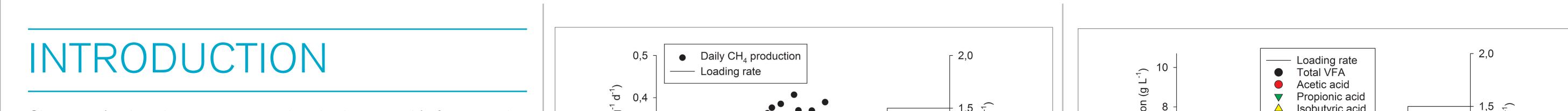
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USE OF DIFFERENT PRE-TREATED CHROMIUM LEATHER SHAVINGS FOR CONTINUOUS BIOGAS PRODUCTION

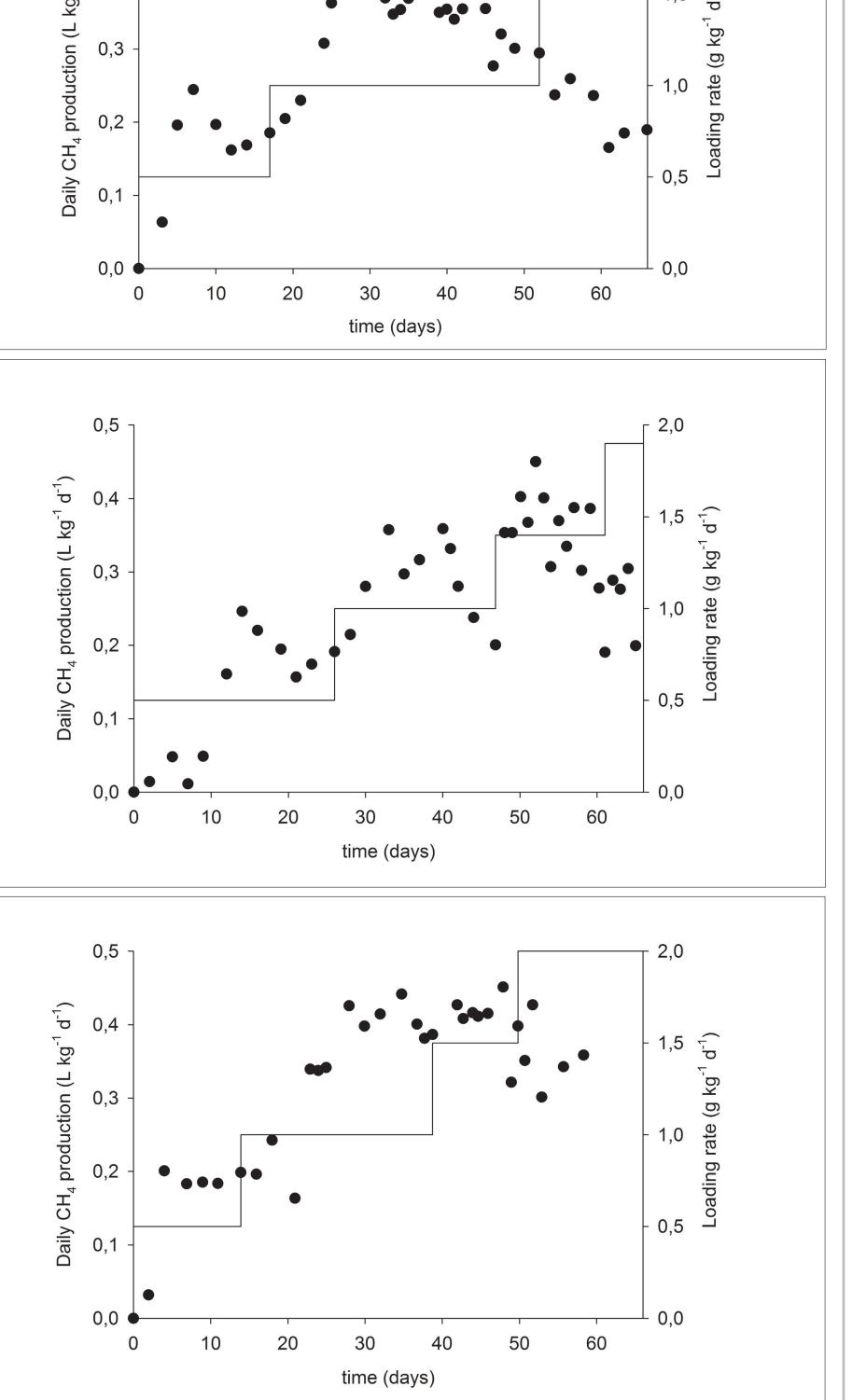


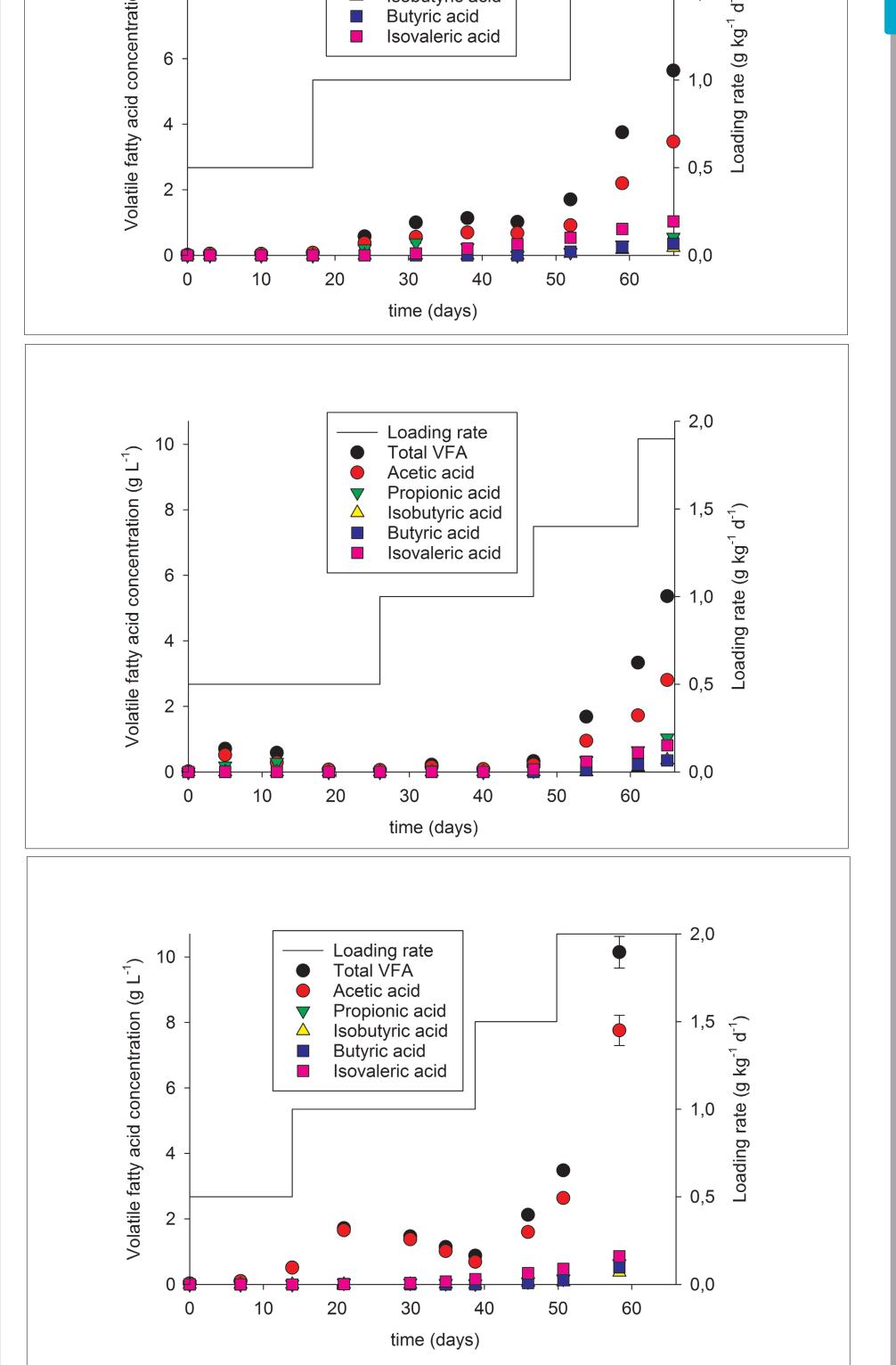
Chromium leather shavings are considered to be too stable for anaerobic degradation due to their structure composed mainly of collagen and chromium cross-links. However, Dhayalan et al. [1] proved that degradation of the waste is possible using anaerobic sludge. To avoid a very slow process and low biogas production it is necessary to denature the collagen fibres present in chromium shavings to enable the anaerobic microorganism to degrade this solid waste [2]. This can be achieved with a pre-treatment. Hitherto there is no published work on continuous reactors for this material, which are essential for adapting the method in the industry. The aim of this study is to investigate the biogas production with untreated and pre-treated chromium leather shavings in a continuous biogas reactor.

METHODS

The chromium shavings tested were shaved from wet chromium tanned leather. The materials were obtained from a local tannery (HEWA Leder). 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.

Different heat and mechanical pre-treatments were tested to denature the chromium shavings and promote degradation. Extrusion, a classical technique from the polymer industry was performed at 100 °C in a continuous process. This method affects the material by heat, mechanical





shear, and pressure. The extrusion of chromium shavings resulted in a powdered material. Continuous hydrothermal treatment is used to plastify wood for the manufacture of composites. The method is based on heat and steam pressure. The process was carried out at 140 °C and 150 °C in saturated steam. Pre-treated samples appeared like a dough.

BIOGAS PRODUCTION TRIALS

Continuous fermentation tests were performed according to the guideline VDI 4630 [3] in a 20 L stirred tank. Temperature was kept under mesophilic conditions. Substrate was added starting at a loading rate of 0.5 g kg⁻¹ d⁻¹. After the daily methane production was constant, loading rate was raised by 0.5 units.

RESULTS

Characterization results show that organic and collagen content in the chromium shavings are barely unchanged after pre- treatment and that collagen was completely denatured by pre-treatment. The organics must be preserved for producing biogas in the digestion.

The pre-treated shavings were tested as substrates for biogas production in a continuous reactor and the results were compared with the performance of the untreated shavings (Fig. 1). The chromium shavings reached the maximum daily methane production, 0.41 L kg⁻¹ d^{-1} , with a loading rate of 1 g kg⁻¹ d^{-1} (Fig. 1a). The extruded shavings reached a higher value, 0.45 L kg 1 d^{-1} , but with a loading rate of 1.4 g kg⁻¹ d^{-1} (Fig. 1b). Similarly, for the shavings treated hydrothermally, the maximum daily methane production was 0.45 L kg⁻¹ d^{-1} with a

Fig. 1: Time plot of fermentation of the untreated shavings (a), extruded shavings (b), and shavings treated hydrothermally (c).

loading rate of 1.5 g kg 1 d⁻¹ (Fig. 1c). Pre-treatment allowed the use of a higher loading rate and increased the maximum daily methane production.

Volatile fatty acids (VFA) were measured along the digestion because they are an indicative of failure of the reactor [4]. The reactor fed with untreated shavings (Fig. 2a) showed an increase of VFA concentration 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 extruded shavings (Fig. 2b) as substrate, the VFA concentration reached an inhibitory concentration at the loading rate of 1.9 g kg⁻¹ d⁻¹, 5.4 g L⁻¹ indicating the failure of the reactor. The reactor fed with shavings treated hydrothermally (Fig. 2c) reached an inhibitory VFA concentration at a loading rate of 2 g kg⁻¹ d⁻¹, concentration increased to up to 10.1 g L⁻¹.

Collagen was efficiently degraded. At shutdown, the reactor fed with untreated shavings reached 95.5% of degradation of added collagen, the extruded shavings reactor reached 96.5%, and the reactor fed with shavings treated hydrothermally reached 95.3%. Fig. 2: Volatile fatty acid concentrations along the anaerobic digestion of untreated shavings (a), extruded shavings (b), and shavings treated hydrothermally (c).

CONCLUSIONS

- Loading rate 40 to 50% higher when using pre-treated shavings;
- Maximum daily methane production 10 % higher when using pretreated shavings;
- The digestion of untreated chromium shavings was also possible but using a low loading rate.

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Results show that the most appropriate loading rate for untreated shavings is 1 g kg⁻¹ d⁻¹, for extruded shavings 1.4 g kg 1 d⁻¹, and for shavings treated hydrothermally 1.5 g kg 1 d⁻¹.

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