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Reduction of Carbon Dioxide into Acetate in a Fully Biological Microbial Electrolysis Cell

Marco Zeppilli, Ilaria Ceccarelli, Marianna Villano, Mauro Majone

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

A microbial electrolysis cell (MEC) was operated in continuous-flow condition to obtain cathodic CO_2 reduction into acetate and methane along with COD anodic oxidation. Under steady-state conditions, most of the electron equivalents produced by COD anodic oxidation (866 mgCOD/Ld) were diverted into current rather than microbial growth, with an average Coulombic efficiency of 95 ± 8 %. In the cathodic chamber, acetate and methane formation from CO_2 reduction accounted for 76% of the equivalents generated in the anodic oxidation reaction. Because a spill of cathodic liquid phase was necessary in order to counterbalance osmotic diffusion across the PEM, it was also possible to spill from the cathodic chamber a concentrated stream of acetate (248 ± 16meq/L). Moreover, as an additional effect, cation transport across the proton exchange membrane (PEM) and the consequent alkalinity generation made it possible to accumulate ammonium nitrogen (242 ± 19 mgN/L) and bicarbonate (22.49 ± 1.45 $gHCO_3^-/L$). Hence, the MEC combined COD and CO_2 removal in addition to nutrients and energy recovery from an anodic influent that simulated an urban wastewater.

1.Introduction

The CO_2 originating from the use of fossil resources continues to accumulate in the atmosphere, accelerating climate change with disrupting impacts on the biosphere. Hence, during 2013 in Europe more than 1900 Mt of CO_2 equivalents (EEA 2013) were released in the atmosphere by human industrial facilities and vehicle transport. Major CO_2 emission are released by combustion, however industrial activities such as pig and iron steel production, oil refining an production of cement clinker, accounted for the 19% of CO_2 equivalents emission in 2013 (EEA 2013). The CO_2 fixation nowadays represents one of the most important goal to enhance sustainability of the human activities. To reduce the CO_2 emissions different approaches of storage and sequestration have been proposed like geochemical storage, physical adsorption or chemical sequestration (Yang et al. 2008). Several biological CO_2 sequestration strategies have been also proposed to reduce CO_2 emissions through the exploitation of autotrophic microorganism such as photosynthetic algae and chemoautotrophic bacteria. In particular, chemoautotrophic microorganisms such as methanogens and homoacetogens, that utilize carbon dioxide as growth substrate, could reduce CO_2 into valuable products such as biofuels and chemicals (Diekert and Wohlfarth 1994; Balch et al. 1979); thus, a bio-process based on the utilization of these microorganisms as renewable and sustainable catalysts represents an attractive route to accomplish both CO_2 fixation and biofuels/chemicals production.

In this general frame, bioelectrochemical systems, in which electroactive microorganisms utilize solid state electrodes as electron donor or acceptor for their metabolisms, can offer a powerful system to convert CO_2 into desired end-products (Lovley and Nevin 2013; Nevin et al. 2010, Marshall et al. 2012). In a microbial electrolysis cell (MEC), through the external control of anode or cathode potential, it is possible to couple COD oxidation at the anode with the production of methane and/or acetate at the cathode chambers of the cell (Villano et al. 2010). The oxidation of COD from wastewater (Rozendal et al. 2008) is also of interest because its supplies part of the energy demand for the cathodic reaction along with allowing the wastewater treatment (Rabaey and Verstraete 2005). Moreover, in comparison with conventional activated sludge process, the COD removal in a MEC shows a considerable reduction in sludge production (Zeppilli et al. 2014) keeping a similar power consumption in terms of kW/kg COD removed (Cheng et al. 2012). Furthermore, in a MEC, the electric

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current promotes additional effects due to ionic mobility and transport across ion exchange membranes; the net alkalinity generation in the cathodic chamber can be used as a strategy to remove and recovery target compounds like the ammonium from liquid effluents (Villano et al. 2013) or phosphorus remobilization (Fischer et al. 2015). Moreover, acetate formation has been also reported in batch experiments, by using methanogenesis inhibition (Kuroda and Watanabe 1995). On the other hand, long terms experiments to test bio-electroacetogenesis performance have not been reported yet.

In this study, a fully bio-catalyzed MEC was utilized to couple COD oxidation and ammonia removal at the anode with CO_2 reduction at the cathode in order to produce both methane and acetate.

2. Experimentals

2.1 Methods

The microbial electrolysis cell (MEC) consisted of a two-chamber reactor made of Plexiglas, as previously described (Villano et al. 2011). The anodic and cathodic chambers were filled with graphite granules and 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 inoculated with 0.10 L of an anaerobic sludge, which had been previously enriched in hydrogenophilic methanogens and homoacetogens in a fill and draw reactor. 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 1080 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 (35 ml/min); however, a daily spill of cathodic liquid was necessary to counterbalance the liquid diffusing from the anode to the cathode through the PEM; the resulting cathodic HRT being 9.3 d. Moreover, in order to supply the inorganic carbon and pH buffering, a N_2/CO_2 mixture with a CO_2 content of 30 % (v/v) was continuously bubbled through the cathodic chamber (this mixture was used to simulate the typical CO_2 content of biogas from anaerobic digestion). The MEC was operated in potentiostatic mode by using a three electrode configuration, where the anode constituted the working electrode while the cathode was the counter electrode; the anode potential was set at +0.2 V vs SHE (standard hydrogen electrode) by using a Bio-Logic potentiostat and an Ag/AgCl reference 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

CO_2 and H_2 were analysed by injecting 50μLof headspace sample into a Dani Master GC (Milan, Italy) gas chromatograph equipped with a thermal conductivity detector (TCD). Methane was analysed by injecting 100 μL of sample headspace (with a gas-tight Hamilton syringe) into a Varian (Lake Forest, CA, USA) 3400 gas-chromatograph. Acetate was analysed by injecting 1 μL of filtered (0.22 μm porosity) aqueous sample into a Dani Master (Milan, Italy) gas chromatograph. Headspace concentrations were converted to aqueous-phase concentrations, by using Henry's law constants (Green and Perry 2008). Chemical oxygen demand (COD) and total nitrogen (TKN) were assessed by using commercial Spectroquant test (Merck Millipore) and a UV-visible spectrophotometer (Shimadzu). Ammonium nitrogen was analyzed by Nessler colorimetric method according to standards method (APHA 1995).Bicarbonate was analyzed by using a TOC analyzer (Shimadzu).

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 utilized to reduce CO_2 to methane or acetate), and the global Coulombic efficiency (GCE, i.e. the ratio of electron equivalents produced by the oxidation that are diverted into reduced products).Mass balance was defined as for COD, ammonium nitrogen and bicarbonate. 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 methane. Further information about calculations are reported elsewhere (Villano et al 2013; Zeppilli et al 2014).

3. Results and discussion

3.1Continuous flow operation

After the inoculation of the anodic and cathodic chambers, the MEC was poised at + 0.2 V vs SHE; in order to speed up the electroactive biofilm formation the anode was continuously fed with acetate as the only organic substrate. During this start up period, the current quickly increased due to electron equivalents deriving from acetate anodic oxidation; these electrons were used to convert CO_2 back into acetate through homoacetogenic activity in the cathodic chamber. Thus, after 10 days of operation, acetate concentration in the cathodic chamber (Figure 1-A) raised to 328 ± 16 meq/L.

Then, the anodic chamber was turned in batch mode for 8 days (i.e. without any anodic feed, with recirculation), in order to decrease the residual acetate in the anodic chamber; the current correspondingly decreased (Figure 1-B). From day 18, the anode was continuously fed with the synthetic mixture of organic substrates. Both the current and cathodic concentration of acetate increased quickly to 100 mA and 246±17 meq/L, respectively.

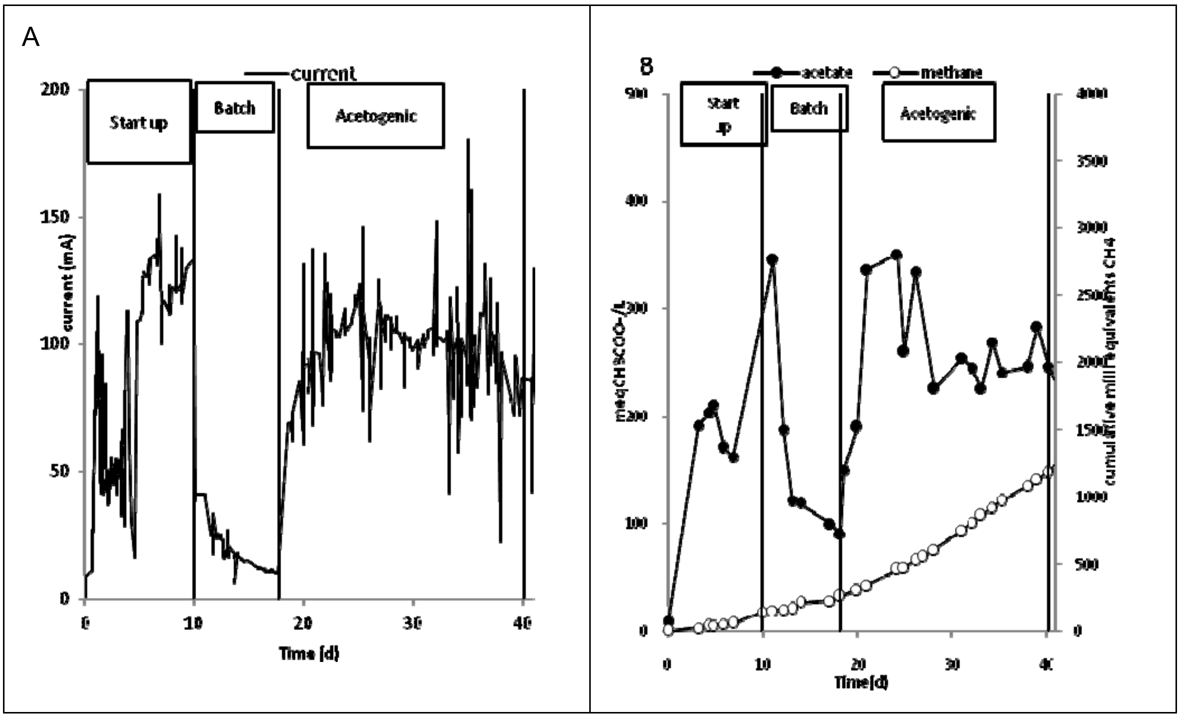

Figure 1: Time course of current time course profile (A) and cumulative methane andacetate concentration in the cathodic chamber (B) during MEC start up, batch and acetogenic period

During a steady-state period of over 20 days (around 36 HRT), an average current of 99 ± 5 mA and a COD removal of 76 ± 2 % were observed in the anodic chamber, which corresponded to a Coulombic efficiency (CE) of 95 ± 8 %.

In the cathodic chamber, both acetate and methane were produced. Acetate was produced at an average rate of 28 meq/Ld corresponding to an average cathodic capture efficiency (CCE) of 26 % whereas the methane was produced at an average rate of 51 meq/Ld, corresponding to a CCE of 50 ± 1%. Combining anodic CE and CCE, the MEC allowed both acetate and methane recovery from a complex mixture of organic substrates with a global coulombic efficiency (GCE) of 73 ± 7%, 25 ± 4 % in terms of acetate and 47 ±3 % in terms of methane. According to the COD mass balance, a similar efficiency was observed, with an average recovery of 24 % and 47% in terms of acetate and methane from the average COD anodic oxidation of 866± 37 mgCOD/Ld. During steady state condition, the produced acetate was removed by the daily spill of the liquid phase from the cathodic chamber, at a concentration of 246 ± 17 meq/L.

With respect to energy recovery from the process, produced methane corresponded to a 33 ± 1 % energy efficiency (i.e the ratio between the electrical energy spent to run the MEC and the energy recovered as methane.)

It is noteworthy that during the start up and the batch phase, the methanogenic activity was negligible, which indicates that methanogens required a quite longer acclimation to the process conditions. On the other hand, after 40 days of operation the homoacetogenic activity strongly decreased while methanogenic activity became the main mechanism (data not reported).

3.2 Nutrients removal and recovery

During the MEC operation, ammonium nitrogen and bicarbonate were daily analyzed in the different streams of the reactor, whose time course is reported in figure 2. The anodic chamber was fed with a TKN concentration of 59 mg/L, composed by both organic and ammonium nitrogen(figure 2-A) while the anodic effluent showed a TKN concentration of 36 mg/L, which was entirely composed by ammonium (thus a complete degradation of peptidic substrates was observed); accordingly, an average nitrogen removal of 42 % was achieved in the anodic chamber. The anodic nitrogen removal corresponded to an increase of ammonium concentration in the cathodic chamber, up to an average concentration of 242 ± 19 mgN/L. This fact indicates the transport of ammonium though the PEM against the concentration gradient, which suggests an active transport driven by the supply of positively charged ions towards the cathodic chamber, in order to maintain the electroneutrality of the system. Even based on this assumption, the ammonium ion accounted for only 2% of the ionic current transported from the anode to the cathode across the PEM. By the daily spill of the cathodic liquid phase, a daily removal of 30 mgN/Ld was obtained. The nitrogen mass balance, summarized in table 1, accounted for 83 % recovery of nitrogen mass flowing through the MEC.

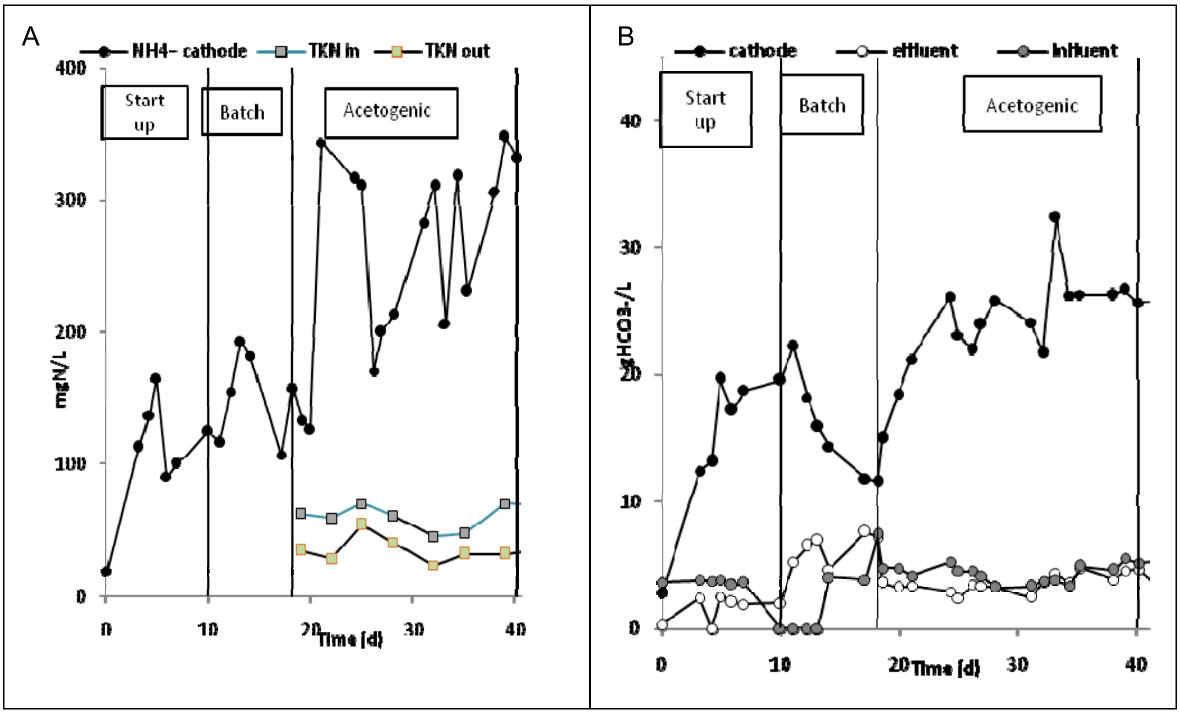

Figure 2: Time course during start up, batch and acetogenic period of ammonium and TKN nitrogen (A) and bicarbonate (B), in the different streams

Table 1: Nitrogen mass balance

$TKN_{in} = TKN_{out} + NH_4^+{}_{cathodic\ spill}$	
Anodic potential	+0.2 V vs SHE
Influent nitrogen (mgN/d)	91
Effluent nitrogen (mgN/d)	53
Cathodic spill (mgN/d)	23
Nitrogen removal (%)	42
Nitrogen recovery (%)	83

Bicarbonate time course, reported in figure 2-B, also showed the accumulation at high concentration in the cathodic chamber, with average concentration of 22.49 ± 1.45 $gHCO_3^-/L$, which was due to CO_2 absorption and dissolution from the concentrated gas mixture (30% CO_2). The CO_2 dissolution was facilitated by slightly alkaline pH (around 8) which was steadily maintained in the cathodic chamber. The latter evidence was likely a consequence of ion transport through PEM which was not only due to protons but also to other cations (including ammonium, as above reported); indeed, the fraction of positive charges transported by cations other than protons generates a net alkalinity which acts as driving force for CO_2solubilization into bicarbonate. In the anodic chamber, influent and effluent bicarbonate did not show a significant variation.

As shown in table 2, a daily CO_2 removal of 61 mmol/d was obtained in the cathodic chamber, which was due to three different mechanisms: CO_2 reduction into acetate (rCH_3COOH) and methane (rCH_4) accounted for 8 and 10% of the overall CO_2 removal whereas CO_2 solubilization into bicarbonate and consequent removal by liquid phase spill accounted for the 56 %, thus resulting the main CO_2 removal mechanism in the system. Overall, the inorganic carbon mass balance for the cathodic chamber showed an average recovery of 75%. On the other hand, in the anodic chamber, influent and effluent bicarbonate did not show a significant variation.

Table 2:Inorganic carbon mass balance

$\Delta CO_2 = rCH_4 + rCH_3COOH + HCO_3^-{}_{cathodic\ spill}$		
	Removal (mmol/d)	Percentage (%)
Overall	61	100
rCH_4	5	8
rCH_3COOH	6	10
$HCO_3^-{}_{cathodic\ spill}$	34	56
Recovery	45	75

4. Conclusions

This research showed the possibility to obtain bioelectro-conversion of CO_2 into acetate and methane by using a fully bio-catalyzed MEC.

The anode chamber removed on average 866 mgCOD/Ld, whose electron equivalents were converted into cathodic reduced end products such as acetate and methane (instead of microbial growth), with an overall efficiency of 71%.

As for acetate, the spill of cathodic liquid phase allowed a recovery of 28 meq/Ld at an average concentration of 248 ± 16 meq/L. Hence, these results show that MEC is a promising bio-based route to convert CO_2 into bio-based chemicals in the general frame of the so-called “carboxylate platform” (e.g. through chain elongation, esterification, or direct conversion of acetate into polyhydroxyalkanoates). Moreover, MEC show a low energy demand, because it is partially supported by the residual chemical energy content in the influent COD (anodic oxidation). In comparison with the biological reduction of CO_2 into acetate, the MEC approach permit to enhance the flexibility of the process by controlling the need of reducing power with electrochemical devices

As for methane production, MEC is a promising candidate to accomplish the energy storage of electric energy, e.g. from temporary overproduction and/or from renewable sources.

Moreover, in addition to acetate and methane production, additional phenomena due to the need of electroneutrality maintenance allowed the removal and the recovery of bicarbonate and ammonium nitrogen in the concentrated cathodic spill (242 ± 19 mgN/L and 22.49 ± 1.45 $gHCO_3^-/L$, respectively).

Hence, the concentrated cathodic spill could be utilized as a feedstock solution for several biotechnological processes such as biopolymer production (polyhydroxyalkanoates from acetate) or algae production (from bicarbonate and ammonium). These features make MEC a flexible and wide-purpose promising technology to accomplish the objectives of the new circular and bio-based economy.

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