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Optimization of hydrolysis and volatile fatty acids production from sugarcane filter cake: Effects of urea supplementation and sodium hydroxide pretreatment

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HIGHLIGHTS

- A dual-pool two-step model was fitted to the batch experiment data.
- 6 g NaOH/100 g FC_{FM} achieved the highest methane potential in batch experiment.
- Urea addition did not enhance VFA yield during semi-continuous experiment.
- Optimum pH for VFA production during semi-continuous experiment was between 5 and 5.5.
- NaOH pretreatment increased the VFA yield by 37% during semi-continuous experiment.

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ABSTRACT

Different methods for optimization the anaerobic digestion (AD) of sugarcane filter cake (FC) with a special focus on volatile fatty acids (VFA) production were studied. Sodium hydroxide (NaOH) pretreatment at different concentrations was investigated in batch experiments and the cumulative methane yields fitted to a dual-pool two-step model to provide an initial assessment on AD. The effects of nitrogen supplementation in form of urea and NaOH pretreatment for improved VFA production were evaluated in a semi-continuously operated reactor as well. The results indicated that higher NaOH concentrations during pretreatment accelerated the AD process and increased methane production in batch experiments. Nitrogen supplementation resulted in a VFA loss due to methane formation by buffering the pH value at nearly neutral conditions (∼6.7). However, the alkaline pretreatment with 6 g NaOH/100 g FC_{FM} improved both the COD solubilization and the VFA yield by 37%, mainly consisted by *n*-butyric and acetic acids.

1. Introduction

Sugarcane is the most produced agricultural commodity (fresh mass basis) in the world (FAO, 2013). It is mainly used for sugar, first-generation bioethanol and bioelectricity production. Nowadays, new developments aim to add value to the underused biomass fractions derived from the cane processing with the intention to diversify the product portfolio of the sugarcane plants in a biorefinery concept (Mariano et al., 2013).

Filter cake (FC), also known as press mud or filter mud, is a solid waste generated during the clarification (physical–chemical process) of sugarcane juice before been used for sugar and first-generation bioethanol production. It is mainly composed of water, inorganic soil particles, residual sugars and small pieces of sugarcane bagasse, which are often intentionally added to improve the permeability during the recovery of sucrose at the rotary vacuum-drum filter. In most cases, FC is applied as organic fertilizer on the sugarcane fields without any previous recovery of value-added products (Elsayed et al., 2008).

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Anaerobic digestion (AD) is a promising strategy to treat such type of waste, since methane and/or platform chemicals for value-added products could be produced as a result of the different syntrophic biochemical phases: hydrolysis, acidogenesis, acetogenesis and methanogenesis (Deublein and Steinhauser, 2008; Merklein et al., 2014). These cascade reactions are performed by various microorganisms, thereby the composition and dynamics of the microbial community is influenced by different process parameters such as organic loading rate (OLR), hydraulic retention time (HRT), pH value, balance of macronutrients and trace elements as well as presence of inhibitors (FNR, 2010; Kayhanian and Rich, 1995).

For optimization of AD, hydrolysis/acidogenesis and acetogenesis/methanogenesis may be improved independently by physical separation of these phases in two reactors (Cysneiros et al., 2012a). It is well known that hydrolysis is often the rate-limiting step during AD when fibrous material, such as filter cake is used as feedstock due to the recalcitrant presence of lignin, which prevents the action of microorganisms and enzymes by its hydrophobic nature (Montgomery and Bochmann, 2014; Yu et al., 2014). One option to improve the hydrolysis of lignocellulosic substrates is to perform a physical (comminution, hydrothermolysis), chemical (acid, alkali, solvents, ozone), physico-chemical (steam explosion, ammonia fiber explosion) or biological (enzymes, fungi) pretreatment process to increase the accessible surface area, to modify the crystalline structure or partially depolymerize cellulose, to solubilize hemicellulose and/or lignin, or to modify lignin structure (Hendriks and Zeeman, 2009; Silverstein et al., 2007).

Only few studies have assessed the effects of different pretreatment methods on methane production from FC in batch systems (López González et al., 2013, 2014). To our knowledge, pretreatment of FC for VFA production in a semi-continuous stirred-tank reactor (SCSTR) has not been studied yet. Only by applying a similar feeding system used during large-scale applications (semi-continuous) it is possible to have a broader understanding of the reactor's behavior in terms of effect of inhibitors, nutrient deficiencies and optimum pH value for a specific AD phase.

Previous studies from our group (Leite et al., 2015) assessed the main characteristics of sugarcane waste along an operating season. Apparently, FC presented a proper C:N ratio for AD, varying from 24 to 41, which is according to several authors (FNR, 2010; Fricke et al., 2007; Weiland, 2010) into the optimum range of around 20–40. However, it is noteworthy that in case of low nitrogen release during fermentation, it could negatively influence the microbial community functioning due to nitrogen deficiency. In the meantime, the sodium concentration of FC was found to be very low (up to maximum 3.7 mg L^{-1}) much lower than recommended values (100–200 mg L^{-1}) by early studies (Mccarty, 1964), which might also negatively affect the microbial growth during the AD process.

The use of sodium hydroxide (NaOH) for substrate pretreatment could be a potential strategy to overcome these possible drawbacks. At the same time cellulose and hemicellulose would become more accessible to hydrolytic enzymes by breaking down the lignocellulosic structure of FC, and sodium as an important macroelement for microbial growth would be provided (Sambusiti et al., 2013a). However, particular attention should be paid to the NaOH dosage, since the ion Na^+ in high concentrations could negatively affect the activity of non-halotolerant microorganisms and interfere with their metabolism (Chen et al., 2008).

Therefore, in this study the effect of alkaline FC pretreatment was previously investigated in batch experiments evaluating the influence of different NaOH concentrations on the short-term AD, followed by fitting the cumulative methane yields to a dual-pool two-step model to provide a preliminary estimation of VFA production. Moreover, a SCSTR was operated as an acidogenic reactor at high OLRs and low HRTs to investigate how VFA production could be optimized providing urea as a NH_4-N source and NaOH pretreatment as a measure to improve the microbial hydrolysis.

2. Methods

2.1. Substrate and inoculum

Sugarcane FC was obtained from a distillery plant in the State of Goiás (Brazil) during the 2013/2014 season, transported to Germany in sealed plastic bags and stored at 4 °C until its use. A large-scale biogas plant that uses maize silage and cattle manure as substrate provided fresh digestate, which was used as inoculum for the batch experiments and the start-up of the semi-continuous reactor. To avoid inlet and outlet pipes from clogging, the digestate was sieved prior to inoculation in the reactors. During the operation of the semi-continuous experiment tap water was utilized to keep the total solids (TS) of the feed in below 15% for wet fermentation process.

2.2. Alkaline pretreatment

For batch experiment, alkaline pretreatment was carried out in 500 mL glass flasks applying different NaOH concentrations (0, 1.5, 3 and 6 g NaOH/100 g FC_{FM}), hereafter referred as to untreated, low, mild and high NaOH concentrations. The substrate TS concentration was 68 g TS L^{-1}. FC and NaOH mixture was stirred for 30 min (100 rpm) at 45 °C using a magnetic stirrer (Heidolph Instruments). After pretreatment, the FC was neutralized with hydrochloric acid and immediately used for subsequent AD trials. The same pretreatment procedure was used prior semi-continuous digestion in a concentration of 6 g NaOH/100 g FC_{FM}.

2.3. PCA analysis

A principal component analysis (PCA) was run on VFA and chemical oxygen demand (COD) concentrations obtained after pretreatment to evaluate the relationship between the effects of the different NaOH concentrations on solubilization of the main substrate components. The analysis was run with the software Statistica 6.0 (Statsoft, Tulsa, OK, USA).

2.4. Batch experiment

The methane yield of the FC pretreated with different NaOH concentrations was obtained through biochemical methane potential (BMP) assays according to VDI (2006) using an Automatic Methane Potential Test System II (AMPTS II, Bioprocess Control, Sweden) under mesophilic temperature (38 °C) during 10 days. Based on the different model derivations presented by Brulé et al. (2014) an exponential dual-pool two-step model (Model D) was used to evaluate the methane production kinetics of the anaerobic batch experiment. This modeling approach differentiates between rapidly and slowly degradable fractions (dual-pool) of the available substrate. Furthermore, it includes the acidification of the two fractions to VFA as well as the degradation of the resulting intermediate VFA concentration to methane (two-step).

Thus, five model parameters and constants needed to be adjusted to depict the respective measurement results: the total methane potential S (mL_N gVS^{-1}), the ratio of rapidly degradable substrate to total degradable substrate α (–) and the three first-order reaction constant for the degradation of rapidly degradable substrate k_F (d^{-1}), slowly degradable substrate k_L (d^{-1}) and the degradation of VFA k_{VFA} (d^{-1}). The model implementation as well as the numeric parameter identification (Levenberg–Marquard