Chemical Engineering Journal 328 (2017) 428–433

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Using effluents from two-phase anaerobic digestion to feed a methane-producing microbial electrolysis

M. Zeppilli [a,*], D. Pavesi [a], M. Gottardo [b], F. Micolucci [c], M. Villano [a], M. Majone [a]

[a] University of Rome "Sapienza", Chemical Department, Piazzale Aldo Moro 5, 00185 Roma, Italy
[b] Department of Environmental Sciences, Informatics and Statistics, University Ca' Foscari of Venice, Via Torino 155, 30172 Venezia, Mestre, Italy
[c] Department of Biotechnology, University of Verona, Strada Le Grazie 15, I-37134 Verona, Italy

HIGHLIGHTS

- A MEC was fed at the anode with real effluents from two-phase anaerobic digestion.
- Digestate from 2nd stage was not effective due to poorly biodegradable COD.
- The MEC showed good performance by using a mix of 1st and 2nd stage effluents.
- Periodical countercurrent backwashing was needed to recover fouling phenomena.
- Depending on nitrogen load, ammonium contributed up to 20% to ionic transport.

ARTICLE INFO

Article history:
Received 26 April 2017
Received in revised form 8 July 2017
Accepted 11 July 2017
Available online 12 July 2017

Keywords:
Two phase anaerobic digestion
Anaerobic digestion effluents
Microbial electrolysis cell
Methane production
Ammonium removal
Volatile fatty acids

ABSTRACT

The integration of a methane-producing microbial electrolysis cell (MEC) into two-phase anaerobic digestion (TP-AD) was investigated, by using effluents from a pilot-scale TP-AD treating the organic fraction of municipal solid waste. The MEC was aimed at exploiting residual COD of TP-AD effluents at the MEC anode in order to support CO_2 removal and methane generation at the MEC cathode (fed by a CO_2-rich gas phase, simulating a biogas). Feeding by 2nd phase digestate caused a loss of MEC performance, due to poor biodegradability of digestate COD under chosen anodic operating conditions (+0.2 V vs SHE, HRT 13 h, organic load 2.3 g COD/L d). On the other hand, by using the 1st phase fermentate (rich in volatile fatty acids, VFA), good MEC performance was recovered with a current of 60 ± 4 mA and a methane production rate of 33 ± 3 meq/L d. However, periodic baskwashing was also necessary to recover fouling effects. Moreover, partial nitrogen removal (228 mg N/L d) from the fermentate was obtained because ammonium was transported across the separation membrane and then recovered through the cathodic concentrated spill (at 3177 ± 97 mg N/L). Cation transport also generated net alkalinity which strongly contributed to CO_2 removal (besides methane generation).

1. Introduction

1.1. Two phase anaerobic digestion for biohythane production

Anaerobic digestion (AD) is one route to achieve the energy and material recovery from the treatment of waste stream such us sewage sludge, agro-zootechnical waste streams, and the organic fraction of municipal solid waste (OFMSW) [1]. Two-phase AD (TP-AD) has been developed aiming at optimizing the overall degradation rate by the separation of hydrolysis and fermentation with the methanogenic step of the anaerobic digestion process [2,3]. The TP-AD offers the advantage of enhancing the overall degradation efficiency by optimizing the conditions (pH, hydraulic retention time, temperature) for the hydrolytic bacteria and for the methanogens [4,5]. However, the utilization of TP-AD also requires a higher investment cost, for the realization and the control of a more complex plant. Moreover, an innovative product obtainable by a TP-AD is offered by the production of the bio-hythane. i.e. a gas mixture composed by hydrogen, methane and carbon dioxide (10%; 60%; 30%) that could be utilized in automotive engines without the upgrading step necessary for conventional biogas [6]. Indeed, the calorific power of the mixture is enhanced by the

* Corresponding author.
E-mail addresses: marco.zeppilli@uniroma1.it (M. Zeppilli), pavesi.1311401@studenti.uniroma1.it (D. Pavesi), marco.gottardo@unive.it (M. Gottardo), federico.micolucci@unvr.it (F. Micolucci), marianna.villano@uniroma1.it (M. Villano), mauro.majone@uniroma1.it (M. Majone).

http://dx.doi.org/10.1016/j.cej.2017.07.057
1385-8947/

presence of the 10% of hydrogen in the mixture that enhance its Wobbe index. Several studies are focused on the biohythane production, by the utilization of TP-AD which in the first step VFA and H_2 are produced by the hydrolyzing and fermentative bacteria, in the second step the methanogenesis produced CH_4 and CO_2, with a residual digestate rich in COD and NH_4^+ [7]. Even if some authors reported biohythane composition with good characteristics to a direct utilization of the mixture in engines, further purification steps are generally required, like for biogas [8].

1.2. Biogas upgrading through bioelectrochemical systems

As an alternative, the biogas from either single or two-phase AD can be refined and upgraded into biomethane (CH_4 > 95%) [9], by removing the CO_2 from the gas mixture in the so called biogas upgrading process [10,11]. However, presently used biogas upgrading processes such as Water Scrubbing and Pressure Swing Absorption (WS and PSA) have a high energy demand (1.12 and 1.40 kWh/N m^3 CO_2 removed [12]) which restricts their economical balance positive only for large or centralized plants [13]. Recently, much research has been devoted into using bioelectrochemical systems, such as microbial electrolysis cells, in order to obtain COD removal from waste and wastewater (anodic reaction) combined to generation of methane or hydrogen (cathodic reaction) [14–16]. In this frame, the possibility to utilize a methane-producing MEC to enhance methane content in biogas and simultaneously recovery nutrients (NH_4^+) by exploiting residual COD in the digestate has been investigated [17], as an attractive way to refine both liquid effluents and biogas from the AD process [18] instead of other approach like struvite crystallization [19] or nutrients removal via denitrification [20].

1.3. Integration of TP-AD with a methane-producing MEC

The integration between AD and MEC technology has been proposed to enhance the energy efficiency of the AD process by increasing the quality of both digestate and biogas with several configurations, either considering in situ integration [21–23] or as a post treatment of AD effluents. In this study, this post-treatment approach is further investigated by using, for the first time, real effluents from a pilot-scale TP-AD, treating the organic fraction of municipal solid waste (OF-MSW).

2. Materials and methods

2.1. Pilot scale two phase anaerobic digestor

Two stainless steel CSTR reactors (AISI 304) were used for volatile fatty acids, hydrogen and methane production. The first reactor (F1), dedicated to the fermentative step (Dark fermentation), had a 200 L working volume and an hydraulic retention time (HRT) of 3.3 days, while the second reactor (F2) dedicated to the methanogenic step had a 380 L working volume and an HRT of 12.6 days. Both reactors were heated by a hot water recirculation system and maintained at 55 °C ± 0.1 using electrical heater controlled by a PT100-based thermostatic probe [24]. The feeding system was semi-continuous, arranged once per day and the average organic load rate for F1 and F2 were 17.8 ± 0.8 and 4.0 ± 0.9 kg VS/m^3 d, respectively. The organic waste was reduced in size using a grinder, mixed with tap water and liquid fraction of sludge recirculation from the entire process and then fed to the first reactor. Acidogenic fermentate (F1 effluent) and the methanogenic digestate (F2 effluent) were filtered at 0.2 mm.

In spite of filtration, digestate had a high concentration of solids (3.1 ± 0.1 g VSS/L). Total COD was 5.6 ± 0.1 g COD/L, the soluble COD (sCOD) being 1.3 g COD/L (23.2%). The fermentate had a higher COD (8.9 ± 0.1 g COD/L), most of which was soluble COD (6.7 ± 0.1 g COD/L, 75% of total COD). Moreover, over 80% of the sCOD was composed by volatile fatty acids (VFA), mainly acetate and propionate. The digestate and the real mix feeding solution (fermentate + digestate) were characterized by an average nitrogen concentration of 932 ± 95 mg N/L and 818 ± 51 mg N/L, mainly composed by ammonium nitrogen.

2.2. Lab scale microbial electrolysis cell

The microbial electrolysis cell (MEC) consisted of a two-chamber reactor made of Plexiglas, as previously described (Fig. 1) [25]. The anodic and cathodic chambers were filled with graphite granules and separated by a Nafion proton exchange membrane (PEM). The empty volume of both chambers was 0.86 L and the bed porosity was 0.48 (as determined by tracer experiments). Hence, by considering that graphite granule were around 0.3 cm on average, it can be estimated that the electrodic surface was not less 820 cm^2 (under the assumption of sfericity 1).

The anodic chamber was inoculated with 0.20 L of activated sludge from the wastewater treatment plant of Rome Nord (Italy), while cathodic chamber was inoculated with 0.10 L of an anaerobic sludge, which had been previously cultured under hydrogenophilic conditions in a fill and draw reactor. The anodic chamber was continuously fed by organic carbon, by using different feeding solution through the experimental run: a synthetic mixture of organic substrates acetate), the anaerobic digestate from a pilot scale TP-AD (treating FORSU) and the fermentate from acidogenic stage of TP-AD (the latter was diluted in the digestate at a ratio of 1:10). The anode hydraulic retention time (HRT) was 0.56 d (with reference to the empty volume). The synthetic mixture was made by a mineral medium composed by NH_4Cl (0.125 g/L); $MgCl_2{\cdot}6H_2O$ (0.1 g/L); K_2HPO_4 (4 g/L); $CaCl_2{\cdot}2H_2O$ (0.05 g/L); 10 mL/L of a trace metal solution; and 1 mL/L of vitamin solution, that contained the following organic substrates: 25% peptone, 10% yeast extract, 55% glucose, and 10% of acetate [26]. Moreover, the total nitrogen content was 70 mg N/L, composed by 50% of ammonium nitrogen and 50% of organic nitrogen (contained in the peptidic substrates).

The cathodic chamber was operated with no liquid influent and with continuous internal 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. Moreover, in order to supply the inorganic carbon, 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 AD. The N_2/CO_2 mixture flow rate was controlled at 13.2 L/d and monitored by a milligascounter (Ritter, Germany). A sampling flask was inserted along the gas line in order to determine the composition of influent gas (N_2; CO_2). Two more flasks were connected to the anodic and cathodic chamber to balance the pressure and make it possible to sample the head space of effluent gas (CO_2, H_2, CH_4).

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; during all over the experimental activity, 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. This potential was chosen because, based on previous research, it allows the quick start-up and acclimation of the electroactive biomass in the anodic chamber [27]. Liquid and gaseous samples of outflows from both anodic and cathodic chambers were daily sampled and analyzed in order to assess the MEC performance. The MEC was operated at room temperature.

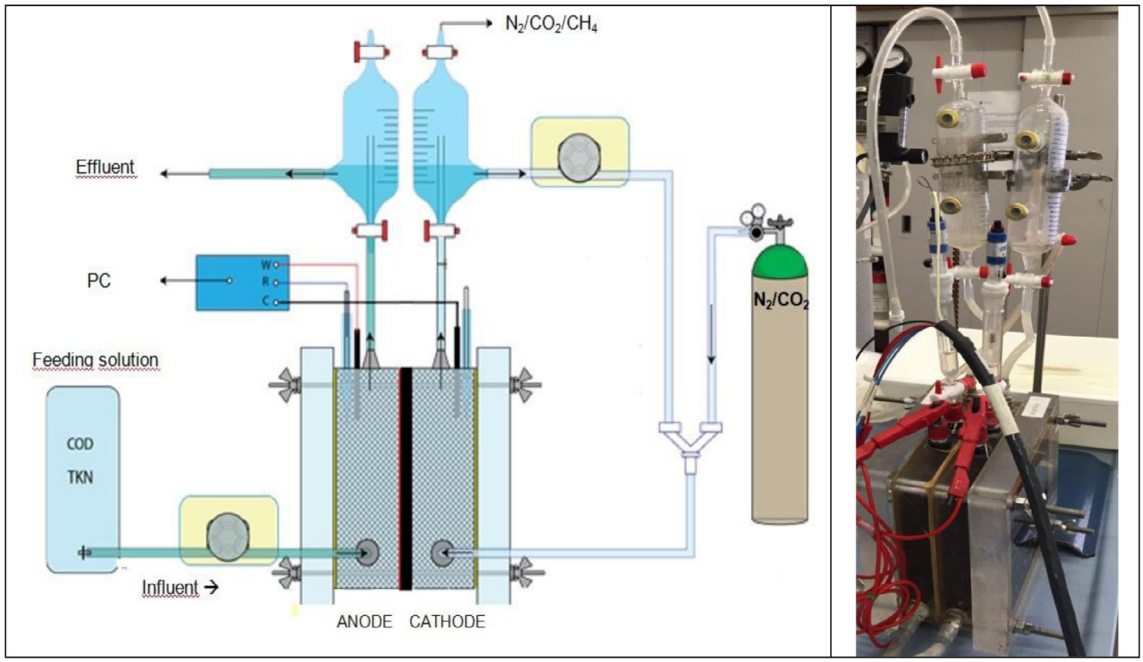

Fig. 1. Schematic representation of the MEC; side view of the lab scale MEC.

Under this configuration, the catalysts for the anodic and cathodic reactions were the electroactive biofilms which developed in the two chambers. The electron produced from substrate anaerobic oxidation by anodic biofilm were transferred to the graphite anode that worked as electron acceptor (instead of typical electron acceptors like oxygen, nitrate, sulphate) while in the cathodic chamber the graphite electrode acted as electron donor to the methanogenic biofilm, either directly or through intermediate electrolytic formation of molecular hydrogen.

2.3. Analytics

CO_2 and H_2 were analyzed by injecting 50 μL of sampling flask headspace into a Dani Master GC (Milan, Italy) gas chromatograph equipped with a thermal conductivity detector (TCD). Methane was analyzed 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 analyzed 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 (TN) were assessed by using commercial Spectroquant kit tests (Merck Millipore) and an UV–visible spectrophotometer (Shimadzu). Ammonium nitrogen was analyzed by Nessler colorimetric method according to standards method [28]. Bicarbonate was analyzed by using a TOC/TIC analyzer (Shimadzu).

2.4. Calculations

The daily amount of COD removed in the anodic chamber were assessed by the difference between the daily influent and effluent COD as:

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

while the COD removal efficiency was calculated as:

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

In both equations, F_{in} and F_{out} (L/d) are the influent and effluent liquid flow rate in the anode chamber, while COD_{in} and COD_{out} (mg/L) are the influent and effluent COD concentration, respectively.

The anodic oxidation of a general organic matter (COD) could be expressed by the follow semi-reaction:

$$\text{ANODIC REACTION}: \ C_xH_yO_z + (2x - z)H_2O \rightarrow xCO_2 + [y + (2x - z)][e^- + H^+]$$

The amount of the oxidized COD which was directly converted into current, was the Coulombic Efficiency (CE, %), and it was calculated as the ratio between the cumulative electric charge transferred at the electrodes (meq_i) and the cumulative equivalents released from COD oxidation (meq_{COD}):

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

Cumulative equivalents released from the oxidation of the organic substrates (meq_{COD}) were calculated from the removed COD, considering the corresponding molar conversion factor of 4 meq/mmol. The cumulative electric charge (meq_i) that was transferred to the anode was calculated by integrating the current over time and dividing by the Faraday's constant (F = 96,485 C/eq).

By considering the cathode semi-reaction,

$$\text{CATHODIC REACTION}: \ CO_2 + 8e^- + 8H^+ \rightarrow CH_4 + 2H_2O$$

the fraction of generated current diverted into methane (or acetate) is called Cathode Capture Efficiency (CCE, %) and it was assessed, as the ratio between the cumulative equivalents of produced methane (meq_{CH4}), calculated by considering the molar conversion factor of 8 meq/mmol$_{CH4}$, and the cumulative equivalents deriving from current

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

Concerning ammonium transport and its contribution to positively charge transport, the daily amount of electric charges transported from the anode to the cathode (cationic current) were assessed by considering the following equation

$$NH^{+}_{4(transf)} = F_{cath} * NH^{+}_{4(cath)} * n * F$$

where F_{cath} and NH^{+}_{4cath} were respectively the liquid spill flow rate (L/d) the concentration of ammonium in the cathode chamber, *n* correspond to the charge of ammonium (+1) and F was the Faraday's constant (F = 96,485 C/eq).

In general, when average values are given from above reported calculations, they are referring to operational runs under unchanged conditions not less than 8 HRTs.

3. Results and discussion

3.1. Anodic performance

After the inoculation, both anode and cathode were operated in a liquid phase recirculation mode with a high rate, in order to promote biofilm formation on the electrodic surface of graphite granules (the anode also received spiked of acetate). After three days from the last acetate spike, the anode was set up in continuous-flow mode and it was feed with the synthetic mix solution at a flow rate of 1.44 L/d, corresponding to an organic load rate (OLR) of 1.08 g COD/L d.

As reported in Fig. 2A and B, after 21 days of operation (named start up period on the graphs), a steady state operation was reached both in terms of anodic COD removal and cathodic methane generation; an average COD removal of 750 ± 80 g COD/d was reached corresponding to a COD removal efficiency of 67 ± 6%. The electron equivalents generated from the COD oxidation were partially converted into an average of 50 ± 1 mA, corresponding to a coulombic efficiency (CE) of 48 ± 7%. This steady-state performance was considered as the reference to assess the process behavior with real substrates. Starting from day 53, the digestate from the methanogenic stage of the TP-AD was fed to the anode chamber by using the same flow rate (1.44 L/d) of previous run with synthetic mix; being the digestate more concentrated, the OLR was 2.3 ± 0.1 g COD/L d (by taking into account the soluble COD only). As reported in Fig. 2A and B, the current quickly drop down and its average value was 23 ± 4 mA for the 21 days of operation with digestate feeding. By taking into account the sCOD only, the average COD removal was 358 ± 99 mg COD/d, corresponding to a COD removal efficiency of 17 ± 4% and a CE of 50 ± 14%. In principle, the sCOD removal could have been underestimated if a fraction of particulate COD was hydrolyzed and converted into more sCOD. However, this additional sCOD should had also given a higher current; on the contrary, the CE was similar between the synthetic mixture and the digestate, which suggests that hydrolysis of particulate COD was not relevant (not unlikely given the short HRT and low temperature). Thus, the digestate feeding caused a significant loss of performance, which can be attributed to fouling phenomena of the electrodic materials and/or by the poor biodegradability of residual compounds in the anodic environment. From day 74 to day 91, transient feeding with the synthetic mixture in the presence or not of digestate along with some backwash cleaning of the anodic chamber were performed. Through this operation, both hypotheses were confirmed: the digestate didn't contain easily biodegradable sCOD but also progressive fouling of electrodic materials/membrane was observed, the latter phenomenon likely due the presence of colloidal.

Given poor performance with the anaerobic digestate, the fermentate from the acidogenic stage was used, which was expected to be a better source of biodegradable sCOD, given that over 80% of the sCOD was composed by VFAs. Due to the high sCOD of fermentate and the need to not reduce the influent flow-rate (to avoid clogging of tubing), the fermentate was diluted into the digestate to a ratio of 1:10.

From day 81 the fermentate-digestate mixture was fed at an OLR of 1.5 g COD/L d by considering only sCOD from the fermentate, i.e. the digestate was considered as an inert medium not significantly contributing to COD load. The current quickly increased and on average it was 60 ± 4 mA. With reference to the sCOD, a daily removal of 360 ± 41 mg COD/d was obtained corresponding to a COD removal efficiency of 28 ± 3% whereas the resulting CE was quite high at 119 ± 28%. Firstly, the high CE can be attributed to that the anodic oxidation of VFAs, and especially acetate, typically presents higher CE than other substrates and often close to 100% [29]; moreover, the CE extra 100% could be reasonably attributed to the hydrolysis the particulate COD, giving additional sCOD not included in the CE calculation (this phenomenon was not observed with the digestate, which is not unlikely due to the additional hydrolysis should have occurred during the second stage with respect to the first one, only). Notably, as reported in Fig. 2, during the operation with fermentate-digestate, the current showed a progressive decrease, which was due to the fouling of electrodic material and membrane; however, a short backwash cleaning of the anodic chamber at high flow rate (over 10 L/d) was able to recover the MEC performance.

3.2. Cathodic performance

The current transferred through the external circuit to the cathodic chamber supplied the reducing power which was utilized by the cathodic biofilm to reduce the CO_2. As reported in Fig. 3, the

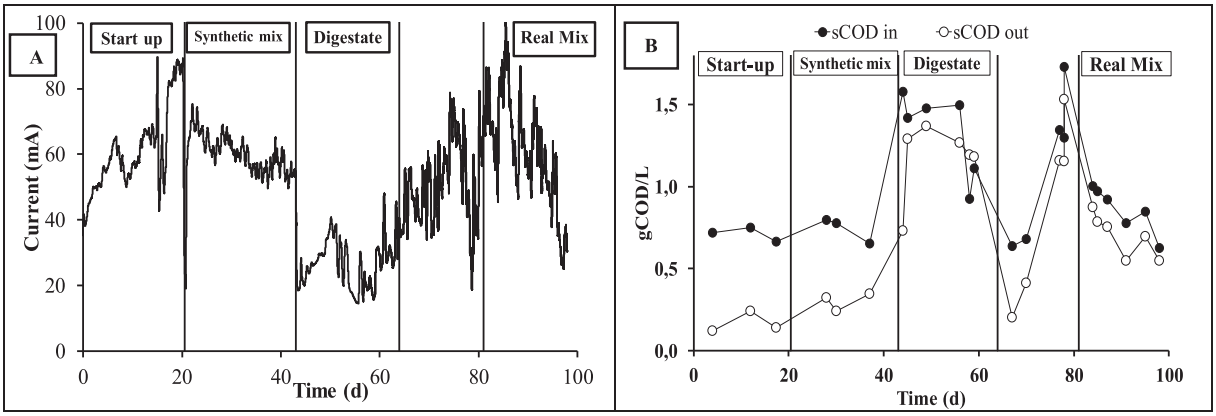

Fig. 2. Time profile of electric current (A) and time course of influent and effluent sCOD in the anodic chamber (B) during the MEC operation.

two reduced products detected were the methane and the acetate. More in detail, homoacetogenic activity was prevailing during the first 15 days of continuous operation (synthetic mix feeding) and the acetate concentration raised up to 800 ± 32 mg/L. After the day 15, a slow decrease until no detectable concentration of acetate was observed whereas methane formation became predominant. During the synthetic mix operation (reference period) an average methane production of 33 ± 2 meq/L d, corresponding to a cathode capture efficiency of 62 ± 1%, was observed. During the period with digestate feeding, the methane production decreased to an average value of 22 ± 2 meq/L d, that corresponds to a CCE of 92 ± 1%. Finally, during the feeding by the fermentate-digestate mixture, the methane production rate increased back to 33 ± 3 meq/L d, that corresponds to a CCE of 51 ± 1%. By the analysis of the cathodic performances, it is clear that the methane production rate was mainly influenced by the average current flowing through the circuit, i.e. from the reducing power from the anodic oxidation of organic substrates.

3.3. Inorganic ionic species transport

Throughout the MEC operation, two inorganic species were also monitored, i.e. the ammonium nitrogen and the bicarbonate; these species were daily monitored in the anodic influent and effluent and in the cathode.

During reference period by feeding the synthetic mixture, the nitrogen load rate was on average 115 ± 12 mg N/L d; it was considered to be practically composed by ammonia nitrogen, due to the rapid hydrolysis of peptidic nitrogen, which also started in the feeding tank. Based on pH in the anodic chamber (6.9), the ammonia nitrogen was mostly present as ammonium, which moved across the PEM and accumulated into the cathodic chamber to an average concentration of 191 ± 16 mg N/L (Fig. 4). Thus, ammonium was transported against its concentration gradient, the driving force being the net cationic flow needed to counterbalance the electron flow across the external electric circuit. However, ammonium transport contributed little by only 2% to the protonic/cationic charge transport needed to maintain electroneutrality. Because a daily spill of cathodic liquid phase was also needed to counterbalance the net osmotic flow of the liquid phase from the anode to the cathode, these combined mechanisms (i.e. transport, accumulation and spill) made it possible to remove ammonium at an average rate of 22 ± 4 mg N/L d (around 19% of the nitrogen influent load). As typical, the anaerobic digestate contained higher concentration of ammonia nitrogen and, by using

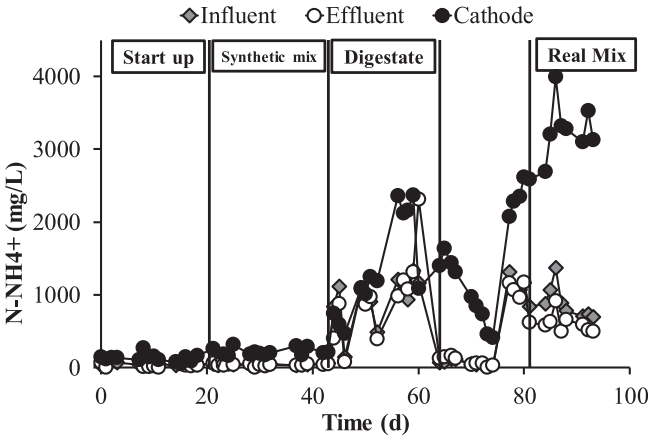

Fig. 4. Ammonium time profiles during MEC operation.

the digestate as anodic feeding solution, nitrogen load rate increased to 1.67 ± 0.11 g N/L d. As a consequence, the cathodic ammonium concentration strongly increased, to an average value of 1368 ± 201 mg N/L (around 7 times more than in the reference period) and it accounted for around 10% of overall ionic current (around 5 times more). However, due to the lower current and the lower daily spill of liquid phase the daily removal of nitrogen increased only to 42 ± 13 mg N/L d (around 2 times more). Finally, during the operation with the fermentate-digestate mixture, the nitrogen load rate was 1.46 ± 0.15 g N/L d. Due to the higher current with respect to digestate only, the cathodic concentration of ammonium raised up to 3177 ± 97 mg N/L and its transport contributed to the ionic current to the 20%. Thanks to the daily cathodic spill, ammonium was removed at 228 ± 32 mg N/L d (although still 15.6% of the influent load only).

With regards to the inorganic carbon, given the average of pH of 6.9 ± 0.1 and 7.9 ± 0.2 for the anode and cathode respectively, in both chambers the predominant species was the bicarbonate ion. While the bicarbonate concentration didn't change significantly between the anodic influent and effluent (Fig. 5), in the cathodic chamber the bicarbonate concentration quickly increased up to an average value of 10.1 ± 0.5 g HCO_3^-/L. This high concentration was a consequence of CO_2 absorption and dissolution in the cathodic liquid phase from the CO_2-rich gas mixture that was continuously fed to the cathode. CO_2 dissolution was also supported by the net alkalinity generation which derived from the transport of positive charges across the PEM, by all cations other than protons.

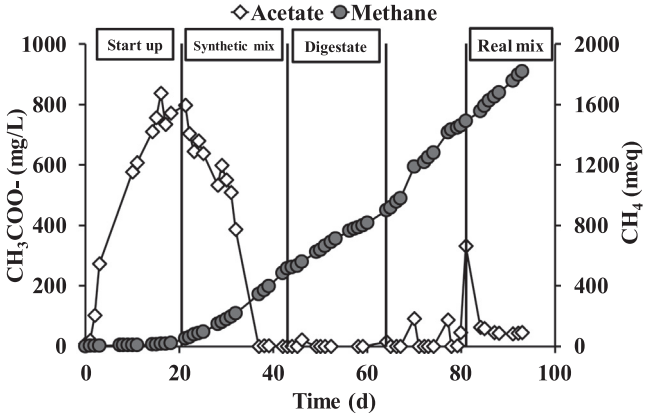

Fig. 3. Acetate and methane time profiles in the cathodic chamber during MEC operation.

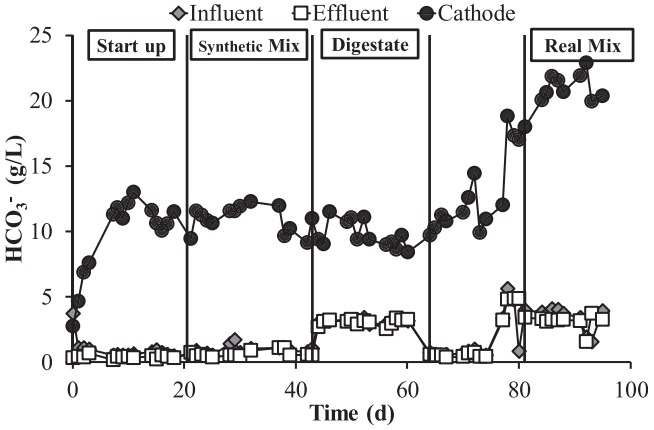

Fig. 5. Bicarbonate time profiles during MEC operation.

During the period by feeding the anode with the digestate, the bicarbonate concentration at the cathode did not change significantly whereas it raised up to 20.7 ± 1.5 g HCO_3^-/L when the anode chamber was fed the fermentate-digestate mixture. The further increase of bicarbonate concentration was driven by the combined effect of both higher current (with respect to the digestate only) and higher ammonium load (with respect to the synthetic mixture); both factors causing a strong increase of ammonium contribution to the positive charge transport other than protons and consequent alkalinity generation.

Given its high bicarbonate concentration, the daily spill of the cathodic liquid phase strongly contributed to overall CO_2 removal from the influent gas mixture. During the reference period with the synthetic mixture, CO_2 reduction into methane and bicarbonate spill contributed to CO_2 removal of 3.5 ± 0.8 mmol C/d and 19 ± 2 mmol C/L d respectively. During the last period with the fermentate-digestate mixture, CO_2 removal was 3.5 ± 0.9 mmol C/d and 25 ± 3 mmol C/L d respectively.

4. Conclusions

For the first time, effluents from a two-phase anaerobic process were utilized to fed the anodic reaction of a methane-producing MEC. After a reference period with a synthetic mixture of organic substrates, the use of the digestate from the methanogenic stage of the anaerobic digestor negatively affected the MEC performance, i.e. the electric current was reduced by the 40% and methane production correspondingly decreased. The performance loss was mostly due to poorly biodegradable COD content of the anaerobic digestate. In order to supply a more suitable COD source for the anodic reactions, the effluent from the first acidogenic phase was used after 1:10 dilution with the digestate. Being the fermentate-digestate mixture much richer in short chain FAs (mainly acetate and propionate), it was possible to recover good performance of the MEC. Moreover, by increasing the nitrogen load rate about 10 times (from 115 ± 12 mg N/L d to 1460 ± 150 mg N/L d) with respect to the control synthetic medium, the nitrogen removal rate and its contribution to ionic transport increased by the same order of magnitude (from 22 ± 4 to 228 ± 32 mg N/L d removed and from 2 to 20% of ionic current transported). Thus, ammonium transportat also caused the alkalinity increase in the cathodic chamber, which corresponded in enhancement of CO_2 absorption and dissolution as bicarbonate.

Based on these results, the effluent from acidogenic step of a two-phase anaerobic digestor is a good feedstock to feed a MEC and to simultaneously obtain nitrogen partial removal and biogas refining (the latter by means of both methane generation and CO_2 absorption and spill).

Acknowledgements

This work has been carried out with the financial support of MIUR through the PRIN 2012 Project "WISE: turning organic Waste into Innovative and Sustainable End-products". Giulio Lucarelli is acknowledged for his skilful assistance with the experimental work.

References

[1] J. Mata-Alvarez, S. Macé, P. Llabrés, Anaerobic digestion of organic solid wastes. An overview of research achievements and perspectives, Bioresour. Technol. 74 (2000) 3–16.
[2] B.K. Ahring, Perspectives for anaerobic digestion, Adv. Biochem. Eng./Biotechnol. 81 (2003) 1–30.
[3] F. Cecchi, C. Cavinato, Anaerobic digestion of bio-waste: a mini-review focusing on territorial and environmental aspects, Waste Manage. Res. 33 (2015) 429–438.
[4] C. Cavinato, D. Bolzonella, F. Fatone, F. Cecchi, P. Pavan, Optimization of two-phase thermophilic anaerobic digestion of biowaste for hydrogen and methane production through reject water recirculation, Bioresour. Technol. 102 (2011) 8605–8611.
[5] C. Cavinato, D. Bolzonella, F. Fatone, A. Giuliano, P. Pavan, Two-phase thermophilic anaerobic digestion process for biohythane production treating biowaste: preliminary results, Water Sci. Technol. 64 (2011) 715–721.
[6] J.R. Bastidas-Oyanedel, F. Bonk, M.H. Thomsen, J.E. Schmidt, Dark fermentation biorefinery in the present and future (bio)chemical industry, Rev. Environ. Sci. Biotechnol. 14 (2015) 473–498.
[7] K.H. Hansen, I. Angelidaki, B.K. Ahring, Anaerobic digestion of swine manure: inhibition by ammonia, Water Res. 32 (1998) 5–12.
[8] E. Ryckebosch, M. Drouillon, H. Vervaeren, Techniques for transformation of biogas to biomethane, Biomass Bioenergy 35 (2011) 1633–1645.
[9] I. Bioenergy, Biomethane Status and Factors Affecting Market Development and Trade, 2014.
[10] F. Bauer, T. Persson, C. Hulteberg, D. Tamm, Biogas upgrading – technology overview, comparison and perspectives for the future, Biofuels, Bioprod. Biorefin. 7 (2013) 499–511.
[11] D. Andriani, A. Wresta, T.D. Atmaja, A. Saepudin, A review on optimization production and upgrading biogas through CO_2 removal using various techniques, Appl. Biochem. Biotechnol. 172 (2014) 1909–1928.
[12] J.D. Hullu, J. Waassen, P. Van Meel, S. Shazad, J. Vaessen, Comparing Different Biogas Upgrading Techniques, Eindhoven University of Technology, 2008, p. 56.
[13] A. Petersson, A. WeLLInGer, Biogas upgrading technologies – developments and innovations, IEA Bioenergy 20 (2009).
[14] B.E. Logan, K. Rabaey, Conversion of wastes into bioelectricity and chemicals by using microbial electrochemical technologies, Science 337 (2012) 686–690.
[15] B.E. Logan, D. Call, S. Cheng, H.V. Hamelers, T.H. Sleutels, A.W. Jeremiasse, R.A. Rozendal, Microbial electrolysis cells for high yield hydrogen gas production from organic matter, Environ. Sci. Technol. 42 (2008) 8630–8640.
[16] S. Cheng, D. Xing, D.F. Call, B.E. Logan, Direct biological conversion of electrical current into methane by electromethanogenesis, Environ. Sci. Technol. 43 (2009) 3953–3958.
[17] M. Villano, S. Scardala, F. Aulenta, M. Majone, Carbon and nitrogen removal and enhanced methane production in a microbial electrolysis cell, Bioresour. Technol. 130 (2013) 366–371.
[18] M. Zeppilli, A. Lai, M. Villano, M. Majone, Anion vs cation exchange membrane strongly affect mechanisms and yield of CO_2 fixation in a microbial electrolysis cell, Chem. Eng. J. 304 (2016) 10–19.
[19] M.S. Romero-Güiza, S. Astals, J. Mata-Alvarez, J.M. Chimenos, Feasibility of coupling anaerobic digestion and struvite precipitation in the same reactor: evaluation of different magnesium sources, Chem. Eng. J. 270 (2015) 542–548.
[20] N. Frison, E. Katsou, S. Malamis, D. Bolzonella, F. Fatone, Biological nutrients removal via nitrite from the supernatant of anaerobic co-digestion using a pilot-scale sequencing batch reactor operating under transient conditions, Chem. Eng. J. 230 (2013) 595–604.
[21] G. Luo, S. Johansson, K. Boe, L. Xie, Q. Zhou, I. Angelidaki, Simultaneous hydrogen utilization and in situ biogas upgrading in an anaerobic reactor, Biotechnol. Bioeng. 109 (2012) 1088–1094.
[22] P. Batlle-Vilanova, S. Puig, R. Gonzalez-Olmos, A. Vilajeliu-Pons, M.D. Balaguer, J. Colprim, Deciphering the electron transfer mechanisms for biogas upgrading to biomethane within a mixed culture biocathode, RSC Adv. 5 (64) (2015) 52243–52251.
[23] M. Villano, F. Aulenta, M. Majone, Perspectives of biofuels production from renewable resources with bioelectrochemical systems, Asia-Pac. J. Chem. Eng. 7 (2012) S263–S274.
[24] F. Micolucci, M. Gottardo, D. Bolzonella, P. Pavan, Automatic process control for stable bio-hythane production in two-phase thermophilic anaerobic digestion of food waste, Int. J. Hydrogen Energy 39 (2014) 17563–17572.
[25] M. Villano, G. Monaco, F. Aulenta, M. Majone, Electrochemically assisted methane production in a biofilm reactor, J. Power Sources 196 (2011) 9467–9472.
[26] M. Zeppilli, M. Villano, F. Aulenta, S. Lampis, G. Vallini, M. Majone, Effect of the anode feeding composition on the performance of a continuous-flow methane-producing microbial electrolysis cell, Environ. Sci. Pollut. Res. Int. 22 (2015) 7349–7360.
[27] M. Cerrillo, M. Viñas, A. Bonmatí, Removal of volatile fatty acids and ammonia recovery from unstable anaerobic digesters with a microbial electrolysis cell, Bioresour. Technol. 219 (2016) 348–356.
[28] APHA, Standard Methods for The Examination of Water and Wastewater, American Public Health Association, Washington DC, 1995.
[29] M. Villano, C. Ralo, M. Zeppilli, F. Aulenta, M. Majone, Influence of the set anode potential on the performance and internal energy losses of a methane-producing microbial electrolysis cell, Bioelectrochemistry 107 (2016) 1–6.