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Anaerobic digestion and electromethanogenic microbial electrolysis cell integrated system: Increased stability and recovery of ammonia and methane

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ABSTRACT

The integration of anaerobic digestion (AD) and a microbial electrolysis cell (MEC) with an electromethanogenic biocathode is proposed to increase the stability and robustness of the AD process against organic and nitrogen overloads; to keep the effluent quality; to recover ammonium; and to upgrade the biogas. A thermophilic lab-scale AD, fed with pig slurry, was connected in series with the bioanode compartment of a two-chambered MEC. In turn, the biocathode of the MEC was poised at −800 mV vs Standard Hydrogen Electrode and fed with CO_2 to increase the methane production of the system. After doubling its organic and nitrogen loading rate, the AD operation became stable thanks to the connection of a recirculation loop with the MEC effluent. Ammonium removal in the anode compartment of the MEC achieved 14.46 g $N\text{-}NH_4^+$ m^{-2} d^{-1}, while obtaining on average 79 L CH_4 m^{-3} d^{-1} through the conversion of CO_2 in the cathode compartment. The microbial analysis showed that methylotrophic *Methanossiliicoccaceae* family (*Methanomassiliicoccus* genus) was the most abundant among the metabolically active archaea in the AD during the inhibited state; while, on the cathode, *Methanobacteriaceae* family (*Methanobrevibacter* and *Methanobacterium* genus) shared dominance with *Methanomassiliicoccaceae* and *Methanotrichaceae* families (*Methanomassiliicoccus* and *Methanothrix* genus, respectively).

1. Introduction

The increasing global demand for fossil fuels, their tendency to be scarcer, and the need to control the greenhouse gas emissions when using them are requiring new strategies for energy production. An alternative to conventional refineries for clean and renewable energy production is the biorefinery. Biorefineries can recover nutrients and other products of interest from energetic crops, organic wastes and other waste fluxes [1]. This concept goes beyond the philosophy of petrochemical refineries, including sustainable management practices and closed cycle processes whenever possible. Wastes, whether domestic, industrial, agricultural or from livestock are a great opportunity to recover water, energy, chemical products and nutrients, and have a big potential for application in biorefineries [2]. Not only meeting environmental protection objectives, but also recovering energy and resources from wastes should be addressed in a circular economy [3].

The combination of anaerobic digestion (AD) and bioelectrochemical systems (BES) is an integrated strategy that can be implemented with different objectives and configurations [4,5] and can attain the goals of the biorefinery concept [6,7]. On the one hand, nutrients can be recovered from ammonium-rich wastewater such as pig slurry or digested pig slurry thanks to cation or anion transport through exchange membranes that takes places in BES [8]. The main example of this application is the recovery of ammonium, which can be reused as fertiliser [9–13]. Otherwise, the AD effluent would need to be processed or managed properly due to its high nutrient content. Ammonia recovery has been demonstrated in various BES including microbial fuel cells (MFCs) [10,11] and microbial electrolysis cells (MECs) [14]. In MECs, a higher current density would greatly enhance ammonium recovery, and thus MECs exhibit a better performance for ammonium recovery than MFCs [15].

On the second hand, BES can operate with low organic loading rates and may be used to polish the effluent of the AD [16–18] or even to absorb higher organic concentrations in the digestates due to AD destabilisation or inhibition [18,19]. Previous work has shown that integrated or multi-step systems can increase the energy

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production from complex substrates [4]. The combination of AD and BES for effluent polishing has been studied mainly using energy recovering MFC, to treat the effluent of a two-stage biogas process [20], digested landfill leachate [21], digested swine wastewater [22], a digested mixture of swine manure and rice bran [23] or digested wastewater from processing potato industries [17]. Instead, the use of MEC mode proposed in this work for AD effluent polishing has been scarcely reported [19].

On the third place, the combination of the previous advantages can be applied to increase the stability of the AD process through the use of a submersible microbial desalination cell [24] or the establishment of a recirculation loop with the BES [25]. The latter strategy has proven to be effective for the control of AD inhibition due to organic and nitrogen overloads, while recovering ammonia and maintaining the effluent quality and the methane production of the AD. Other studies have reported an increased stability of the AD process when inserting electrodes in the reactor [26–28]. However, this latter configuration does not allow for ammonia recovery, as proposed in the present work.

Finally, BES have been applied to increase the methane content of the biogas produced in the AD by the use of MECs with electromethanogenic biocathodes [29,30]. Since biogas consists mainly of methane (CH_4, 40–75%) and carbon dioxide (CO_2, 15–60%) it needs upgrading prior to its use as vehicle fuel or for injection in the natural gas grid intended to adjust the calorific value. Conventional techniques for biogas upgrading focus on CO_2 removal without changing CH_4 mass [31], while electromethanogenesis performed in MEC allows for the conversion of CO_2 into CH_4 [32–34]. An alternative configuration to electromethanogenic MECs, by inserting electrodes in the AD reactor and applying a potential, allows for the in situ biogas upgrading, reporting an increase in methane yield [26,35–37]. An increase of 59.7% in methane yield was achieved in a AD-MEC coupled system compared to the AD alone [38]. MECs for CO_2 conversion to methane have been operated mainly with synthetic medium [39,40] and there is a lack of studies with real high strength wastewater fed for the anode compartment. The present study contributes to the body of knowledge by using a real high strength wastewater, digested pig slurry, to feed the anode compartment.

The multiple ways of AD and BES combination suggest that a more comprehensive strategy can help to settle most of the limitations of the AD process, which up to now has not been assessed. Several studies have addressed the use of BES with a combined objective, such as Zepilli et al. [40], who operated a methane-producing MEC with a synthetic solution of soluble organic compounds, simulating the composition of a municipal wastewater, with the purpose of COD and ammonium removal, and methane production. Instead, the scientific novelty of this study was to investigate an integrated AD-MEC system fed with a high strength wastewater, such as pig slurry, and designed with a multiple purpose: i) to increase the stability and robustness of the AD process against organic and nitrogen overloads, ii) to keep the effluent quality, iii) to recover nutrients, and iv) to upgrade the biogas. None of the reported bioelectrochemical systems has simultaneously addressed these four purposes. Therefore, the application of MEC technology could be also implemented to overcome simultaneously the main limitations of AD. Furthermore, further study on the active microbial populations enriched in the bioanode and biocathode of the BES is needed to gain insight on potential resilience strategies as well as to complement previous studies [30,40]. Until now, studies were centred on the description of the most predominant existent microorganisms on methanogenic biocathodes [29,32,34,41,42], while this study presents a novel focus on the metabolically active biomass. This novel approach bridge the gap to distinguish those active microorganisms from total microbial community in the biofilm communities in MECs.

The main aim of this study was to assess the performance of a lab-scale AD-MEC integrated system as a strategy to stabilise a pig slurry thermophilic AD under an organic and nitrogen overload, recover ammonia and increase the methane content of the biogas produced by the AD, in terms of chemical oxygen demand and ammonia removal, methane yield and energy efficiency of the process. The evolution of the active microbial community of the AD and the MEC bioelectrodes (both the anode and the cathode) was evaluated in terms of composition and activity by means of high throughput sequencing (16S rRNA *versus* 16S rDNA based Illumina-Miseq) and quantifying total and metabolically active populations (*16SrRNA* and *mcrA* gene and transcripts) by qPCR.

2. Materials and methods

2.1. Experimental set-up

A 4 L lab-scale thermophilic anaerobic continuous stirred tank reactor (AD) was used in the assays. It consisted of a cylindrical glass reactor (25 cm diameter) with a 4 L working volume. The digester was fitted with a heat jacket with hot water circulating to keep the temperature at 55 °C. The AD reactor was connected in series with the anode compartment of a two-chambered MEC (0.5 L in each compartment) and had a recirculation loop between both reactors. The anode of the MEC was carbon felt (dimensions: 14 × 12 cm; thickness: 3.18 mm; Alfa Aesar GmbH & Co KG, Karlsruhe, Germany) that had been inoculated with anode-inoculum from a mother MFC and had been operated with digested pig slurry as feeding solution for 9 months. The cathode chamber was filled with granular graphite with diameter ranging from 1 to 5 mm (Typ 00514, enViro-cell Umwelttechnik GmbH, Oberursel, Germany), leaving a net volume of 265 mL. Prior to being used, in order to remove metals and organic residues, the granular graphite was treated as described in Sotres et al. (2016) [43]. An A304 stainless steel mesh was used as electron collector in each compartment (dimensions: 14 × 12 cm; mesh width: 6 × 6 mm; wire thickness: 1 mm; Feval Filtros, S.L., Barcelona, Spain). The anode and cathode compartments were separated by a cation exchange membrane (CEM) (dimensions: 14 × 12 cm; Ultrex CMI-7000, Membranes International Inc., Ringwood, NJ, USA). The cathode compartment was inoculated with 30 mL of a resuspension of the anaerobic granular sludge of an UASB (volatile suspended solids content of 33 g L^{-1}) that had been operated with methanol in order to enrich the biomass in methanogenic archaea, as described elsewhere [44]. The resuspension was done by vortex mixing during 10 min in a 50 mL tube containing 30 g of granular sludge and 25 mL of Ringer 1/4 sterilised solution. A three electrodes configuration was used, where the anode was the counter electrode, the cathode was the working electrode and an Ag/AgCl reference electrode (Bioanalytical Systems, Inc., USA, +197 mV vs. standard hydrogen electrode (SHE)) was inserted in the cathode compartment. All potential values in this paper are referred to SHE. A potentiostat (VSP, Bio-Logic, Grenoble, France) was used for data monitoring, which was connected to a personal computer for electrode potentials and current recording every 5 min using EC-Lab software (Bio-Logic, Grenoble, France). The anode was fed with filtered digested pig slurry (125 μm) from the AD and the cathode compartment was fed with a synthetic solution which contained (per litre of deionised water): 5 g L^{-1} of $NaHCO_3$, NH_4Cl, 0.87 g; $CaCl_2$, 14.7 mg; KH_2PO_4, 3 g; Na_2HPO_4, 6 g; $MgSO_4$, 0.246 g; and 1 mL L^{-1} of a trace elements solution as described elsewhere [45].