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

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Italy’s tannery industry accounts for 23% of the global value of leather.

From raw hide to the finished leather, 1.46 kg of waste (of which 18% is sludge) is created for each m² of finished product.
Urban area

Tannery Industry effluents

Physical-Chemical pre-treatment

Primary Settling

Biological C-N removal

Secondary Settling

Solid-Liquid Separation

Tannery Sludge

Removal of solids, sulphides, chromium,… to improve biological treatment

civil wastewaters (10% v/v)

treated water

WWTP of Montebello Vicentino (northeast Italy)
wastewater from 23 tannery plants (∼10000 m³/d) are treated
Tannery sludge from Montebello Vicentino WWTP

Sludge is classified as a special non-hazardous residue, disposed of in second-class type B controlled landfill (D.Lgs. 04/06).

37,000 ton/y tannery sludge

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Average</th>
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</thead>
<tbody>
<tr>
<td>Total Solid (TS, g/kg)</td>
<td>830 ± 14</td>
</tr>
<tr>
<td>Volatile Solid (VS, g/kg)</td>
<td>590 ± 4</td>
</tr>
<tr>
<td>COD (g COD/kg TS)</td>
<td>793 ± 18</td>
</tr>
<tr>
<td>Total Kjeldahl Nitrogen (TKN; g N/kg TS)</td>
<td>32.8 ± 0.9</td>
</tr>
<tr>
<td>Total Phosphorus (P; g P/kg TS)</td>
<td>7.9 ± 0.4</td>
</tr>
</tbody>
</table>

Total Cr = 19.000 – 22.000 mg/kg
Aim of the Research

Landfilling means
☞ wasting all the high-quality organic material that characterizes this waste
☞ high economic impact for the industries
☞ significant environmental impacts

Mostly unexplored material
Circular economy perspectives
Work flow

1. Mild-hydrolysis tests (pre-treatment) ➡ Evaluate the sludge biodegradability and selection of most appropriate $\text{H}_2\text{O}_2$ dosage

2. Acidogenic fermentation in batch ➡ Selection of most appropriate temperature (T) and hydraulic retention time (HRT)

3. Semi-continuous acidification tests (CSTR)

4. Biomethanation potential tests (BMP) in batch (post-treatment) ➡ Recovery of methane from solid-rich acidified residue
(1) **H₂O₂ Pretreatment (mild-hydrolysis)**

- Oxidizes organics through OH⁻ free radicals
- Oxidizing the sulphide (S) species in the sludge
- H₂O₂ dosages: 0.1, 0.2, 0.4, 0.6 g H₂O₂/g TS.

\[
\frac{dS}{dt} = -k_h S \\
\ln \frac{B_\infty - B}{B_\infty} = -k_h t
\]

0.4 g H₂O₂/g TS chosen dosage
2 h reaction time
Acidogenic Fermentation….

Parameters of batch acidification tests

- Temperatures: 15, 25, 30, 40 and 50 °C
- Pre-treatment dosage (2 h): 0.4 g H₂O₂/g TS
.... to short chain fatty acids production

40°C chosen T $\rightarrow$ HRT of 4.0 and 8.0 d

The chosen $\text{H}_2\text{O}_2$ dosage together with $T$ above 30 °C facilitate the anaerobic fermentation of the organics
(3) Semi-continuous process sCSTR

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Run 1</th>
<th>Run 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>HRT (d)</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>OLR (g VS/L d)</td>
<td>17.5</td>
<td>8.4</td>
</tr>
<tr>
<td>H$_2$O$_2$ dosage (g/g TS)</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>40</td>
<td>40</td>
</tr>
</tbody>
</table>

**Monitored parameters**
- SCFAs concentration (g COD/L)
- SCFAs/COD$_{\text{SOL}}$ ratio (COD/COD)
- $Y_{\text{SCFAs}}$ (g COD$_{\text{SCFA}}$/g VS)
- pH
- Total Cr (mg/L)

The semi-continuous processes were performed to define the required data for the final mass-balance assessment.
Run 1 (HRT 4.0 d)

COD$_{SOL}$: $18.2 \pm 0.2$ g/L
SCFAs: $12.8 \pm 0.1$ g COD$_{SCFA}$/L
$Y_{SCFA}$: $0.25 \pm 0.01$ g COD$_{SCFA}$/g VS

Acetic acid 62 % (COD basis);
Propionic acid 19.7 %

Run 2 (HRT 8.0 d)

COD$_{SOL}$: $21.8 \pm 0.5$ g/L
SCFAs: $16.0 \pm 0.3$ g COD$_{SCFA}$/L
$Y_{SCFA}$: $0.32 \pm 0.01$ g COD$_{SCFA}$/g VS

Acetic acid 67 % (COD basis);
Propionic acid 13.2 %
··· fate of the chromium···

☞ Cr was partially released after the oxidative pre-treatment (119 ± 11 mg Cr/L)

☞ Consequences:

✓ the utilization of tannery sludge fermentation liquid did not any have environmental-safety issues related to the chromium;

✓ SCFAs did not act as organic ligands, no Cr presence in the liquid phase

Hao et al., 2022. Ecotoxic. Env. Safety
(4) Biochemical Methane Potential (BMP)

Biochemical Methane Potential (BMP)

0.4 g H₂O₂/g TS post-treatment

SGP: 0.48 m³ biogas/kg VS (at HRT 20 days)
Conclusions

- Tannery sludge can be employed to produce **SCFAs** and **biogas**
- **Pre-** and **post-treating** the sludge with **0.4 g H₂O₂/g TS** improves the overall efficiency and production **SCFAs** \( Y_{SCFA} \) **0.32 COD_{SCFA}/g VS** and **biogas** \( SGP = 0.48 \text{ m}^3/\text{kg VS} \)

Preliminary bass-energy balance revealed a potential 50% of tannery sludge **reduction** with a revenue >4,000,000 €/y from SCFAs production
Acknowledgements

A special thanks to Medio Chiampo S.p.a. for providing the raw material for this research.

Financial support of the European Union - Next Generation EU: PON “Ricerca e Innovazione” and Project ECS000043 - Innovation Ecosystem Program “Interconnected Northeast Innovation Ecosystem” (iNEST) CUP H43C22000540006.

Thank you!

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