Bioelectromethanogenesis reaction in a tubular Microbial Electrolysis Cell (MEC) for biogas upgrading

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Abstract

The utilisation of bioelectrochemical systems offers an innovative biogas upgrading approach through the CO_2 biological methanization in the biocathode of a Microbial Electrolysis Cell (MEC). The bioelectromethanogenesis reaction permits the reduction of the CO_2 into CH_4 by using a polarized electrode (i.e. the cathode) as electrons donor for the methanogenic microorganisms. In this study, a biogas upgrading system has been developed by using a MEC in which the bioelectromethanogenesis reaction occurred in the biocathode converting the CO_2 into CH_4, while the electroactive oxidation of the organic matter occurred in the bioanode partially sustain the energy demand of the process. A tubular MEC configuration has been developed by using a tubular anion exchange membrane (AEM) and graphite granules as electrodic material, the tubular MEC has been tested under laboratory condition with synthetic substrates (i.e. synthetic wastewater and synthetic biogas) showing the capability of COD removal, CH_4 production and CO_2 removal. Two different polarization strategies of the tubular MEC have been explored, i.e. the conventional three-electrode configuration, in which a reference electrode is utilized to control the potential of the working electrode, and a two-electrode configuration in which a fixed potential difference is applied between the anode and the cathode. The tubular MEC showed interestingly performances regarding the COD and CO_2 removal during the +0.2 V vs SHE condition with an energy consumption of 0.47 kWh/kgCOD and 0.39 kWh/Nm^3 of CO_2 removed, resulting in lower energy consumption with respect the available technologies on the market.

1.Introduction

A potential innovative route for the biological CO_2 methanization[1], i.e. the conversion of CO_2 into CH_4, involved the utilization of bioelectrochemical systems (BES) in which the microorganism's metabolism is controlled through an electrochemical device[2]. The microbial metabolism control is based on the electron exchange between a microorganism and an electrode by the extracellular electron transfer mechanism (EET)[3]. The electrochemical interface constituted by the electrode and the microorganisms can be named bioelectrode; if the electrodic material act as electron acceptor, the interface is called bioanode while in the case of an electrodic material working as electron donor, the interface is defined a biocathode[4]. Several environmental applications of BES are recently reported in the literature like the electricity production from wastewater[5], the removal of toxic and persistent contaminants in the groundwater [6]and the biological production of hydrogen[7], methane[8]. The bioelectromethanogenesis reaction involved the utilization of a biocathode in which the electroactive microorganisms are capable to reduce the CO_2 into CH_4 by using an electrode as electron donor[9]. The potential application of the bioelectromethanogenesis reaction for the energy storage of electrical power [10] under CH_4 is currently receiving attentions in several research groups with the development of the Bioelectrochemical power to gas concept (BPtG)[11]. In the (BPtG) concept, the bioelectrochemical production of CH_4 can be adopted for the utilization of the electricity surplus production from renewable resources (i.e. photovoltaic or wind electricity)[12] to reduce the CO_2 into CH_4, which can be easily stored and distributed with the existing facilities. In this context the biogas upgrading process [13], i.e. the removal of the CO_2 from the biogas produce by the anaerobic digestion, results an interesting application of the bioelectrochemical reduction of the CO_2 into CH_4 due to the high percentage of CO_2 in the biogas [14]. Several authors proposed the utilization of a MEC for the biogas upgrading into biomethane with different configuration including in-situ approaches, i.e. the direct insertion of polarized electrodes in the anaerobic digestion reactor [15,16], or an ex-situ approach in which a post treatment of the liquid and gaseous effluents of the digester are separately treated in the MEC [17-19]. In addition to the CO_2 reduction, another CO_2 removal mechanism have been recently identified in the CO_2 sorption as HCO_3^- ion caused by the alkalinity generation the biocathode [20], more in details, the alkalinity generation in the biocathode is a direct consequence of the transport of ionic species different from protons and hydroxyls for the electroneutrality maintenance [21]. Even if the CO_2 sorption results the main CO_2 removal mechanisms, the CO_2 reduction into CH_4 along with the anodic reaction are necessary for the electrical current generation which in turn stimulate the ionic transport for the electroneutrality maintenance [22]. The CO_2 removal through the bioelectromethanogenesis reaction coupled with the anodic bioelectrochemical oxidation of the organic matter have been explored in bench scale reactors under several operating conditions including different substrates[23], different organic load rates [24]and different anodic potentials[25], here, in this study a first scale up system with a tubular geometry has been developed for the biogas upgrading through the bioelectromethanogenesis reaction coupled with the oxidation of COD in the anodic chamber. The tubular geometry of the MEC here proposed have been adopted to simulate a sorption column in which the alkalinity generation bioelectrochemically generated by the reactions, enhance the CO_2 sorption without the use of any additional chemicals. Two different polarization strategies have been adopted for the operation of the tubular MEC, i.e. a three-electrode configuration, in which the anodic potential is controlled using a reference electrode and a potentiostat, and a two-electrode configuration in which the potential difference between anode and cathode is fixed by the potentiostat. The reason of the utilization of a two-electrode configuration resulted by the fact that usually industrial electrochemical processes are conducted under fixed potential or fixed current using a power supplier, a simpler device instead of a potentiostat able to work with a three-electrode configuration.

2.Material and methods

2.1 Tubular MEC set up

The tubular MEC has been set-up using a plexiglass cylindric reactor of 12 L, the inner anodic chamber (3.14 L) was separated from the external cathodic chamber (8.86 L) by a tubular anion exchange membrane (Fumasep FAD-PEEK, FumatechGmbH). Both anodic and cathodic concentric chambers were filled with graphite granules giving by a bed porosity of 0.57; the anodic and cathodic compartment were equipped with a sampling-glass chamber for the liquid and the gas sample collection. The anodic chamber was inoculated using 1 L of activated sludge (10.5 gVSS/L) coming from a full-scale wastewater treatment plant, while the cathodic chamber was inoculated with 1 L of an anaerobic sludge (7.3 gVSS/L) coming from a thermophilic anaerobic digester. By using a peristaltic pump, the anode was continuously fed with a synthetic mixture of organic substrates with a flow rate of 6 L/d, resulting in a hydraulic retention time (HRT) of 12.6 h for the anodic chamber. The synthetic mixture was composed by: peptone (0.138 g/L), yeast extract (0.075 g/L), sodium acetate (0.088 g/L), glucose (0.34 g/L), NH_4Cl (0.125 g/L), $MgCl_2$ $6H_2O$ (0.1 g/L), K_2HPO_4 (4 g/L), $CaCl_2$ $2H_2O$ (0.05 g/L), 10 mL/L of a trace metal solution, and 1 mL/L of a vitamin solution.. The cathodic chamber was fed continuously with a gas mixture composed of CO_2 at 30% and N_2 at 70% to simulate a biogas. A digital barometer was used to determine the operating pressures at which the samples were analysed. In the cathodic compartment, the liquid phase was continuously recirculated using a peristaltic pump. The water diffusion through the AEM forced a daily refill of the cathodic chamber with mineral medium. The reactor operated at controlled laboratory temperature of 25°C. A three electrodes configuration was adopted by using a AMEL model 549 potentiostat and a reference Ag/AgCl electrode (+0.2 V vs. SHE) placed in the anodic chamber, i.e. the anode resulted the working electrode while the cathode acted as counter electrode. Two additional multimeters (Aim-TTI 1604) were connected to the circuit to measure the flowing current and the potential difference between the two electrodes (ΔV). During the two-electrode operation, the reference electrode was shorted with the counter electrode, with this configuration the potentiostat acted like a simple voltage power supplier.

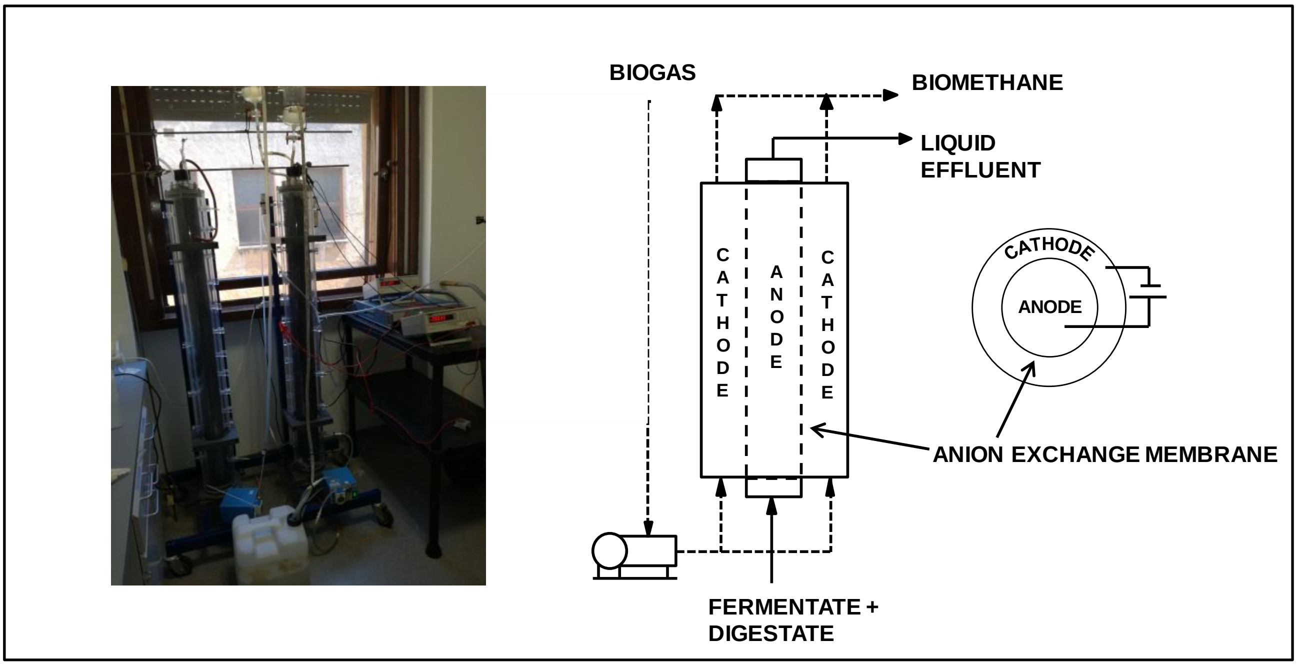

Figure 1. Photography and schematic representation of the tubular MEC

2.2 Analytical methods

The chemical oxygen demand (COD) content in the anode influent and effluent streams were assessed by using commercial COD cell test (Merck, Darmstadt, Germany). The methane content of the gas phase has been analysed, sampling 50 µL of the headspace of the compartments by a gas-tight Hamilton syringe and injecting it into a Varian (Lake Forest, CA, USA) 3400 gas-chromatograph (GC; 2m × 2 mm glass column packed with 60/80 mesh Carbopack B/1% SP-1000; He carrier gas at 18 mL/min; oven temperature at 50 °C; FID temperature 260 °C). The CO_2 determination has been performed by injecting 50 µL of gaseous sample into a Dani Master gaschromatograph (stainless-steel column packed with molecular sieve; He as carrier gas 18 mL/min; oven temperature 180 °C; thermal-conductivity detector (TCD) temperature 200 °C). The inorganic carbon was measured by TOC (Total Organic Carbon Analyzer)-V CSN (Shimadzu) on filtered samples (0.2 µm).

2.3 Calculations

The daily COD removal in the anodic chamber was assessed as the difference between the daily amount of influent and effluent COD (mg/d), according to the following equation:

$$COD_{removed} = F_{in} * COD_{in} - F_{out} * COD_{out}$$

in which COD_{in} (mg/L) and COD_{out} (mg/L) represent respectively the anodic influent and effluent COD while F_{in}(L/d) and F_{out}(L/d) are the influent and effluent flow rates in the anodic chamber (L/d). The COD removal efficiency can be also evaluated by:

$$COD_{removal\ efficiency} = \frac{F_{in} * COD_{in} - F_{out} * COD_{out}}{F_{in} * COD_{in}}$$

The COD oxidation reaction can be expressed with the following general equation:

$$C_xH_yO_z\mathrm{N} + (2\mathrm{x} - \mathrm{z})\mathrm{H_2O} \rightarrow \mathrm{xCO_2} + [\mathrm{y} + (2\mathrm{x} - \mathrm{z})]\ [\mathrm{e^-} + \mathrm{H^+}\ ] + \mathrm{NH_3}$$

According to the water oxidation reaction, the daily amount of COD diverted into current was also expressed as equivalents of electrons

$$\mathrm{2H_2O} \rightarrow \mathrm{O_2} + 4\mathrm{e^-} + 4\mathrm{H^+}$$

The meq_{COD} was calculated by using a conversion factor of 4 meq/32 gO_2.

The Coulombic Efficiency (CE%) represents the amount of oxidized COD directly converted into current; it was calculated as the ratio between the cumulative electric charge transferred at the electrodes (meqi) and the cumulative equivalents released by the COD oxidation (meqCOD):

$$CE = \frac{meq_i}{meq_{COD}}$$

The cumulative electric charge (meqi) was calculated by integrating the current (A) over time and dividing by the Faraday's constant (F = 96485 C/eq).

The methane production rate $rCH_{4(mmol)}$ (mmol/d) was also expressed in terms of equivalents $rCH_{4(eq)}$ (meq/d), considering the conversion factor of 8 meq/$mmol_{CH4}$, which derives from the following semi-reaction:

$$\mathrm{CO_2} + 8\mathrm{e}^- + 8\mathrm{H}^+ \rightarrow \mathrm{CH_4} + 2\mathrm{H_2O}$$

$$rCH_{4(mmol)} * 8 = rCH_{4(meq)}$$

About the cathodic performance, the fraction of generated current diverted into methane, also named Cathode Capture Efficiency (CCE, %), was calculated by the ratio between the cumulative equivalents of produced methane (meq_{CH4}) and the cumulative equivalents of current (i.e. the charge):

$$CCE = \frac{meq_{CH4}}{meq_i}$$

2.4 Inorganic carbon mass balance

The CO_2 daily removal (ΔCO_2, mmol/d) by each cathodic chamber has been evaluated by the following equation:

$$\Delta CO_2 = Qcat_{in} * CO_{2\,in} - Qcat_{out} * CO_{2\,out}$$

in which Q_{cat}in (L/d) and Q_{cat}out (L/d) are the influent and effluent gas flow rates, respectively whereas CO_2in and CO_2out (mmol/L) represent respectively the CO_2 concentrations in the influent and effluent gaseous cathodic streams.

Since different forms of inorganic carbon (i.e. CO_2 and HCO_3^- ion) were present, the methane production and the CO_2 sorption (as HCO_3^- ion in the cathodic liquid phases) were both representing the main cathodic CO_2 removal mechanisms. The HCO_3^- ion in the cathodic chamber is removed by the migration of HCO_3^- ion from the cathodic chamber to the anode across the AEM membrane.

The following expression represents the overall inorganic mass balance in the reactor:

$$Qcat_{in} * CO_{2\,in} + F_{in} * HCO_{3\mathrm{in}}^- = Qcat_{out} * (CO_{2\,out}) + r_{\mathrm{CH4(mmol)}} + F_{out} * HCO_{3\mathrm{out}}^-$$

where Q (L/d) are and F (L/d) are the volumetric flow rates of the gaseous and the liquid streams, respectively while CO_2 and HCO_3^- indicate the molar concentrations in gaseous and liquid phases expressed as inorganic carbon. Q_{cat}in is the influent gaseous flow rate in the cathodic chamber while Q_{cat}out is the outlet flow rate from the cathodic chamber; F_{in} and F_{out} are the anodic influent and effluent flow rates, F_{refill} is the refill flow rate of the cathodic chamber and $HCO_3^-{}_{MM}$ is the concertation of bicarbonate in the mineral medium. The term $rCH_{4(mmol)}$ (mmol/d) represents the rate of the overall methane production.

The estimation of the ionic transport contribution of the HCO_3^- from the AEM cathode to the anode, is calculated from the overall inorganic mass balance by using the following expression:

$$HCO_{3\mathrm{(transf)}}^- = F_{out} * HCO_{3\mathrm{out}}^- - F_{in} * HCO_{3\mathrm{in}}^-$$

then, it is possible to convert the molar daily amount of HCO_3^- transferred in terms of current by

$$HCO_3^-{}_{(mA)} = HCO_3^-{}_{\mathrm{(transf)AEM}} * n * \frac{F}{86400}$$

where n is the charge of the bicarbonate ion, F is the Faraday constant and 86400 represents the seconds in a day.

3.Results and discussions

3.1 Start-up and +0.2 V vs SHE MEC operation

After the inoculation of the anodic and cathodic chamber of the tubular MEC, a start-up period characterized by the polarization of the anodic chamber at +0.2 V vs SHE with a three-electrode configuration has been adopted to stimulate the anodic biofilm growth on the graphite granules, during the start-up period, synthetic organic mixture solution was continuously recirculated in the anodic chamber under batch mode. After the start-up period that showed the capability of the anodic chamber to oxidize the organic matter by using the electrodic material as electron acceptor, the anode chamber configuration of the tubular MEC was shifted in a continuous flow mode with an average flow rate of 6 L/d, that corresponds to an HRT of 0.52 days. The continuous flow mode with the anodic chamber poised at +0.2 V vs SHE was maintained for 20 days (i.e. 38 HRT) to characterize a steady state condition of the reactor with the three-electrode configuration, that represent the conventional operation mode for the bioelectrochemical reactors. During the +0.2 V run, an average COD removal of 4850 mgCOD/d was obtained (Figure 2-B), corresponding to a COD removal efficiency of 56 %. Considering the remove COD and the current output of the tubular MEC (Figure 2-A), that resulted on average 86 mA the coulombic efficiency during the +0.2 V vs SHE run, resulted only in the 13 %. The main reduction product produced in the cathodic chamber of the tubular MEC was the methane, that was produced with an average rate of 300 meq/d; the corresponding coulombic efficiency of the cathodic reaction, also named cathode capture efficiency (CCE) resulted on average 390 %, a value higher than the 100 % that suggested the presence of an additional mechanism of methane production. The other methane production mechanism was the acetoclastic activity of the cathodic biofilm, due to the presence of a stable COD concentration of 500 mgCOD/L in the cathodic chamber of the MEC (Figure 2-B). By considering the methane overproduction by acetoclastic activity, a daily diffusion of 1800 mgCOD/d from the anode to the cathode chamber was determined. The COD migration from the anode to the cathode resulted in a loss of efficiency of the bioelectrochemical reactions introducing a COD shortcut inside the reactor.

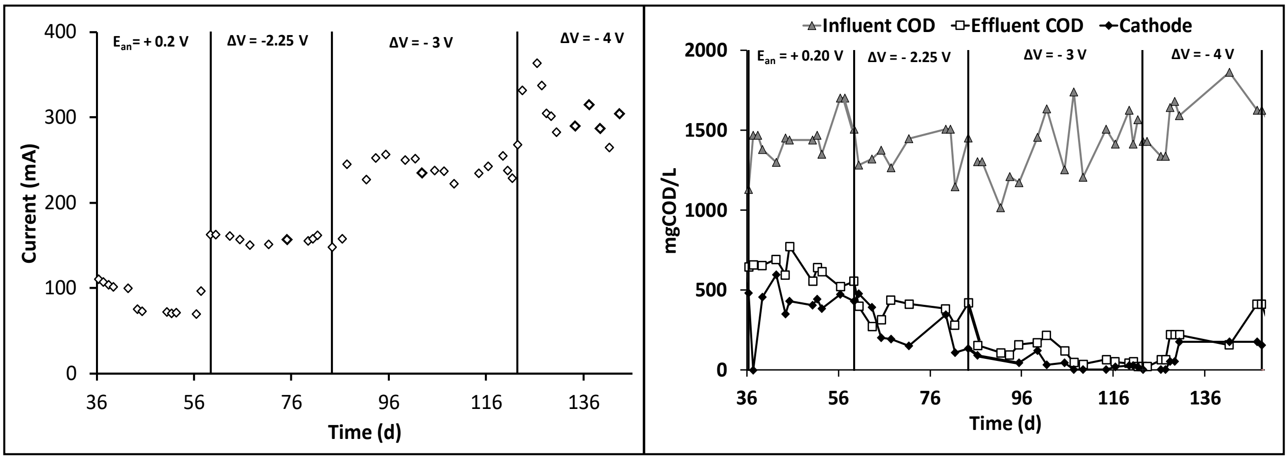

Figure 2. Current time profile (A) and COD time profile of the different reactor streams (B) during all the potentiostatic conditions explored

3.2 Two electrode configuration at different applied voltages

After the characterization of the +0.2 V vs SHE run, to perform a more conventional potentiostatic control of a large-scale electrochemical process with a simpler apparatus, the potentiostatic control of the tubular MEC was changed to a two-electrode configuration in which the potential difference between the anode and the cathode is fixed to the desired value. The potential difference has been set to -2.25 V and maintained for 24 days; the average current raised up to the value of 154 mA, along with the increase of the current, the removed COD in the anode chamber and the methane production in the cathodic chamber increased up to the average value of 5982 mgCOD/d and 449 meq/d, respectively. Those values permitted the assessment of an average CE of and a CCE of 18% and 325% for the potentiostatic condition at -2.25 V. In order to increase the reaction rates in the anodic and cathodic chamber the potential difference was further increase to -3 and -4 V, maintaining the potentiostatic condition at least for 20 days (i.e. a number of HRT higher than 38); the average current obtained at -3 and -4 V resulted 237 and 282 mA, respectively. While the COD removal in the anodic chamber showed an increase with the increase of the potential difference, with average values of 7631 and 8360 mgCOD/d corresponding in a removal efficiency of 92 and 92 % of the COD, the methane production decrease with the increase of the potential difference and consequently the current increase, to average values of 367 and 261 meq/d. During the latter two potentiostatic condition, the coulombic efficiency of the anodic chamber reached slightly higher values corresponding to 22 and 24 % low values, around 20%, while the cathode capture efficiency (CCE) decrease from the value of 325 to 103 %. The recorded values for the cathodic methane production were probably influenced by the dynamic of the microbial population, in which the acetogenic methanogens converted the organic substrates coming from the anodic chamber into methane. The coulombic efficiency of both anodic and cathodic reactions resulted strongly influenced by the COD shortcut from the anodic and cathodic chamber.

	+ 0.2	**- 2.25**	**- 3.00**	**- 4.00**
Current (mA)	86	154	237	282
COD removed (mgCOD/d)	4850	5982	7631	8360
COD removal efficiency (%)	56	72	92	90
Coulombic Efficiency (CE, %)	13	18	22	24
Methane production (meq/d)	300	449	367	261
Cathode Capture Efficiency (CCE, %)	390	325	173	103

Table 1. Main parameters obtained during the different potentiostatic conditions explored

3.3 CO_2 removal and bicarbonate transport

During all over the potentiostatic conditions explored, the CO_2 removal in the cathodic chamber showed similar values with average values in the range of 300 mmol/d. As before mentioned, two CO_2 removal mechanisms, i.e. the methane production and the CO_2 sorption as HCO_3^- ion in the cathodic chamber, occurred in the MEC cathodic chamber. Throughout all of the conditions explored, the HCO_3^- profile in the different reactor streams (Figure 3) shows a higher HCO_3^- concentration in the cathodic chamber of the tubular MEC with respect the anodic HCO_3^- concentration, moreover, the HCO_3^- concentration in the anodic effluent, resulted higher with respect the influent HCO_3^- concentration of the feeding solution, indicating a net transport of HCO_3^- from the cathode to the anode chamber. The HCO_3^- transport from the cathode to the anode chamber can be attributed to two different mechanisms, the diffusion of the bicarbonate due to the concentration gradient between anode and cathode chamber, and the migration of the HCO_3^- for the electroneutrality maintenance from the cathode to the anode due to the presence of an AEM membrane. Considering the difference of HCO_3^- concentration between the influent and the effluent, the flux of bicarbonate transported across the AEM membrane have been determined in all the potentiostatic conditions explored. Even if, is not possible to distinguish the two different mechanisms, due to the similar HCO_3^- transport values obtained in the different condition, the hypothesis of the predominance of a diffusion mechanism resulted by the evidence of a drop down of the HCO_3^- contribution to the ionic current transport (around 36 mmol/d in all the condition) from 46 % to 16% of the overall current flowing in the circuit in the different potentiostatic condition.

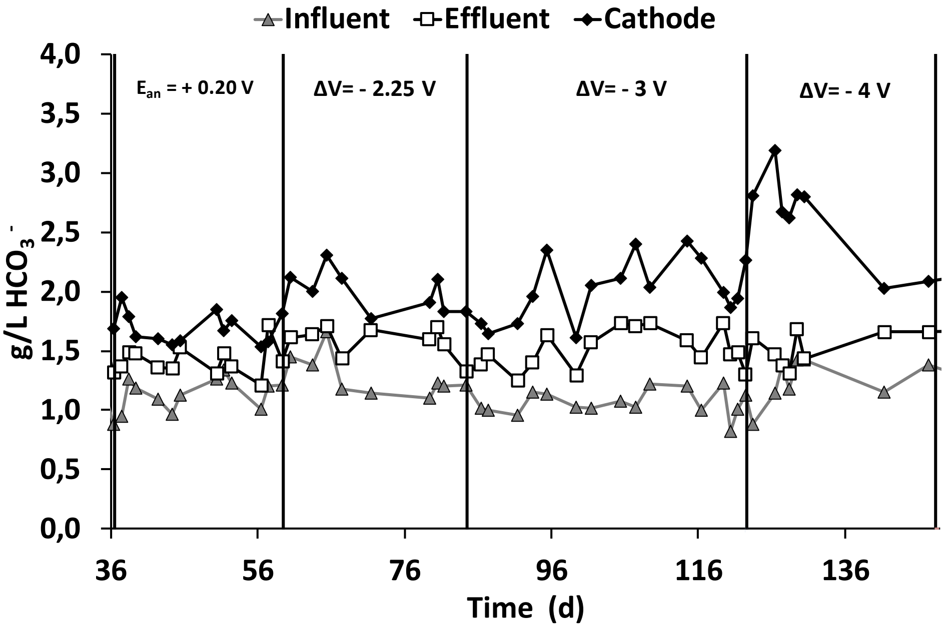

Figure 3. Bicarbonate time course in the different reactor streams during all the potentiostatic conditions explored

	+ 0.2	- 2.25	- 3.00	- 4.00
CO_2 removal (mmol/d)	303	292	299	321
rCH_4 (mmol/d)	38	56	46	33
$HCO_{3\ transf}^-$ (mmol/d)	30	33	43	38

Table 2. CO_2 removal CH_4 production and HCO_3^- transport obtained during the different potentiostatic conditions

3.4 Energy evaluation of the process

The energy consumed by the tubular MEC was assessed by measuring the applied voltage and the average current flowing in the circuit; the kWh consumed per day were utilised for the assessment of the energetic cost of each single operation, i.e. the COD removal in the anodic chamber and the CO_2 removal by the external cathodic chamber. Concerning the COD removal, the +0.2 V vs SHE (e.g. three electrode configuration) and the -2.25 V condition showed lower and similar energy consumption with respect the two benchmark technologies (i.e. activated sludge for the COD removal and Water scrubbing for the CO_2 removal) with average values of 0.47 and 1.39 kWh/kgCOD removed and 0.39 and 1.27 kWh/Nm^3 of CO_2 removed respectively. By increasing the potential applied to the MEC at -3 and -4 V (Figure 4), only a significant increase in the energy consumption of the process has been obtained instead of an increase in the COD and CO_2 removal from the MEC. Table 3 summarized the energetic parameters calculated in each potentiostatic condition explored.

	+ 0.2	**- 2.25**	**- 3.00**	**- 4.00**
i (mA)	86	154	237	282
ΔV (V)	- 1.1	- 2.25	- 3.00	- 4.00
kWh/Nm^3CO_2	0.33	1.27	2.54	3.77
kWh/kgCOD	0.47	1.39	2.24	3.24

Table 3. Energy consumption for COD and CO_2 removal obtained in the different potentiostatic conditions

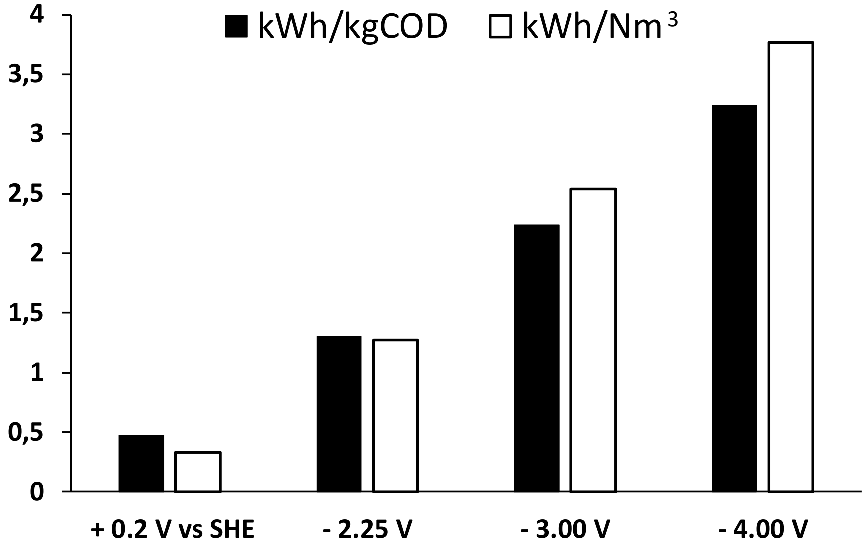

Figure 4 Energy consumption for COD and CO_2 removal obtained during the different potentiostatic conditions

4. Conclusions

The results obtained with the tubular MEC showed the feasibility of the process with the tubular geometry that permitted the anodic oxidation of substrates coupled with the CO_2 reduction into CH_4, however, with respect previous experiments performed in a flat bench scale reactor a consistent loss of efficiency in terms of conversion of organic matter oxidation into current (i.e. the coulombic efficiency) have been obtained. On other hand, the cathodic performances, particularly the CO_2 removal, resulted highly increased by the tubular geometry with an average CO2 removal of 300 mmol/d corresponding to the removal of 13.2 gCO_2/d, during the different potentiostatic conditions explored. The most promising application of the tubular MEC resulted the CO_2 removal also for the low energy consumption of 0.33 kWh/Nm^3 CO_2 removed obtained during the three-electrode configuration at +0.2 V vs SHE. The three-electrode configuration with the anode potential controlled at +0.2 V vs SHE showed the better energetic performance with energy consumptions for the COD removal and CO_2 removal of 0.47 and 0.33 kWh/Nm^3 that resulted lower values with respect the energy consumption of the commercially available technologies on the market that results 1.2 kWh/kgCOD [26] for the activated sludge process and 0.8 kWh/Nm^3 CO_2 for the Water Scrubbing technology [27].

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