PROFESSOR MIKE REDWOOD YOUNG LEATHER SCIENTIST GRANT 2021 SUSTAINABILITY/ENVIRONMENTAL AWARD

FINAL REPORT

HYDROCARBONS AND CARBOHYDRATES RELEASE DURING THE BIODEGRADATION OF SOLID WASTE FROM TANNERIES FOR BIOGAS PRODUCTION

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1. Introduction

Anaerobic digestion (AD) of organic waste is a method of producing renewable energy, i.e. biogas, with simultaneous waste treatment. Biogas is attracting significant attention as an increasingly interesting renewable and sustainable energy technology [1]. Biogas has the advantage of not having geographical limitations or requiring new technology for producing energy to the other renewable energy sources [2]. Biogas production is the first category where potential process innovations are sought and analyzed. Within this category a significant number of studies have been published over the last few years. Topics address various ways of enhancing, controlling and optimizing AD and improving biogas yield and/or biogas quality. Crucial points for improving the efficiency of biogas production that are frequently emphasized throughout the literature are associated with facilitating access to cheap raw materials [3]. However, many biogas plants operate at sub-optimal loading rates to ensure a stable process at the expense of digester productivity [4]. There are issues during AD, such as process instability, long lag time, low biogas yield, and methane concentration. There are a number of factors that affect AD performance including environmental conditions (e.g., temperature, pH, carbon/nitrogen – C/N ratio), process by-products (e.g., volatile fatty acids and ammonia), and physical and chemical properties of the feedstock (e.g., VS (volatile solids), nutrient content, complex chemical structure) [5]. Biomass is a sustainable renewable energy source including a broad range of organic waste such as: animal manure, forestry and agricultural residues, municipal and industrial solid waste [2]. Tannery waste consists of wastewater, solid waste shavings and sludge. The on-site anaerobic treatment of solid tannery waste to produce biogas has become an attractive option for the tannery industry [6].

Research carried out on this issue has studied AD of tannery solid waste. Thermophilic AD of fleshing, hide trimmings and wastewater sludge were investigated [6], with chromium addition, in 1,160 mL vessels; The specific methane production potential was estimated to be 0.617 m^3/kg of volatile suspended solids (VSS) for tannery waste sludge, 0.377 m^3/kg for tannery leather trimmings and 0.649 m^3/kg for fleshing. Different proportions of fleshing and primary sludge were subjected to mesophilic AD in 100 mL bottles [7]; VS destruction between 41 and 52%, specific gas production between 0.419 and 0.635 L/g volatile solids feed and methane yield between 71 and 77% were achieved. In the AD of fleshing and mixtures of primary and secondary sludge in 650 mL bottles [8], biogas generated per gram of VS added was on average 410 mL/g. In mesophilic AD of substrates (soybean meal, hydrolyzed collagen, hide powder and wet-blue leather shavings) containing different concentrations of chromium in 300 mL bottles [9], the maximum rate of biogas production reached a yield of 162.2 mL/g of VSS and a methane fraction of 73.7%. Some of our previous researches were focused on studying the feasibility of the AD of mixtures of shavings and sludge in co- digestion processes, addition of tannery wastewater for nutritional supplementation, assessment of a semi-pilot scale procedure, cost saving analysis, influence of the presence of the tanning agent and high-throughput sequencing, co-digestion with agricultural crop residues. Tannery waste with chromium presence proved to be significantly more suitable for AD than waste without chromium. Biogas yields between 21 and 30 mL/gVSS, maximum methane content of 59% v/v, and a total organic carbon (TOC) reduction between 68 and 76% was obtained. A linear consistency of methane production was found in the assessed scale-up and a two-fold biodegradation rate to a five-fold volume of treated waste. In the conditions studied in semi-pilot scale, a midsize tannery could reduce 6.8% of electric and 1.6% of thermal energy consumption besides the great cost savings of disposal of this waste. The highest amount of biomethane observed was related to the archaeal family *Methanosaetaceae* and bacterial order *Bacteroidales* [10–12].

However, the quantities of biogas produced by tannery residues are still lower when compared to other more bioavailable residues, such as food residues [13], where the biogas production reaches up to 15 times greater. Once anaerobic digestion is fully established, as methane is being produced, a gap remains in the initial stage of hydrolysis, where the organic load of the residues does not appear to be completely broken down into smaller hydrocarbons to be bioavailable for microorganisms.

The aim of this study is to evaluate the evolution of the hydrocarbon and carbohydrates release, the energy efficiency and the efficiency of treatment of AD of the solid waste of tanneries. The originality of this study is the innovative study regarding on how chemical, physical and environmental parameters work. This is an important step in improving the efficiency and process stability of anaerobic digesters in order to adjust in which step of the batch process the continuous

process must be designed and which pretreatments are most suitable to increase the carbon depletion of the waste.

2. Materials and methods

2.1. Batch digester

Chromium-tanned leather shavings and sludge with chromium salts were obtained from tannery factories and their respective wastewater treatment plant (WWTP) located close to Porto Alegre, Brazil. They were kept at room temperature (25°C) prior to use.

Twenty-two independent and identical replicates of batch co-digestion of tannery waste were prepared containing:

- 25 mL of sludge (beamhouse + chromium tanning), also acts as inoculum (Fig 1.a);
- 1 g of chromium-tanned leather shavings (Fig 1.b);
- 200 mL of nutrient solution (2 g/L of yeast extract, 1 g/L of peptone, 7 g/L of K_2HPO_4, 3 g/L of KH_2PO_4);

The ratio of the quantity of sludge/shavings of 25 mL/1 g in the assays was adapted by local research carried out with tanneries of the region following the proportional amount of waste produced. The nutrient solution was employed to ensure favorable conditions for the growth and metabolism of the microorganisms. The bioreactors were incubated at 35 °C in a microorganism culture oven (DeLeo).

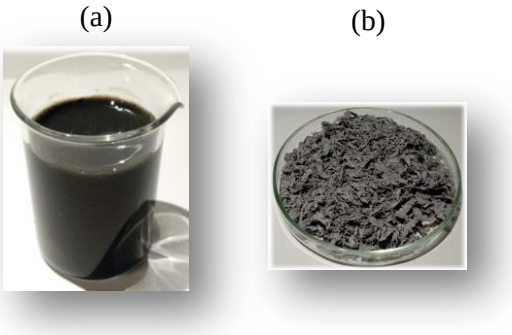

Fig. 1. (a) sludge and (b) chromium-tanned leather shavings.

2.2. Periodic sampling

As the analyses were destructive and required a large volume of sample, every 10 days a duplicate of bioreactors was opened for collection of the liquid and precipitate reaction medium, starting on day 0 and ending on day 100. The supernatant reaction medium was collected in Falcon tubes

and stored at 4 °C until analysis. The precipitated solid was filtered, dried and stored in Falcon tubes at 4 °C until analysis.

2.3. Biogas monitoring

Biogas volume was measured every 2 days by water displacement with a device based on the Mariotte principle [10]. The proportion of biogas components was accessed weekly through a gas chromatograph (GC-2014 Shimadzu, Japan) equipped with a ShinCarbon column (ST 100/120 2 m 1 mm ID 1/16" OD Silco) and TCD detector. Helium (White Martins 5.0, United Kingdon) 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.

2.4. Monitoring waste destruction

The hydrocarbon and carbohydrates release were measured with NIR spectra [14]. The range of the spectra measured by the instrument was between 4000 cm^{-1} to 12,000 cm^{-1}. Total organic carbon (TOC), inorganic carbon (IC) and total nitrogen (TN) were measured in a TOC analyzer (Shimadzu TOC-L, Japan) equipped with a TN measuring unit (Shimadzu TNM-L) and 8-port sampler (Shimadzu OCT-L). Biological oxygen demand (BOD5) was manometrically measured with a VELP Scientifica BOD Sensor System 6 (VELP, Brazil). Solid contents (volatile suspended solids (VSS) and volatile dissolved solids (VDS)) were determined with gravimetric method with the assistance of a digital analytical balance (Edutec EEQ9003F-B, Brazil), a drying oven (DeLeo, Brazil) and a muffle furnace (Quimis Q318M, Brazil). pH was determined with a Digimed pHmeter (DM-22, Digimed, Brazil). Chromium (III) oxide concentrations were determined according ABNT NBR13341 method for residual bath. The denaturation temperature of the assays was determined using a Perkin Elmer differential scanning calorimeter (DSC 6000, EUA) in a nitrogen atmosphere with a flow of 20 mL/min. The samples underwent a temperature increase from 5 to 110 °C with a heating speed of 10 °C/min using a close aluminium pan of 20 µL. Image analysis was accomplished with a Stereo Microscope SZX16 Olympus equipped with Olympus LG-PS2 (Japan) light sources with resolution of 900 line pair/mm and zoom of 1.6x with dual turret.

A carbon-based mass balance was performed to calculate the percentage of carbon conversion throughout the experiment, taking into account the initial and final TC (converted to moles) and the carbon that left the system in the biogas (CH_4 and CO_2, in moles).

3. Results and discussion

The cumulative biogas generation per gram of VSS added (average of the unopened assays at each point) is shown in Fig. 2. The daily evolution and the composition of the biogas produced (average of the unopened assays at each point) are shown in Fig. 3.

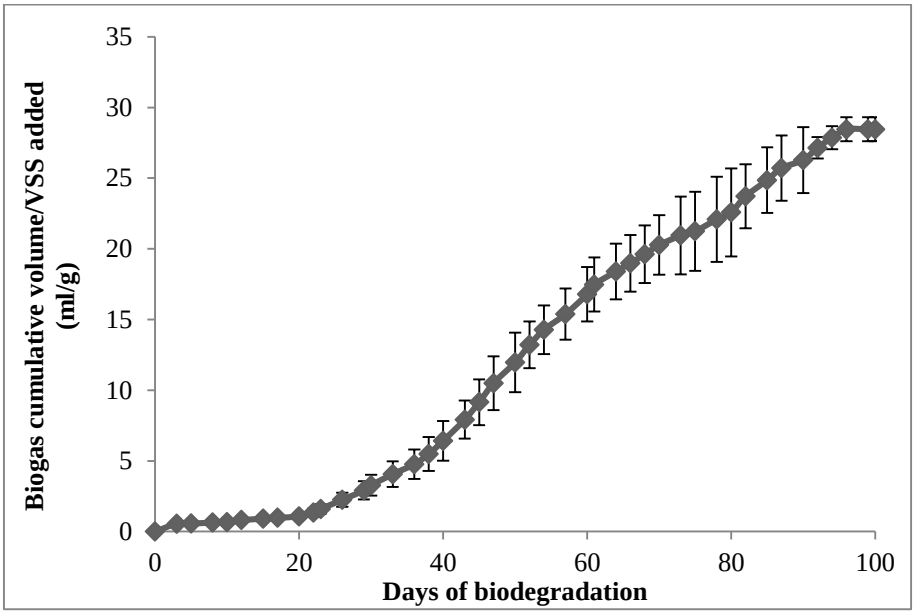

Fig. 2. Biogas cumulative production per gram of VSS added in the biodegradation of tannery waste — average of the unopened assays.

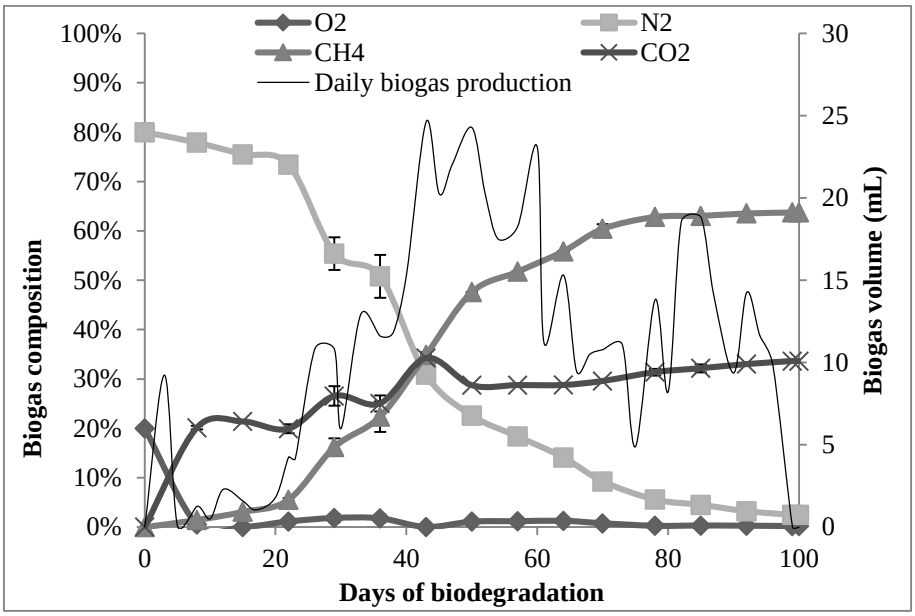

Fig. 3. Mean biogas composition and daily production during the assays — average of the unopened assays.

The assays produced on average 28.5 ± 0.8 mL of cumulative biogas/g of VSS added (16.4 g) with a maximum percentage of 63.7% of methane. The cumulative production of biogas was

characteristic of a closed culture, confirming the complete establishment of anaerobic digestion [10]. The biogas cumulative volume from tannery waste is similar to the cumulative volume produced by other waste such as swine manure, which produced 30 mL of biogas/g VSS in 100 days [15].

Lag phase is regarded as a period for the adaptation to the new environment. The greater the lag phase, the greater the recalcitrance of the substrate [16]. The lag phase was very long, approximately 20 days (Fig 2). This long lag phase is not observed in less recalcitrant residue such as urban wastewater [17] and dairy waste [18], which did not present any lag phase in its anaerobic digestion, showing that the recalcitrance and complexity of the tannery waste caused the hydrolysis phase to take longer to complete.

Log phase is regarded as a period of complete adaptation and high availability of substrate, without microbial competition. In this phase, the higher the biogas production rate, the greater the bioavailability of the residue [16]. Similarly, the log phase was also long, beginning at day 20 of incubation and ending at day 95, and also not having a large slope, again due to the complexity of the residues, so that the microbiological biomass could not quickly metabolize the waste (Fig. 2). The concentration of O_2 was rapidly wiped out. However, even with small inlets of oxygen in the system (around 30 and 60 days of assay), the CH_4 concentration was not affected, since oxygen has a very low power of penetration in dense media [19], such as the case of these wastes, oxygen was only in the gas phase, not affecting the anaerobiosis of the medium. The N_2 concentration was also slowly being wiped out as the pressure was relieved (Fig. 3). As it is an inert gas to AD, its presence had no effect on methane production. The concentrations of CO_2 and CH_4, as expected [11], rose throughout the experiment. The CO_2 concentration increases first, since the acidogenesis and acetogenesis stages were stable before the methanogenesis stage, reaching 21.4%, and then, at the end of the process, stabilized in 33.6%. The methane concentration rose along with the biogas production (Figs. 2 and 3) as expected for a well-established AD process. Its percentage showed the same growth as the biogas production growth, reaching a maximum of 63.7% at the end of the log phase. The daily production of biogas showed a characteristic behavior [20]; the highest daily production was between days 40 and 70, within the log phase, when the maximum daily production reached 24.6 mL of biogas and 15 mL/day on average.

The visual representation of the assays throughout the process is shown in Fig. 4. There are three distinct phases of the process. Up to day 30, the shavings are practically intact, so that the microorganisms are adapting to the waste and the hydrolysis has not yet fully completed. From day 40 to day 70, there is a great degradation of the shavings; however it is still possible to see blue spots. From day 80, it is no longer possible to visualize the shavings, so that they were completely metabolized by the microorganisms.

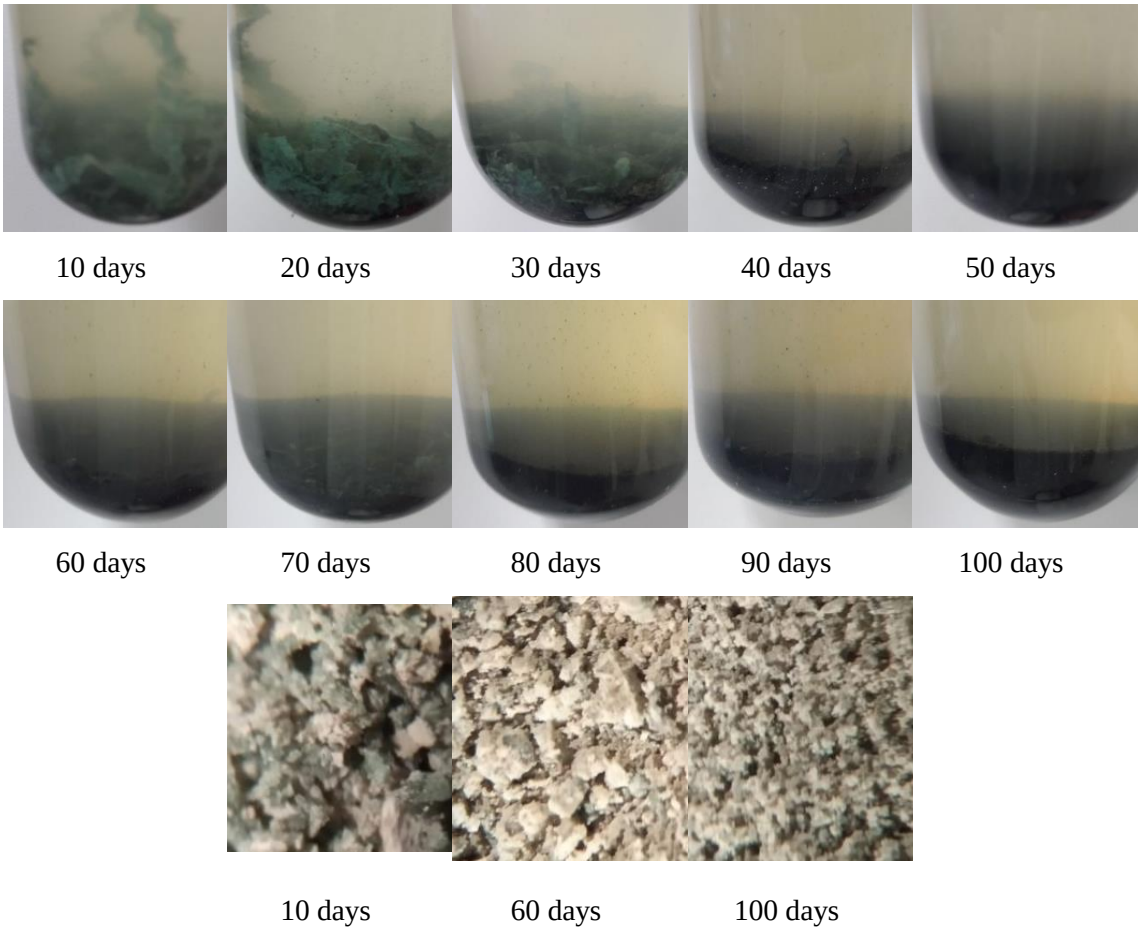

Fig 4. Visual representation of the bioreactors throughout the experiment with (a) picture of bioreactors bottom and (b) Stereo Microscope images (1.6x).

The hydrocarbons and carbohydrates percentage calculated using FT-NIR spectrometry concurs very well with the actual percentage and the total concentrations are relatively similar [21]. Fig. 5 shows the transmittance spectra obtained for the mixture of hydrocarbons and carbohydrates released during the biodegradation assays at different stages of the process. As can be seen, transmittance spectra vary according to the stage of the process. Intensity of bands and consequently concentration of hydrocarbons and carbohydrates released in the medium have the highest concentration in the 1° phase of the process (until 20 days), with a maximum percentage of 27% at 20 days of the process. This is due to the initial solubilization of the residues, attributed to the hydrolysis and disintegration of macromolecular biopolymers to soluble monomers [22]. In the 2° phase of the process (between 20 and 70 days), the percentage of hydrocarbons and carbohydrates gradually decreases, reaching the minimum value of 21% in 70 days, as the log phase of the process is established. In the 3° final phase of the process, the percentage of hydrocarbons and carbohydrates rises to an intermediate value of 24% in 90 days. This can be explained by the total metabolization of residues, depleting the medium's nutrients and causing cell lysis that releases unmetabolized monomers back into the medium.

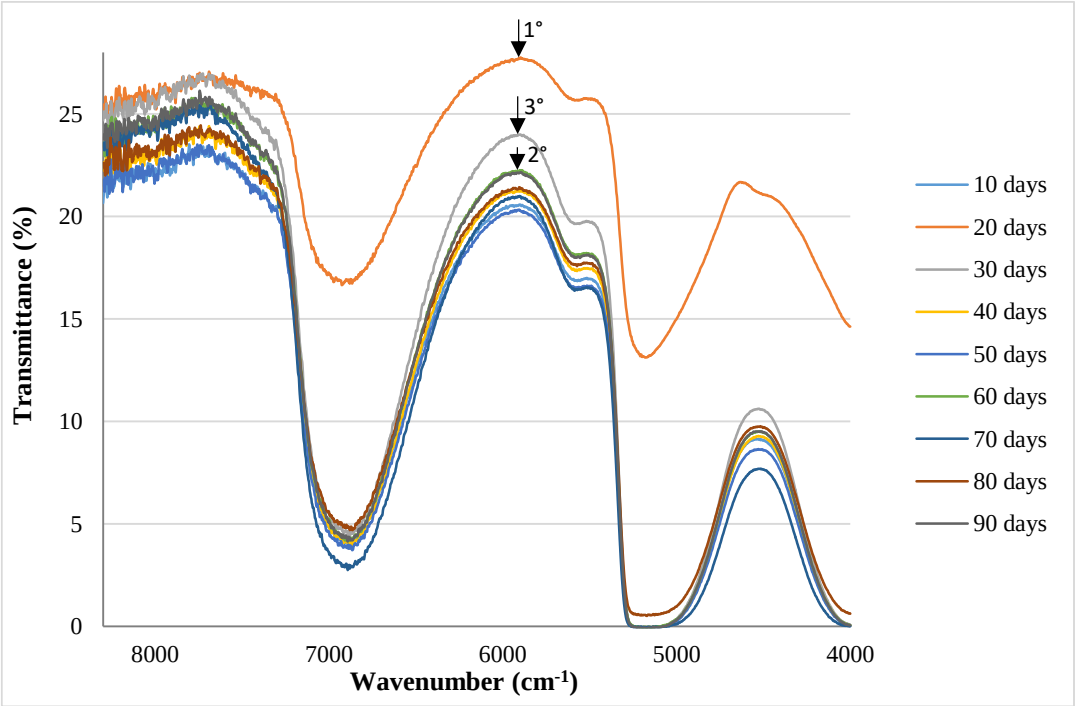

Fig 5. Infrared spectra of hydrocarbons and carbohydrates released from leather shavings mixed with tannery sludge for biogas production, indicating (1°) 20 days, (2°) 60 days and (3°) 90 days.

The concentrations of TOC, IC, TN, BOD as well as the C/N ratio along the anaerobic incubation are shown in Fig. 6. The BOD concentration reflects all the available organic matter present for the microorganisms. Despite the recalcitrance of the waste, the assays presented an initial high BOD of 2,040 ± 110 mg/L, which slightly increased throughout the trials, due to hydrolysis of the most recalcitrant compounds, reaching the maximum of 2,550 ± 368 mg/L and then, due to complete metabolization, reducing to 1,620 ± 30 mg/L. The concentration of TOC showed a strongly similar behavior to BOD. The initial TOC concentration of 1,165 ± 29 mg/L slightly increased to 1,380 ± 30 mg/L due to hydrolysis at 40 days of process, and at the end of the process, after the metabolization of the waste, reduced to 428 ± 61. Although they exhibit very similar behaviors, BOD and TOC concentrations have two major differences: (i) the concentration of BOD is much greater than the concentration of TOC throughout the process, since while TOC represents only carbon, BOD represents the sum of all organic components; and (ii) while the BOD concentration showed a reduction of only 20% throughout the process, the concentration of TOC reduced by more than 60%, as it leaks a lot of carbon, in the form of CH_4 and CO_2, and other organic compounds remain in the middle and in cell biomass. The behavior of IC and TN concentrations were also strongly similar, as expected, as both increased throughout the process. The initial IC concentration of 145 ± 1 mg/L increased steadily throughout the process reaching 927 ± 12 mg/L, a six-fold increase, characteristic of the metabolization and mineralization of the waste, transforming the organic carbon into inorganic. The TN concentration started at 609 ± 7

mg/L and increased steadily during the first 30 days, when it jumped to the maximum concentration of 1,314 ± 31 mg/L, together with the maximum daily biogas production, and then remained constant, reaching the end of the process at 1,290 ± 9 mg/L, a two-fold increase. The concentration of TN did not increase as expressly as IN concentration since TN is not actually produced along the process as IC, but it only remains in the same gross quantity, and since there is a large reduction in volume due to large carbon output (biogas), it increases in concentration. The initial C/N ratio of 2.2 is far below ideal for AD — ~ 20 to 30 [23] —, as tannery waste is a nitrogen-rich material, coming from animal hide. However, even with this low C/N ratio, AD was established without the need to add a carbon-rich substrate. The C/N ratio was gradually reduced throughout the process, reaching the value of 1.0 at the end of the assay.

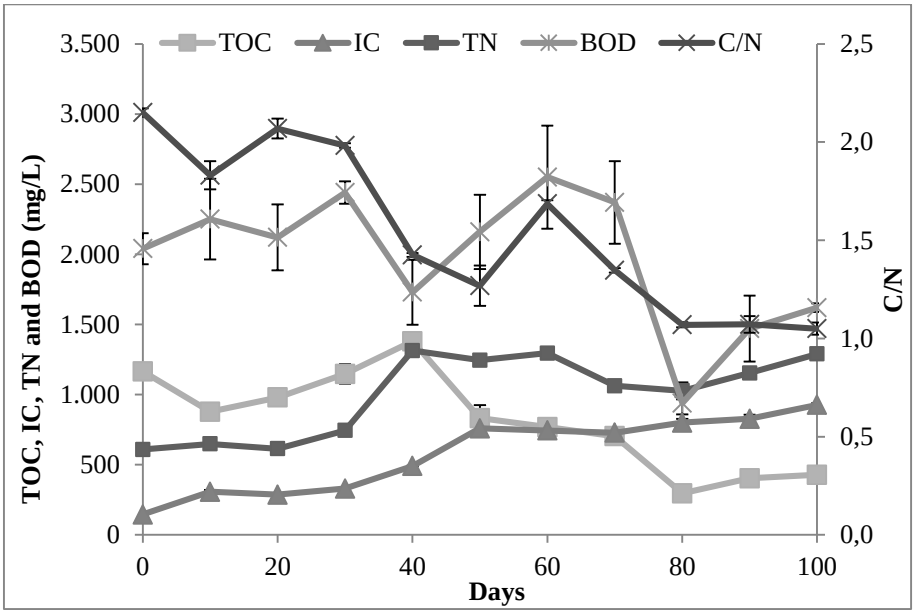

Fig. 6. TOC, IC, TN and BOD concentrations and C/N ratios throughout the assays.

A balance that involves TC (TOC + IC) was carried out for the mixtures in bioreactors in order to compare the amount of initial carbon with the amount of carbon that was converted to methane or carbon dioxide throughout the experiment. The results are detailed in Table 1. Up to the 30th day of the experiment, the conversion was less than 5%, probably due to temperature variations and experimental errors. After, the conversion gradually increased until reaching 36% conversion at the end of the experiment.

Table 1

Carbon-based mass balance considering an initial carbon amount of 0.48 g and 0.04 moles.

Day of experiment	C (moles) CH_4	C (moles) CO_2	C conversion
0	0.0	0.0	0%
10	0.000003	0.00004	0.1%
20	0.00001	0.0001	0.3%
30	0.0002	0.0005	2%
40	0.001	0.001	4%
50	0.002	0.002	11%
60	0.004	0.003	18%
70	0.01	0.004	23%
80	0.01	0.004	27%
90	0.01	0.005	33%
100	0.01	0.006	36%

The volatile solids represent the organic matter dissolved and suspended in the system, giving an idea of the migration of the organic matter initially complex and precipitated in the residues, which underwent hydrolysis to the point of lowering the molar mass and being able to solubilize in the medium, to being metabolized by microorganisms. The variation of VSS and VDS throughout the assays is shown in Fig. 7. Initially, the suspended solids (waste) presented 63.2% of volatile solids, due to its high organic load; this percentage was maintained until day 40 of the experiment, as well as lag phase. Then there was a big drop to 36.7%, showing the end of the hydrolysis stage, and so kept up, reaching 33.6% at the end of the process. The dissolved solids, on the other hand, started with 25.0% of volatile solids and were gradually reducing to 12.3% at the end of the process. This behavior gives the fact that once the organic compound is dissolved, it is rapidly metabolized by the microorganisms.

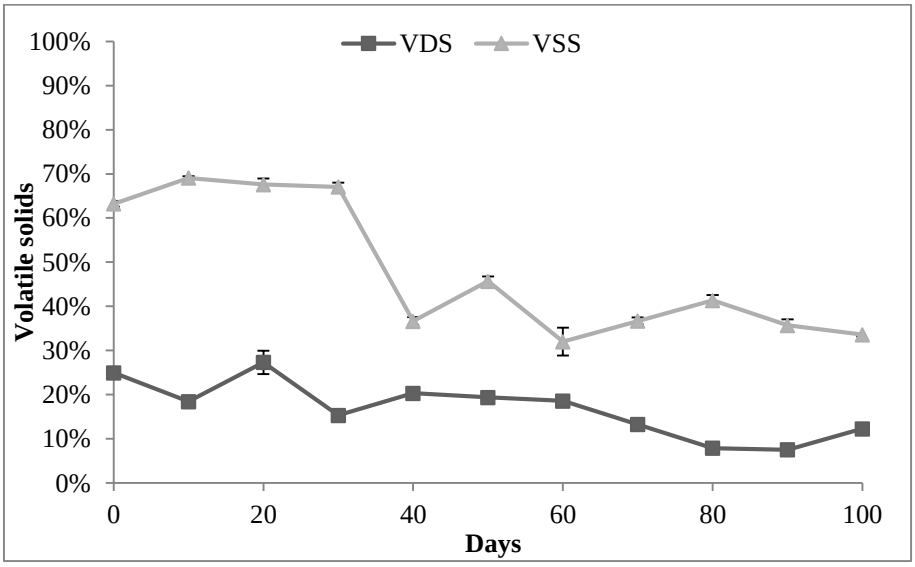

Fig. 7. Volatile dissolved and suspended solids throughout the experiment.

The DSC analysis results and the reduction of denaturation temperature throughout the experiment are shown in Fig. 8. Initially the residue (raw shaving) had a high denaturation temperature, of 106.2 °C, characteristic of tanning waste due to the presence of chromium, which stabilized the material [24]. From 10th day, the denaturation temperature of the mixture dropped sharply to 63.7 °C and slowly reduced until reaching 53.3 °C in 70th day of experiment. From 80th day, the residue was completely denatured, with no denaturation peaks.

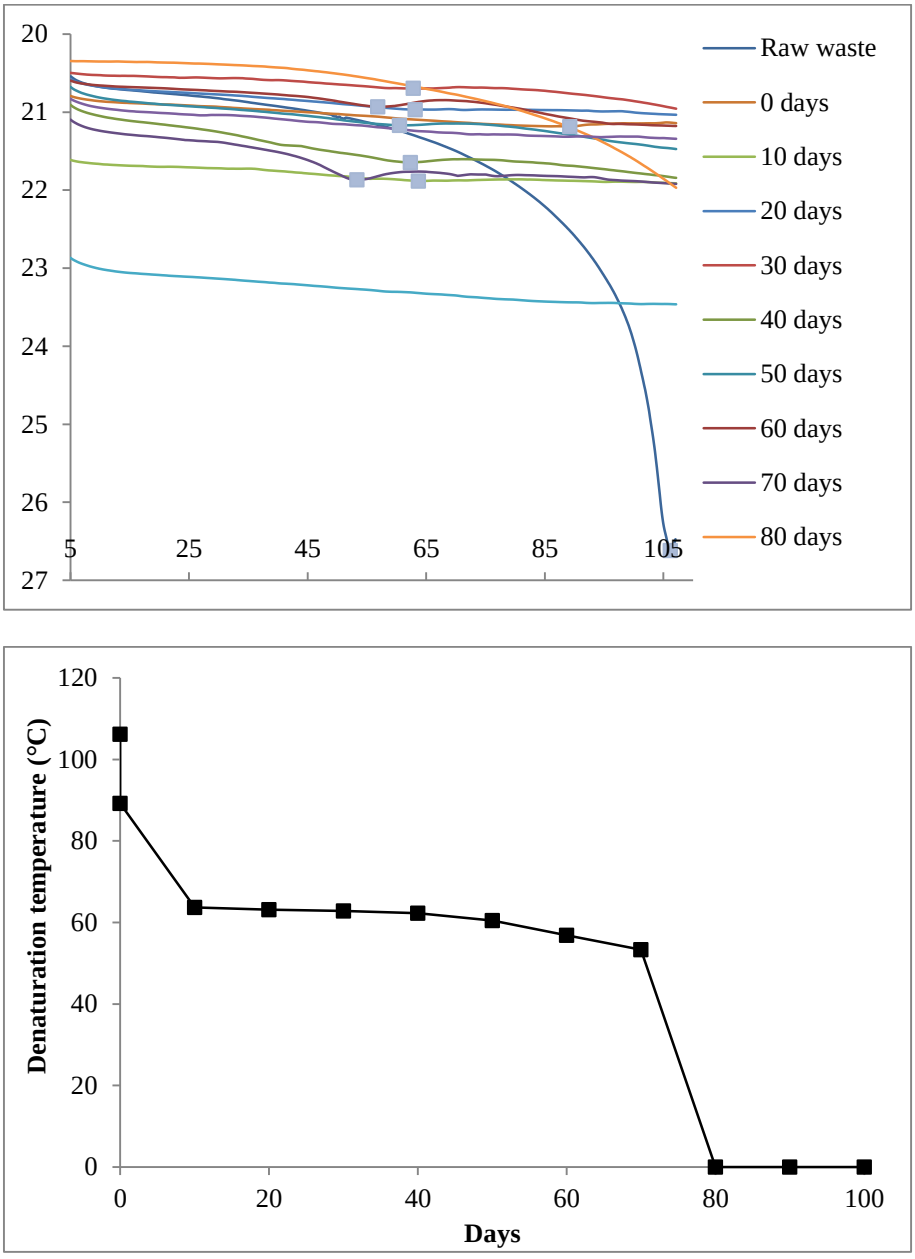

Fig. 8. (a) DSC analyzes results and (b) denaturation temperature throughout the experiment.

The pH is a parameter affected by many factors of the process, so that it is not an efficient parameter to describe the process, but to control if there is any discrepancy that can cause the total inhibition of AD, that is, if the pH is outside the range 7–8 [25]. In summary, the main factors affecting pH in AD are the volatile fatty acids produced during the hydrolysis stage that tend to

reduce the pH and the alkalinity generated by methanogenic activity. In addition, it is worth emphasizing that in order to measure the pH of the assays, it was necessary to open the bioreactor and to stop the experiment, exposing it to the atmosphere and releasing the CO_2, so that variations may have occurred. The pH measured throughout the assays is shown in Fig. 9. The initial pH of 7.3 initially acidified until reaching 7.2 on day 30, due to hydrolytic activity. On day 40, together with the beginning of biogas production and consequent high CO_2 production, the pH began to subside and remained within the expected range throughout the process. The point outside the appropriate range on day 90 is probably due to experimental errors, since biogas production was not affected in this period.

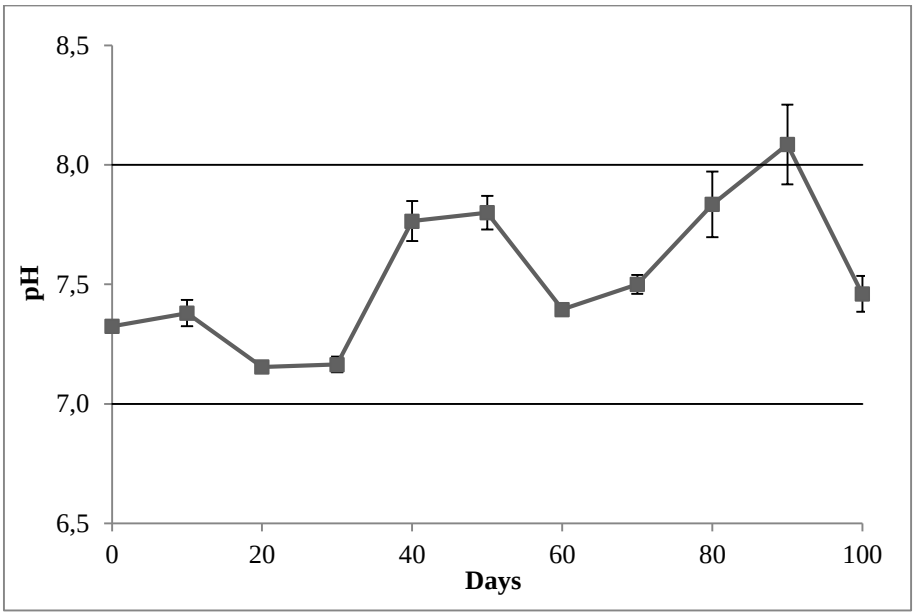

Fig. 9. pH throughout the experiment.

The concentration of chromium present in the assays comes from the tanning leather process, where chromium salts were used. The concentration of chromium throughout the experiment is shown in Fig. 10. Despite the great amount of chromium used for tanning the hides, little amount of chromium is diluted in the reaction medium because chromium has a very strong interaction with the hide. The initial concentration of 3.7 ± 0.6 mg/L, well below the limiting concentration for microorganisms of 100 mg/L [26], was gradually increased, as the shavings were being degraded. On day 80, a jump in concentration occurred, which increased to 45.6 ± 2.5 mg/L and at the end the process at 44.0 ± 0.9 mg/L. This jump may be due to total degradation of the shavings, which can be seen visually (Fig. 3), so that all the chromium present dissolved in the reaction medium.

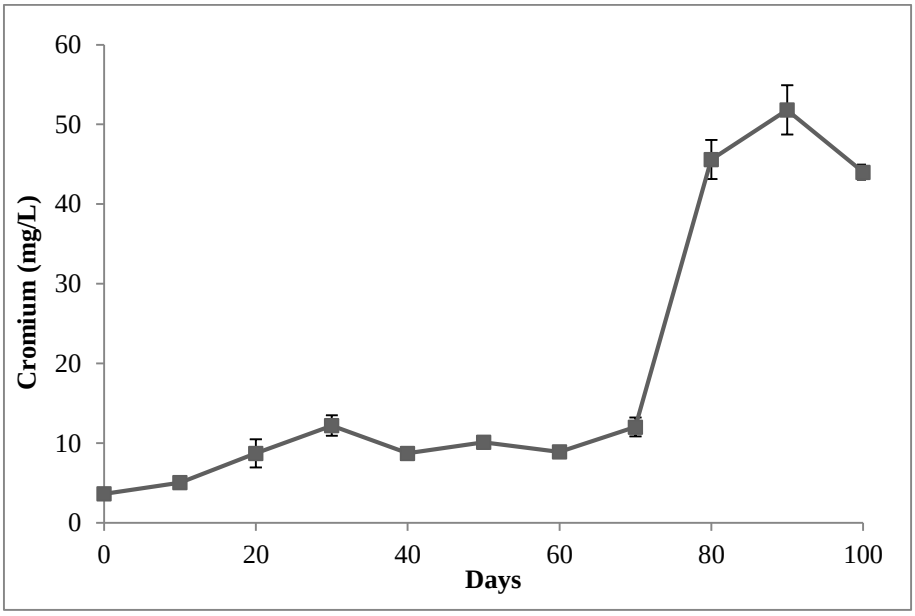

Fig. 9. Chromium throughout the experiment.

4. Conclusions

The results show that the AD of the tannery solid waste can be separated into three phases: (1°) a long lag phase of 20 days, where the microorganisms slowly adapt to the waste, due to its high recalcitrance; hydrocarbons and carbohydrates reach their maximum percentage of 27% due to waste solubilization and hydrolytic action; (2°) a log phase with a low metabolic rate of 15 mL/day, due to the complexity of the waste, where much of the chromium present is bound or adsorbed to the shavings, not inhibiting the process and hydrocarbons and carbohydrates reach their minimum percentage of 21% since the metabolic action of anaerobic microorganisms is fully established; and (3°) the final phase where all the shavings were metabolized and all the chromium dissolves in the reaction medium; with the depletion of nutrients, cell lysis also occurs, which releases hydrocarbons and carbohydrates back into the medium, reaching a final intermediary value of 24%.

Acknowledgements

The author is grateful to IULTCS for the financial support granted through the Professor Mike Redwood Young Leather Scientist Grant 2021 Sustainability/Environmental Award. The author would also like to acknowledge Prof. Dr. Mariliz Gutterres for all the support along her trajectory.

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