Use of Different Pre-treated Chromium Leather Shavings to Produce Biogas in Continuous Scale

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Abstract. Leather goods are noble and sustainable but leather production may bear a potential for pollution. During leather manufacture, high amounts of chromium shavings, wet by-products of the leather industry, are produced worldwide. They are disposed of at landfill sites which results in long-term environmental problems. They are stable towards temperatures of up to 110 °C and enzymatic degradation, preventing anaerobic digestion in a biogas plant. This stability is due to the three-dimensional native structure, typical for collagen, and additional chemical cross-links between the collagen fibres achieved by Cr^{3+} salts in the tanning step in tanneries. Hitherto, chromium shavings are not utilized industrially to produce biogas. In order to ease enzymatic degradation, necessary to produce biogas, a previous denaturation of the native structure has to be carried out. Otherwise, the generation of biogas is hindered. In our projects, chromium shavings were pre-treated thermally and mechanically by extrusion and hydrothermal methods. In previous works, we intensively studied the use of these shavings to produce biogas in batch scale and significant improvement was reached when using pre-treated shavings. In this work, a scale-up of the process was performed in a continuous reactor using pre-treated and untreated shavings to examine the feasibility of the considered method. Measuring different parameters along the anaerobic digestion, namely organic matter, collagen content, and volatile fatty acids content, it was possible to show that a higher methane production can be reached and a higher loading rate can be used when feeding the reactor with pre-treated shavings instead of untreated shavings, which means a more economical and efficient process in an industrial scenario.

1 Introduction

The disposal of chromium leather waste is one of the most important ecological challenges in the leather industry. Due to their structure composed mainly of collagen and chromium cross-links, this solid waste is considered to be too stable for anaerobic degradation. However, Dhayalan et al. (2007) studied the anaerobic digestion of chromium leather and concluded that degradation of the waste is possible using anaerobic sludge. The problem is that using this substrate leads to a very slow process and low biogas production.

Currently, there are no biogas plants in the industry using chromium leather waste as a main substrate. However, the tannery SÜDLEDER (Rehau, Germany) already has a biogas plant in operation using their own organic waste (hair, protein, fat, and chromium loaded sludge) to produce energy (Schuberth-Roth, 2013). This kind of initiative illustrates the interest of the industry in biogas production. Nevertheless, using a complex substrate as chromium leather waste needs to be further developed.

Collagen molecules are endowed with mechanical and thermal stability of the fibrous network and high stability to enzymatic degradation (Reich, 2007). Additionally, the chromium tanning process makes the material even more stable (Usha and Ramasami, 2000). Hence, it is necessary to denature the collagen fibres present in chromium leather waste to enable the anaerobic microorganism to degrade this solid waste (Kanagaraj et al., 2006). A pre-treatment can be used to denature the collagen and enable degradation in order to reduce the digestion time and increase the biogas yield.

While some studies treated chromium leather waste under batch conditions (Dhayalan et al., 2007; Ferreira et al., 2010; Agustini et al., 2015 and 2018; Priebe et al., 2016; Gomes et al. 2017 and 2019), there is no published work on continuous reactors for this material. Continuous tests simulate long-term process conditions and are essential for adapting the method in the industry

since most large-scale industrial digesters work in continuous mode as this allows the digester to continually produce biogas (Gamble et al., 2015). These tests enable to investigate capabilities and loading limits of the process, mean residence time as well as formation and accumulation of metabolic intermediates and their influence on process stability (VDI 4630, 2006).

1.1 Objectives

The aim of this study is to investigate the biogas production with untreated and pre-treated chromium leather wastes in a continuous biogas reactor. Pre-treatment was performed by different heating and mechanical technologies.

2 Materials and Methods

2.1 Materials

The chromium leather waste tested were chromium shavings shaved from wet chromium tanned leather. The materials were obtained from a local tannery (HEWA Leder, Freiberg, Saxony, Germany). The chromium shavings used in this work have already been air-dried to some extent and present a water content of almost 20%.

For the biogas trials, mesophilic anaerobic sludge from the tannery SÜDLEDER was used as inoculum. Since the sludge was produced in a tannery, this inoculum was already adapted to chromium residues and collagen as substrate.

2.2 Pre-treatment of the chromium shavings

In order to denature the materials and promote the waste degradation and biogas production, different heat and mechanical pre-treatment techniques were tested. Extrusion, a classical technique from the polymer industry, and a continuous hydrothermal treatment, which is commonly used to plastify wood for the manufacture of wood composites, were used to pre-treat and denature the chromium shavings. While extrusion affects the material by heat, mechanical shear, and pressure, the hydrothermal treatment is based on heat and steam pressure only. During the process, temperatures higher than the denaturation temperature were achieved in order to enable enzymatic degradation to produce biogas.

2.2.1 Extrusion

Extrusion was performed on chromium shavings with a co-rotating twin screw-extruder Werner & Pfleiderer ZSK 25 at 100 °C in a continuous process. This extrusion process starts by feeding the sample from a hopper into the barrel of the extruder. The material is gradually degraded by the mechanical energy generated by turning screws and by heaters arranged along the barrel. The conversion of mechanical energy into heat makes it possible to use this process even under the denaturation temperature of chromium shavings (105 °C to 110 °C). The extrusion of chromium shavings resulted in a powdered material (Figure 1) with a water content of about 15%. The process takes approximately 3 minutes.

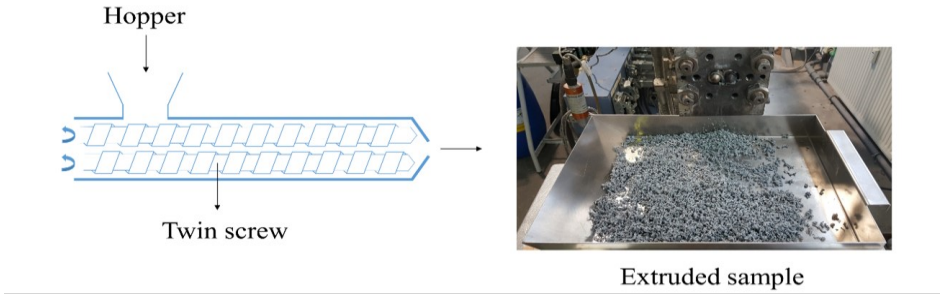

Fig. 1. Operation of the extruder machine.

2.2.2 Hydrothermal treatment

The chromium shavings were subjected to hydrothermal treatment through a continuous autoclave system attached to a refiner (Andritz CPH 12-1) at the Institut für Holztechnologie (Dresden, Germany). Usually, this equipment is used to plastify wood chips but it is also adequate to process a variety of organic materials. The process was carried out at 140 °C and 150 °C in saturated steam. The material was dosed into a digester in which it was denatured with steam under pressure. The pre-treatment time was around 45 seconds.

The pre-treated samples appeared like a dough with a high water content of about 80%. The direct use of these samples in the biogas trials was not possible due to their high water content. Therefore, drying and manual grinding of the material was necessary.

2.3 Characterization of the pre-treated shavings

The pre-treated materials were characterized regarding their inorganic matter (DIN EN ISO 4047, 1998), chromic oxide content (DIN EN ISO 5398-1, 2007), and collagen content by determination of the hydroxyproline content (Stegemann, 1958). Thermal profiles in fully hydrated state of the materials were taken using differential scanning calorimetry (DSC 1 STARe System Mettler Toledo) to verify that the pre-treated materials were completely denatured. The enthalpy calculated from this method represents the necessary energy to break down the hydrogen bonds that stabilize the triple helix. If no enthalpy was observed, there is no triple-helical collagen present in the sample. Results were compared with the values found for the untreated chromium shavings.

2.4 Biogas production trials

Continuous fermentation tests were performed according to the guideline VDI 4630 (2006). The continuous reactors consisted of a 20 L gastight stirred tank with infeed and outlet, and a gas offtake connection to collect the formed biogas (Figure 2). Temperature was kept under mesophilic conditions (37 °C ± 2 °C) using a circulation thermostat (Huber CC-202C), and the biomass was constantly mixed at 50 rpm using a paddle stirrer (Heidolph RZR 2041). The biogas formation in norm litres per kg of sludge (L kg^{-1} d^{-1}) was measured daily using a drum-type gas meter (Ritter TG05/5), and the quality of the gas and the hydrogen sulphide concentration was measured using an electronic analyser (OPTIMA 7 BIOGAS) once every two days excluding weekends. The hydrogen sulfide concentration was controlled by the addition of iron (III) chloride hexahydrate (Merck), which works as an H_2S scavenger, when necessary. Mesophilic anaerobic sludge from the SÜDLEDER tannery was used as inoculum.

Fig. 2. Continuous fermentation test apparatus (source: MyFerm I manual – Landgraf Laborsysteme HLL GmbH).

At the beginning of the test, the reactor was filled with approximately 20 kg of inoculum (wet basis). Substrate was added once every two days excluding weekends via a dip tube located at the head end of the reactor, starting at a loading rate of substrate per kg of sludge of 0.5 g kg^{-1} d^{-1} (substrate mass in organic dry matter). After the daily methane production was constant, the loading rate was raised by 0.5 units and the process was repeated until the gas production no longer increased.

Once a week a sample of biomass was taken for characterization regarding its pH, inorganic matter (DIN EN ISO 4047, 1998), chromic oxide content (DIN EN ISO 5398-1, 2007), and collagen content (Stegemann, 1958). The biomass was also analysed chromatographically by HPLC (Shimadzu prominence Serie 20, equipped with a refractive index detector RID-10A and a photodiode array detector SPD-M20A) to determine its volatile fatty acids content.

3 Results and Discussion

3.1 Characterization of the pre-treated shavings

The characterization of the pre-treated samples gives important information for the biogas trials. Only organics are capable of producing biogas and, therefore, it is important to quantify the organic and inorganic content. The characterization of the samples is presented in Table 1.

Table 1. Characterization of the untreated and pre-treated chromium shavings.

	Organic matter (%)*	Chromium (%)*,**	Collagen (%)*	Denaturation enthalpy (J g^{-1})
Chromium shavings	88.8 ± 0.1	4.6 ± 0.0	77.0 ± 0.6	61.8 ± 0.6
Extruded shavings	88.9 ± 0.0	4.6 ± 0.0	74.2 ± 0.9	0
Shavings treat. hydrothermally	89.5 ± 0.4	4.4 ± 0.0	74.2 ± 0.8	0

*Dry basis; mean ± standard deviation, n = 3
**Measured as chromium oxide

The organic matter in the samples remains the same after pre-treatment. This is important because the organics must be preserved for producing biogas in the anaerobic digestion. The collagen content is also barely unchanged after pre-treatment. This protein is the main component of the chromium shavings, only about 12% of the samples are different types of organics, for instance fats. Therefore, collagen is the most important parameter to calculate the substrate degradation after anaerobic digestion. DSC results show that the collagen in the chromium shavings was completely denatured by pre-treatment. Consequently, chromium shavings are more easily accessible to enzymatic degradation. This is explored in more detail in a previous work (Gomes et al., 2017).

Almost half of the inorganic part of the samples is chromium oxide. Chromium also remains the same after pre-treatment. Other inorganics in the samples come from the chemicals used in tanneries.

3.2 Biogas production trials

3.2.1 Productivity of the reactors

The pre-treated samples were tested as substrates for biogas production in a continuous reactor and the results were compared with the performance of the untreated shavings. Figure 3 shows the time plot of digestion for the studied substrates.

Two of the biogas trials showed a drop in the daily methane production along digestion, indicating technical problems. The methane production drops can be seen on the 7th day of digestion for the reactor fed with extruded shavings (Figure 3b) and on the 21st for the reactor fed with shavings treated hydrothermally (Figure 3c). The former was caused by an oxygen infiltration on day 5 due to the rupture of the dip tube used to feed the reactor; the latter by an agitation failure, which resulted in the uneven heating of the reactor. Even though there is a drop in the methane production, the system recovered its former stability and appeared to function normally after a few days. The reactor fed with shavings treated hydrothermally needed only 2 days to recover, and the reactor fed with extruded shavings needed 5 days, that is more time to recover probably because the ingress of oxygen occurred very early in the digestion process. The daily methane production became very unstable for the extruded shavings when using loading rates higher than 1.4 g kg^{-1} d^{-1} and for the shavings treated hydrothermally for loading rates of 2.0 g kg^{-1} d^{-1}.

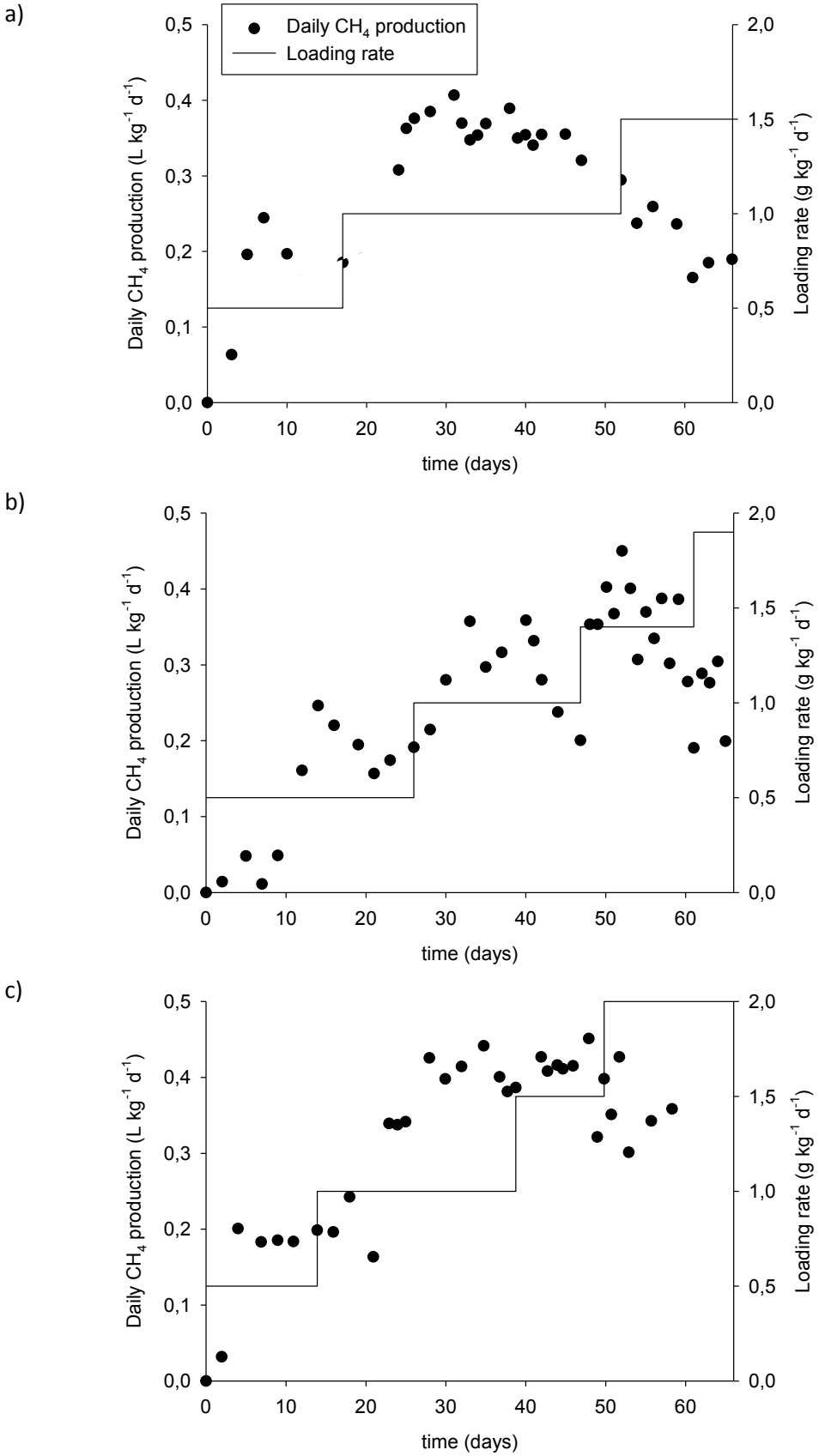

Fig. 3. Time plot of continuous fermentation of the untreated chromium shavings (a), extruded shavings (b), and shavings treated hydrothermally (c).

The production of a second batch of extruded shavings was necessary to feed the reactor starting on the 42nd day. This second batch of the substrate was not completely denatured because the use of the same extruder was not possible. DSC results still showed a denaturation enthalpy of 12.6 J g^{-1} compared to 61.8 J g^{-1} for untreated chromium shavings (Table 1).

Pre-treatment allowed the use of a higher loading rate and increased the maximum daily methane production. The trial with untreated chromium shavings (Figure 3a) had to be stopped at a loading rate of 1.5 g kg^{-1} d^{-1} but the extruded shavings (Figure 3b) could be tested up to a loading rate of 1.9 g kg^{-1} d^{-1} and the shavings treated hydrothermally (Figure 3c) up to 2.0 g kg^{-1} d^{-1}. The chromium shavings reached the maximum daily methane production, 0.41 L kg^{-1} d^{-1}, on day 31 of digestion with a loading rate of 1.0 g kg^{-1} d^{-1}. The extruded shavings reached a higher value, 0.45 L kg^{-1} d^{-1}, on day 52 of digestion but with a loading rate of 1.4 g kg^{-1} d^{-1}.

Similarly, for the shavings treated hydrothermally, the maximum daily methane production was 0.45 L kg^{-1} d^{-1}, on day 48 of digestion with a loading rate of 1.5 g kg^{-1} d^{-1}.

No studies covering the anaerobic digestion of chromium leather waste in continuous trials could be found for comparison. Some authors studied the digestion of tannery waste in continuous (López et al., 2015a and 2015b) or semi-continuous mode (Berhe and Leta, 2018; Kameswari et al., 2015; Zupančič and Jemec, 2010) but the material was always collected from tanneries prior to the tanning step and this is known to be already in use industrially (Schuberth-Roth, 2013). These studies mainly used fleshings as substrate, which are also not suitable for comparison due to a high fat content.

3.2.2 Inhibition of digestion

In order to monitor the reactor stability and possible inhibitions, biomass samples were collected weekly and analysed regarding their concentration of volatile fatty acids. Figure 4 shows the results for the three anaerobic reactors.

Volatile fatty acids are intermediate products resulting from anaerobic digestion. However, they could inhibit the methane production at high concentrations (Gomes et al., 2019). To avoid failure of a fermenter, the total concentration of volatile fatty acids should be lower than 4 g L^{-1}. The acetic acid concentration should be lower than 3 g L^{-1}, the isobutyric acid concentration lower than 0.5 g L^{-1}, and the propionic acid concentration lower than 1 g L^{-1} (Kaiser et al., 2008) but a concentration of propionic acid higher than 0.3 g L^{-1} is enough to disturb the anaerobic digestion (Deublein and Steinhauser, 2008).

The reactor fed with untreated shavings (Figure 4a) showed a stable total volatile fatty acid concentration for a loading rate up to 1.0 g kg^{-1} d^{-1} but the concentration increased at a loading rate of 1.5 g kg^{-1} d^{-1} to more than 4 g L^{-1}, corresponding to the drop in daily methane production. For the final collected sample, the acetic acid concentration was 3.5 g L^{-1} and the propionic acid concentration reached 0.6 g L^{-1} indicating a complete failure of the reactor at this loading rate.

Similarly, for the extruded shavings (Figure 4b) as substrate, the total volatile fatty acid concentration was low for a loading rate up to 1.0 g kg^{-1} d^{-1}. There was a small increase of acid concentration at the first loading rate, corresponding to the ingress of oxygen registered for this reactor but the system recovers its former stability and the acid concentration drops again. The acid concentration started increasing at a loading rate of 1.4 g kg^{-1} d^{-1} without reaching an inhibitory concentration, which could explain the unstable daily methane production values at this loading rate. Finally, at the last loading rate, the total acid concentration reached 5.4 g L^{-1} and the propionic acid concentration reached a value of 1 g L^{-1} indicating the failure of the reactor. The acetic acid and isobutyric acid concentrations were also high in this last sample but without reaching an inhibitory concentration.

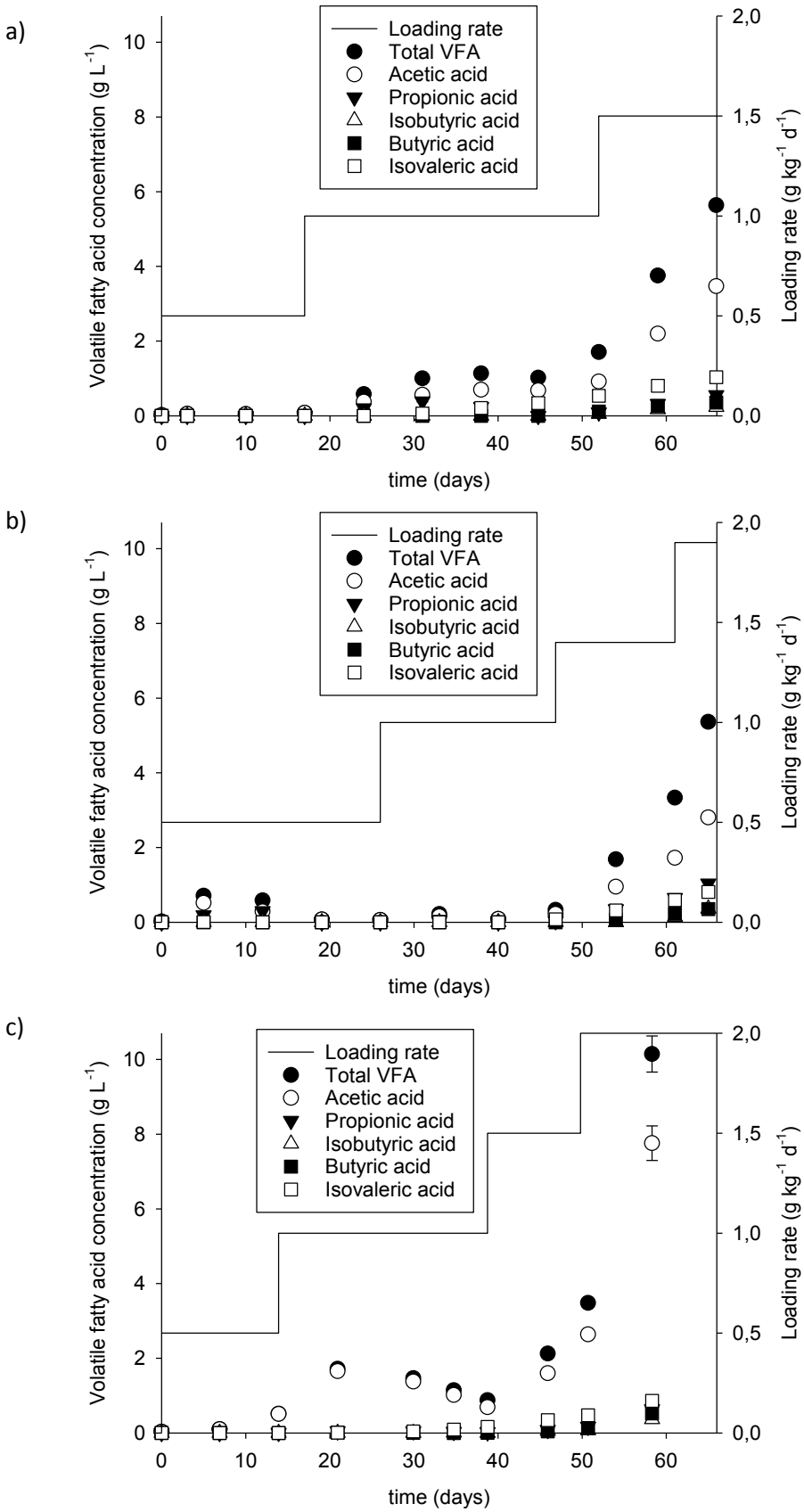

Fig. 4. Volatile fatty acid concentrations along the anaerobic digestion of untreated chromium shavings (a), extruded shavings (b), and shavings treated hydrothermally (c).

Table 2. pH and chromium content of the samples collected along the continuous digestion.

Chromium shavings			
Time (days)	Loading rate (g kg^{-1} d^{-1})	pH	Chromium (%)*
0	0.5	8.1	1.1
3			1.0 ± 0.0
10		7.9	1.4 ± 0.1
17		7.9	1.6 ± 0.1
24	1.0	7.9	1.9 ± 0.0
31		8.0	2.4 ± 0.1
38		8.1	2.7 ± 0.0
45		8.1	3.5 ± 0.0
52		8.1	3.3 ± 0.1
59	1.5	8.1	3.9 ± 0.1
66		8.0	4.3 ± 0.1
Extruded shavings			
Time (days)	Loading rate (g kg^{-1} d^{-1})	pH	Chromium (%)*
0	0.5	8.3	1.0 ± 0.0
5		7.8	1.3 ± 0.1
12		7.9	1.6 ± 0.0
19		8.0	2.0 ± 0.1
26		7.9	2.5 ± 0.0
33	1.0	8.0	3.1 ± 0.1
40		8.1	3.5 ± 0.1
47		8.0	3.8 ± 0.1
54	1.4	8.0	4.7 ± 0.1
61		8.1	4.9 ± 0.4
65	1.9	8.0	4.5 ± 0.0
Shavings treated hydrothermally			
Time (days)	Loading rate (g kg^{-1} d^{-1})	pH	Chromium (%)*
0	0.5	8.1	1.2 ± 0.0
7		8.0	1.6 ± 0.0
14		8.0	1.7 ± 0.0
21	1.0	7.8	2.3 ± 0.0
30		8.1	2.8 ± 0.1
35		8.1	3.1 ± 0.0
39		8.1	3.1 ± 0.0
46	1.5	8.1	3.5 ± 0.1
51		8.1	4.7 ± 0.0
58	2.0	8.0	4.7± 0.0

*Dry basis; mean ± standard deviation, n = 2; measured as chromium oxide

The reactor fed with shavings treated hydrothermally (Figure 4c) also showed a small increase of the volatile fatty acid concentration due to the agitation failure at a loading rate of 1.0 g kg^{-1} d^{-1}. Again, the reactor recovers stability and the acid concentration drops. Otherwise, the reactor showed stable volatile fatty acid concentrations. The concentration only increased in the last collected biomass sample at a loading rate of 1.5 g kg^{-1} d^{-1}. Inhibition began at the last loading rate and daily methane production dropped. The total volatile fatty acid concentration increased to up to 10.1 g L^{-1},

the acetic acid concentration to up to 7.8 g L^{-1}, propionic acid to up to 0.6 g L^{-1}, and isobutyric acid to up to 0.4 g L^{-1}.

The chromium content could also cause inhibition of the methane production in the reactors. Cr^{3+} ions could inhibit the methanogenic archaea without affecting the acidogenic bacteria, resulting in the accumulation of volatile fatty acids. Chromium could also have other negative effects on the anaerobic digestion such as a decrease in the total gas production rate, a fall in pH, a decrease in the percentage of methane in the gas produced, and an accumulation of organic matter (Alkan et al., 1996). The pH and chromium content of the collected biomass samples was analysed and results are shown in Table 2.

The pH of the biomass during digestion was very stable, between 7.8 and 8.3, causing no disturbance in the system. At the end of the trials, a total chromium content of almost 5% was achieved in all reactors, which appears not to affect digestion. The inoculum for the reactor fed with chromium shavings had a chromium content of 324 mg L^{-1}, the extruded shavings reactor had a chromium content of 233 mg L^{-1}, and the reactor fed with shavings treated hydrothermally had a content of 369 g L^{-1}. The bacteria present in the initial sludge were already adapted to high quantities of chromium prior to digestion. The determination of a limit would only be possible with a long-term trial at an appropriate loading rate, without other inhibitions.

3.2.3 Degradation of the substrate

The degradation of the substrate was evaluated analysing the biomass samples collected weekly along the anaerobic digestion. Table 3 shows the characterization of the collected biomass samples. The samples were analysed regarding their collagen, organic matter, and chromium content.

An increase in the organic matter content in the collected sludge would indicate the accumulation of unprocessed substrate and, therefore, inefficiency of the process. As seen in Table 3, the reactor fed with untreated chromium shavings showed a constant value of organic matter content (around 40%) for most of the time. An increase to 45% was detected at the end of the trial at a loading rate of 1.5 g kg^{-1} d^{-1}, indicating that the reactor was overloaded. The methane production is very low and the added substrate accumulates.

The reactor fed with the extruded shavings had an organic matter content of around 39% at a loading rate of 0.5 g kg^{-1} d^{-1}. At a loading rate of 1.0 g kg^{-1} d^{-1} the organic matter content remained constant at 40% and showed a slight increase to 42% at the end of this rate. In a next step, an increase in organic matter to around 44% was observed at a loading rate of 1.4 g kg^{-1} d^{-1}. Finally, in the last step, the organic matter content increased to 47% at a loading rate of 1.9 g kg^{-1} d^{-1}. With regard to the shavings treated hydrothermally, the reactor started with around 38% of organic matter at the first loading rate. Progression to the next step increased the organic matter content of the reactor to about 40%. The loading rate of 1.5 g kg^{-1} d^{-1} resulted in an increase to 45% and the last loading rate led to 48%. The increase of organic matter at the last loading rate when methane production slows indicates accumulation.

At the end of digestion, the collagen content was almost as low as it was prior to adding substrate at the beginning of the process for all reactors, showing that collagen was degraded and that there is no accumulation of collagen in the reactor. Therefore, the collagen of the added substrate was metabolized. However, the inorganic part of the samples accumulated, and the chromium content in the reactor increased.

Although a second batch of extruded shavings was used, which were not completely denatured, the reactor accomplished degradation of the substrate. When the reactor was shut down, it contained 33.7 g of collagen (dry basis), which represents a final degradation of 96.5% of all of the added collagen (953.8 g of added collagen). The reactor fed with untreated shavings contained 45.6 g of collagen (dry basis) at shutdown, equating to 95.5% of degradation (1014.4 g of added collagen) and the reactor fed with shavings treated hydrothermally showed a final amount of collagen of 58.3 g (dry

basis) meaning that 95.3% of the added collagen were degraded (1233.4 g of added collagen). That leads to the conclusion that there is efficient degradation of collagen notwithstanding the observed accumulation of organic matter (Table 3).

Table 3. Biomass characterization of the samples collected along the continuous digestion.

Chromium shavings			
Time (days)	**Loading rate (g kg^{-1} d^{-1})**	**Collagen (%)***	**Organic matter (%)***
0	0.5	2.9 ± 0.3	39.5 ± 1.4
3		4.3 ± 0.9	41.4 ± 1.2
10		4.4 ± 0.4	41.2 ± 1.8
17		5.8 ± 0.6	38.7 ± 0.2
24	1.0	6.3 ± 0.7	41.1 ± 0.3
31		5.1 ± 0.4	40.8 ± 0.0
38		3.6 ± 0.4	40.2 ± 0.3
45		2.5 ± 0.1	40.3 ± 0.2
52		2.3 ± 0.1	41.3 ± 0.2
59	1.5	2.6 ± 0.2	44.6 ± 0.3
66		3.3 ± 0.0	45.4 ± 0.1
Extruded shavings			
Time (days)	**Loading rate (g kg^{-1} d^{-1})**	**Collagen (%)***	**Organic matter (%)***
0	0.5	2.7 ± 0.3	38.3 ± 0.3
5		3.2 ± 0.1	38.4 ± 1.2
12		3.3 ± 0.1	38.5 ± 0.3
19		3.6 ± 0.1	39.6 ± 1.4
26		3.4 ± 0.1	37.9 ± 0.1
33	1.0	3.4 ± 0.3	40.2 ± 0.5
40		4.5 ± 0.2	40.3 ± 0.2
47		6.5 ± 0.3	42.0 ± 0.1
54	1.4	3.4 ± 0.1	43.7 ± 0.2
61		3.1 ± 0.1	44.4 ± 0.1
65	1.9	2.8 ± 0.0	46.9 ± 0.1
Shavings treated hydrothermally			
Time (days)	**Loading rate (g kg^{-1} d^{-1})**	**Collagen (%)***	**Organic matter (%)***
0	0.5	3.3 ± 0.0	37.4 ± 0.2
7		3.7 ± 0.0	39.1 ± 0.3
14		4.0 ± 0.1	37.9 ± 0.1
21	1.0	5.6 ± 0.0	40.7 ± 0.3
30		4.8 ± 0.3	39.8 ± 0.6
35		5.1 ± 0.1	39.8 ± 0.4
39		5.2 ± 0.1	40.6 ± 0.5
46	1.5	4.9 ± 0.1	42.3 ± 0.3
51		5.0 ± 0.0	45.3 ± 0.4
58	2.0	4.0 ± 0.1	48.0 ± 0.1

*Dry basis; mean ± standard deviation, n = 3

The organic matter present in the final biomass is formed from organics from the inoculum and intermediate products from the hydrolysed substrate, such as volatile fatty acids, amino acids, and peptides. In a previous work (Gomes et al., 2017), it was shown that the anaerobic digestion of

inoculum without adding substrate leads to a final biomass of about 40% of organic content from which the conclusion can be drawn that part of the initial organic matter will remain unprocessed. The increase in organic matter content along the digestion is a consequence of the accumulation of unprocessed substrate in the form of intermediate products, which are not transformed into biogas probably due to inhibition of the anaerobic bacteria.

Considering that the highest daily methane production for the untreated shavings was reached at a loading rate of 1.0 g kg^{-1} d^{-1}, the conclusion can be drawn that this is the most appropriate loading rate for this material. The reactor fed with extruded shavings showed the highest daily methane production at a loading rate of 1.4 g kg^{-1} d^{-1} proving to be the most suitable loading rate for the extruded sample among the studied rates. Finally, the reactor fed with shavings treated hydrothermally reached its highest daily methane production at a loading rate of 1.5 g kg^{-1} d^{-1} showing that this rate should be aimed at. Accumulation of organic matter and the increasing concentrations of volatile fatty acids verified in the collected biomass samples for the last tested loading rates lead to the same conclusion. Nevertheless, long-term trials of one year or more should prove this observation.

Pre-treatment of the chromium shavings allows for a higher loading rate of substrate in the reactor and a higher daily methane production. This increases the capability of reducing solid waste and the generation of energy. Consequently, the feasibility of chromium shavings to be digested for producing biogas in tanneries increases. It is also possible to digest untreated chromium shavings in continuous systems to produce methane but using a low loading rate. However, an explanation for this observation is still missing and this conflicts with the common doctrine that untreated shaving cannot be digested in biogas reactors. An economical evaluation to verify if the pre-treatment costs are compensated by the energy gains should be done. However, reduction of the disposal of final waste, which would otherwise generate costs, makes this method very attractive for industry purposes.

4 Conclusions

The production of biogas in continuous reactors was tested for two different pre-treated chromium shavings and untreated chromium shavings. Pre-treatment was carried out to denature the stable collagen structure of chromium shavings in order to enhance anaerobic digestion when using this waste as substrate to produce biogas. The reactors fed with pre-treated shavings showed a higher methane production than those using chromium shavings as substrate. For pre-treated shavings a loading rate could be used which was 40 to 50% higher than that for untreated chromium shavings, and the maximum daily methane production could be increased by almost 10%. A higher loading rate leads to a more economical process, and it can be expected that, on an industrial scale, the loading rate could be increased by 40 to 50% through pre-treatment of the chromium shavings or, in contrast, the reactor volume for a given loading rate could be decreased.

5 Acknowledgements

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References

1. *Agustini, C., Costa, M., Gutterres, M.: 'Biogas production from tannery solid wastes - Scale-up and cost saving analysis', J. Clean. Prod., 187, 158–164, 2018*
2. *Agustini, C., Neto, W., Costa, M., Gutterres, M.: 'Biodegradation and biogas production from solid waste of tanneries', XXXIII IULTCS Congress, Novo Hamburgo, Brazil, 2015*
3. *Alkan, U., Anderson, G. K., Ince, O.: 'Toxicity of trivalent chromium in the anaerobic digestion process', Water Res., 30, 3, 731 – 741, 1996*
4. *Berhe, S., Leta, S.: 'Anaerobic co-digestion of tannery waste water and tannery solid waste using two-stage anaerobic sequencing batch reactor: focus on performances of methanogenic step', J. Mater. Cycles Waste Manag., 20, 1468–1482, 2018*
5. *Deublein, D., Steinhauser, A.: Biogas from Waste and renewable Resources An Introduction, Wiley-VCH, Weinheim, 2008*
6. *Dhayalan, K., Fathima, N. N., Gnanamani A., Rao J. R., Nair B. U., Ramasami T.: 'Biodegradability of leathers through anaerobic pathway', Waste Manage., 27, 760–767, 2007*
7. *DIN EN ISO 4047: 'Leather - Determination of sulphated total ash and sulphated water-insoluble ash', German Institute for Standardization, Berlin, Germany, 1998*
8. *DIN EN ISO 5398-1: 'Leather - Chemical determination of chromic oxide content', German Institute for Standardization, Berlin, Germany, 2007*
9. *Ferreira, M. J., Almeida, M. F., Pinho, S. C, Santos, I. C.: 'Finished leather waste chromium acid extraction and anaerobic biodegradation of the products', Waste Manage., 30, 1091–1100, 2010*
10. *Gamble, K. J., Houser, J. B., Hambourger, M. S., Hoepfl, M. C.: Anaerobic Digestion from the Laboratory to the Field: An Experimental Study into the Scalability of Anaerobic Digestion, ASEE Southeast Section Conference, Gainesville, USA, 2015*
11. *Gomes, C. S., Repke, J-U., Meyer, M.: 'Different pre-treatments of chrome tanned leather waste and their use in the biogas production', XXXIV IULTCS Congress, Chennai, India, 2017*
12. *Gomes, C. S., Repke, J-U., Meyer, M.: 'Diauxie during biogas production from collagen-based substrates'. Renew. Energ., 141, 20-27, 2019*
13. *Kaiser, F., Metzner, T., Effenberger, M., Gronauer, A.: Sicherung der Prozessstabilität in landwirtschaftlichen Biogasanlagen, Bayerische Landesanstalt für Landwirtschaft (LfL), Freising-Weihenstephan, 2008*
14. *Kanagaraj, J., Velappan, K. C., Babu, N. K. C., Sadulla, S.: 'Solid wastes generation in the leather industry and its utilization for cleaner environment - A review'. J. Sci. Ind. Res., 65, 541 -548, 2006*
15. *Kameswari, K. S. B., Kalyanaraman, C., Thanasekaran, K.: 'Optimization of organic load for co-digestion of tannery solid waste in semi-continuous mode of operation', Clean Technol. Envir., 17, 693–706, 2015*
16. *López, I., Passeggi, M., Borzacconi, L.: 'Validation of a simple kinetic modelling approach for agro-industrial waste anaerobic digesters', Chem. Eng. J., 262, 509-516, 2015 (a)*
17. *López, I., Passeggi, M., Borzacconi, L.: 'Variable kinetic approach to modelling an industrial waste anaerobic digester', Biochem. Eng. J., 96, 7–13, 2015 (b)*
18. *Priebe, G. P. S., Kipper, E., Gusmão, A. L., Marcilio, N. R., Gutterres, M.: 'Anaerobic digestion of chrome-tanned leather waste for biogas production', J. Clean. Prod., 129, 410–416, 2016*
19. *Reich, G.: From collagen to leather – the theoretical background, BASF Service center Media and Communications, Ludwigshafen, 2007*
20. *Schuberth-Roth, V. T.: 'Erster Schritt in neue Energie-Ära', Frankenpost, Rehauer Tagblatt, [https://www.frankenpost.de/lokal/hofrehau/rehau/Erster-Schritt-in-neue-Energie-Aera;art2452,2627816], 2013*
21. *Stegemann, H.: 'Microdetermination of hydroxyproline with chloramine-T and p-dimethylaminobenzaldehyde', Hoppe-Seyler's Zeitschrift für physiologische Chemie, 311, 41, 1958*
22. *Usha, R., Ramasami, T.: 'Effect of crosslinking agents (basic chromium sulfate and formaldehyde) on the thermal and thermomechanical stability of rat tail tendon collagen fibre', Thermochim. Acta, 356, 59-66, 2000*
23. *VDI 4630: 'Fermentation of organic materials, Characterization of the substrate, sampling, collection of material data, fermentation tests', The Association of German Engineers, Düsseldorf, Germany, 2006*
24. *Zupančič, G. D., Jemec, A.: 'Anaerobic digestion of tannery waste: Semi-continuous and anaerobic sequencing batch reactor processes', Bioresour. Technol., 101, 26–33, 2010*