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Minimizing tannery sludge in landfilling through a mixed microbial culture approach: Effect of oxidizing pretreatment, temperature and hydraulic retention time on process performances and chromium fate

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ABSTRACT

Exploiting tannery sludge as potential source of short-chain fatty acids (SCFAs) and biogas offers a promising solution for a new management of this waste, which is currently landfilled due to chromium presence. This study assessed the optimal hydrogen peroxide (H_2O_2) dosage, temperature (T) and hydraulic retention time (HRT) through hydrolysis and acidification tests to maximize SCFAs production and to recover biogas from the solid-rich fermentation residue.

A dosage of 0.4 g H_2O_2/g TS and mesophilic T (40 °C) were the most suitable conditions to promote sludge biodegradability and SCFAs production in batch tests. Afterwards, among the two investigated HRT (4 and 8 days) in the semi-continuous processes, longer HRT increased SCFAs concentration and acidification yield up to 16.0 g COD_{SCFAs}/L and 0.32 g COD_{SCFA}/g VS_0, respectively. Chromium was initially released in the liquid phase, but completely removed in less than 5 HRTs, allowing the utilization of fermentation liquid without environmental-safety issues. Finally, the solid-rich residue showed its potential as biogas source, having a specific gas production (SGP) of 0.48 m^3/kg VS. According to the mass balance assessment, more than 50% of sludge can be saved from landfill, with potential economic benefit close to 2,700,000 €/y compared to the current management practice.

1. Introduction

The tannery industry has an important role in many countries where it has contributed significantly to employment and economic expansion [1]. However, this industry is still known for its high environmental impact related to the large water consumption and production of wastewater, which is characterized by a high content of chemical compounds, such as dyes, chromium salts and solvents [1]. In particular, chromium Cr(III) sulfate is widely used as a tanning agent as it imparts thermal stability, chemical resistance, and endurance to the finished leather products [2]. Cr(III) can also exist in the effluents in its hexavalent state [Cr(VI)], which is more toxic, mobile, and soluble [3].

According to the UNIC sustainability report of 2021, Italy's tannery industry accounts for 23% of the global value of leather and is regarded as the industry's global leader [4]. Wastewater from this industry typically undergoes treatment in wastewater treatment plants (WWTP). Here, physical–chemical primary treatments followed by activated sludge-based processes are performed to obtain a final effluent amenable to be discharged in the surface water bodies. The main waste derived from these processes is the tannery sludge, which is then dried out and disposed of in second-class type B controlled landfills due to its toxic nature. The volume of dried sludge sent to landfilling is very significative since 1.46 kg of waste (of which 17.5% is sludge) is created for each squared meter of finished product [4].

Abbreviations: AD, Anaerobic Digestion; AF, anaerobic fermentation; ANOVA, analysis of variance; BMP, biochemical methane potential; CHP, combined heat and power unit; COD, chemical oxygen demand; EU, European Union; FID, flame ionization detector; GC, gas chromatograph; GHG, greenhouse gases; HRT, hydraulic retention time; OM, organic matter; sCSTR, semi-continuous stirred tank reactors; SCFAs, short chain fatty acids; SRT, sludge retention time; SGP, specific gas production; COD_{SOL}, soluble COD; T, temperature; TKN, total kjeldahl nitrogen; TP, total phosphorus; TS, total solids; VS, volatile solids; VSS, volatile suspended solids; WWTP,, wastewater treatment plant.

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Nowadays, anaerobic digestion (AD) is the only fully established technology that allows the production of biogas and fertilizers from organic waste while reducing their mass or solids' content. Tannery sludge could be a great candidate for similar microbial technology. The first three stages of AD (hydrolysis, acidogenesis, and acetogenesis) are characterized by the production of short-chain fatty acids (SCFAs) and CO_2 from the breaking down of organic matter (OM) by fermentative bacteria, along with the production of H_2 [5]. In the final step of AD (methanogenesis), biogas is produced mainly using CO_2 as a carbon source and H_2 as the electron donor [6]. In the case of tannery waste, it has been observed that methanogenesis can be negatively impacted by inhibitors deriving from the tanning process, such as hydrogen sulfide (H_2S), ammonia (NH_3), and toxic metals [7]. Additionally, Achouri et al. [8] observed that the main limitation in treating solid-rich tannery effluent with AD was the particularly low hydrolysis rate, probably due to the presence of high-molecular-weight substances.

One of the most promising methods to increase the rate of the hydrolysis stage is the use of hydrogen peroxide (H_2O_2) to oxidize the high-molecular-weight compounds [9]. This process is achieved through the oxidizing action of the OH free radicals on the OM, which are formed by the breakdown of oxygen-oxygen single bonds [10]. As a consequence, the biodegradability of the OM increases due to the creation of lower-molecular-weight and bioavailable-to-microorganisms compounds [9]. This pretreatment has been previously employed with promising results due to its effectiveness, low costs, as well as easy availability, conduction, and harmless by-products generation [10,11].

Considering the no more sustainable disposal of tannery sludge, exclusively destined for a landfill, this study is aimed at its exploitation for the production of SCFAs, as value-added products and marketable platform chemicals trough anaerobic fermentation (AF) process [12]. The biogas recovery from any residual flux is necessary for a further reduction of the sludge, and in turn, for the minimization of the landfilling. In this study, a thorough analysis of tannery sludge as a substrate for microbial anaerobic processes has been performed. A first assessment of batch hydrolysis tests was aimed to evaluate the ideal H_2O_2 dosage to promote sludge biodegradability, quantified by the hydrolysis constant (k_h) [13]. In addition to its effect on the OM, H_2O_2 has also the potential of reducing the sulfur species in the sludge (H_2S), freeing the elemental S that could also be eventually recovered [14]. According to the chosen H_2O_2 dosage, a round of acidification batch tests was then focused on the effect of the temperature (T) on the SCFAs production, utilizing the pre-oxidized sludge previously obtained. Based on these assessments, two semi-continuous fermentation tests were performed at 4 and 8 days as hydraulic retention times (HRT) and at mesophilic T (40 °C) to compare SCFAs production (concentration and yield) and composition. Moreover, Cr fate was discussed through its quantification in the semi-continuous fermentation effluents. Biochemical methane potential (BMP) batch tests were performed to simulate the AD on the solid-rich AF residue, to quantify the biogas production and to define the whole tannery sludge reduction trough the final mass-energy balance. The latter was applied on the hypothetical two-steps anaerobic treatment (AF+AD) to quantify the mass reduction of landfilled sludge and the potential economic income from the produced SCFAs.

2. Materials and methods

2.1. Rationale of the approach

The designed flowchart consisted of a) hydrolysis potential assessment of the tannery sludge to increase its biodegradability; b) AF step for SCFAs production and fermentation yield maximization; c) solid/liquid separation, to obtain a SCFAs-rich liquid stream and a solid-rich fraction to be used in the subsequent AD step; d) AD for the production of biogas from the solid-rich fraction; e) a final drying step for the quantification of the solids abatement. Real data coming from hydrolysis tests, AF and AD steps have been discussed together with some assumptions to give a first idea about the technical and economic viability of the technology value chain through a detailed mass-energy balance as discussed below.

2.2. Substrate's characteristics and inoculum

A mixture of primary and secondary tannery sludge coming from the wastewater treatment plant (WWTP) of Montebello Vicentino (northeast Italy) was used as a carbon source. The WWTP treats different wastewaters produced by more than 20 tannery plants (about 10000 m^3/d), both with primary treatment (alkaline flocculation) and secondary biological treatment (anoxic/aerobic process). The tannery sludge was firstly subjected to a dewatering and drying step; its chemical and physical characteristics were the following: total and volatile solids content of 830 ± 14 g TS/kg and 590 ± 4 g VS/kg respectively; chemical oxygen demand (COD) 793 ± 18 g COD/kg TS; total phosphorus (TP) and nitrogen (as TKN) were 7.9 ± 0.4 g P/kg TS and 32.8 ± 0.9 g N/kg TS, respectively; total chromium (Cr) was equal to 19155 ± 310 mg Cr/kg TS.

2.3. Experimental setup and parameters of the hydrolysis tests

The hydrolysis tests were set up in 250 mL glass bottles sealed with a cap with a silicon plug, with 180 mL working volume, and each test was performed in duplicate. As anaerobic inoculum, 50 mL of mesophilic anaerobic digestate from a full-scale digester located in Treviso (northeast Italy) was used (35 g VS/L) and was previously incubated at 40 °C for one week to reach the endogenous methane production. Similarly, 50 mL of thermophilic inoculum from a parallel laboratory-scale digester was utilized for the thermophilic (55 °C) experiments. The tests were performed at neutral pH. Tannery sludge was added following the methodology proposed by Angelidaki et al. [13]; in particular, the substrate to inoculum (S/I) ratio was set at 0.3 (VS basin) for all the experiments. For the oxidative pretreatment of the sludge, four different H_2O_2 dosages were chosen: 0.1, 0.2, 0.4, 0.6 g H_2O_2/g TS (using a H_2O_2 solution at 35% w/w [11]). Since tannery sludge is rich in complex and slowly biodegradable substances, it has been treated with H_2O_2 to boost its hydrolysis. The oxidizing pretreatment was carried out in open bottles (250 mL) maintained under mixing for 2 h. The hydrolysis tests have been also conducted on the untreated tannery sludge (0.0 g H_2O_2/g TS). In each test, the biogas production was daily monitored; the data have been elaborated by the model described elsewhere [13] to monitor the sludge's hydrolysis rate, which was quantitatively represented by the hydrolysis constant k_h (d^{-1}).

2.4. Experimental setup and parameters of the batch acidogenic fermentation tests

The AF batch tests was conducted at different T, to investigate its effect on SCFAs production. According to the hydrolysis tests, a single H_2O_2 dosage was chosen for the oxidizing pretreatment (0.4 g H_2O_2/g TS), which was as previously explained for the hydrolysis tests.

A fixed aliquot of dried tannery sludge was used as inoculum to fix a S/I ratio of 8.0 w/w (VS basin) in 200 mL working volume [15]. All the bottles were sealed with a silicon plug-equipped cap and placed in a different water bath at five different temperatures: 15, 25, 30, 40, and 50 °C. Each test was conducted in triplicate. The bottles were manually mixed twice a day and a fixed-volume aliquot (around 10 mL) was regularly sampled to measure pH, $COD_{SOL,}$ and SCFAs concentration. In particular, the SCFAs concentration was monitored until the plateau was reached, as indication of the maximal SCFAs production in batch.

2.5. Semi-continuous acidogenic fermentation

The AF semi-continuous tests were conducted according to the best performances obtained in the hydrolysis and AF batch tests. The dosage of 0.4 g H_2O_2/g TS for the hydrolysis and the T of 40 °C were chosen.

Two parallel semi-continuous stirred tank reactors (sCSTR) of 1.5 L working volume were inoculated with tannery sludge, diluted with tap water at 20 g VS/L. The two sCSTR were maintained at the fixed T with water recirculation into an external thermostatic jacket and stirred with a mechanical impeller at 100 rpm. A pre-established mesophilic lag phase of one week was chosen for the inoculum's acclimation (only stirred); afterward, both reactors were fed once per day with H_2O_2 pre-pretreated tannery sludge, and maintained at two different hydraulic retention times (HRT) of 4.0 and 8.0 days (Run 1 and Run 2 respectively). The HRTs were equal to sludge retention time (SRT) since no settling phase was performed. The two HRTs were chosen based on the observed SCFAs trends in the AF batch tests; in particular the required times to achieve at least the 75% and 90% (roughly) of the maximum SCFAs production were considered. A fixed aliquot (according to the chosen HRT) was withdrawn for the effluent characterization, in terms of COD_{SOL}, SCFAs, N-NH_4^+, pH, and Cr. Regarding the SCFAs production, in addition to their concentration, the fermentation yield (Y_{SCFA}^{CSTR}) and the ratio between the SCFAs concentration and the COD_{SOL} (COD_{SCFA}/COD_{SOL}) were monitored. Total Cr was analyzed in the liquid phase at the end of the H_2O_2 pretreatment and regularly in the effluents to quantify any possible Cr release. The pH was naturally maintained neutral by the sludge itself which has a pH buffer characteristic due to the presence of lime ($CaCO_3$) [15].

2.6. Biochemical methane potential (BMP) tests

The BMP tests were set up in duplicate as indicated in the methodology of the hydrolysis tests. Similarly, 50 mL of mesophilic anaerobic digestate from the Treviso full-scale digester was used (35 g VS/L) as inoculum after one week of incubation (40 °C) to reach the endogenous methane production. The tests were performed at neutral pH, by using the solid-rich fraction of the fermentation effluent taken from Run 2 as substrate. The S/I ratio was set at 0.3 (VS basin). To investigate the effect of the oxidizing treatment on biogas production, parallel BMP tests were also conducted on hydrolyzed solid-rich fraction, which was treated with H_2O_2 (0.2 and 0.4 g H_2O_2/g TS) in open bottles (250 mL), maintained under mixing for 2 h before being inoculated. Biogas production and CH_4 content was daily monitored to quantify the maximum specific gas production (SGP; m^3/kg VS) achievable and the hypothetical HRT to be considered in the scaled-up continuous AD process, according to the model described elsewhere [16].

2.7. Analytical methods

The analyses were carried out according to the Standard Methods for the quantification of total solids (TS), volatile solids (VS), soluble COD (COD_{SOL}), ammonia, total nitrogen (as TKN), phosphorous (TP), total Cr and Cr(VI) [17].

Ammonium ions were measured on filtered samples (0.2 μm porosity) using the Nessler spectrophotometric method (Varian DMS 90 UV-Visible Spectrophotometer; absorbance at the wavelength of 420 nm). The COD_{SOL} analyses were also carried out on filtered samples (0.2 μm porosity) by using specific kits (Merck-VWR). For TKN and TP, a small aliquot of dried sludge (0.1 g) was firstly subjected to an acidic digestion with in a top-louder microwave (Speedwave XPERT, Berghof); the following spectrophotometric methods for ammonia and orthophosphate were adopted for the quantification [17].

Total Cr analysis was performed on samples previously basified, centrifuged, and filtered with a 0.2 μm porosity filters; the quantification was carried out with an inductively coupled plasma-mass spectrometry (ICP-MS) NexION 350X (Perkin Elmer) coupled with the autosampler seaFAST (ESI). The Cr(VI) analyses were also performed on filtered samples (0.2 μm porosity) with the direct spectrophotometric determination Cr(VI) by diphenylcarbazide [17]; the absorption measurements were carried out at 540 nm wavelength.

The SCFAs were analyzed using an Agilent 6890 N gas chromatograph (GC) equipped with a flame ionization detector (FID) at a temperature of 250 °C. An Agilent J&W DB-FFAP fused silica capillary column (DB-FFAP; 15 m length, 0.53 mm ID, 0.5 μm film thickness) was utilized as a stationary phase. Hydrogen was utilized as carrier. The inlet was set in split mode, with a split ratio of 20:1. The instrument was designed to operate with ramp temperature, from 80° to 100°C, at 10 °C per minute. Before GC analysis, each sample was centrifuged for 10 min at 4500 rpm and the supernatant was filtered through 0.2 μm acetate-cellulose filter porosity (Whatman).

CH_4 analyses were performed with the same GC reported above, which was also equipped with HP-PLOT MOLESIEVETM column (30 m x 0.53 m ID x 25 μm film thickness) and with a thermal conductivity detector (TCD) at 250 °C. The injector was maintained at 120 °C and 70 kPa. Gas samples (200 μL) were taken with a gas-type syringe; the analyses were conducted at 40 °C (oven temperature) for 8 min, by using Argon as gas carrier.

2.8. Calculation and statistical analysis

The degradation kinetic of the hydrolysis tests was evaluated in terms of the hydrolysis rate (k_h; d^{-1}), which was calculated according to the linear regression of the logarithmic equation of generated gas vs time, according to the first order kinetic model described elsewhere [13].

In the acidogenic fermentation batch tests, the acidification performances were evaluated by the ratio between the SCFAs and the COD_{SOL}, and the fermentation yield (Y_{SCFA}^{batch}), which was calculated considering the produced SCFAs over time ("t") and VS_0 as the initial VS concentration in the batch tests:

(1) $Y_{SCFA}^{batch} = [COD_{SCFA}]_t/VS_0$.

In the sCSTR experiments, the ratio between the SCFAs and the COD_{SOL}, as well as the fermentation yield (Y_{SCFA}^{CSTR}) and rate (q_{SCFA}^{CSTR}), ammonia release, and SCFAs volumetric productivity (P_{SCFA}^{CSTR}) were also quantified according to the following equations:

(2) $Y_{SCFA}^{CSTR} = [COD_{SCFA}]_t/VS_0$;
(3) $q_{SCFA}^{CSTR} = [COD_{SCFA}]_t/(VS_0 \bullet HRT)$;
(4) N-NH_4^+ release (%) $= [\text{N-}NH_4^+]_t/TKN_0$;
(5) $P_{SCFA}^{CSTR} = [COD_{SCFA}]_t/HRT$.

The BMP tests were assessed with regards to the SGP (m^3_{biogas}/kg VS), which was analyzed as a function of the modeled HRT to be adopted in the AD process, according to the methodology described in Jensen et al. [16].

The parameters characterizing the performances of AF batch and semicontinuous reactors were reported as mean values (with standard deviation). The *t*-test, the analysis of variance (ANOVA) and Tukey HSD post hoc tests were conducted to detect the results' significance. Shapiro–Wilk test was carried out to see if the data were normally distributed; Bartlett test and F-test were used to determine the homoscedasticity between the several data groups. All the statistical analyses were performed with R open-source program (The R Foundation for Statistical Computing, version 4.0.3).

The parameters for the mass and energy balance were set considering a production of 37000 tons/year of tannery sludge, which was the total amount from the two tannery WWTPs (Medio Chiampo S.p.a. and Acque del Chiampo S.p.a.). Reference parameters and boundary conditions are given in a previous work [18]. For the economic feasibility assessment, the disposal cost of the dried sludge was assumed to be 250 €/ton. The electrical energy required (0.237 €/kWh) to recover SCFAs from fermentation broth was considered 0.8 kWh/m^3, with an efficiency of 70% and the average SCFAs selling price of 2000 €/ton [19]. For tap water and H_2O_2, a price of 0.55 €/m^3 and 0.30 €/kg were respectively considered.

3. Results and discussion

3.1. Hydrolysis tests

The hydrolysis rate, represented by the k_h, is a pivotal information about the substrate biodegradability and its utilization as SCFA source. This parameter was analyzed for four different dosages of H_2O_2 (Fig. 1). Only one example described the benefit of using H_2O_2 on tannery sludge for the production of SCFAs [15]; however, the adopted pretreatment was combined with microwave application, and it foresaw a single H_2O_2 dosage (0.2 g H_2O_2/g TS). In addition, no investigation on the sludge biodegradability and k_h data was performed. Given the poor literature information, a wider range of H_2O_2 has been explored here, together with a quantitative evaluation of the k_h values.

For the mesophilic conditions (40 °C), the k_h of the untreated tannery sludge was 0.177 ± 0.04 d^{-1}; for the pretreated oxidized sludge, the k_h values were 0.189 ± 0.03, 0.187 ± 0.03, 0.197 ± 0.04, and 0.196 ± 0.03 d^{-1} at increasing H_2O_2 dosage respectively. Compared to untreated sludge, a remarkable improvement in the tannery sludge biodegradability was obtained at the dosage of 0.4 g H_2O_2/g TS. This appeared the ideal condition in a perspective of reagents and cost-saving approach, considering the comparable result obtained at the highest H_2O_2 dosage.

In the thermophilic tests (55 °C), the k_h values did not show a significative increase: they were equal to 0.182 ± 0.04 d^{-1} (no pretreatment), 0.189 ± 0.04 d^{-1} (0.1 g H_2O_2/g TS), 0.197 ± 0.04 d^{-1} (0.2 g H_2O_2/g TS), 0.206 ± 0.04 d^{-1} (0.4 and 0.6 g H_2O_2/g TS). According to the k_h data, the increase of the performances appeared relatively limited, and potentially not favorable for a cost-saving approach. However, the data from the thermophilic conditions also confirmed the dosage of 0.4 g H_2O_2/g TS as the best option and it was chosen in the following batch AF tests. In addition, since a clear indication from the optimal T was not reached in terms of hydrolysis rate, the following batch AF tests were conducted under a wider T range.

The k_h values obtained here were higher than mesophilic k_h values related to primary or secondary municipal sludge (0.110 – 0.170 d^{-1}), indicating the good biodegradability of tannery sludge also without any pretreatment [20]. Other organic sources not linked to the activities of the water utilities also showed similar k_h values: 0.250 d^{-1}, 0.095 d^{-1}, and 0.121 d^{-1} for kitchen waste, paper, and garden waste, respectively [21]. Generally, all the k_h values were evaluated in perspective of biogas production during the established AD process; to the best authors' knowledge, this is the first work where the quantification of the k_h was performed as additional information for the AF process.

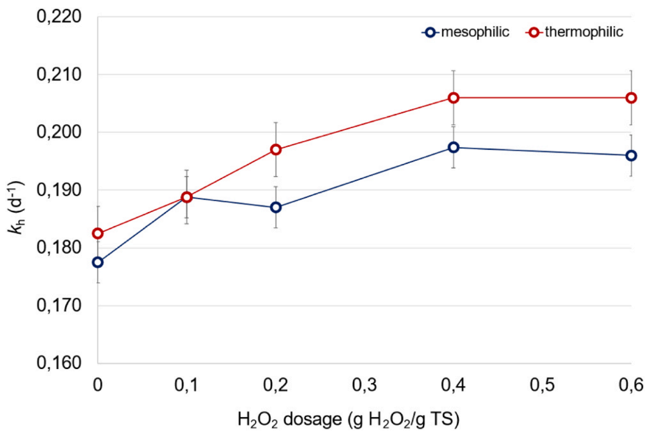

Fig. 1. Hydrolysis rate (k_h) of tannery sludge at different H_2O_2 dosages and temperature.

3.2. Production of SCFAs in the batch tests

The following Fig. 2(a) shows the trend of the total SCFAs concentration over time in batch AF. Independently from the adopted T, the production of the SCFAs started from the first day, without any lag-phase period or inhibition phenomena. At the lowest T (15 °C), the SCFAs trend showed the lowest initial kinetic, according to the SCFAs profile in the first 4 days. A remarkable improvement in the initial kinetics and in the SCFAs concentration was observed at higher T. The series with intermediate T (25 and 30 °C) were characterized by similar performances: the SCFAs concentration heavily increased over the first 4–5 days, with a modest increase occurring after that. The series conducted with higher T (40 and 50 °C) showed a comparable trend, even though the SCFAs concentration reached values above 14.0 g COD_{SCFA}/L. This fact indicated that the chosen H_2O_2 dosage, together with T > 30 °C boosted the acidification of the OM, which would otherwise remain only scarcely hydrolyzed. In fact, since the waste produced by the leather industry (proteins, oils, dyes, hair, lime, tannins, etc.) is commonly conveyed to centralized WWTP [22], the final sludge is quite rich in proteins. This can limit the SCFAs production if the OM is not efficiently hydrolyzed or properly balanced by carbohydrates or starch-based by-products addition [23]. Given the increase of the COD_{SOL}, generally caused by an hydrolysis step, it becomes crucial to measure the effectiveness of the acidification process through a comparison between the SCFAs and COD_{SOL} values [12]. As depicted in Fig. 2(b), both the SCFAs/COD_{SOL} ratio and yield (Y_{SCFA}^{batch}) had the same trend as a function of the T. The low T did not ensure an effective acidification performance since almost 50% of the solubilized COD remained unconverted. The final SCFAs concentration was 9.5 ± 0.3 g COD/L. The conversion yield was also the lowest achieved (0.16

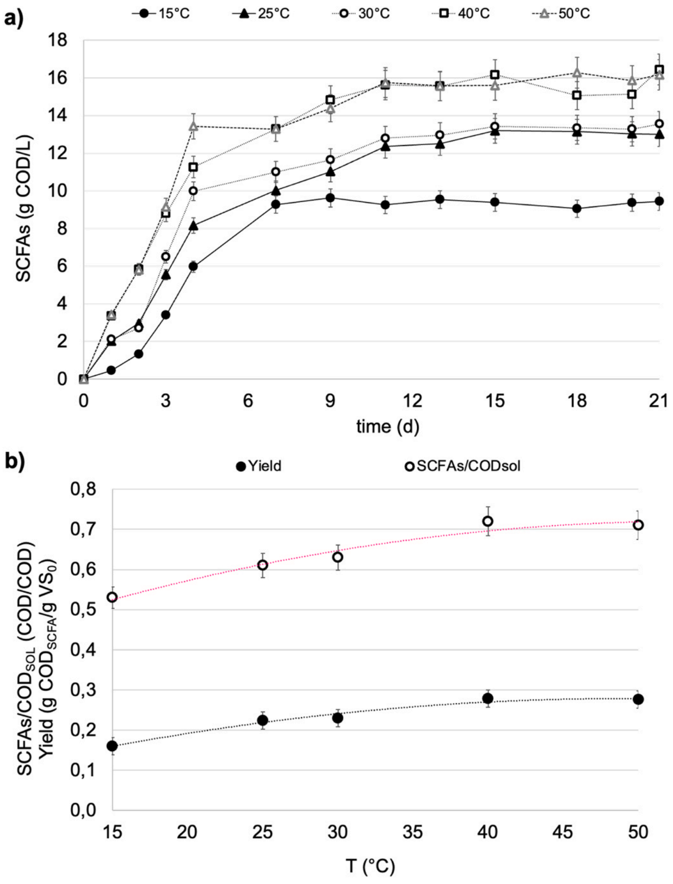

Fig. 2. Evolution of produced SCFAs in the batch acidogenic fermentation tests (a); trend of the Y_{SCFA}^{batch} and SCFA/COD_{SOL} ratio at different H_2O_2 dosages (b).

± 0.01 g COD_{SCFA}/g VS_0). Higher T improved both parameters: the SCFAs/COD_{SOL} ratio was equal to 0.61 ± 0.04, 0.63 ± 0.04, 0.73 ± 0.04, 0.72 ± 0.04 COD/COD at 25, 30, 40 and 50 °C respectively (ANOVA test, Tukey HSD post hoc test, $\alpha = 0.05$); the Y_{SCFA}^{batch} increased up to 0.22 ± 0.02 and 0.23 ± 0.02 g COD_{SCFA}/g VS_0 at 20 and 30 °C, and up to 0.28 ± 0.03 g COD_{SCFA}/g VS_0 at 40 and 50 °C (ANOVA test, Tukey HSD post hoc test, $\alpha = 0.05$). In practice, the series with the highest T were similar in terms of acidification performances; hence, the T value of 40 °C was chosen as the preferred one for the following semi-continuous process in a perspective of a cost and energy-saving approach. Both SCFAs/COD_{SOL} ratio and Y_{SCFA}^{batch} can be considered satisfactory and in line with values obtained in previous studies conducted with raw and thermally pretreated sewage sludge, a comparable substrate produced in water utility sector: 0.44 – 0.82 COD/COD and 0.15 – 0.29 g COD_{SCFA}/g VS_0 for SCFAs/COD_{SOL} ratio and Y_{SCFA}^{batch} respectively [24,25]. In addition, sewage sludge fermentation liquids are generally characterized by lower SCFAs concentration (up to 11 g COD/L [25]) compared to the values obtained in this study (roughly up to 16 g COD/L). This was probably due to the presence of a certain amount of primary treatment derived tannery sludge, more putrescible and fermentable compared to the sludge coming from the biological wastewater treatment.

3.3. Production of SCFAs in the semi-continuous CSTR

Based on the results from the AF batch tests, the two HRTs of 4 and 8 days were selected for the mesophilic semi-continuous fermentation tests. The HRT values were chosen according to the trend of SCFAs concentration observed in the AF batch tests (paragraph 2.5). The two reactors were both characterized by a short acclimation time to reach a steady-state production of SCFAs, namely around 8–9 days in Run 1 (HRT 4 days) and 13 days in Run 2 (HRT 8 days) (Fig. 3a-b). Afterward, the production was maintained stable for the whole duration of the experiment, probably favored by the stability of the pH. The latter was naturally maintained between 6.5 and 7.5, confirming the already observed characteristic of tannery sludge to act as a pH buffer [15]. Once the steady state was reached, the COD_{SOL} were 18.2 ± 0.2 g/L and 21.8 ± 0.5 g/L in Run 1 and Run 2 respectively (*t*-test, $\alpha = 0.05$). The difference between these two values was quite contained and, even if higher HRT allowed for higher OM solubilization, the oxidizing pretreatment already had the most impact on the COD_{SOL} values.

The process conducted at higher HRT (Run 2) was characterized by

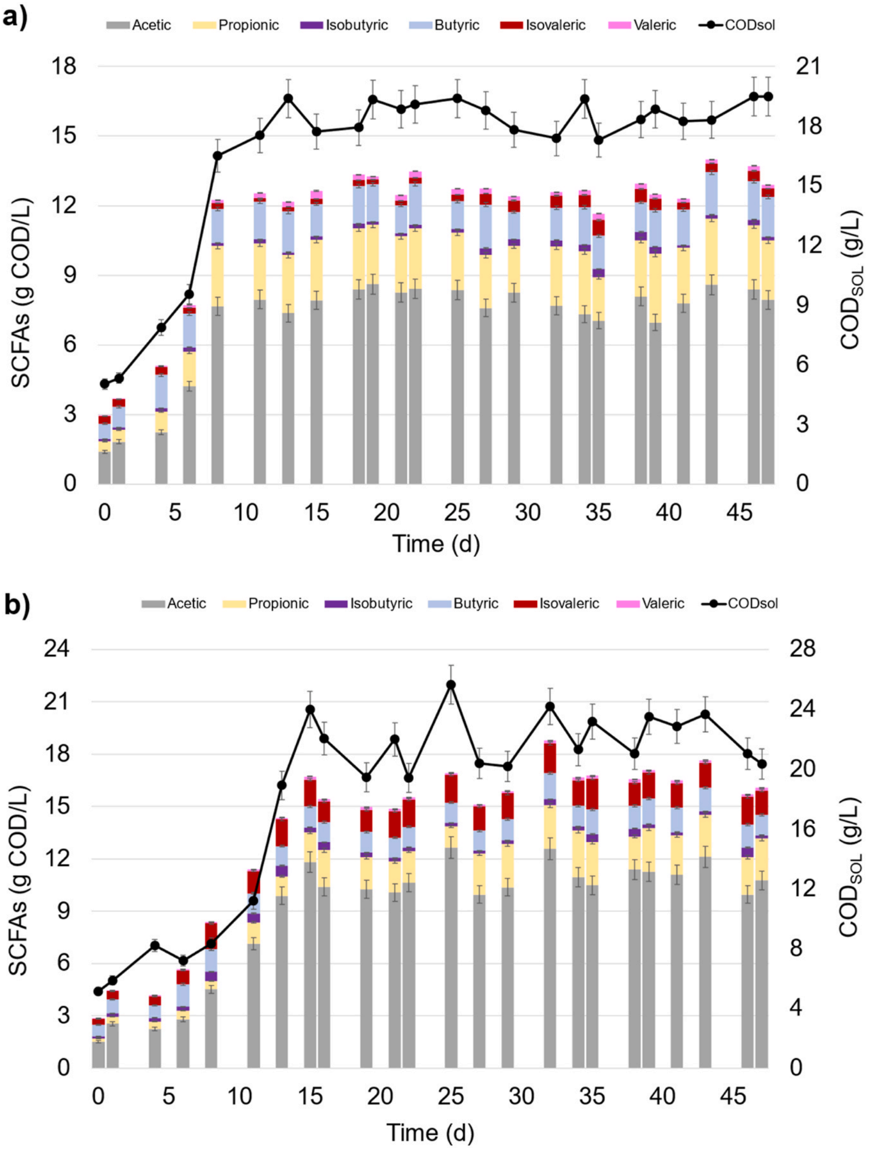

Fig. 3. Trends of the COD_{SOL} and SCFAs concentrations at 4.0 days (a) and 8.0 days (b) as HRT.

higher SCFAs average values (16.0 ± 0.3 g COD_{SCFA}/L) compared to Run 1 (12.8 ± 0.1 g COD_{SCFA}/L) (*t*-test, α = 0.05), but the SCFAs/COD_{SOL} ratio were both satisfying (~0.70 COD/COD), demonstrating the effectiveness of the oxidizing pretreatment to favor the acidification in a semicontinuous process.

Although Run 2 performed better in terms of SCFAs concentration than Run 1, its rate and productivity were lower than values in Run 1. This fact agreed with the culture adaptation at lower HRTs, which typically exert selective pressure on the kinetically faster microorganisms that can survive at high-rate processes [24]. The specific fermentation rate in Run 1 was 63.1 ± 0.6 mg COD_{SCFA}/(g VS d), roughly 50% higher than rate in Run 2 (40 ± 1 mg COD_{SCFA}/(g VS d)); similarly, the SCFAs productivity was 2.58 ± 0.02 and 1.63 ± 0.03 g COD_{SCFA}/(L d) in Run 1 and Run 2 respectively (*t*-test, α = 0.05). On the contrary, the fermentation yield (Y_{SCFA}^{CSTR}) showed the opposite behavior: 0.32 ± 0.01 vs 0.25 ± 0.01 g COD_{SCFA}/g VS_0 in Run 2 and Run 1, respectively (*t*-test, α = 0.05).

Lower HRT favored the selection of microorganisms' consortia with a high rate but a lower efficiency in the conversion of OM, which required a longer time for efficient conversion into SCFAs. Given the importance of the Y_{SCFA}^{CSTR} its implication in the mass-balance assessment and in the overall economy of the approach, higher HRT has to be considered in the value chain in order to minimize the amount of unconverted OM. On the other hand, high HRT means high reactor's volume, which in turn affects the energy balance (discussed below). The literature furnished very limited information about the exploitation of tannery sludge as SCFAs source. A forerunner article evaluated the combined microwave-H_2O_2 pretreatment on SCFAs production only in batch tests [15]. The authors reported a maximum SCFAs concentration of 26 g COD_{SCFA}/L but the long time required was unsustainable for the technology implementation in a continuous mode. Compared to sewage sludge (also produced within WWTPs), tannery sludge appeared a more profitable source in terms of SCFAs production, being partially derived from primary treatments and, in turn, consisting of a more fermentable OM [26]. A largely adopted practice consisting of the thermal hydrolysis gave lower performances in terms of SCFAs production and OM conversion compared to the tannery sludge: Castro et al. [27] obtained 8.0 ± 0.9 g COD_{SCFA}/L from acidified thermally pretreated sewage sludge, with a yield of 0.26 g COD_{SCFA}/g VS_0; Zhang et al. [28] obtained 7.57 and 9.63 g COD_{SCFA}/L in the acidification process of raw and thermally pretreated sewage sludge respectively, with a conversion yield in the range 0.15–0.22 g COD_{SCFA}/g VS_0 in mesophilic conditions. Two recent works reported a range of SCFAs concentration and Y_{SCFA}^{CSTR} in the range 7.3–8.4 g COD_{SCFA}/L and 0.30–0.38 g COD_{SCFA}/g VS_0 respectively, after thermophilic AF of thermally treated sewage sludge [24,25]. Due to the utilization of raw sewage sludge (no pretreatment), Presti et al. [29] obtained a low SCFAs concentration (< 3.0 g COD_{SCFA}/L) and a yield of 0.38 g COD_{SCFA}/g VSS_0 (volatile suspended solids). This yield was exclusively calculated on the VSS, and it was certainly lower than fermentation yields obtained with pretreated municipal and tannery sludge.

3.3.1. SCFAs composition

The composition of the SCFAs in the effluent remained relatively constant once it reached the steady phase and it was comparable for both HRTs. A remarkable dominance of acetic acid was obtained, probably favored by the utilization of a pretreated sludge, accounting for approximately 62.1 ± 0.6% and 67 ± 1% (COD basis) of the total SCFAs in Run 1 and Run 2 respectively. Propionic acid was next, accounting for 19.7 ± 0.4% (Run 1) and 13.2 ± 0.6% (Run 2); butyric acid was less than 10% in both runs. The other acids were present in lower amounts. The low amount of butyric acid was not surprising as protein-rich substrates like tannery sludge, usually produce less of this acid compared with carbohydrate-rich substrates [30]. Given that acetic and propionic acids covered 80% of the total COD_{SCFA} (roughly), the SCFAs spectrum was not heavily fragmented, facilitating the downstream processes necessary to concentrate and/or separate the SCFAs in the fermentation broth [31]. The downstream steps are necessary to improve the marketability of the SCFAs, at least for applications that require purified products such as pharmaceuticals' manufacturing, plasticizers, production of esters or conversion into fine chemicals [32]. Even though many options have been reviewed (among others extraction and distillation, adsorption, membrane-based technologies), this aspect still needs more investigation and efforts to improve the cost-effectiveness of the technologies.

3.4. Fate of the chromium in the semi-continuous process

The presence of Cr was evaluated in the liquid fraction of the oxidized tannery sludge, which was then utilized as carbon source for the two sCSTR. The Cr was partially released after the oxidative pretreatment, having a concentration of 119 ± 11 mg/L (total Cr); no Cr (VI) was observed, indicating that the H_2O_2 dosage was not sufficient to oxidize the released Cr or the Cr initially associated to the sludge. Apart from the stringent regulation on potable waters and the related Cr limit (0.05 mg/L for total Cr; EU Directive 2020/2184), this value (119 mg/L) is rather higher than the maximum discharge limit to the aquatic environment in Europe, which is equal to 5 mg/L for total Cr [33].

The trend of the Cr is depicted in Fig. 4, for both investigated HRTs. The peak of the maximum Cr concentration was found at different times (4 and 8 days), according to the adopted HRT. However, after the period of one HRT was covered, the Cr concentration started to progressively decrease until its disappearance in the liquid effluent. This occurred approximately after 20 and 40 days of operation in Run 1 and Run 2 respectively (roughly 5 HRTs in both runs). The literature reported that OM (both colloidal and soluble) can play a significant role in the distribution of Cr, especially in its most common state of Cr(III) [34]. The leather industry is one of the most important contributors of OM-Cr(III) complexes, usually utilized to obtain the required color, strength or softness of the leather. The OM-Cr(III) structures are usually characterized by high complexation affinity and stability over a wide pH range [35]. On the other hand, these complexes can be not completely fixed, entering the wastewater, and remaining in the final sludge. Given the presence of Cr in the liquid phase of H_2O_2-treated tannery sludge, the maximum Cr concentration should have been equal to that of oxidized sludge (119 mg/L) in both reactors if no removal phenomena had occurred. The observed decrease in Cr concentration can be explained hypothesizing a two-steps mechanism: (i) the anaerobic consortium was responsible for the OM degradation (and its conversion into SCFAs) and the destruction of the OM-Cr(III) complexes; (ii) the free Cr was presumably removed via precipitation as $Cr(OH)_3$, due to the neutral pH of the fermentation broth and the lime presence (source of OH^-) in the tannery sludge. In support of this interpretation, the Pourbaix diagram shows how Cr is present in the form of hydroxides for pH greater than 3.5 and, in addition, negative redox potential (typical for anaerobic processes) causes the formation of $Cr(OH)_3$ as the most frequent precipitate under neutral pH [36]. Independently from the fermentation rate of the two consortia, a complete Cr removal was obtained approximately in 5 HRTs. Before this time, a post-treatment on the fermentation broth could be eventually necessary to remove the Cr and to utilize the SCFA-rich stream for the targeted applications. The Cr removal from industrial wastewater is mainly based on chemical, physic, or combined approach such as chemical precipitation, adsorption, Fenton and Fenton-like oxidation, advanced oxidation processes, and electrocoagulation with post-oxidation [37].

These results were useful for supporting two important outcomes: a) the utilization of tannery sludge fermentation liquid did not any have environmental-safety issues related to the Cr initially present in the sludge (at least under the tested conditions); b) the produced SCFAs did not act as organic ligands (in the form of OM-Cr(III)) and they did not contribute to the Cr presence in the liquid phase. Hence, even though SCFAs can have an important role in governing the Cr mobility in the environment, showing a certain potential for complexation with Cr [38],

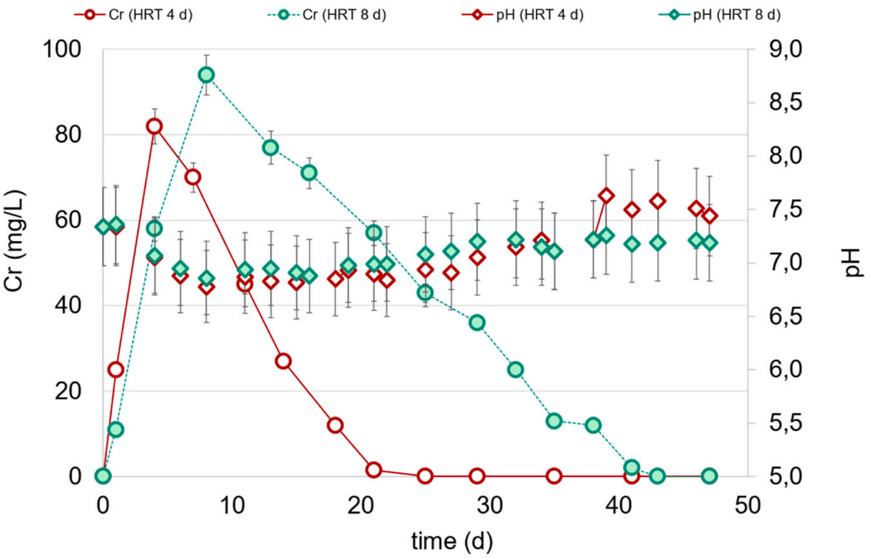

Fig. 4. Trends of the Cr and pH in the two semi-continuous reactors at different HRT.

the investigated working conditions allowed to valorize the tannery sludge without concerns about the Cr speciation and fate.

3.5. BMP tests of the solid-rich pre-fermented tannery sludge

The BMP tests were implemented to assess the potential biogas production from the solid-rich pre-fermented fraction. The importance of this step is related to the possibility of further reducing the sludge's mass and to recover energy from the residue part coming from the AF step. In vision of a full-scale process, the energy generation should be at least sufficient to sustain the thermal energy requirement of AF and AD steps, both conducted at controlled T. The cumulative biogas production and the modeled Specific Gas Production (SGP) of each mesophilic BMP test are reported in Fig. 5a-b. The volumetric biogas production was 0.21 ± 0.01, 0.36 ± 0.02, and 0.40 ± 0.02 mL after 30 days in the tests conducted with 0.0, 0.2, and 0.4 g H_2O_2/g TS as dosage, respectively. The data showed again a positive effect of the oxidizing treatment and a progressive increase in the performance with the increasing H_2O_2 dosage. The best performance was obtained at the highest H_2O_2 dosage, which gave a maximum SGP of 0.52 m^3/kg VS (in 30 days). To the best authors' knowledge, the literature does not furnish data about the biogas production potential of treated or untreated tannery sludge (given its landfilling as the only disposal practice) and the H_2O_2 utilization has never been discussed as a potential pretreatment agent to improve sludge biodegradability and biogas production. A recent study described how biogas production can be increased when waste from the leather industry (shavings and sludge) is mixed with other sources (agricultural waste) due to the improved nutrient balance [39]. Leather shavings were also subjected to mesophilic anaerobic digestion with tannery sludge [40], showing a remarkable benefit in biogas production when tanning agents were present (chromium among others).

The modeled SGP provided some noteworthy information. With 20 days as HRT, the untreated solid-rich fraction was characterized by an SGP of 0.25 m^3/kg VS. Considering the same HRT, the dosage of 0.2 and 0.4 g H_2O_2/g TS increased the SGP up to 0.43 and 0.48 m^3/kg VS respectively, doubling the biogas production compared to the solid-rich fraction utilized without the post hydrolysis. The obtained SGP corresponded to 80% (roughly) of the maximum biogas achievable; if HRT > 20 d had been chosen, this percentage would be increased due to the prolonged biodegradation of the OM, concomitant with alkalinity and biogas production [41]. On the other hand, higher HRTs brings to the increase of reactor's volume and associated costs. The choice of the HRT is a matter of compromise between the biogas potentially obtainable and the volumetric limitation to be established through a detailed mass-energy balance. The CH_4 content was approximately similar in all the text (independently from the H_2O_2 dosage), being in the range 51–56% v/v in the whole length of the BMP tests. These results are in line with the available literature SGP values and CH_4 content of tannery sludge (up to 0.20 m^3/kg VS and 50–60% v/v respectively), which was not subjected to any pretreatment step [42]. Not pretreated secondary

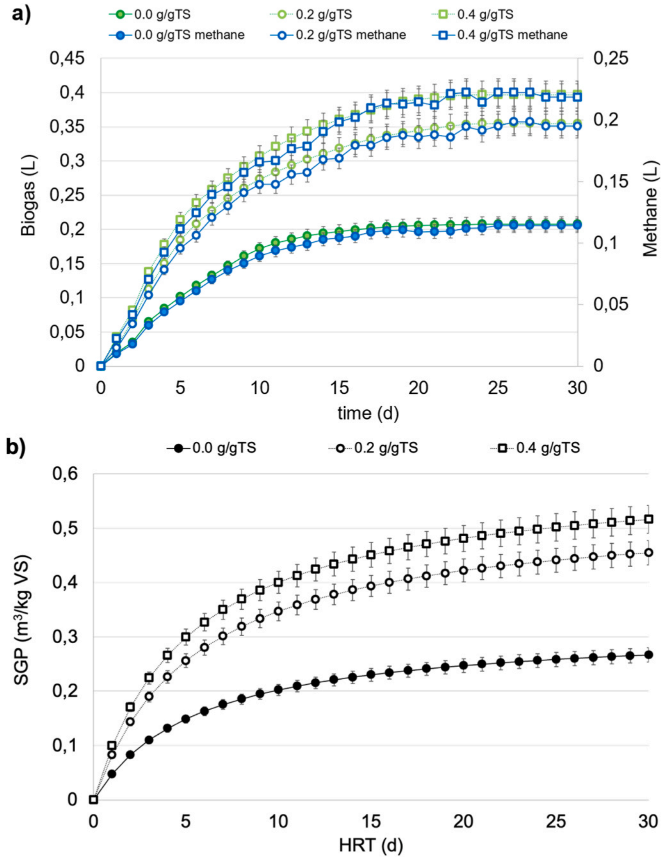

Fig. 5. Evolution of produced biogas (a) and theoretical SGP values (b) modeled in the three experiments at different H_2O_2 dosages under mesophilic conditions.

tannery sludge (with lower biodegradability compared to primary sludge) exhibited a biogas production in the range 0.11–0.22 m^3/kg VS (~55% CH_4 v/v) [43]. Compared to sludge utilization, mixture of tannery and slaughterhouse wastewater produced more biogas (0.23–0.36 m^3/kg VS as SGP) but with considerably lower CH_4 level (20–45% v/v) [7].

3.6. Mass-energy balance and economic consideration

The mass-energy balance was performed starting from a production of 37,000 ton/y of tannery sludge; according to its features reported in paragraph 2.2, the TS and VS flow rates are 99,065 kg TS/d and 70,419 kg VS/d (currently disposed of in landfills). In the proposed approach (Fig. 6), this sludge is firstly subjected to a pre-hydrolysis step where water tap water (1,308,089 kg/d) and H_2O_2 (39,625 kg/d; at 0.4 g H_2O_2/kg TS) are added, while also being heated to 37 °C, which is the T maintained for the subsequent AF process.

After the oxidizing pretreatment, the sludge flow rate is 1,467,070 kg/d (roughly at 7% w/v of solids' content), entering a CSTR with a volume of 11,737 m^3 (HRT 8 d). In this stage, the VS flow rate is reduced to 58,236 kg VS/d, due to a small aliquot of generated gas (SGP 0.1 m^3/kg VS [44]). The resulting SCFAs-rich effluent (8.00 ton SCFAs/d, due to the P_{SCFA}^{CSTR} of 1.63 g COD_{SCFA}/(L d); Run 2, Table 1) is then treated through a solid/liquid separation unit, obtaining two streams: the liquid fraction (1,142,392 L/d; employed to extract the SCFAs), and the solid-rich residue (roughly at 25% w/v of TS content). The latter has to be diluted and treated (post-hydrolysis at 0.4 g H_2O_2/kg TS dosage) before entering the AD step. The flow rate of this residue is 324,678 kg/d, which becomes 1,088,150 L/d after dilution (~7% w/v TS content). The volume and the operating conditions of the CSTR anaerobic digester are established according to the BMP results (SGP 0.48 m^3/kg VS; Volume 21,763 m^3, HRT 20 days, 37 °C). The consequent amount of produced biogas is 26,115 m^3/d, corresponding to a VS content of 29,368 kg/d (based on the average composition of 55%−45% v/v of CH_4-CO_2 respectively). The residual digestate was also subjected to another liquid/solid separation before being dried up to a TS content of 83% w/v (approximately similar to the initial value). Overall, the final amount of dried sludge to be disposed of in the landfill is 56,996 kg/d, corresponding to less than 50% of the tannery sludge in input.

In the energy balance, the option of employing the biogas in a boiler was chosen as the final drying step (290,906 MJ/d); the utilization of a combined heat and power unit (CHP) to valorize the AD-derived biogas does not allow to obtain a positive thermal balance. Since the boiler has an efficiency of 90%, the production of 540,875 MJ/d of thermal energy has been estimated. The required thermal energy for the whole process is around 498,694 MJ/d, according to the chosen mesophilic conditions for the AF and AD (energy and cost-saving approach), and the final drying unit. Hence, the thermal balance was characterized by a net energy production of 42,181 MJ/d, completely covering the needs of the process without additional costs. It is noteworthy that almost 60% of the required thermal energy is necessary for the final drying step.

In terms of the economic feasibility of the whole value chain, the current disposal cost (37,000 tons/y in landfilling) sustained by the tannery industries is around 9,250,000 €/y. With the implementation of this flowchart, the main costs would be represented by the utilization of the H_2O_2 (6,704,702 €/y), tap water (347,666 €/y), and electricity (67,117 €/y), while the disposal costs would drop to 4,417,162 €/y. The profit instead would derive from the sale of the SCFAs which would be around 4,957,982 €/y, in other words an economic saving of 2,671,335 €/y compared to the current scenario. Table 2 summarizes all the energy and economic-related items discussed above. In addition to the economic factors, this process has different environmental benefits in terms of greenhouse gases (GHG) emissions. In particular, fossil fuel energy is totally excluded since CH_4 is produced from the sludge itself and there is no additional CO_2 production from external C-source; also, unintentionally CH_4 release (from old landfills) is surely reduced due to the obtained sludge reduction.

4. Conclusions

A first-of-kind approach for the tannery sludge valorization and related outcomes has been proposed in this study. Tannery sludge was effectively utilized as a renewable carbon source to produce SCFAs as added-value products along with biogas. Hydrolysis and AF batch tests highlighted the optimal dosage of H_2O_2 (0.4 g H_2O_2/g TS) for pretreatment and T (40 °C) for acidification. The following mesophilic experiments conducted in the sCSTR at an HRT of 8 days allowed to obtain a SCFA-rich stream at a content of 16.0 g COD_{SCFA}/L, dominated by acetic acid (67% COD basin), and corresponding to an acidification yield of 0.32 g COD_{SCFA}/g VS_0. Environmental or toxicity issues concerning the Cr presence in the fermentation broth were not significant, since Cr was not transferred from the sludge to the liquid matrix, despite its partial release in the oxidizing pretreatment.

Given the quantified biogas production (0.48 m^3/kg VS) from the solid-rich residue, separated after the AF step, the proposed multi-steps process has the potential to strongly reduce the tannery sludge of more than 50% without the need of external fossil fuel sources for the energy requirements. As a consequence, the landfilling, currently the only disposal practice, can be significantly downsized with a yearly economic saving higher than 2,600,000 € for the tannery industries and associated water utilities, compared to the existing state.

Even though a new direction for tannery sludge management has been indicated in this study, a margin of improvement is still possible, especially on the hydrolysis step (needed amount of the oxidizing agent and associated cost), and on the acidification yield (roughly 30% of the VS has been converted into SCFAs). Different pretreatment (including thermal) or even H_2O_2-combined ones addressed to increase the VS

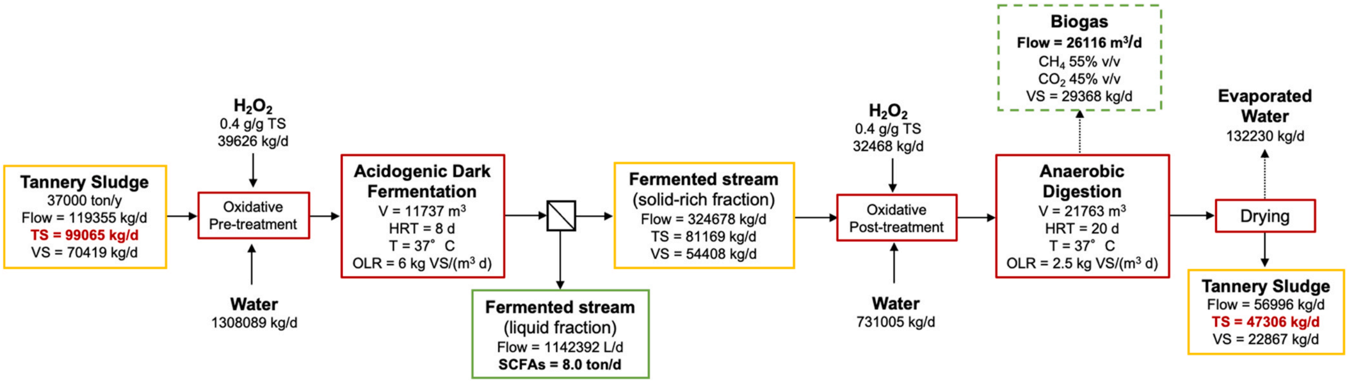

Fig. 6. Mass balance of the whole value chain in perspective of tannery sludge utilization.

Table 1
Summary of the effluent's characteristics and reactors' performances under batch and semi-continuous acidogenic fermentation conditions.

Parameter	Unit	Batch *(0.4 g H_2O_2/g TS)*					sCSTR *(0.4 g H_2O_2/g TS; 40 °C)*	
		T (°C)					HRT (days)	
		15	25	30	40	50	4.0	8.0
COD_{SOL}	g/L	17.9 ± 0.2	20.6 ± 0.3	20.4 ± 0.7	22.3 ± 0.5	22.7 ± 0.1	18.2 ± 0.2	21.8 ± 0.5
COD_{SCFA}	g/L	9.5 ± 0.3	13.2 ± 0.4	13.5 ± 0.5	16.4 ± 0.7	16.3 ± 0.3	12.7 ± 0.1	16.0 ± 0.3
COD_{SCFA}/COD_{SOL}	g/g	0.53 ± 0.03	0.61 ± 0.04	0.63 ± 0.04	0.73 ± 0.04	0.72 ± 0.04	0.69 ± 0.01	0.73 ± 0.01
Acetic acid	g COD/L	4.2 ± 0.1	5.8 ± 0.6	6.1 ± 0.5	7.8 ± 0.3	7.7 ± 0.3	7.93 ± 0.11	10.66 ± 0.21
Propionic acid	g COD/L	1.6 ± 0.3	2.2 ± 0.3	2.1 ± 0.4	2.7 ± 0.2	3.2 ± 0.2	2.51 ± 0.06	2.11 ± 0.09
Butyric acid	g COD/L	1.9 ± 0.5	2.8 ± 0.3	2.9 ± 0.1	3.0 ± 0.3	2.7 ± 0.3	1.54 ± 0.05	1.25 ± 0.03
Valeric acid	g COD/L	1.0 ± 0.3	1.6 ± 0.6	1.6 ± 0.2	1.8 ± 0.4	1.7 ± 0.4	0.21 ± 0.01	0.15 ± 0.01
Isovaleric acid	g COD/L	0.9 ± 0.3	0.8 ± 0.2	0.7 ± 0.3	1.1 ± 0.2	1.0 ± 0.2	0.36 ± 0.03	1.47 ± 0.03
Y_{SCFA}^{batch}	g COD_{SCFA}/(g VS_0)	0.16 ± 0.01	0.22 ± 0.02	0.23 ± 0.02	0.28 ± 0.03	0.28 ± 0.03	-	-
q_{SCFA}^{CSTR}	mg COD_{SCFA}/(g VS d)	-	-	-	-	-	63.1 ± 0.6	40 ± 1
Y_{SCFA}^{CSTR}	g COD_{SCFA}/(g VS_0)	-	-	-	-	-	0.25 ± 0.01	0.32 ± 0.01
P_{SCFA}^{CSTR}	g COD_{SCFA}/(L d)	-	-	-	-	-	2.58 ± 0.02	1.63 ± 0.03
$N\text{-}NH_4^+$ release	mgN-NH_4^+/g TKN	-	-	-	-	-	42 ± 1%	53 ± 2%

Table 2
Energy and economy-related items in the new scenario of tannery sludge valorization.

Parameter		**Unit**	**New scenario**	**Current scenario**
Tannery sludge production		ton/y	37,000	37,000
SCFAs production		ton/y	2,879	-
CH_4 production*		m^3/y	5,170,890	-
Required Energy	Acidogenic Fermentation	MJ/d	119,449	-
	Anaerobic Digestion	MJ/d	88,340	-
	Drying	MJ/d	290,906	-
Produced Energy		MJ/d	540,875	-
Cost* *	Disposal	€/y	4,417,162	9,250,000
	Tap Water	€/y	347,666	-
	H_2O_2	€/y	6,704,702	-
	Electrical Energy	€/y	67,117	-
Revenue		€/y	4,957,982	-

*from SGP 0.48 m3/(kg VS) and CH4 content of 55% v/v.
* *The electrical energy is related to the SCFAs extraction and recovery; the disposal is related to the tannery sludge.

solubilization and to decrease the H_2O_2 dosage should be deeply investigated along with other reactor's configuration, such as decoupling HRT and SRT to increase the SCFAs yield and productivity.

CRediT authorship contribution statement

Giulia Adele Tuci: Investigation, Formal analysis, Writing – original draft, Writing – review & editing. **Francesco Valentino**: Funding acquisition, Project administration, Supervision. **Aditi Chitharanjan Parmar**: Formal analysis, Visualization. **Paolo Pavan**: Visualization, Funding acquisition. **Marco Gottardo**: Conceptualization, Methodology, Investigation, Formal analysis, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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