Tannery sludge valorization through biological processes: preliminary evaluation of biogas and short-chain fatty acids (SCFAs) production

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Italy is one of the leading countries in the tannery industry, with a value of production of 3.5 billion euros in 2020 (UNIC, 2020). In addition, according to the Italian tannery industry sustainability report of 2020, Italian tanneries generate an average of 1.65 kg of wastes per square meter of leather produced, with the 20.8% of it being sludge. The obtained sludge contains high amounts of organics and inorganics such as toxic metal salts, employed in the tanning process (Mpofu et al., 2021), and is consequently classified as a special non-hazardous residue, according to Italian legislation and its current destination is to a second-class type B controlled landfill (D.Lgs. 04/06). As a result, the environmental impact of this industry is non-negligible, and the costs sustained by the tannery industries to dispose of the generated waste are very high, creating the need to find more sustainable and less costly alternatives. However, at the moment this substrate has not been thoroughly investigated yet, so its potential remains untapped.

Anaerobic digestion is a very promising technology that allows the recovery of bio-products such as short-chain fatty acids (SCFAs) and biogas from waste, while significantly reducing the mass of the waste, thus decreasing the disposal costs and the environmental impact. Consequently, tannery waste is a great candidate for this process due to its high organic load and high costs for its disposal. The purpose of this work is to provide a viable alternative to the wasteful disposal of tannery sludge in landfills and use it instead to produce added-value products, namely biogas and SCFAs.

As first screening, lab-scale batch tests (180 mL; pH 7; T 38°C) were performed to find the best option in terms of biogas production. The tannery sludge samples were pretreated with 4 different amounts of H\textsubscript{2}O\textsubscript{2}, namely 0.1, 0.2, 0.4, and 0.6 g H\textsubscript{2}O\textsubscript{2}/g TS, based on previous work on different substrates (Tyagi et al., 2011). Hydrogen peroxide pretreatment was proven to be one of the most promising methods to increase the speed of the hydrolysis stage to oxidize the organic compounds and increase their availability to the microorganisms. H\textsubscript{2}O\textsubscript{2} has also the potential of reducing the S species in the sludge, which can negatively impact the methanogenesis, freeing the elemental S that could also be eventually recovered. This pretreatment has been previously employed with good results due to its promising characteristics, namely its effectiveness, low costs, easy availability and conduction, and harmless by-products (Achouri et al., 2021; Ambrose et al., 2020).

Figure 1 shows the specific gas production for the BMP trials for tests TQ, 0.1, 0.2, 0.4, and 0.6: their cumulative biogas productions are 129.7, 185, 189.7, 195.7, and 204 mL respectively.

The batch test trials revealed that the hydrogen peroxide pretreatment proved to be effective both in increasing the biogas production and the velocity of the process, especially with the higher doses of 0.4 and 0.6 g H\textsubscript{2}O\textsubscript{2}/gTS, reaching a biogas production of 195.7 and 204 mL, and an SGP of 0.24 and 0.25 m\textsuperscript{3}/kgVS, respectively, with an HRT of 19 days.

The obtained results prove that these resources can be employed to produce biogas and provide a viable alternative to landfilling.

Figure 1: specific gas production of the 5 batch tests
After this first assessment, a comprehensive acidogenic fermentation batch tests assay has been developed, where the effect of temperature (38-55°C), pH (5-7-9-11), microwave and H₂O₂ pretreatment and total solids (TS; 8-12%) concentration has been investigated on SCFAs production (rate, yield and concentration) and distribution. The batch test trials revealed that the combined microwave and hydrogen peroxide (MW- H₂O₂) pretreatment followed by thermophilic conditions gave the best results, in terms of the acidification yield (0.31 gCOD_{SCFA}/gVS₀) and maximal SCFA concentration (above 26 g COD_{SCFA}/L). In the tests conducted without pretreatment, the mesophilic temperature seems to be preferable since the acidification performances were comparable to or even better than their thermophilic counterparts. The SCFA composition analysis showed that in mesophilic fermentation, tannery sludge can generate up to 50% acetic acid (COD_{Ac}/COD_{SCFA}), if previously pretreated (MW- H₂O₂).

Figure 2: SCFAs concentration in the different tests.

Overall, these results show the feasibility of employing tannery sludge for anaerobic digestion to obtain both biogas and SCFAs, opening the road for further research to optimize the process to eventually move towards larger scale applications. This research acts as a forerunner for the appropriate handling of this resource, to employ it for the development of a new tannery industry focused on a circular approach, rather than to simply dispose of it in landfills.

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References