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Carbon Dioxide Abatement and Biofilm Growth in MEC Equipped With a Packed Bed Adsorption Column

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In this study, a lab-scale microbial electrolysis cell (MEC) aimed to the biogas upgrading through a methanogenic biocathode has been integrated with an adsorption column to test the possible increase of the biocathode CO_2 removal capacity. In the adopted MEC configuration, the oxidation of the organic matter by an anodic biofilm was utilized to partially sustain the energy demand of the bioelectromethanogenesis reaction in the cathodic chamber. Anodic and cathodic biofilms were characterized by cyclic voltammetry (CV) technique which allowed the electron transfer mechanisms characterization in the anodic and cathodic bioelectrochemical reactions. More in detail, while the anodic biofilm showed the presence of a potential direct electron transfer, the cathodic CV suggests a hydrogen mediated mechanism for the CO_2 reduction into CH_4. The integration of a sorption column and the MEC biocathode showed a negligible effect in the overall biocathode CO_2 removal, suggesting the control of the CO_2 sorption by a chemical reaction through the alkalinity generation mechanism instead of the gas-liquid mass transfer.

1. Introduction

Biogas, the main product of the anaerobic digestion (AD) process, is a gas mixture mainly composed by carbon dioxide and methane. To obtain biomethane, with a high percentage of methane (>95%), is necessary a purification step to remove the impurities such as NH_3, H_2S, and an upgrade step to increase CH_4 percentage by removing the CO_2 (Angelidaki et al., 2018). The characteristics of the biomethane are similar to those of the compressed natural gas and it may find applications as a vehicle fuel or injected in the distribution grid (Andriani et al., 2014; Bauer et al., 2013). The standard upgrading systems are based on physiochemical procedures, which exploit the higher solubility of CO_2 compared to CH_4 solubility into water or organic solvents (Ryckebosch et al., 2011). However, these technologies often require high cost, along with the evaluation of several conditions, such as the biogas composition and its quality, the energy uptake, the recovery of the CO_2 and the compatibility with existing equipment (Sarker et al., 2018). An innovative strategy for biogas upgrading consists in the utilization of a microbial electrolysis cell (MEC) in which the reduction of carbon dioxide to methane is performed by the bioelectromethanogenesis reaction (Zeppilli et al., 2020b). The bioelectromethanogenesis reaction consists in the use of a biocathode to supply the reducing power to a methanogenic biofilm growing on the electrode surface (Cheng & Logan, 2013). The bioelectromethanogenesis reaction proceeds by means of two different limit mechanisms for the CO_2 reduction: the direct electron uptake from the electrode or the hydrogen mediated mechanism, in which hydrogen is produced via abiotic proton reduction and then consumed by the methanogenic microorganisms present on the electrode surface (Villano et al., 2010). Moreover, in a MEC biocathode an additional CO_2 removal mechanism consists in the CO_2 sorption as HCO_3^- in the catholyte due to the generated alkalinity. Alkalinity is generated by the migration of other species than protons or hydroxyls through the membrane. CO_2 sorption results the main removal mechanism responsible for the removal of the 90 % of the overall CO_2 (Zeppilli et al., 2016b). In a biocathode, the CO_2 sorption can be driven by the chemical reaction between a hydroxyl ion and a CO_2 molecule, or it can be affected by the surface area available for the mass transfer from the gas to the liquid phase. In this study, the use of a fully biological MEC to study the CO_2 removal by a biocathode has been evaluated with the introduction of a sorption column which allows for the maximization of

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the surface area available for the gas – liquid mass transfer. Finally, the cyclic voltammetry potentiodynamic technique has been adopted for the anodic and cathodic electron transfer mechanism characterization.

2. Material and methods

2.1 Microbial Electrolysis Cell operation

The Microbial Electrolysis Cell (MEC) consists in a two chamber MEC with a filter press configuration already described in a previous experiment (Zeppilli et al., 2015). During the entire study, the MEC was operated by a three-electrode configuration by using an anodic potential of +0.200 V vs SHE (Standard Hydrogen Electrode). The anodic chamber, in which the organic matter was oxidized by electroactive microorganisms, received a continuous flow of a synthetic feeding solution (Zeppilli et al., 2016a) with an average flow rate of 1.84 L/d corresponding to an HRT of 0.47 d. During the MEC operation without the sorption column, the cathodic chamber electrolyte (i.e. the catholyte) was continuously recirculated in the cathodic chamber while the N_2/CO_2 gas flow was directly inserted in the cathodic chamber. The sorption column consists in a plastic tube of 5,1 cm of diameter with a length 84 cm giving an empty volume of 1715 cm^3. The column was filled with a plastic packing material which allow for a porosity of 0.51. The sorption column was flushed from the bottom with the N_2/CO_2 gas mixture simulating the CO_2 content of a biogas while the catholyte was continuously recirculated with a counter-current flow configuration from the top to the bottom of the column. A gas counter allowed for the determination of the outlet gas flow rate while two gas sampling ports permitted the characterization of the gaseous stream. During the sorption column operation, the catholyte did not complete flood the sorption column according to the maximization of the contact area between gas and liquid phase and a daily spill was necessary to counterbalance the electroosmotic diffusion of water from the anodic to the cathodic chamber. To prevent the autotrophic microalgae growth, the sorption column has been covered to prevent external light diffusion.

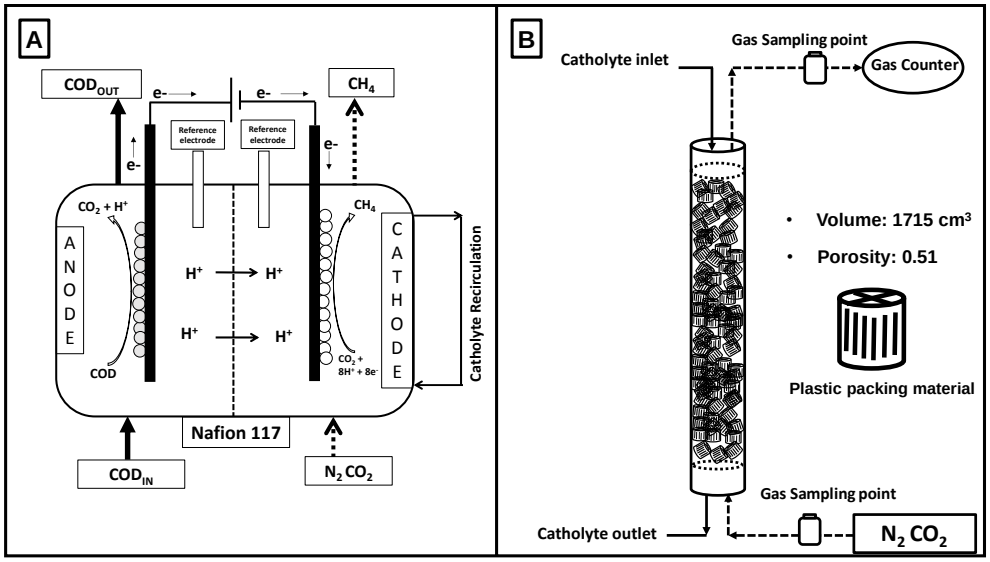

Figure 1: Schematic representation of the continuous flow Microbial Electrolysis Cell (MEC) (A) and schematic view of the sorption column with the detailed representation of the packing material (B)

2.2 Cyclic Voltammetry

Cyclic voltammetry (CV) was applied at the anode and cathode chamber by a SP300 BioLogic Potentiostat, the anodic CV was applied between +0.5 to -0.2 V vs SHE while the cathodic CV range was -0.3 to -1.2 V vs SHE. Both anodic and cathodic CVs were replicated three times at 60 – 40 -20 - 5 mV/min scan rate. The CVs conducted in presence of substrate (turnover conditions) were conducted with the anodic chamber continuously fed by the organic substrate feeding solution while the CV in absence (non-turnover condition) of substrate have been conducted with the same mineral medium without any organic substrate.

2.3 Analytical methods and calculations

Analytical methods for COD, CH_4, H_2, CO_2, and HCO_3^- determination has been already described in (Zeppilli et al., 2017b; Zeppilli et al., 2019b). Main calculation related to the anodic and cathodic bioelectrochemical

reactions are summarized in Table 1, a more detailed calculation description has been also reported in (Zeppilli et al., 2020a; Zeppilli et al., 2017a).

Table 1. Main parameters calculations

COD removal (mgCOD/d)	$COD_{removed} = F_{in} * COD_{in} - F_{out} * COD_{out}$
- **COD_{in}** and **COD_{out}** (mg/L)*:* influent and effluent COD concentrations - **F_{in}** and **F_{out} (L/d)**: influent and effluent flow rates in the anodic chamber	
Coulombic Efficiency, CE (%)	$CE = \frac{meq_i}{meq_{COD}}$
- **meq_i**: cumulative electric charge - **meq_{COD}**: cumulative equivalents from COD oxidation	
CH_4 and H_2 production rate ($rCH_{4(eq)}$ $rH_{2(eq)}$)	- $rCH_{4(mmol)} = \frac{mmol_{CH4}}{d} * 8 = \frac{meq_{CH4}}{d}$ - $rH_{2(mmol)} = \frac{mmol_{H2}}{d} * 2 = \frac{meq_{H2}}{d}$
- **$rCH_{4(mmol)}$ $rH_{2(mmol)}$** (mmol/d): daily moles of methane or hydrogen produced - **8 meq/mmol$_{CH4}$ 2 meq/mmol$_{H2}$** conversion factor	
Cathode Capture Efficiency, CCE (%)	- $CCE_{CH4} = \frac{meq_{CH4}}{meq_i}$ $CCE_{H2} = \frac{meq_{H2}}{meq_i}$
- **meq_{CH4}**: cumulative equivalents of produced methane or hydrogen - **meq_i**: cumulative electric charge	
CO_2 removal (mmol/d)	$\Delta CO_2 = Qcat_{in} * CO_{2\,in} - Qcat_{out} * CO_{2\,out}$
- **$Qcat_{in}$** and **$Qcat_{out}$ (L/d):** influent and effluent gas flow rate in and from the cathode chamber - **CO_{2in} and CO_{2out} (mmol/L):** CO_2 concentration in the influent and effluent gaseous streams	
HCO_3^- cathode (mmol/d)	$HCO_{3\,(cathode)}^- = F_{cathode} * HCO_3^-\,cathode$
- **$F_{cathode}$ (L/d):** flow rate of the catholyte daily spill - **HCO_3^- cathode (mmol/L):** $CHCO_3^-$ concentration in the catholyte	

3. Results and discussion

3.1 Characterization of the anodic and cathodic biofilm through Cyclic Voltammetry technique

The characterization of the anodic and cathodic biofilm through the cyclic voltammetry (CV) techniques has been performed after a long startup of the MEC which has been already described in the literature (Zeppilli et al., 2019a). Figure 2 reports the CVs of the anodic chamber conducted under turn over (presence of substrate) vs the CVs under non turnover conditions (absence of substrate) at the selected scan rates. The CVs showed a clear effect of the presence of substrate, which enabled the current generation through the organic substrate oxidation. In the CVs conducted in presence of substrate, the scan rate decrease promoted the shift of the maximum peak to less oxidative potentials, i.e. figure 2- B-C-D clearly showed the maximum peak of current at +0.2 V vs SHE (40 mV/min), +0.12 V vs SHE (20 mV/min) and +0.05 V vs SHE (5 mV/min). The decrease of the potential corresponding to the current peak was probably caused by the minimization of the capacitive current (which results from electrode charging) obtained using lower scan rates, which probably enabled the better identification of the faradic processes (i.e., the oxidation of substrates into current). Moreover, the CVs shapes indicates the non-reversibility of the anodic reaction due to the presence of the oxidation peak related to organic substrates oxidation. This, along with the CV profiles obtained under non turnover conditions, strongly suggests the presence of an electroactive biofilm on the surface of the bioanode.
On the contrary, as reported in figure 3, the cathodic CVs showed a different behavior with respect the anodic CVs, in which the absence of reduction peaks and the asymptotic trend, suggested the proximity of a limit current which indicates the predominance of mass transport limitations of the substrate. The condition described by the cyclic voltammetry of the cathode clearly shows a typical situation of the reduction of the proton in an aqueous media, which suggest a hydrogen mediated mechanism for the CO_2 reduction into CH_4.

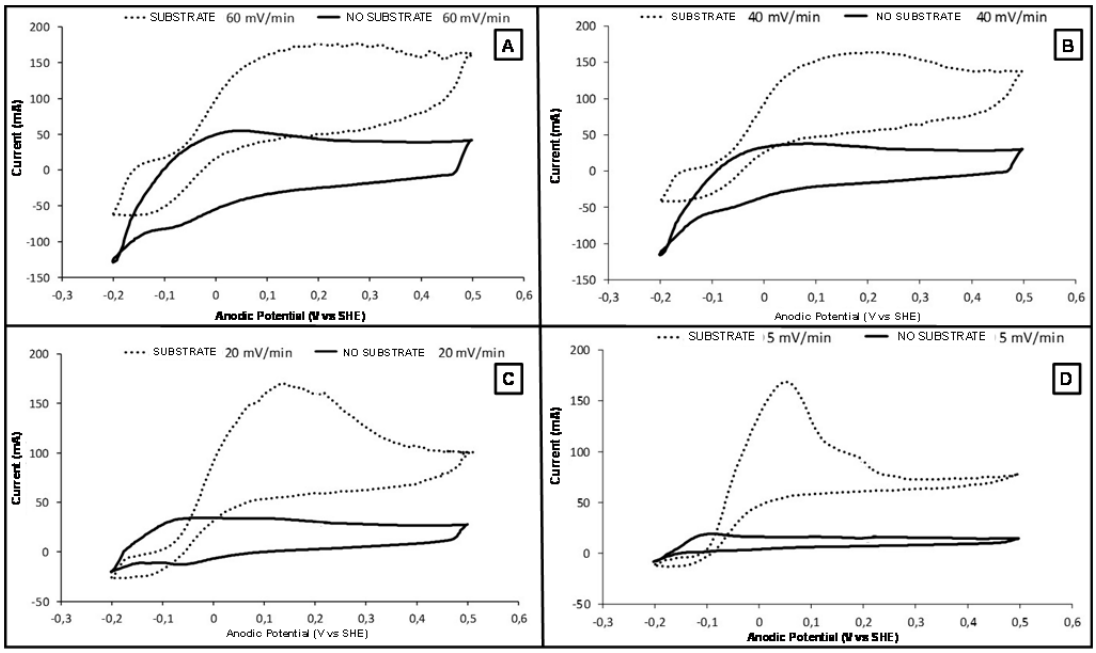

Figure 2: Cyclic Voltammetry of the anodic chamber conducted in presence (black dots) and in absence of substrate (black line) at 60 mV/min (A) 40 mV/min (B) 20 mV/min (C) and 5 mV/min (D)

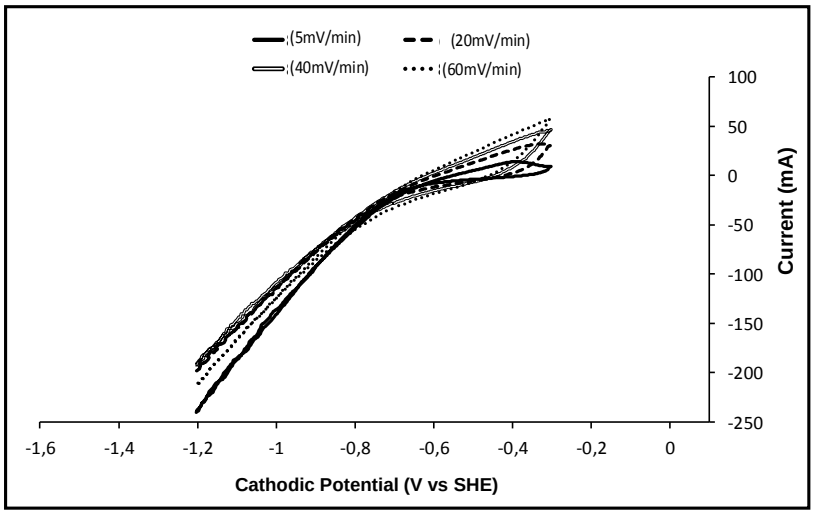

Figure 3: Cyclic Voltammetry of the cathodic chamber conducted at the different scan rates

3.2 Potentiostatic run at +0.20 V vs SHE

During the two operating conditions, the MEC bioanode continuously received the feeding solution with an average flow rate of 1.84 L/d and it was polarized at +0.20 V vs SHE. Each operating condition has been maintained for approximately 30 days which corresponded to 64 HRT. The COD removal and the consequent current generation in the anodic chamber resulted similar in the two investigated periods, as reported in Table 2. The coulombic efficiency for the anodic reaction resulted 59 ± 3 and 78 ± 9 % during the operation of the MEC without and with the sorption column, respectively. As expected, the insertion of the sorption column did not affect the anodic bioelectrochemical reaction.

Table 2: Bioelectrochemical performance of the anodic biofilm during the two operating periods

Sorption column	Current (mA)	COD removal (mgCOD/d)	Coulombic Efficiency (%)
NO	67 ± 6	0.61 ± 0.08	59 ± 3
YES	59 ± 7	0.71 ± 0.11	78 ± 9

Regarding the main cathodic products, hydrogen and methane were the two reduced species detected in the outlet of the cathodic chamber (during the operation without sorption column) or in the outlet of the sorption column. As reported in table 3, also cathodic performances of the MEC resulted almost the same during the operation with and without the sorption column. The cathodic performances, resulted in an overall cathode capture efficiency of 42 ± 3 and 59 ± 6 % of the average current was diverted into hydrogen and methane, a quite low efficiency with respect the anodic chamber.

Table 3 Bioelectrochemical performance of the cathodic biofilm during the two operating periods

Sorption column	rH_2 (meq/d)	rCH_4 (meq/d)	Cathodic Capture Efficiency (%)
NO	10 ± 1	15 ± 3	42 ± 3
YES	12 ± 3	19 ± 5	59 ± 6

3.3 CO_2 removal and inorganic carbon balance

The CO_2 removal obtained during the two operating periods resulted similar with an average CO_2 removal of 110 ± 9 and 118 ± 12 mmol/d, showing a negligible effect of the sorption column insertion. In figure 4-A, the average HCO_3^- concentration in the anode and cathode chamber clearly showed the CO_2 sorption into HCO_3^- due to the alkalinity generation in the cathodic chamber (Zeppilli et al., 2016b).

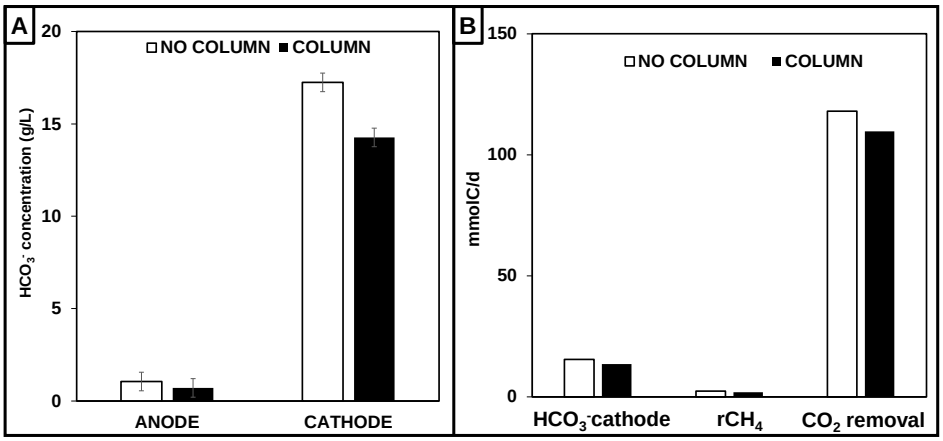

Figure 4: Schematic representation of the continuous flow Microbial Electrolysis Cell (MEC) (A) and schematic view of the sorption column with the detailed representation of the packing material (B)

Figure 4-B reports the inorganic carbon mass balance, according to the literature (Zeppilli et al., 2016b), the CO_2 reduction into CH_4 accounted for a small percentage of the overall CO_2 removal, (less than 2% in both the operating periods), while the HCO_3^- daily spilled from the cathodic chamber accounted for about 10% of the overall CO_2 removal. By the analysis of the identified CO_2 removal mechanisms, only the 14 % of the overall CO_2 removal resulted characterized, indicating the presence of other removal mechanisms. A possible important contribution to the overall CO_2 removal could be offered by the possible presence of high concentration of bivalent ions like calcium and magnesium which promoted the formation of insoluble carbonate salts (Cristiani et al., 2020).

Table 4 CO_2 removal mechanisms in the two different operating periods

Sorption column	CO_2 removal (mmol/d)	rCH_4 (mmol/d)	HCO_3^- Cathode (mmol/d)
NO	110 ± 9	2 ± 1	14 ± 3
YES	118 ± 12	2 ± 1	15 ± 4

4. Conclusions

The characterization of the bioelectrochemical interphases, i.e., the anodic and cathodic chamber, by the CV technique allowed for the description of the electron transfer mechanisms involved in the MEC. The anodic chamber CVs showed the dependence of the current production by the presence of organic substrates which are probably oxidized by a direct electron transfer mechanism between the electroactive biofilm and the electrodic material. On the contrary, the CVs applied to the cathodic chamber suggested the presence of a hydrogen mediated mechanisms of CO_2 reduction, due to the absence of reduction peaks and to the tendency of an asymptotic limiting current that indicates the proton reduction reaction in an aqueous media. Moreover, the integration of a sorption column and a biocathode for the CO_2 removal did not increase the average CO_2 removal of the process. The latter experimental results suggest the predominance of a CO_2 sorption mechanism controlled by the chemical reaction (alkalinity production in the cathodic chamber) instead of a mass transfer limitation between the gas liquid interphases.

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