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Microbial Electrolysis Cell to Enhance Energy Recovery from Wastewater Treatment

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Energy intensive activate sludge treatment is the most utilized technology for municipal wastewater treatment. However, an innovative way to harvest part of the energy contained in municipal wastewater is offered by the utilization of microbial electrolysis cells (MECs). In an MEC, through the utilization of electro active microorganism, is possible to couple the oxidation organic matter with the generation of value-added reduced products, such as methane, similar to the anaerobic digestion process. MECs typically consist of a bio-anode and a (bio)-cathode separated by an ion exchange membrane (IEM). The addition of external energy usually is required to make the cathodic reaction thermodynamically feasible. Here, a continuous flow methane-producing MEC equipped with an anion exchange membrane was operated in a continuous flow mode for over 60 d at two different poised anode potentials (+ 0.20 and -0.10 V vs. standard hydrogen electrode, SHE) and with a fixed organic load rate (1.08 gCOD/Ld). The MEC showed a high COD removal efficiency (92 ± 1%), with a net energy recovery (122 ± 3 %, at -0.1 V) and low sludge production (0.09 gCOD/gCOD), making its utilization attractive in the frame of low strength wastewater treatment.

1. Introduction

Nowadays wastewater treatment represents a considerable energy cost for the society. In this frame, a new approach aimed to enhance energy efficiency and reduce the economic impact is to consider wastewater treatment plants (WWTP) and, in general, sanitation systems as sustainable resource recovery systems. However, as recently reported in the literature (Guest et al. 2009), this approach needs a paradigm shift focused on what must be removed from wastewater to what can be recovered. In this scenario, anaerobic digestion (AD), that permits the biomethane production from waste materials, surely represents the "energy engine" for the treatment plant in future. AD applications increased over the last years with the possibility to apply the co-digestion of sewage sludge with other waste materials such as the organic waste of municipal solid waste (OF-MSW) or zoo-technical effluents, in order to enhance the biomethane production. However, a critical aspect of the AD technology is the need to operate digesters at temperature at or above 35 °C that makes the technology economically feasible only for concentrated streams. Thus, municipal low-strength wastewaters cannot be utilized as feedstock for AD process and are typically treated in energy intensive activate sludge systems, with an average energy consumption of about 0.7 - 2 kWh/kgCOD (Cheng et al. 2012). Both chemical (in the form of reduced carbon substances and nutrients) and thermal energy (associated with the temperature of the wastewater) contained in municipal wastewaters could be in principle exploited through innovative technologies such as bioelectrochemical systems (BES) (McCarty et al. 2011). In a BES electro-active microorganisms utilize a solid state electrode as final acceptor or donor of electrons involved in their metabolism. BESs can be utilized to produce electrical power, as occurs in microbial fuel cells (MFCs), or to generate valuable reduced products, as occurs in microbial electrolysis cells (MECs). In the latter case, an external energy input is generally required in order to make thermodynamically feasible the cathodic reduction (Logan and Rabaey 2012). Particularly, the possibility to couple the oxidation of organic matter (at the anode) to methane production (at the cathode) in an MEC brings several advantages and the performance of a two chamber methane-producing MEC, operated at different organic load rates (OLR)

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(Villano et al. 2012) and composition of feeding solution (Zeppilli et al. 2014), has been largely investigated over the last years. Data collected have been obtained by using a high selective protonic exchange membrane (Nafion® 117) as separator of the anodic and cathodic compartments. However, the type of membrane used is a key-parameter affecting the performance of BESs (Rozendal et al. 2008). Along this line, the present research has been mainly focused on evaluating the performance of a methane producing MEC equipped with an anion exchange membrane (Fumasep - FAD) and operated at an OLR of 1.08 gCOD/Ld with acetate as the only substrate for anodic oxidation. The performance of the MEC in long term experiments has been mainly assessed trough electrons, mass, and energy balance.

2 Materials and methods

2.1 Microbial electrolysis cell setup and operation

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 compartments were filled with graphite granules with a diameter between 2 and 6 mm, and separated by a Fumasep-FAD, which is a quaternary ammonium based anionic exchange membrane (AEM). The AEM was pretreated at 35°C for 24 h in a NaCl solution (5 % w/v) in deionized water. Both compartments were equipped with a graphite rod current collector and a KCl saturated Ag/AgCl reference electrode (+0.2 V vs. standard hydrogen electrode, SHE) (Amel s.r.l., Milan, Italy), in order, respectively, to guarantee the external electrical connection and to measure or control the potential of individual electrodes. In order to sample both headspace and liquid phase of anolyte and catholyte, a glass chamber equipped with sampling ports sealed with butyl rubber stoppers and aluminum crimps was placed in the outlet of each compartment. Furthermore, the cathodic glass chamber was connected to a milliGas counter (Ritter, Germany), in order to record the volume of the gas fluxed trough the cathode compartment. The anode of the MEC was inoculated with 0.2 L of activated sludge from a local municipal wastewater treatment plant (Rome, Italy), having a biomass concentration of approximately 4 g/L as volatile suspended solids (VSS). The cathodic compartment was inoculated with an anaerobic sludge enriched in hydrogenophilic methanogens in a fill and draw reactor (0.4 L, working volume), having a biomass concentration of approximately 8 g/L as VSS. The anode was operated in continuous-flow mode with a feeding solution containing acetate as the only carbon source. The anolyte composition was (g/L): CH_3COONa (0.82); NH_4Cl (0.125); $MgCl_2•6H_2O$ (0.1); K_2HPO_4 (4); $CaCl_2•2H_2O$, (0.05); 10 mL/L of a trace metal solution (Balch et al. 1979), and 1 mL/L of vitamin solution (Zeikus 1977). Before being used, the feeding solution was flushed with a N_2/CO_2 (70:30 v/v) gas mixture in order to establish anaerobic conditions. The anodic feeding flow rate was 1.44 L/d, resulting in an hydraulic retention time (HRT) of 0.57 d (referred to the empty volume of the anode compartment).The cathode compartment was operated under batch conditions, with a high internal recirculation rate in order to overcome concentration gradients. The catholyte composition was the same of the anolyte except for the acetate. Furthermore, to ensure pH control and to supply the carbon for the cathodic reduction process (Villano et al 2013), a mixture of N_2/CO_2 (70 %:30 %) gas was continuously bubbled inside the cathodic compartment. Throughout all the experimentation, the MEC was operated in potentiostatic mode, by a three electrode configuration where the anode compartment constituted the working electrode. The anode potential was controlled at +0.2 V and -0.1 V vs. SHE with a potentiostat (Bio-Logic, Grenoble, France), which also allowed measuring and recording the electrical current and the cumulative charge flowing in the system. The difference of potential between the anode and cathode compartments, as well as the value of the cathode potential, were daily monitored with a digital multimeter (Fluke, Holland). All over the manuscript potentials are reported with respect to the standard hydrogen electrode (SHE).

2. 2 Chemical analysis and calculation

Acetate was analysed by injecting 1 μL of filtered (0.22 μm porosity) aqueous sample into a Dani Master (Milan, Italy) gas chromatograph. 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. Headspace concentrations were converted to aqueous-phase concentrations using tabulated Henry’s law constants (Green and Perry 2008). The concentration of microorganisms in the anode effluent as well as in the cultures used to inoculate the MEC was determined as volatile suspended solids (VSS), according to standard methods (APHA 1995). All calculations referred to electrons, mass, and energy balance were performed as reported elsewhere (Zeppilli et al 2014).

3. Results and discussion

3.1 MEC operation in potentiostatic mode

The MEC was operated for more than 60 days with the anode potentiostatically controlled at the desired value (Figure 1). From day 0 to day 33, the anodic potential was poised at +0.2 V and, during this operational time, a steady state condition was obtained after around 2 d of operation in terms of both acetate removal (expressed as COD, chemical oxygen demand) and methane production. More in detail, as reported in Figure 1 - A, the average influent acetate concentration varied between 598 and 828 mgCOD/L, while the concentration in the effluent stream accounted for 58 ± 7 mgCOD/L, with an average COD removal efficiency of 91 ± 1%. Electric current was generated from substrate oxidation, indicating the ability of microorganisms present in the anode compartment to use the polarized electrode as electron acceptor. The average value of current was 72 ± 3 mA, with a resulting columbic efficiency (CE), i.e the percentage of electrons deriving from substrate oxidation and converted into current, of 64 ± 3 %. Furthermore, the average concentration of biomass in the effluent liquid phase from the anodic compartment was 38 mgVSS/L and, by assuming a steady state condition whereby the biomass daily discharged from the reactor can be considered equal to the novel produced biomass, the observed growth yield in the anodic compartment of the MEC accounted for 0.09 gCOD/gCOD. This clearly indicated that only a very little fraction of the removed substrate was diverted into microbial growth. Throughout the operational period the main product detected in the cathodic compartment was methane, with an average production rate of 79 ± 3 meq/Ld (figure 1 – B), whereas neither acetate nor hydrogen were detected. The cathode capture efficiency (CCE), which represents the amount of electrons recovered as products at the cathode, was 95%, giving a further confirmation that methane was the predominant reduced product. On average, the global capture efficiency (GCE), which represents the degree of conversion of the anodic COD into cathodic products, raised a value of 64 ± 3 %. A key parameter to evaluate the process performance is represented by its energy consumption, which is dependent on the value of potential difference established between the cathode and the anode, as well as on the value of current flowing in the system. With the anode potentiostatically controlled at +0.20 V, the difference of potential measured between the two compartments of the MEC was on average 1.46 V. As a consequence the energy efficiency (ηE), i.e. the ratio between the energy recovered as methane and the external energy input, was 69 ± 3 %. On the basis of a previous research (Zeppilli et al. 2014), starting from day 32 the anodic potential was shifted to a less oxidative value, in order to improve the MEC energy efficiency. To accomplish this objective, day 33 to day 63 of operation the MEC was run with the anode potential poised at -0.10 V. During this second potentiostatic condition, the influent acetate concentration varied between 608 and 906 mgCOD/L while the value of acetate concentration in the effluent was on average 60 ± 7 mgCOD/L (Figure 1 - A); thus, the average value of COD removal efficiency was 92 ± 1 %. As for current generation, the observed average value (53 ± 3 mA) was lower than that obtained with the anode potential controlled at +0.20 V, and this resulted also in a lower average value (49 ± 3 %) of the CE. No significant effect of the applied anode potential was detected on the calculated observed growth yield. Indeed, both the average biomass concentration in the anodic effluent and the observed growth yield were very similar to values obtained at +0.20 V. As for the performance of the the cathode, also in this case methane was the only reduced product, with an average production rate of 57 meq/Ld (Figure 1B), which is slightly lower than that observed at the more oxidative applied value of the anode potential; even though the CCE was very high (102 ±1 %).This was likely due to the lower availability of electrons deriving from the lower current generation. On other hand, the recovery of methane with respect to the COD oxidation, did not show a dependence by the applied anodic potential, in fact GCE was 49 ± 3 % on average during the -0.10 V condition. Finally, due to the potential difference established between the anode and the cathode (-0.89 ±0.02 V), substantially lower than that established in the previous run, the value of ηE was 122 ±3 % indicating a theoretically net energy production from the MEC. Main parameters obtained during the entire period of the MEC operation at the two applied anode potentials are summarized in Table 1.

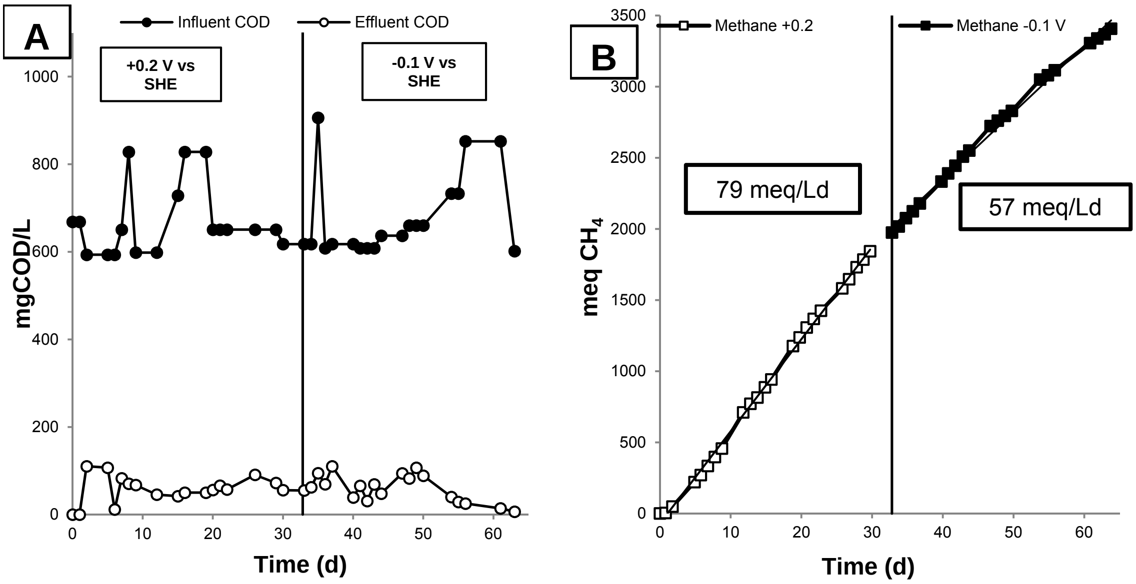

Figure 1: Time course of COD concentration in the anodic influent and effluent (A) and cumulative equivalents of methane generated at the cathode (B) during the entire period of the MEC operation at two applied anode potentials.

Table 1: Main parameters obtained during the entire period of the MEC operation at two applied anode potentials.

	Anion Exchange membrane	
Anodic potential (vs SHE)	+ 0.2	- 0.1
i (mA)	72 ± 3	53 ± 3
Influent COD (mg/L)	632 ± 13	699 ± 19
Effluent COD (mg/L)	58 ± 7	60 ± 7
VSS anodic effluent (mg/L)	38 ± 2	39 ± 1
Growth Yield (gCOD/gCOD)	0,09	0,09
COD removal efficiency (%)	91 ± 1	92 ± 1
Coulombic efficiency (%)	64 ± 3	49 ± 3
Methane production rate (meq/Ld)	79 ± 3	57 ± 3
Cathode capture efficiency (%)	95 ± 2	102 ± 1
Global coulombic efficiency (%)	64 ± 3	49 ± 3
Potential difference (ΔV)	1.46 ± 0,07	0.89 ± 0,02
Energy efficiency %	69 ± 3	122 ± 3

3.2 COD mass balance

Data collected during 60 days MEC operation have been used to perform a COD mass balance of the process. The different mechanisms considered in the balance are: methane production, biomass production and “lost” COD, i.e. the COD removed through unknown pathways. The latter was obtained by difference between the COD removed and the COD recovered as biomass and methane production. The main results of COD mass balance are summarized in Table 1. During the run with the anode polarized at +0.20 V, on average the COD removal rate was 1.052 gCOD/Ld, while biomass growth and methane production rates were respectively 0.094 and 0.634 gCOD/Ld; representing on average 60 % of the oxidized COD and 9 % of the removed COD, respectively. As a result, 31 % of the removed COD was not recovered or involved in other detectable mechanisms. The “lost" COD was probably due to non-electroactive pathways or unknow processes, like microbial storage as intracellular or extracellular polymer or adsorption or entrapment in the anodic biofilm. Moreover, during the less oxidative explored condition (-0.10 V), the COD removal rate was on average 1.033 gCOD/Ld; even though the portion of the removed COD converted into microbial growth was the same as the previous run (9 %), only about 45 % of COD was recovered by cathodic methane production. As a consequence, the “lost" COD represented 46 % of total removed COD. This difference, in terms of "lost" COD and methane production in the two potentiostatic conditions, was likely due to the different oxidative environment established in the anode compartment. At +0.20 V, probably the more oxidative environment enhanced the electrocatalytic activity of anodic biomass that, through the oxidation of the influent acetate, transferred a higher amount of equivalents to the cathodic reaction. In a less oxidative environment, indeed, other competitive processes to COD utilization could be more impacting on the overall performance of the MEC.

Table 2: COD mass balance during the during entire period of the MEC operation at two applied anode potentials

COD mass balance				
Mechanism	+ 0.2 vs SHE		- 0.1 vs SHE	
	Rate	Percentage	Rate	Percentage
COD removed (gCOD/Ld)	1.052	100	1.033	100
Methane production (gCOD/Ld)	0.634	60	0.459	45
Biomass production (gCOD/Ld)	0.094	9	0.096	9
Lost COD (gCOD/Ld)	0.324	31	0.478	46

3.3 Energy Balance

The evaluation of the energy consumption of the lab scale methane-producing MEC was calculated by the product of the difference of potential established between the anode and the cathode and the average value of current flowing in the system. The calculated energy consumption (as kWh/d) was normalized with respect to the removed COD (kgCOD/d) in the anodic chamber. During the two potentiostatic conditions, the energy consumption accounted for 2.92 kWh/kgCOD and 1.34 KWh/kgCOD at +0.2 V and -0.1 V, respectively. However, by taking into account that part of the consumed energy was recovered as methane at the cathode of the MEC, the net energy consumption substantially decreased at both operating conditions. Indeed, a net energy consumption of 0.96 kWh_{net}/kgCOD was estimated at +0.2 V and no net energy consumption was calculated when the anode potential was poised at -0.1 V. This was due to the very high value of the energy efficiency obtained at this potential, which significantly overcame 100 % indicating that the energy recovered from methane was higher than the energy provided to produce it.

4. Conclusions

A two-chamber methane producing MEC operated with the anode potential controlled at +0.2 V and -0.1 V (vs. SHE) resulted in a stable performance, both in terms of COD removal and methane production, over 60 d of operation. In both the explored conditions, over 90 % of the influent COD was removed in the anodic compartment and mostly utilized for current generation instead of biomass growth. The high COD removal efficiency was likely due to the utilization of acetate as model substrate and, importantly, was not affected by the value of the anode potential. The latter, however, surely influenced the capability of the biomass to utilize graphite granules as final electron acceptor. Indeed, even though the amount of removed COD was similar under the different operating conditions, the coulombic efficiency (i.e., the yield of COD conversion into current) was 64 ±3% at +0.2 V and 49 ±3% at -0.1 V. This experimental result suggests the possibility of microorganisms to utilize acetate also in different non electro active pathways. In agreement with this hypothesis, the COD mass balance confirmed that the “lost COD”, i.e. the COD not involved in electroactive pathways, became higher at less oxidative potential. As for the cathode performance, methane production resulted in a high conversion of generated current into cathodic products (i.e., the cathode capture efficiency, CCE) at both potentiostatic conditions, with values of 95 ± 2 and 102 ± 1 %. However, the CCE could be partially overestimate because a small amount of acetate ions likely diffused from the anode to the cathode where acetoclastic methanogens could utilized acetate to methane production. This fact, on the contrary, could cause an underestimation of the coulombic efficiency. The MEC reactor showed interesting results in the frame of the applicability of the process to perform an energy recovery from the treatment of low-strength wastewater, furthermore, another advantage of the MEC is related to the low sludge production. In fact, the aerobic biomass (with typical growth yield in the range of 0.5 gCOD/gCOD) inoculated at the MEC anode, showed a low growth yield of 0.09 gCOD/gCOD in both the explored conditions. Moreover, the energy consumption of the reactor was maintained in the range of activate sludge process (Cheng et al. 2012) with values of 2.92 and 1.34 kWh/kgCOD for the two potentiostatic conditions explored. Finally, with the anode controlled at -0.1 V the MEC showed a net energy production, whereby the energy theoretically recovered by methane production was higher than the electrical input spent to operate the reactor.

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