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Carbon and nitrogen removal and enhanced methane production in a microbial electrolysis cell

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HIGHLIGHTS

- A two-chamber methane-producing microbial electrolysis cell (MEC) is investigated.
- 94% of the influent acetate was oxidized at the anode with 91% coulombic efficiency.
- Methane was microbially produced at the cathode with 79% electron capture efficiency.
- Low-strength wastewater treatment with good energy efficiency and low sludge production.
- Good potential to refine both liquid effluent and biogas from anaerobic digestors.

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ABSTRACT

The anode of a two-chamber methane-producing microbial electrolysis cell (MEC) was poised at +0.200 V *vs.* the standard hydrogen electrode (SHE) and continuously fed (1.08 gCOD/L d) with acetate in anaerobic mineral medium. A gas mixture (carbon dioxide 30 vol.% in N_2) was continuously added to the cathode for both pH control and carbonate supply. At the anode, 94% of the influent acetate was removed, mostly through anaerobic oxidation (91% coulombic efficiency); the resulting electric current was mainly recovered as methane (79% cathode capture efficiency). Low biomass growth was observed at the anode and ammonium was transferred through the cationic membrane and concentrated at the cathode. These findings suggest that the MEC can be used for the treatment of low-strength wastewater, with good energy efficiency and low sludge production.

1. Introduction

Harnessing (even only partially) the energy contained in waste streams would mitigate the burden and costs associated with wastewater treatment, while simultaneously generating clean and renewable energy (Heidrich et al., 2011; Angenent et al., 2004); however, in order to convert undefined and often diluted waste organic substrates into clean fuels and/or chemicals a platform of selective and energy-efficient (bio) catalytic routes needs to be developed, optimized, and properly integrated.

Anaerobic digestion (AD), the microbially catalyzed conversion of (waste) organic substrates into a gas mixture primarily consisting of methane and carbon dioxide, is one of the most attractive routes to sustainable bioenergy production from waste substrates (Rittmann, 2008; Kleerebezem and van Loosdrecht, 2007; Verstraete and Vandevivere, 1999). Unfortunately, the well-established AD technology is constrained by the susceptibility of methanogenic microorganisms to toxic compounds, the need to operate the bioprocess at temperatures generally at or above 35 °C which restricts its applicability to high-strength wastewater only, inefficient nutrient removal, and difficulty in removing the organic substrates down to low residual concentrations (Pham et al., 2006). For the latter reason, in order to meet stringent effluent discharge limits, AD systems require a "polishing" post-treatment step, that is typically achieved in energy-intensive activated sludge systems, where the residual organic matter is aerobically oxidized to carbon dioxide and water, with concomitant production of considerable amounts of sludge.

Bioelectrochemical systems such as microbial electrolysis cells (MECs), have emerged as another highly versatile technology which enables coupling wastewater treatment to the generation of energy carriers and chemicals (Pant et al., 2012). In a microbial electrolysis cell, "electro-active" microorganisms use a solid-state anode as terminal electron acceptor for the oxidation of organic waste substrates to carbon dioxide, while simultaneously releasing protons to the solution. Electrons flow from the anode to the cathode

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through an external circuit while protons diffuse to the cathode through a proton-exchange membrane separating the two electrode compartments. At the cathode, in the presence of a suitable (bio)catalyst, the electrons combine with a soluble electron acceptor, generating a target product (Rabaey and Rozendal, 2010). In most cases, MECs require the potential generated from substrate oxidation at the anode to be boosted with an external power supply in order to make the cathodic reaction thermodynamically feasible. Even though the need for external power decreases the net energy balance with respect to the traditional AD process, the MEC approach brings some specific advantages, such as the possibility to deal with diluted wastewaters and to operate the process even at ambient temperature. Moreover, besides H^+, NH_4^+ is also transported across the cation exchange membrane (even against a concentration gradient) from the anode to the cathode compartment of other bioelectrochemical systems, such as microbial fuel cells, to maintain the electroneutrality during sustained operation (Kuntke et al., 2011, 2012; Cord-Ruwisch et al., 2011). If confirmed also in an MEC setup, this finding could offer the opportunity to concentrate and recover NH_4^+ from the influent stream. Furthermore, the possibility to integrate the AD process with bioelectrochemical systems has also been proposed and it seems to be particularly interesting when AD is combined with a methane-producing MEC (Pham et al., 2006; Clauwaert et al., 2008; Villano et al., 2010, 2011).

The aim of the present study was to investigate whether a methane-producing MEC can be used for treatment of low-strength wastewater, with good energy efficiency and low sludge production. For this purpose the performance of a two-chamber methane-producing MEC, continuously fed (at the anode) with a diluted stream containing acetate (0.64 gCOD/L) as model substrate for low-strength wastewater was analyzed in terms of substrate removal efficiency, current and methane generation, and energy yield. A nitrogen mass balance was also performed in order to preliminary assess the potential for ammonia recovery.

2. Methods

2.1. Microbial electrolysis cell design and setup

The setup consisted of a two-chamber microbial electrolysis cell (MEC) made of Plexiglas as previously described (Villano et al., 2011). The two chambers (i.e., the anode and cathode compartments) were separated by a Nafion® 117 proton exchange membrane (PEM) and filled with graphite granules with a diameter between 2 and 6 mm, giving a bed porosity of 0.48. The total empty volume of each chamber was 0.86 L. Prior to being used, both the PEM and the graphite granules were pretreated as described elsewhere (Villano et al., 2011).

A graphite rod current collector (5 mm diameter, Sigma–Aldrich, Italy) and a KCl saturated Ag/AgCl reference electrode (+0.199 V *vs.* standard hydrogen electrode, SHE) (Amel s.r.l., Milan, Italy) were placed in each compartment, in order to guarantee the external electrical connection and to measure or control the potential of individual electrodes, respectively.

A glass chamber, equipped with sampling ports sealed with butyl rubber stoppers and aluminum crimps, was placed in the outlet of each compartment in order to sample the headspace and the liquid phase of both the anode and the cathode. In the latter case, the glass chamber was connected to a milliGas Counter (Ritter, Germany), which recorded the volume of the produced gas.

2.2. Microbial electrolysis cell operation

The experimentation was performed with microorganisms already present in the MEC, from previous inocula. Specifically, the anode compartment had been inoculated with 0.2 L of activated sludge collected from a local full-scale municipal wastewater treatment plant (Rome, Italy), having a biomass concentration of approximately 2 g/L as volatile suspended solids (VSS). The inoculum used for the cathode compartment was anaerobic sludge (0.05 L) from the full-scale wastewater treatment plant of Treviso (Italy), with a biomass concentration of approximately 8 g/L as VSS.

Throughout the study, the anode was operated in continuous-flow mode by using a peristaltic pump. The feeding solution (anolyte) contained (g/L): CH_3COONa, 0.82; NH_4Cl, 0.125; $MgCl_2{\cdot}6H_2O$, 0.1; K_2HPO_4, 4; $CaCl_2{\cdot}2H_2O$, 0.05; 10 mL/L of a trace metal solution (Balch et al., 1979), and 1 mL/L of vitamin solution (Zeikus, 1977). Prior to being supplied to the anode, the feeding solution was flushed with a N_2/CO_2 (70:30 v/v) gas mixture and the pH was adjusted to values between 7.00 and 7.10 by adding a $NaHCO_3$ solution (10% w/v), resulting in a final bicarbonate concentration of approximately 1 g/L. The feeding flow rate was 1 mL/min, resulting in an hydraulic retention time (HRT) of 0.60 d (referred to the empty volume of the anode compartment). The corresponding organic load rate (OLR) was 1.08 gCOD/L d, the acetate being the sole electron donor for the anodic culture. In a few cases, the acetate feed was shortly interrupted to verify the dynamic response of the system and then established again.

The MEC cathode was operated in a semi-batch mode with the liquid phase (catholyte) being continuously recycled at a flow-rate of 30 mL/min, using a peristaltic pump, in order to prevent the establishment of products concentration gradients. The composition of the catholyte was the same as for the anolyte, except that acetate was omitted. On average, 103 mL of catholyte were removed daily in order to counterbalance the liquid volume diffusing from the anode to the cathode compartment through the PEM; this resulted in an HRT of 8.35 d (with respect to the empty volume of the cathode compartment). These volumes were carefully accounted for in the mass balances. From day 15 onwards, the liquid phase in the cathode compartment was continuously bubbled with a gaseous stream (at a flow rate of around 10 L/d) containing carbon dioxide (30 vol.%, N_2 as balance), which simulated the biogas derived from an anaerobic digester.

In order to smooth temperature variations, both the influent line (to the anode) and the recycle line (through the cathode) were passed through glass heat exchangers; the temperature was typically around 24–26 °C. Throughout the experiments, the anode was controlled at +0.200 V (*vs.* SHE) with a potentiostat (Bio-Logic, Grenoble, France), which also allowed measuring and recording the electrical current flowing in the system. This relatively high anode potential was chosen because it falls within the range of redox conditions typically occurring in conventional aerobic wastewater treatment processes, e.g. the activated sludge process. The final aim was to achieve and maintain substrate removal efficiencies as high as those reported for aerobic oxidation, since they are a key prerequisite for a MEC to be competitive with currently applied wastewater treatment technologies.

The potential of the cathode was periodically monitored with a digital multimeter (Keithley Instruments, Cleveland, Ohio). Potentials are reported with respect to SHE.

The MEC was operated for 72 d without changing the operating conditions, but for the addition of the gas mixture to the cathodic compartment, and short interruptions of the acetate feed. After any change, a steady state was quickly reached, as verified through the invariance of the time-profile of all monitored parameters (such as current, pH, effluent acetate and ammonia).

2.3. Chemical analyses

Acetate was analyzed by injecting 1 μL of filtered (0.22 μm porosity) aqueous sample into a Dani Master (Milan, Italy) gas-chromatograph (2 m × 2 mm glass column packed with Carbopack,