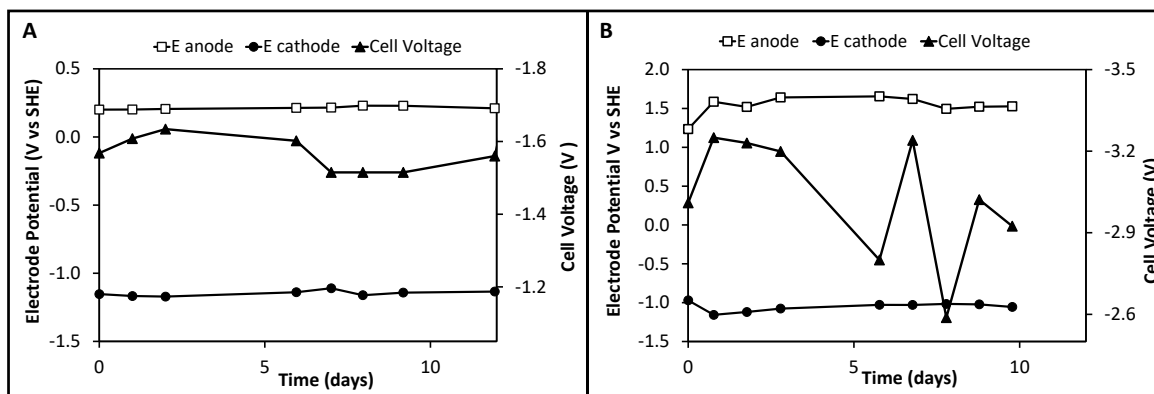|	Potentiostatic	Galvanostatic
Anode potential (V vs SHE)	+ 0.21	+ 1.53 ± 0.06
Cathode potential (V vs SHE)	-1.15 ± 0.02	-1.05 ± 0.03
Cell Voltage (V)	-1.56 ± 0.05	- 3.03 ± 0.05
Hydrogen production (kWh/Nm^{3}H$_2$)	9 ± 1	49 ± 5
COD removal (kWh/kgCOD$_{removed}$)	2.3 ± 0.5	66.7 ± 0.8

Figure 3. Electrochemical electrode potential and cell voltage time course during the potentiostatic (A) and galvanostatic (B) operation of the MEC

During the potentiostatic conditions operation, the MEC showed an energy efficiency (i.e. the ratio between the energy recovered as hydrogen and the energy applied) of 35%, moreover, the specific energy consumption for hydrogen production reached 9 ± 1 kWh/Nm^3 of hydrogen produced, while the cost for the removal of COD resulted 2.3 kWh/kgCOD$_{removed}$. Due to the increase in cell voltage after the loss of the biological COD oxidation, the specific energy consumption for hydrogen production increased to 49 ± 5 kWh/Nm^3 H$_2$, showing the effectiveness of the bioanode approach for green hydrogen production. Indeed, despite the actual cost of hydrogen production through alkaline electrolyzer results 5 kWh/Nm^{3}H$_2$ (Son et al., 2021), the MEC approach for the generation of green hydrogen resulted attractive.

4. Conclusions

In this work, a continuous experimental work was conducted on a microbial electrolysis cell capable of converting organic matter into hydrogen. Under potentiostatic conditions, a COD removal efficiency of 55% was obtained, with a removal rate of 0.90 gCOD/Ld. The obtained current had an average value of $64 \pm$ mA, resulting in a coulombic efficiency of 50 ±%. After the shift the into galvanostatic condition, the kinetic limitations present in the anodic biofilm promote the increase of the anodic potential to $+ 1.53 \pm 0.06$ V and a potential difference of $- 3.03 \pm 0.05$ V. Concerning energy consumption, the benefit of using the microbial electrolysis cell under potentiostatic conditions becomes even clearer since under galvanostatic conditions there is a consumption of hydrogen more than 5 times higher (49 kWh/Nm^3 vs 9 kWh/Nm^3). All these collected data showed clearly the advantage in the use a MEC under potentiostatic conditions to preserve biological activity of the anodic biofilm which is responsible for the organic matter oxidation and conversion into hydrogen. Moreover, as already described previously (Zeppilli et al., 2019), the potentiostatic condition at the anode set the potential level of the electron acceptor, i.e. the graphite granules, preserving the biological activity in the anodic chamber, on the contrary different strategies like shifting the potentiostatic conditions from the anode to the cathode could be considered in the energetic optimization of the process.

Reference

Apha, Standard methods for the examination of water and wastewater. American public health association, Washington DC, 1995.

Badia-Fabregat, M., et al., 2019. Hydrogen production from crude glycerol in an alkaline microbial electrolysis cell. International Journal of Hydrogen Energy. 44, 17204-17213.

Cristiani, L., et al., 2024. Enhancing energy efficiency and H2 production in lab-scale dual chamber microbial electrolysis cells: A focus on catholyte composition and voltage losses. Journal of Environmental Chemical Engineering. 12, 111782.

222

Gao, Y., et al., 2017. The 2 °C Global Temperature Target and the Evolution of the Long-Term Goal of Addressing Climate Change—From the United Nations Framework Convention on Climate Change to the Paris Agreement. Engineering. 3, 272-278.

Holladay, J. D., et al., 2009. An overview of hydrogen production technologies. Catalysis Today. 139, 244-260.

Koroneos, C., et al., 2004. Life cycle assessment of hydrogen fuel production processes. International Journal of Hydrogen Energy. 29, 1443-1450.

Logan, B. E., et al., 2008. Microbial electrolysis cells for high yield hydrogen gas production from organic matter. Environ Sci Technol. 42, 8630-40.

Logan, B. E., et al., 2006. Microbial fuel cells: methodology and technology. Environ Sci Technol. 40, 5181-92.

Rabaey, K., et al., 2009. Bioelectrochemical systems: from extracellular electron transfer to biotechnological application. Water Intelligence Online. 8, 9781780401621.

Rozendal, R. A., et al., 2008. Towards practical implementation of bioelectrochemical wastewater treatment. Trends in Biotechnology. 26, 450-459.

Son, S., et al., 2021. Comparison of hydrogen production and system performance in a microbial electrolysis cell containing cathodes made of non-platinum catalysts and binders. Journal of Water Process Engineering. 40, 101844.

Villano, M., et al., 2013. Carbon and nitrogen removal and enhanced methane production in a microbial electrolysis cell. Bioresource Technology. 130, 366-371.

Zeppilli, M., et al., Reduction of carbon dioxide into acetate in a fully biological microbial electrolysis cell. Chemical Engineering Transactions, Vol. 49, 2016, pp. 445-450.

Zeppilli, M., et al., 2021. Potentiostatic vs galvanostatic operation of a Microbial Electrolysis Cell for ammonium recovery and biogas upgrading. Biochemical Engineering Journal. 167, 107886.

Zeppilli, M., et al., 2019. Anodic vs cathodic potentiostatic control of a methane producing microbial electrolysis cell aimed at biogas upgrading. Biochemical Engineering Journal. 152, 107393.