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Influence of ultrasound irradiation pre-treatment in biohythane generation from the thermophilic anaerobic co-digestion of sugar production residues

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ABSTRACT

The objective of this study was to evaluate the effects of sonication on the biogas production dynamics of sugarcane straw and vinasse in an anaerobic digestion. Two different ultrasound pretreatments were evaluated namely 180 W of ultrasonic power irradiated at 37 kHz for 30 min (PBU) and 800 W of ultrasonic power irradiated at 19 kHz for 15 min (PSU). Significant differences were observed in the biogas compositions of the PBU and PSU pretreatments and their respective controls. A continuous increase in methane concentration of the biohythane (biohydrogen and methane combined) was recorded in the PBU reactors (60–80% by volume). The main effect of ultrasound pretreatment was on the composition biohydrogen, methane and carbon dioxide (biohythane) produced.

1. Introduction

Many renewable technologies are currently used as alternatives to fossil fuels such as hydropower, solar, wind, and biomass. One of the most promising types of renewable energy generation is the reuse of biomass, such agricultural residues. One of the main crops produced in Brazil is sugarcane which is then used mainly for the production of sugar and alcohol [1]. The main by-products obtained are the filter cake, sugarcane straw and vinasse [2]. Recently, it has been agreed that rising ethanol production induces statistically significant positive impacts on the sugarcane agroindustry [3]. However, an increased reliance on mechanical harvesting has led to the increased production of sugarcane straw that can be harnessed for bioenergy production [3]. Additionally, up to 15 L of vinasse per liter of alcohol is produced [4,5]. Although vinasse can be used for irrigation, an excessive use can cause land contamination [6]. A large amount of sugarcane straw and vinasse produced, can be used in anaerobic co-digestion to generate renewable energy [7], as an alternative to reduce the net environmental impact which vinasse causes in soils and the environment when applied directly to land [8].

Anaerobic digestion is an organic matter degradation process in the absence of molecular oxygen by the action of microorganisms mediating biochemical reactions to produce bioenergy in the form of ATP [9–11]. The technology of anaerobic digestion promotes the simultaneous co-digestion of two or more materials. Therefore, the anaerobic digestion process adds to the existing microorganisms in the system a variety of substrates and biodegradable substances [12]. Anaerobic co-digestion of sewage sludge and other biodegradable organic matter could increase the production of biogas and the degradation of organic matter [13]. Other advantages of the co-digestion are the buffering capacity of the mixture, an increase in the biodegradable content and a wider diversity of microorganisms present in the process [14].

Therefore, the co-digestion of vinasse may prove to be a potential sustainable process because it will attempt to solve the current problem of correctly disposing of the huge amounts of residues. However, depending on the characteristics of the biomass, some pretreatment may be required, and this has been regularly been noticed to be the case of an enhanced kinetics of biogas or biohythane is desired. Several types of pretreatments can be used including extraction with supercritical fluids, microwave irradiation, biological treatment, chemical treatment and recently the use of ultrasound irradiation [15,16]. The use of ultrasound irradiation as pretreatment is based on the cavitation dynamics of bubbles formed by the passage of ultrasonic waves through an aqueous or slurry-type medium. As waves pass through the medium, expansion (rarefaction) and compression regions are formed forcing the dissolved gasses into bubbles. With each cycle of the wave irradiation, the bubble oscillates and accumulates more energy until a point where

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it implodes to release huge amounts of localized energy which then greatly enhance diffusion.

There are several examples of the use of ultrasound irradiation (i.e. sonication) as pretreatment for different processes namely for the dehydration of fruits [17], biological degradation of wastewaters [18], disintegration of wastes [19], treatment of lignocellulosic wastes to improve ethanol and biogas production [20], chemical modification of sugarcane bagasse [21], and cellulolytic activity of cellulose complex [22]. However, there is no information available presently on the effects of sonication pretreatment on the anaerobic co-digestion of sugarcane straw and vinasse. In this context, the purpose of this study has been to assess the effect of ultrasound irradiation pre-treatment on the anaerobic co-digestion process of vinasse and sugarcane straw substrates under thermophilic conditions (55 °C) in a semi-continuous system. This work had attempted to bring fresh data on the application of low frequency ultrasound irradiation as an effective pre-treatment for anaerobic digestion. The novelty of this work also resides in the substrates being used for the sonication-assisted bioprocessing and in the generation of a biogas which is enriched with biohydrogen. It is thus hoped this work increments knowledge in the specific field of biohythane production from waste biomass pretreated in a green manner.

2. Materials and methods

2.1. Substrates and sample preparation

The substrates used in this study were vinasse, sludge from the mesophilic reactor and sugarcane straw. All have been obtained from an industrial sugarcane plant (Cosmópolis, São Paulo, Brazil). The sugarcane straw was milled using a vertical rotor mill with mobile and stationary knives (Marconi, model MA340). Subsequently, it was sieved using a magnetic stirrer with round sifters (Bertel, model 220), and at a mesh opening of 1.00 mm. The sieved sugarcane straw was stored in a freezer at −14 °C for its later use in experiments. Physicochemical analyses of the substrates were done according to the Standard Methods for the Examination of Water and Wastewater [23]. The primary characteristics of the substrates are shown Table 1.

2.2. Ultrasound irradiation pre-treatment

Two different sonication pre-treatments were applied. The first pretreatment (PBU) was performed in an ultrasonic bath (Elmasonic Singen, model P60H,) operating with a frequency of 37 kHz and 180 W of power at a temperature of 75 °C and for 30 min of processing time. The second pretreatment (PSU) was performed in the Extract-US multipurpose unit equipped with an ultrasonic horn (Unique, Indaiatuba, Brazil) operating at a frequency of 19 kHz and 800 W of power at a temperature of 30 °C and for 15 min of processing time.

Table 1
Average physical characteristics of substrates used.

Parameters	Substrates		
	vinasse	sugarcane straw	sludge
pH	4.52	–	5.32
Moisture (%)	95.87 ± 0.01	5.44 ± 0.22	97.53 ± 0.51
Total solids (%)	4.13 ± 0.01	94.56 ± 0.22	2.47 ± 0.51
Volatile solids (%)	3.31 ± 0.07	76.08 ± 2.92	1.96 ± 0.04
Fixed solids (%)	0.82 ± 0.08	18.48 ± 3.14	0.81 ± 0.09
N-NH_3 (mg NH_3/g)	37.33 ± 6.46	–	280.00 ± 0.00
COD (mg O_2/g)	51.88 ± 2.30	–	11.75 ± 0.00

2.3. Experimental pilot unit

For the co-digestion process of vinasse and sugarcane straw, two stainless steel jacketed reactors of 4.3 L with an agitation system were used. A jacketed glass reactor of 3.7 L with an agitation system was used for the storage of the inoculum or sludge from the mesophilic reactor obtained from an industrial sugarcane plant (Cosmópolis, São Paulo, Brazil). A thermostatic bath kept the system operating in thermophilic conditions (55 °C). The Fig. 1 shows the schematic configuration of each reactor for the co-digestion process under the thermophilic semi-continuous system. All the processes of anaerobic co-digestion were carried out at thermophilic conditions (55 °C) and with a stirring speed of 500 rpm. The pH control was done manually, each three days, using a solution of HCl or NaOH (6.0 N).

2.4. Physicochemical analyses

The methods applied to characterize the substrates and evaluate the process control were: pH (4500-H+ B), total alkalinity (ALK) (2320B), total solids (TS) (2540B), total volatile solids (VS) (2540E), total Kjeldahl nitrogen (4500Norg-B), ammonium nitrogen (N-NH3) (45000NH_3-C) and chemical oxygen demand (COD) (4520D), and proteins were determined by multiplying the TKN content by 6.25 all according to the Standard Methods for the Examination of Water and Wastewater [23].

2.5. Volatile fatty acids (VFA) analysis

The analysis of VFAs was carried out in a gas chromatogram equipment coupled with a mass spectrometer QP 505A (GC–MS, model 17A, Shimadzu Corporation, Kyoto, Japan). The GC–MS method used a DBWAX capillary column (Agilent Technologies, California – United States) with the following dimensions: length of 30 m, the internal diameter of 0.25 mm, and the film thickness of 20 μm. The carrier gas was helium at a flow rate of 1 mL min^{-1}. The samples were injected manually with Hamilton gas-tight syringes. The injection volume was 2 μL per sample in split mode (1:100). The temperature of the injector was maintained at 250 °C. An isotherm of 80 °C (held 3 min) up to 180 °C at 15 °C 1/min (held 2 min) was used for VFAs separation in the analytical column. It was used a mass range of *m/z* 12 to *m/z* 120 for the development of analytical curves used for each VFA evaluated. Total analysis time for VFAs was 20 min. The VFAs evaluated were acetic acid, valeric acid, butyric acid and, propionic acid (all Sigma-Aldrich). A working solution of 10 g/L of VFAs was used for the construction of all analytical curves.

2.6. Biohythane analysis

The analysis of the components of biohythane (H_2, O_2, CH_4, and CO_2), was carried out in a gas Chromatogram (GC 2014, Shimadzu Corporation, Japan, model CG 2014) equipped with a thermal conductivity detector (TCD) and a packed column (ShinCarbon ST 50/80 mesh). To determine the biohythane content, the following chromatographic conditions were used: the injector and detector temperatures were both set to 200 °C; initial temperature of GC column was 50C (held for 3 min) and with increments of 5 °C min^{-1} to 180 °C (held for 5 min). The sample volume injected was 0.5 mL, and N_2 was used as carrier gas (35 mL min^{-1}, 5 bar), and total analysis time for biohythane was 45 min.

2.7. Field emission scanning electron microscopy (FESEM)

Field emission scanning electron microscopy (FESEM) was used to analyze the microstructure of the initial and final bioreactor composition. Based on Dias et al. [24], the FESEM was equipped with a field emission gun (Quanta 650, FEI, Hillsboro, Oregon, USA). Before