Resources, Conservation & Recycling 130 (2018) 51–59

Contents lists available at ScienceDirect

Resources, Conservation & Recycling

journal homepage: www.elsevier.com/locate/resconrec

Full length article

# Biogas production for anaerobic co-digestion of tannery solid wastes under presence and absence of the tanning agent

Caroline Borges Agustini[a,*], Franciela Spier[a], Marisa da Costa[b], Mariliz Gutterres[a]

[a] Laboratory for Leather and Environmental Studies – LACOURO, Chemical Engineering Department, Federal University of Rio Grande do Sul, Brazil
[b] Bacteriology Laboratory, Microbiology Department, Institute of Basic Health Sciences – ICBS, Federal University of Rio Grande do Sul, Brazil

A R T I C L E I N F O

*Keywords:*
Anaerobic co-digestion
Chromium
Vegetable tannin
Tannery solid waste
Beamhouse waste

A B S T R A C T

The influence of the presence of the tanning agent in co-digestion of leather shavings mixed with sludge before and after the tanning stage was examined. Chromium and vegetable tannin are the main tanning agents used and the presence of both was evaluated in two orthogonal arrays. The energy efficiency was evaluated through biogas and methane production. The efficiency in waste treatment was evaluated through the variation of TOC, IC, TN and the concentration of the tanning agents. Sludge with chromium proved to be significantly more suitable for AD than sludge without it, producing 27.9 mL of biogas/g of VSS with 60% of methane; a reduction of 62.8% of TOC; and a 325.0% increase of IC, showing that the initial 7.6 mg/L of chromium in these tests was beneficial. Shavings with chromium also proved to be significantly more suitable for AD, even though with a higher initial 16.4 mg/L of chromium, producing 10.7 mL of methane/g of VSS and a 55.2% reduction of TOC, confirming that the concentrations of chromium in the residues were not inhibitory. Shavings with vegetable tannins were unfavorable to the mineralization of the wastes through anaerobic digestion, showing significantly poorer results than shavings without it. They produced 4.1 mL of methane/g of VSS, confirming the establishment of anaerobic digestion. However, they increased the TOC by 23.7%, showing that the initial hydrolytic activity occurred, but the waste was not mineralized by the other phases of the process due to the high initial concentration of 590 mg/L of tannins.

## 1. Introduction

Research into different residues acting as biomass sources which could mitigate environmental and economic issues related to conventional energy crops, while sustaining and improving bioenergy production, has been increasingly investigated (Meyer et al., 2014). The leather-making process generates substantial quantities of solid waste before and after the tanning stage, which are a potential source which could meet this goal. The main solid residues are hide and leather shavings (Piccin et al., 2016) and sludge from wastewater treatment plants (WWTPs) (Mella et al., 2016). Some important characteristics of these residues include the high organic load and the difficulty of degradation of recalcitrant and poorly biodegradable compounds (Mannucci et al., 2010). The most common way to manage these solid wastes is by disposing of them at landfill sites. The stringent restrictions imposed on the disposal of residues of chromium and vegetable tannin − the two main tanning agents used in many parts of the world and also the presence of valuable modified protein in these residues necessitates the development of alternative waste management strategies (Pillai and Archana, 2012). Biogas is a biofuel that can be generated during waste anaerobic treatment and contribute to a more renewable and local energy system (Ammenberg and Feiz, 2017).

Leather processing is mainly divided into three stages: beamhouse, tanning and finishing. The beamhouse processing of leather production involves multiple mechanical and chemical unit processes. Its objective is to remove dirt, hair, epidermis, non-collagenous proteins and grease from rawhide/skin, and open up collagen fibers so as to favor the subsequent tanning process. After the beamhouse process, the hide is pickled when the action of deliming (alkalinity removal) and bating (enzymatic cleaning) is interrupted, and the collagen fibers are prepared for easy penetration of tanning agents by acidification of the hide in acid saline solution (Gutterres and Mella, 2015; Wang et al., 2016). Tanning is the operation in which the tanning agents react with the collagen matrix, stabilizing it (Fuck et al., 2011). Tanning processes are classified according to the type of tanning reagent (mainly tannins or chromium) used to crosslink the collagen fibers. The finishing steps vary according to the application of the leather (Mannucci et al., 2010).

Chrome tanning is the most important tanning method used to

* Corresponding author.
*E-mail address:* agustini@enq.ufrgs.br (C.B. Agustini).

https://doi.org/10.1016/j.resconrec.2017.11.018
Received 4 July 2017; Received in revised form 21 November 2017; Accepted 22 November 2017
Available online 23 November 2017

obtain light, inexpensive leathers of high thermal and bacterial resistance, using basic chromium sulfate as the tanning agent. The inhibition of the bioprocess of wastewaters treatment in the WWTP due to the presence of chromium has been demonstrated for concentrations of 140 mg/L, which cause a 50% reduction of bacterial activity. The other tanning agent class, which is popularly used, is based on vegetable tannins, which are extracted from plants. A concentration of tannins higher than 0.2 g/L in wastewater strongly inhibits microbial activity, while 2 g/L of tannins will completely inhibit it. The toxicity is proven for tannin concentrations up to 914 mg/L (Kalyanaraman et al., 2015). The toxicity of tannins can be associated with several mechanisms such as enzyme inhibition, substrate deprivation and loss of metal ions (Bhoite and Murthy, 2015). A high concentration of tannins causes a reduction in both the removal of the organic matter and the production of biogas. The organic load removal is more sensitive to condensed tannins concentrations than to hydrolysable tannins. A decrease in the removal of organic load was observed for tannins concentrations exceeding 790 mg/L (Dhayalan et al., 2007).

The tannery residues characteristics suggest that anaerobic digestion is a potential alternative treatment. The use of anaerobic processes to treat tannery wastewater is an interesting alternative choice compared to aerobic processes, as the sludge production and the energy consumption are both lower. Anaerobic digestion can occur during waste treatment and is a biochemical process that converts complex organics into biogas in the absence of oxygen under the effect of anaerobic microorganisms (Jia et al., 2017). In anaerobic digestion, which occurs in four anaerobic digestion phases (hydrolysis, acidogenesis, acetogenesis and methanogenesis), the sludge is also used as a microbiological source (C. B Agustini et al.,2017). The main advantages of anaerobic treatment applied to solid wastes are: lower energy consumption because forced aeration is not required; the organic matter of the substrate is converted into biogas that can be used as an energy source; and a smaller amount of biomass remains, resulting in lower costs for sludge disposal. This final sludge can also be used as a source of organic matter and nutrients for agricultural activity (Appels et al., 2008).

Biogas comprises 55–70% methane ($CH_4$), 30–45% carbon dioxide ($CO_2$) and traces of other gases. The use of energy from biogas proves to be energetically and environmentally interesting for heat/power generation and for the reduction of environmental impacts (Priebe et al., 2016). Biogas is an important biofuel because it can contribute to a transition toward a more circular and bio-based economy by delivering biomaterials and bioenergy (Feiz and Ammenberg, 2017). These can be used for onsite heating or electricity generation, thereby reducing external energy requirements, greenhouse gas emissions and dependence on fossil fuels (Schoen and Bagley, 2012). Several authors describe the use of thermal pre-treatment to enhance the anaerobic digestion of industrial residue. Heat applied during thermal treatment disrupts the chemical bonds of the cell wall and membrane, thus solubilizing the cell components. Studies report a positive impact of thermal pre-treatment on anaerobic digestion of WWTP sludge (Carrère et al., 2010; Sapci, 2013).

In the literature, investigations and reports on anaerobic digestion of sludge from WWTP and the mixture of WWTP sludge with shavings from the tannery process are found (C. B. Agustini et al.,2017; Priebe et al., 2016). However, the mixture of residues before and after the tanning stage has not been reported (Akyol et al., 2015; Sri Bala Kameswari et al., 2011; Thangamani et al., 2010). The purpose of this research was to investigate the influence of the tanning agent in co-digestion along tests of the two solid wastes of the leather industry of major concern: leather shavings and sludge from tannery WWTP, both before and after the tanning stage. The effect of the mixture of shavings and sludge before and after tanning for two tanning agents (chrome and vegetable tannin separately) were analyzed using two orthogonal arrays. The motivation behind this study stems from the assessment of how the presence of the tanning agent affects: (i) biogas and methane production and (ii) organic and inorganic loads variation of the tanned solid wastes biodegradation compared to tests with residues from stages prior to the tanning stage. Specifically, the objectives were to:

1 Confirm the capability of anaerobic treatment of tannery waste regardless of the presence of tanning agent,
2 Determine and compare the biogas and methane potential of tannery waste with and without tanning agent, and
3 Evaluate the influence of the tanning agent present with varying organic load and recalcitrance of wastes.

## 2. Methods

### 2.1. Solid waste collection and preparation

The leather shavings and the sludge were obtained from tannery factories and their respective WWTP located close to Porto Alegre. The samples of leather shavings collected were: pickled hide shaving (not tanned), chromium tanned leather shaving and vegetable (condensed tannin − acacia) tanned leather shaving. The samples of sludge from the tannery WWTP were: sludge from the beamhouse processing stage and sludge after the entire final leather processing with chromium salts as tanning agent. Sludge can also act as inoculum. They were kept at room temperature prior to use. To facilitate the availability for biodegradation of already stabilized hide due to the tanning, thermal pre-treatment was applied to the chromium and vegetable tannin tanned leather shavings through an autoclave at 121 °C (1 atm) for 5 min. Vegetable tannin sludge was not tested due to its high toxicity to bacteria, meaning that it was unable to provide the inoculum to the tests, as verified in previous studies for the authors.

### 2.2. Biodigestion experiments

The experiments were assembled to analyze the influence of the presence/absence of the tanning in two independent orthogonal arrays of the mixture of shavings with sludge. The ratio of the quantity of sludge/shavings of 25 mL:1 g was stipulated, this being the industrial rate generated by local research carried out with the tanneries of the region. Biodigestion was performed in 300 mL hermetically sealed bench scale bioreactors built in cylindrical glasses provided with two points for internal gas sampling. This study consisted of the co-digestion of 2 types of sludge with 3 types of shavings, resulting in 6 conditions and totaling 12 tests as shown in Table 1. All tests were performed in duplicate. In addition, 200 mL of nutrient solution (2 g/L of yeast extract, 1 g/L of peptone, 7 g/L of $K_2HPO_4$, and 3 g/L of $KH_2PO_4$) was employed to ensure favorable conditions for the growth and metabolism of the microorganisms (C. B. Agustini et al.,2017). The bioreactors were maintained at 35 °C (mesophilic temperature range). After 200 days of incubation, the bioreactors were opened and the liquid and solid samples were collected. To analyze the organic and inorganic loads of the biomass mixture before biodegradation, the same tests were assembled in closed bottles, shaken for 1 h in a Wagner shaker, and left to settle for 24 h at 4 °C until their opening and the collection of liquid and solid samples. In order to identify the main effects and interactions of the selected variables, two $2^2$ full factorial designs were used. The independent variables were:

1 Origin of sludge (processing stage) from WWTP: before and after tanning;
2 Origin of shavings (processing stage): picked hide (before tanning) and after tanning.

In order to evaluate the influence of the presence/absence of the tanning agent, various parameters were taken into account. The efficiency was expressed in terms of the following response variables: