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Dark fermentation, anaerobic digestion and microbial fuel cells: An integrated system to valorize swine manure and rice bran

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ABSTRACT

This work describes how dark fermentation (DF), anaerobic digestion (AD) and microbial fuel cells (MFC) and solid-liquid separation can be integrated to co-produce valuable biochemicals (hydrogen and methane), bioelectricity and biofertilizers. Two integrated systems (System 1: AD + MFC, and System 2: DF + AD + MFC) are described and compared to a traditional one-stage AD system in converting a mixture (COD = 124 ± 8.1 g_{O2} $kg^{-1}_{Fresh\ Matter}$) of swine manure and rice bran. System 1 gave a biomethane yield of 182 L_{CH4} $kg^{-1}_{COD\text{-}added}$, while System 2 gave L yields of bio-hydrogen and bio-methane of 27.3 ± 7.2 L_{H2} $kg^{-1}_{COD\text{-}added}$ and 154 ± 14 L_{CH4} $kg^{-1}_{COD\text{-}added}$, respectively. A solid-liquid separation (SLS) step was applied to the digested slurry, giving solid and liquid fractions. The liquid fraction was treated via the MFC-steps, showing power densities of 12–13 W m^{-3} (500 Ω) and average bioelectricity yields of 39.8 W h kg^{-1}_{COD} to 54.2 W h kg^{-1}_{COD}.

1. Introduction

The substitution of fossil fuels by biofuels has been proposed in the European Union (EU) as part of a strategy to mitigate greenhouse gas emissions from road transport, increase security of energy supply and support development of rural communities (Ryan et al., 2006). As a consequence of that, biofuels production is nowadays strongly debated and issues related to food/feed vs. energy production, economic sustainability and changed land use are becoming important for the future of the agriculture sector (Koonin, 2006).

Among types of renewable energy, biogas has aroused great interest (Zuo et al., 2015), and four million tonnes oil equivalent (Mtoe) of biogas primary energy were produced in EU during 2013, which is 1.2 Mtoe more than in 2012, representing 10.2% growth (EurObserv'ER, 2014).

Anaerobic digestion (AD) at farm level is nowadays a reality in many EU countries, and has been demonstrated to be a valid step in this direction (Plöchl and Heiermann (2006)). For mixed and highly-humid (<50% dry matter content) waste materials, AD is now the best alternative at full-scale to simultaneously obtain organic matter mineralization and stabilization, odor and atmospheric emissions control (Scaglia et al., 2011), nutrient and recalcitrant carbon preservation (Tambone et al., 2010) and carbon re-utilization through the production of high-value bio-fuels (biogas or bio-methane).

However, biogas production above all at farm level, benefits from incentives by national governments without which it cannot be run from an economic point of view (Schievano et al., 2015). Reducing costs to achieve parity with those of the grid is a condition of giving a future to biogas, as benefits are no longer sustainable and governments have started to reduce them greatly.

An approach to reducing biogas costs consists of diversifying products coming from anaerobic digestion by developing a biogas-biorefinering model (Ragauskas et al., 2006), such as recently proposed for the bioethanol sector (Moraes et al., 2014).

A biorefinery consists of a cascade process in which waste coming from a previous step becomes the feedstock for the next one, reducing waste production (zero waste concept) (Demirbas, 2009). A first approach to a biogas biorefinery came from Manenti and Adani (2014), who proposed the use of digestate to produce energy (gasification), bio-based compounds (syngas reforming) and fertilizers (chemical physical treatment). Nevertheless, that

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approach was only a theoretical premise as biogas refinery has yet to be demonstrated from a scientific point of view.

The first step to biogas refinery development has already been made at full scale with the use of bio-methane for purposes other than on-site electricity production. Biogas up-graded to bio-methane, free of CO_2 and other trace compounds, can be injected into methane gas distribution grids and be used as a renewable counterpart of fossil-derived natural gas for both industrial (as reactant for chemical synthesis), household (as fuel) and automotive uses.

Upstream, dark fermentation (DF) is an option to diversify gaseous products (separate a stream of H_2-rich biogas) and, optionally, to use solubilized organic matter for different bio-refinery purposes (Manzini et al., 2015). Bio-H_2 production from DF has great potential to contribute in substituting for fossil-based hydrogen in refinery processes. In traditional fossil-based refinery chains, molecular Hydrogen (H_2) is an intermediate with a relevant role both as a product and as a reactant (Pandey, 2013). Besides, today a new model of refinery is arising, based on renewable carbon and on the concept of circular, instead of linear materials/energy streams, as the principle of overall sustainability (Rabaey and Ragauskas, 2014), and bio-based H_2 may play relevant roles in this developing perspective.

When bio-H_2 is produced separately by DF and all residual organic matter is sent to AD, the process is normally called in the literature a two-stage process (DF + AD) (Schievano et al., 2012). The integration of DF and AD has been extensively experimented upon with a wide variety of substrates, types of digesters and process parameters (Schievano et al., 2012; Manzini et al., 2015). In the last decades, various authors have shown benefits from the integration of DF and AD (Koutrouli et al., 2009). Recently, Schievano et al. (2014) demonstrated possible increases of bio-energy recovery from biomass, with a dependency on biomass composition. The co-digestion of animal manure with a carbohydrate-rich substrate is needed to produce interesting amounts of H_2. Here we chose rice bran (a widely available secondary product of one of the most important crops worldwide) in addition to swine manure, according to previous experimental evidence (Schievano et al., 2014).

AD of waste streams like animal manure has been extensively reported as fundamental to reduce methane and ammonia emissions during open-air storage, as well as to improve their properties as fertilizers and soil amendments (Rehl and Müller, 2011; Tambone et al., 2010). After AD, a lot has still to be done to optimize the use of digestate as a resource for conditioning agricultural soils and the production of renewable fertilizers. Ammonia nitrogen and other soluble nutrients should be recovered and made full use of as valuable fertilizers for crop cultivation. Especially in some regions, excessive geographical intensity of farming would necessitate nutrients re-distribution to nearby regions, with lower presence of concentrated livestock and with a lack of available nutrients and organic matter (Ledda et al., 2013). The high water contents of digested slurries often represent an impediment for their viable transportation. For this reason, different strategies are being studied and implemented to separate both suspended and soluble substances from water and to sustainably return the largest fraction of the liquid to the local environment; examples are solid-liquid separations (SLS) by filtration, centrifuges, ultrafiltration, reverse osmosis, biological nitrification-denitrification, etc. However, this residual organic matter in digestates, especially its soluble fraction (especially mineral nitrogen), is difficult to separate and most systems (reverse osmosis, biological treatments, etc.) are not yet economically and energetically feasible at a commercial scale (Ledda et al., 2013).

Recently, Microbial Fuel Cells (MFC) have been proposed as an innovative option to treat the supernatant fraction of digestates, to simultaneously degrade residual soluble/suspended organic matter, reduce nitrogen content (Virdis et al., 2010) and produce bio-electricity (Fradler et al., 2014). In particular, air-cathode MFC were demonstrated to have potentially high COD-removal efficiency with a variety of liquid streams (Fradler et al., 2014; Pepé Sciarria et al., 2015; Kim et al., 2015) and, additionally, to act simultaneously as nitrification-denitrification systems (Virdis et al., 2010).

Coupling MFC to DF and AD, is a relatively new concept and only a few studies have described in depth this approach (AD + MFC or DF + AD + MFC). To our knowledge, the first exhaustive study was presented by Premier et al. (2013) who focused their efforts mainly on COD removal, with little attention on nitrogen and on the overall mass balance, energy conversion efficiency (ECE) and energy recovery (ER). Fradler et al. (2014) followed the same path and demonstrated more comprehensively the performance of a 4-module tubular MFC applied after a DF + AD system as a polishing stage. However, on one hand the overall flows of mass and chemical energy of the integrated system was not shown and on the other hand, the performance of the MFC was not satisfactory. Using a four-module tubular MFC, with HRT of around 8 h, and the influent concentration being 1029 mg COD L^{-1}, the COD-removal remained below 10%, with a relatively low energy recovery per raw influent volume (92 J L^{-1}). In addition, when working at higher concentrations of COD, to avoid high dilutions of the AD effluent, the MFC performed even worse. In both the Premier et al. (2013) and Fradler et al. (2014) contributions, also, nothing is reported about the nitrogen/ammonium balance and its fate throughout the MFC step (Fradler et al., 2014; Kim et al., 2015).

As discussed above, new technology and biotechnology can be applied to the biogas sector in order to diversify obtainable products, increase the value of goods and reduce waste produced. Nevertheless, these new approaches need to be integrated in more complex system, i.e. a biorefinery. Up to now, integrated approaches to developing a biogas refinery have not yet been proposed, apart from the integration of two different technologies, i.e. biogas-biohydrogen production, biogas-MFC or biogas-biofertilizers production (Schievano et al., 2012; Ledda et al., 2013; Premier et al., 2013; Fradler et al., 2014).

This work represents an effort to fill in the gaps existing in the development of a biogas biorefinery by proposing at lab-scale, the integration of DF, AD, MFCs and mechanical treatment of digestate to diversify the products obtainable from agricultural waste and promote a circular economy at farm level. Organic matter and nitrogen balances will be investigated within the integrated process, as well as the properties of intermediate products and performance parameters of individual processes. Results obtained can be useful for further discussion on the future feasibility of biogas refinery on a larger scale.

2. Materials and methods

2.1. Experimental plan

A mixture of swine manure (SM, 89% wet weight) and rice bran (RB, 11% wet weight) was used as input material, to keep the experimental work and the results particularly focused on the farming sector. SM was sampled in a farm (around 5000 pigs) in the Lodi district, Italy, and used as-it-is in the experimental work. RB was sampled from a rice farm, Pavia district, Italy, and used as-it-is for the tests. The mixture was treated in parallel by: (1) a traditional one-stage AD system (reactor R1); (2) a two-stage system (AD + MFC, in reactors R1 and R2), hereafter System 1; (3) a integrated system (DF + AD + MFC, in reactors R3, R4 and R5, respectively), hereafter System 2. The feeding procedure of AD reactors