MONITORING OF BIOGAS PRODUCTION AND REDUCTION OF BIODEGRADABILITY FROM TANNERY SOLID WASTES ANAEROBIC CO-DIGESTION

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Abstract. The understanding of how chemical, physical and environmental parameters work during anaerobic digestion production and waste treatment is an important step in improving the efficiency and process stability. This study provides the biogas production and the reduction of biodegradability of the treatment of the anaerobic digestion of solid wastes of tanneries. Leather shavings and sludge from wastewater treatment plants substrates were considered in the study. The findings suggest that the biodegradability of the residues practically did not change during the biodegradation tests, since the biodegradable part was transformed into microbial biomass.

1 Introduction

Renewable energy deriving from biomass sources has great potential for growth to meet our future energy demands. Biogas is a very important source of renewable methane. It is produced from anaerobic digestion (AD) of biomass in the absence of oxygen[1]. Compared to other renewable energy sources such as wind energy or photovoltaics, biogas is generated independently from weather phenomena and can be stored, making it available on demand. Furthermore, bio-methane is a valuable substitute for limited natural gas using the same, already well established gas distribution system. Additionally, in view of the waste management, biogas is more favorable than composting, since fossil fuels can be substituted and the CO_2 emissions can be reduced[2].

Raw biogas consists mainly of methane (CH_4, 40-75%), with lower heating value between 15 and 30 MJ/Nm^3, and carbon dioxide (CO_2, 15-60%). Trace amounts of other components such as water (H_2O, 5-10%), hydrogen sulfide (H_2S, 0.005-2%), siloxanes (0-0.02%), halogenated hydrocarbons (VOC,<0.6%), ammonia (NH_3, <1%), oxygen (O_2,0-1%), carbon monoxide (CO, <0.6%) and nitrogen (N_2,0-2%) can be present and might be inconvenient when not removed[3].

AD is the consequence of a series of metabolic interactions among various groups of microorganisms: hydrolytic, acidogenic, acetogenic and methanogenic[2]. The process is carried out in digesters that are maintained at temperatures ranging from 30 to 65°C, where the mesophilic range (30-35 °C) is the most cost-effective. Co-digestion – the digestion of two or more substrates – is a very attractive solution for improving the process, as it results in better distribution of nutrients and trace elements, supporting microbial activity and providing potential for higher methane yield[4,5].

The leather making process generates substantial quantities of solid waste (cuts of hides and skins, fats, shavings and trimmings, buffing dust) and sludge from wastewater treatment plants, which in most cases contain chromium, the main chemical used in the tanning process[6,7]. These residues are usually disposed of in hazardous industrial landfills, which are characterized as places of waste confinement where the residues undergo undesired and uncontrolled biological treatment[8]. As they are organic matrices, they also correspond to an interesting substrate for the implementation of AD[9].

This research attempts to evaluate the feasibility of the AD of tannery solid wastes (mixtures of shavings and sludge) in co-digestion processes. The aim of this work is the assessment of biogas production and

reduction of BOD/COD ratio in the anaerobic co-digestion of leather shavings and sludge from wastewater treatment plants.

2 Materials and Methods

2.1 Biodegradation assays

Biodegradation assays on a scale five times smaller than Agustini[1] were performed in 50 mL vials and biogas production was monitored with the aid of a graduated syringe, as shown in Fig. 1.

Fig 1. Biodegradation test in 50 mL flask with monitoring of biogas production with graduated syringe.

The proportion of biogas components was accessed weekly through a gas chromatograph (GC-2014 Shimadzu) equipped with a ShinCarbon column (ST 100/120 2 m 1 mmID 1/16" OD Silco) and TCD detector. Helium (White Martins 5.0) was used as the carrier gas at a flow rate of 10 ml/min. The injector and detector temperatures were held at 200 and 250 °C, respectively. The oven program was: 40 °C (3 min), ramp at 15 °C/min to 150 °C, and hold for 0.67 min.

2.2 Biochemical oxygen demand - BOD

The microorganisms present in a liquid sample containing biodegradable organic matter consume oxygen for their metabolic activity and produce an equivalent amount of carbon dioxide. If the process occurs in a closed system and the carbon dioxide is absorbed by a strong alkali, a progressive reduction of internal pressure can be observed. The determinations of the biochemical oxygen demand (BOD) were carried out with a pressure sensor (BOD Sensor) from VELP Scientifica equipped with a

system of agitation (System 6). The composition of materials and reagents for the analyzes is shown in Table 1. After assembly, the vials were incubated at 20°C for 5 days. A sample with only water (blank) was always performed to obtain the BOD value relative to the seed only.

Table 1. Composition of solutions for BOD analysis.

Solution	Amount
Sample (dilution 1:20)	
Water	237.5 mL
Sample	12.5 mL
Sample pretreatment	
Sodium sulphate 1.58 g/L - removal of chlorides	1 mL
2-Chloro-6 (trichloromethyl) pyridine 350 g/L - inhibition of nitrifying agents	1 mL
Seed	
Sludge from tanning wastewater treatment plant that used chrome salts and vegetable tannins in the tanning process	2 mL
Nutrient Solution	
FeCl3 · 6 H2O 0.25 g/L	0.25 mL
CaCl2 27.5 g/L	0.25 mL
MgSO4 · 7 H2O 22.5 g/L	0.25 mL
KH2PO4 8.5 g/L	
Na2HPO4 · 7 H2O 33.4 g/L	0.25 mL
K2HPO4 1.7 g/L	

2.3. Chemical Oxygen Demand - COD

Chemical oxygen demand (COD) measurements were performed using the closed-loop colorimetric method (5220 - Standard Methods) where the organic and inorganic materials present in the sample are oxidized by means of the oxidizing agent potassium dichromate (K2Cr2O7). The COD is quantified because it is linearly proportional to the color change of the medium as the chromium is reduced (Cr^{6+} to Cr^{3+}).

The composition of materials and reagents for the analyzes is shown in Table 2. After addition of the solutions in glass tubes with digestion threads, the tubes were closed and arranged in a heating plate model ECO25 from VELP Scientifica for 2 h at 150°C. After cooling, the absorbance of the sample was read on a spectrophotometer model T80 + UVVis Spectrometer from PG Instruments at 600 nm. A sample with only water (blank) was always performed. The calculation of the COD concentration was performed using the equation of the straight line obtained from the standard calibration curve with potassium biftalate (1000 ppm = theoretical COD of 1000 ppm of O_2).

Table 2. Composition of solutions for COD analysis.

Solution	Amount
Sample (dilution 1:2)	
Water	1 mL
Sample	1 mL
Digestive solution	
Potassium dichromate (K2Cr2O7) 10.216 g in 500 mL of distilled water	
Sulfuric acid (P.A.) 167 mL	1.2 mL
Mercury Sulfate II (HgSO4) 33.3 g	
Avolume in 1000 ml of distilled water	
Catalytic solution	
Silver Sulfate (Ag2SO4) 10.12 g/L in sulfuric acid (P.A.)	2.8 mL

3 Results and discussion

3.1 Biogas production

The daily production and composition of the biogas produced are shown in Fig. 2. The triplicate assays yielded on average 10.18 mL of accumulated biogas/g SVS added (mean value of triplicate ± standard deviation) with a maximum percentage of methane of 40.9 ± 0.05% (by volume). This maximum percentage, however, did not remain until the end of the experiment and the oxygen concentration did not remain at zero throughout the experiment, showing that the flask was not able to seal the oxygen inlet and, because it was a small scale experiment, oxygen was able to penetrate the reaction medium and partially inhibited methanogenic activity.

The analysis of the results of the accumulated biogas production is shown in Fig 3. Comparing these results with the that obtained from scale studies of Agustini[1], by statistical inference of variance (F test with a significance level of 0.05), it was found that there was a significant difference (Fbiogas (34.32) > Fcritical (5.14)) between this scale in relation to the others, so that the linear consistency was not maintained, proving that these tests were partially inhibited by the oxygen present. The log phase of these trials (slope of 0.142) was 1.6 times lower than the laboratory scale (slope of 0.2375) and ended approximately 20 days later, maintaining the ratio that the solids concentration influences the DA velocity.

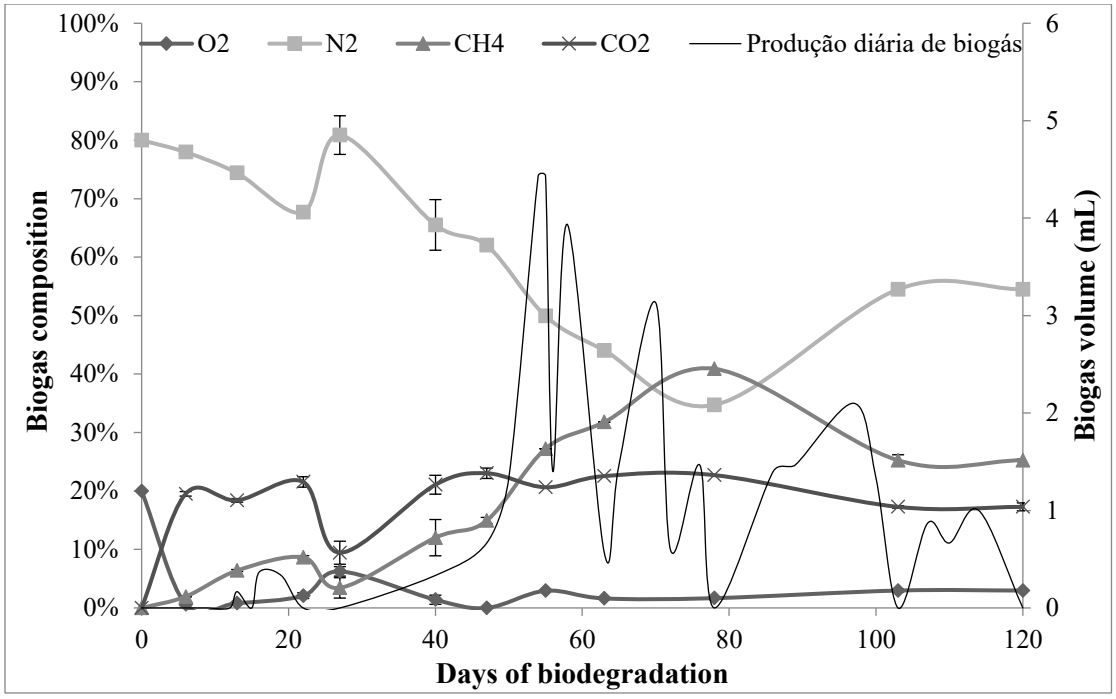

Fig. 2. Average composition and daily production of biogas.

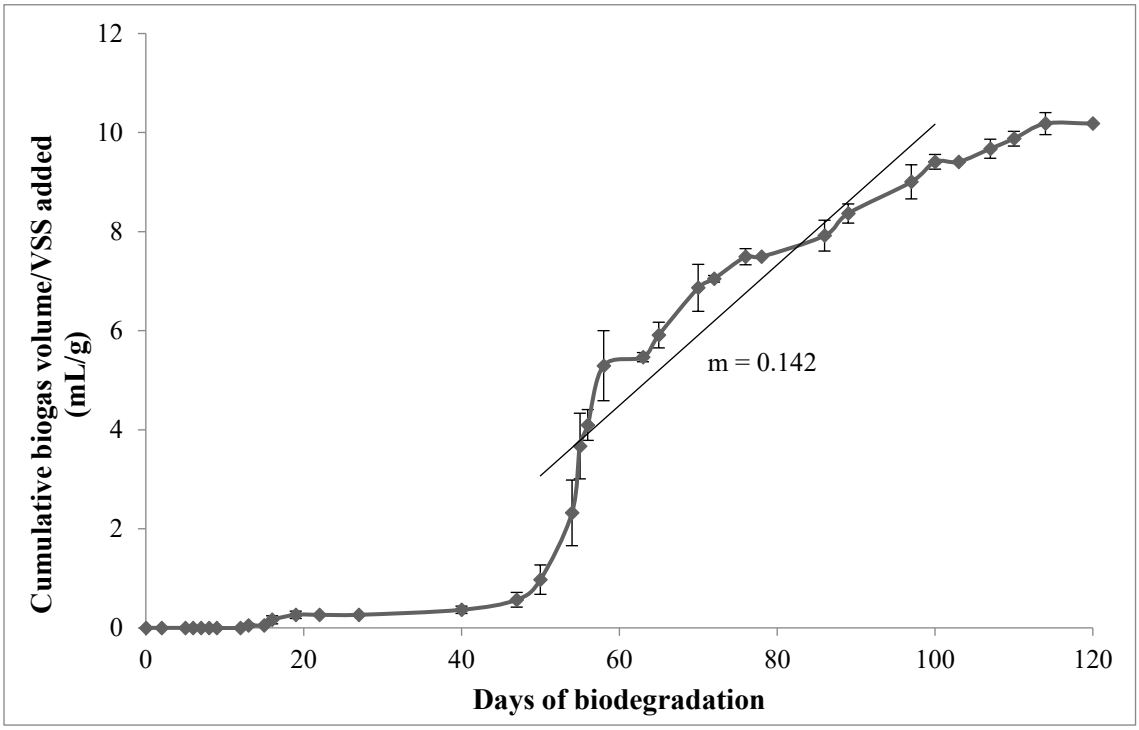

Fig. 3. Cumulative biogas production and indication of slope of the log phase.

The variation of VDS and VSS is shown in Fig 4. VDS, as expected, remained constant. The triplicate assays reduced 13.4 ± 0.6% SVD (mean value in three replicates ± standard deviation). VSS, as expected, reduced. The triplicate assays reduced 39.3 ± 1.0% SVS (mean value in three replicates ± standard deviation). Despite the large reduction, VSS remained approximately 30% at the end of the experiment, while on the larger scales[1], VSS almost reached zero, confirming that AD was partially inhibited by aerobiosis and that very small reaction volumes are more easily influenced by the presence of oxygen.

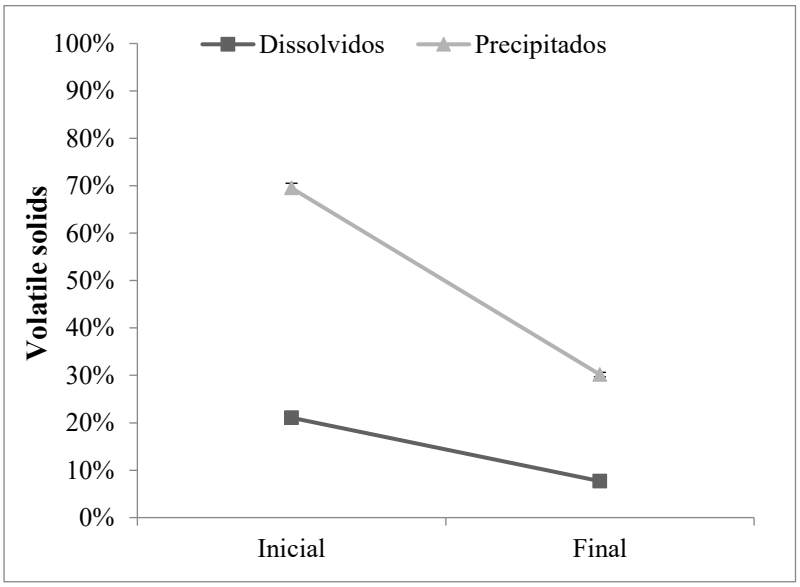

Fig. 4. Volatile solids dissolved and precipitated.

3.2 Reduction of biodegradability – BOD/COD ratio

Table 3 shows the BOD, COD and BOD/COD values before and after DA.

Table 3. Comparison between the BOD and COD parameters.

	Initial	Final
BOD (ppm)	2.040 ± 110	1.090 ± 65
COD (ppm)	2.519 ± 17	1.131 ± 7
BOD/COD	1.23	1.04

Dissolved COD, like BOD, reduced by more than half. A reduction of 1,388 ± 30 ppm (55%) COD concentration (mean value of triplicate ± standard deviation). The analysis of the COD reduction results obtained, using statistical inference of variance (F test with significance level of 0.05), did not show significant differences (FCOD (0.46) < Fcritical (18.51)). The COD is related to many parameters of the biodegradable and recalcitrant organic matter, so that no difference between the COD reductions was detected.

The BOD/COD ratio is an indicator of biodegradability and tends to decrease throughout the AD process. For tannery residues, typical BOD/COD values range from 0.6 to 1.7[10]. The initial BOD/COD value obtained of 1.23 is within the range expected for tannery waste. A reduction of 0.20 ± 0.01 (16%) BOD/COD ratio (mean value of triplicate ± standard deviation) was observed. The analysis of the results of the reduction of the BOD/COD ratio obtained, using statistical inference of variance (F test with a significance level of 0.05), showed no significant differences (FCOD/BOD (7.70) < Fcritical (18.51)). The small reduction of the BOD/COD ratio for the high amount of biogas that left the system may be due to the formation of microbial biomass that kept the BOD values close to that of COD.

4. Conclusions

The findings suggest that small production scales can be impaired by the possible entry of O_2 to affect the process, due to the oxygen penetration power being sufficient, in small scale means, to reach the anaerobic zones and, thus, inhibit the methanogenic activity. The biodegradability of the residues practically did not change during the biodegradation tests, since the biodegradable part was transformed into microbial biomass.

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