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

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Tannery industry

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 m^2 of finished product

Tannery Industry effluents

Urban area

civil wastewaters (10% v/v)

Physical-Chemical pre-treatment

Primary Settling

Biological C-N removal

Secondary Settling

treated water

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

Solid-Liquid Separation

Tannery Sludge

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

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

Total Cr = 19.000 – 22.000 mg/kg

Aim of the Research

Landfilling means

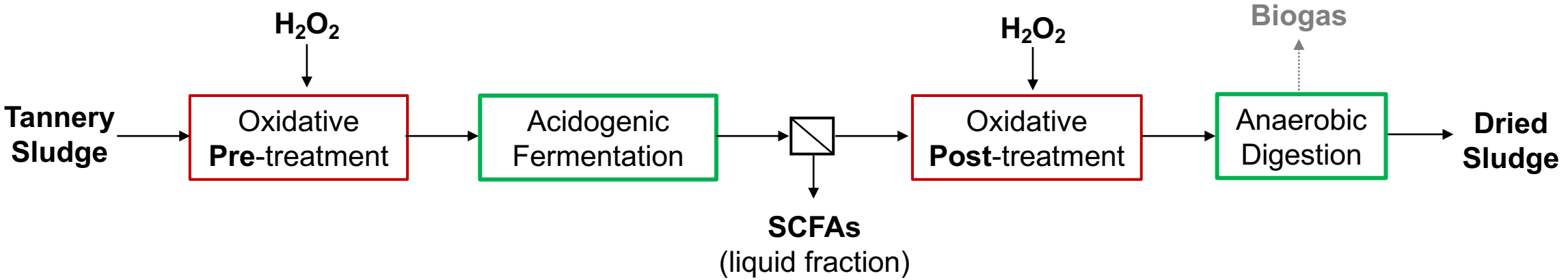
☞ wasting all the high-quality organic material that characterizes this waste

☞ high economic impact for the industries

☞ significant environmental impacts

Mostly unexplored material

Circular economy perspectives



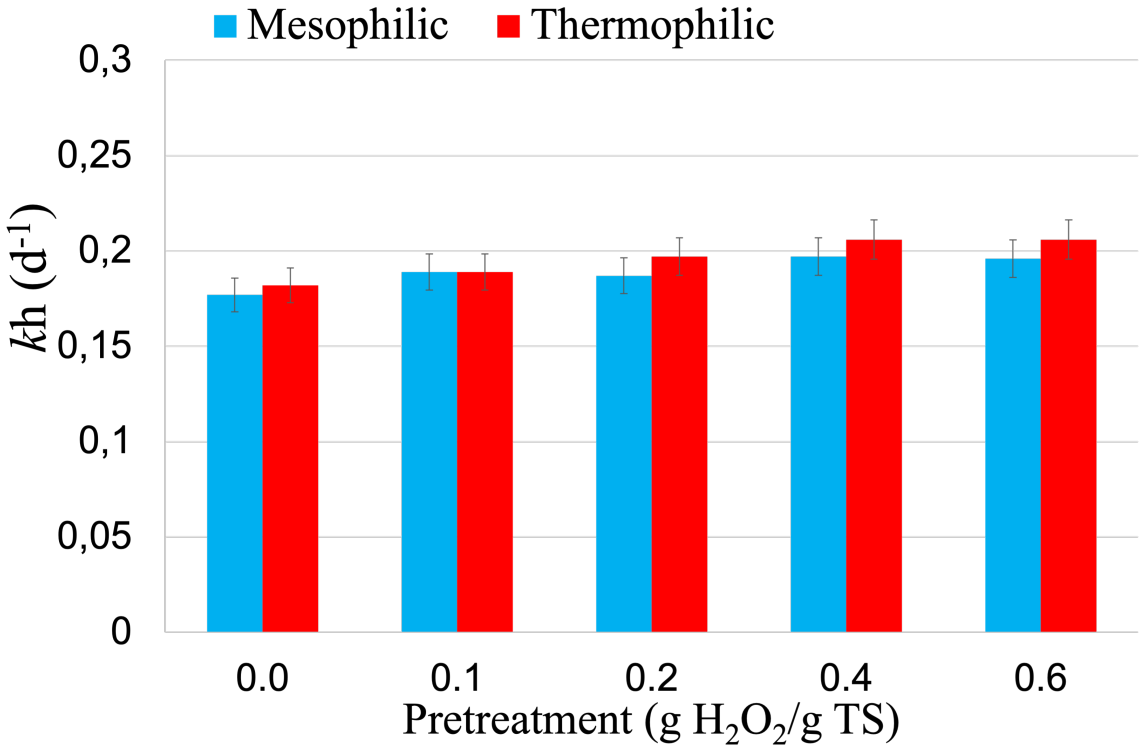
Work flow

1. Mild-hydrolysis tests (pre-treatment) → Evaluate the sludge biodegradability and selection of most appropriate H_2O_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) H_2O_2 Pretreatment (mild-hydrolysis)

- oxidizes organics through OH• free radicals
- oxidizing the sulphide (S) species in the sludge
- H_2O_2 dosages: 0.1, 0.2, 0.4, 0.6 g H_2O_2/g TS.

$$\frac{dS}{dt} = -k_h S \qquad \ln \frac{B_\infty - B}{B_\infty} = -k_h t$$



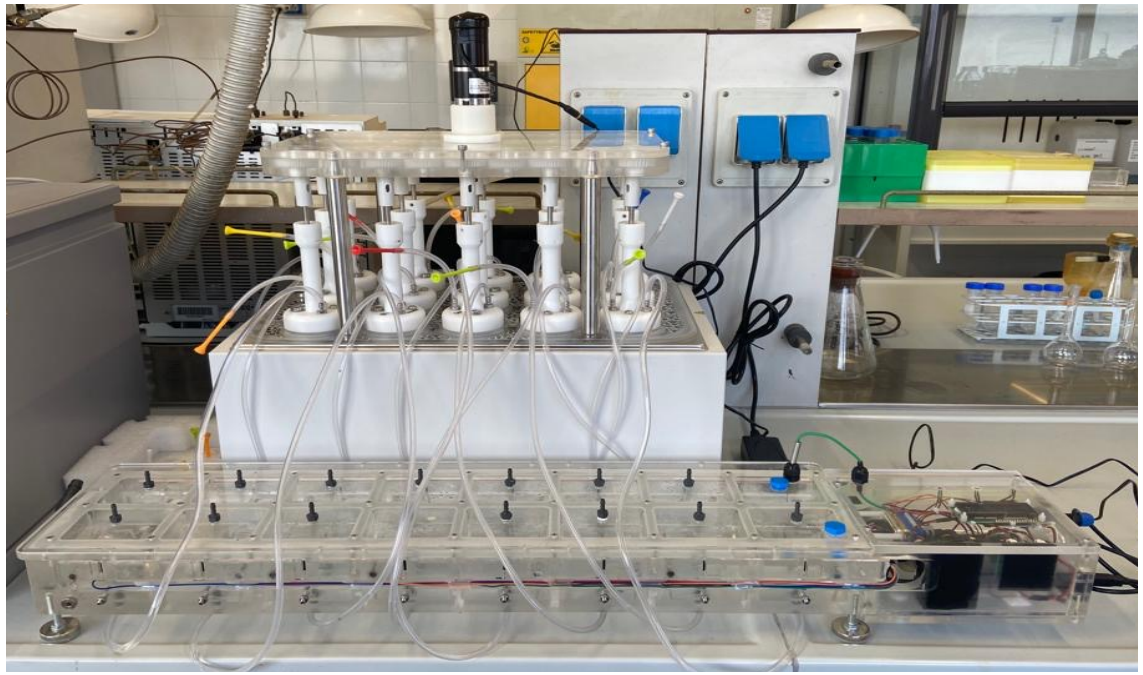
0.4 g H_2O_2/g TS chosen dosage
2 h reaction time

(2) Acidogenic Fermentation….

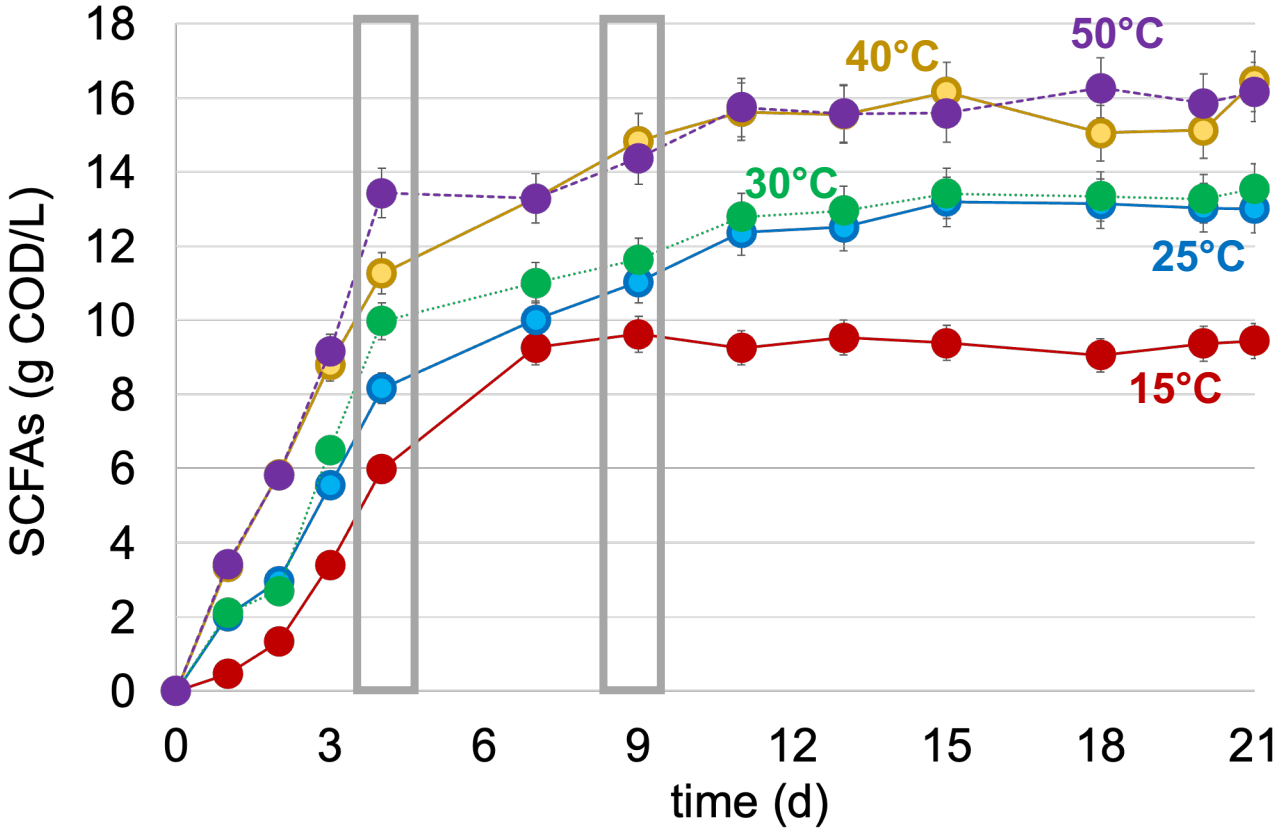
Parameters of batch acidification tests

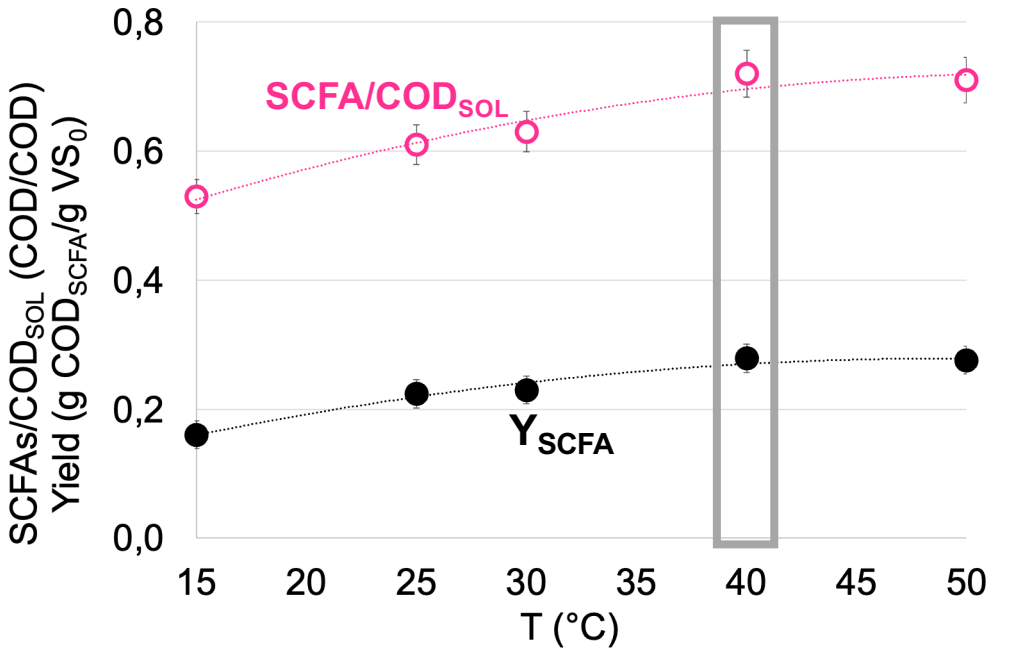
☞ Temperatures: 15, 25, 30, 40 and 50 °C

☞ Pre-treatment dosage (2 h): 0.4 g H_2O_2/g TS



…. to short chain fatty acids production



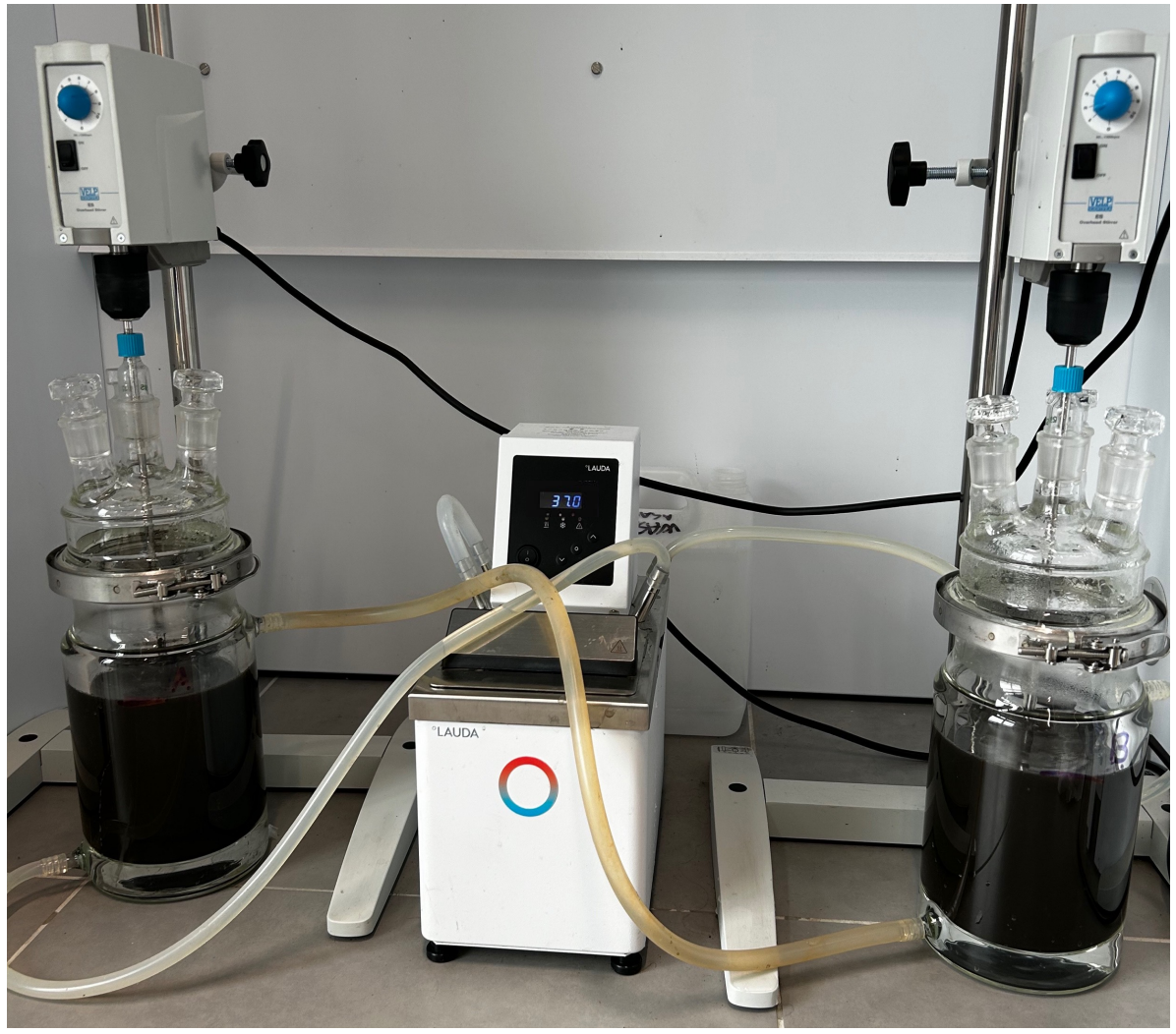


40°C chosen T → HRT of 4.0 and 8.0 d

The chosen H_2O_2 dosage together with T above 30 °C facilitate the anaerobic fermentation of the organics

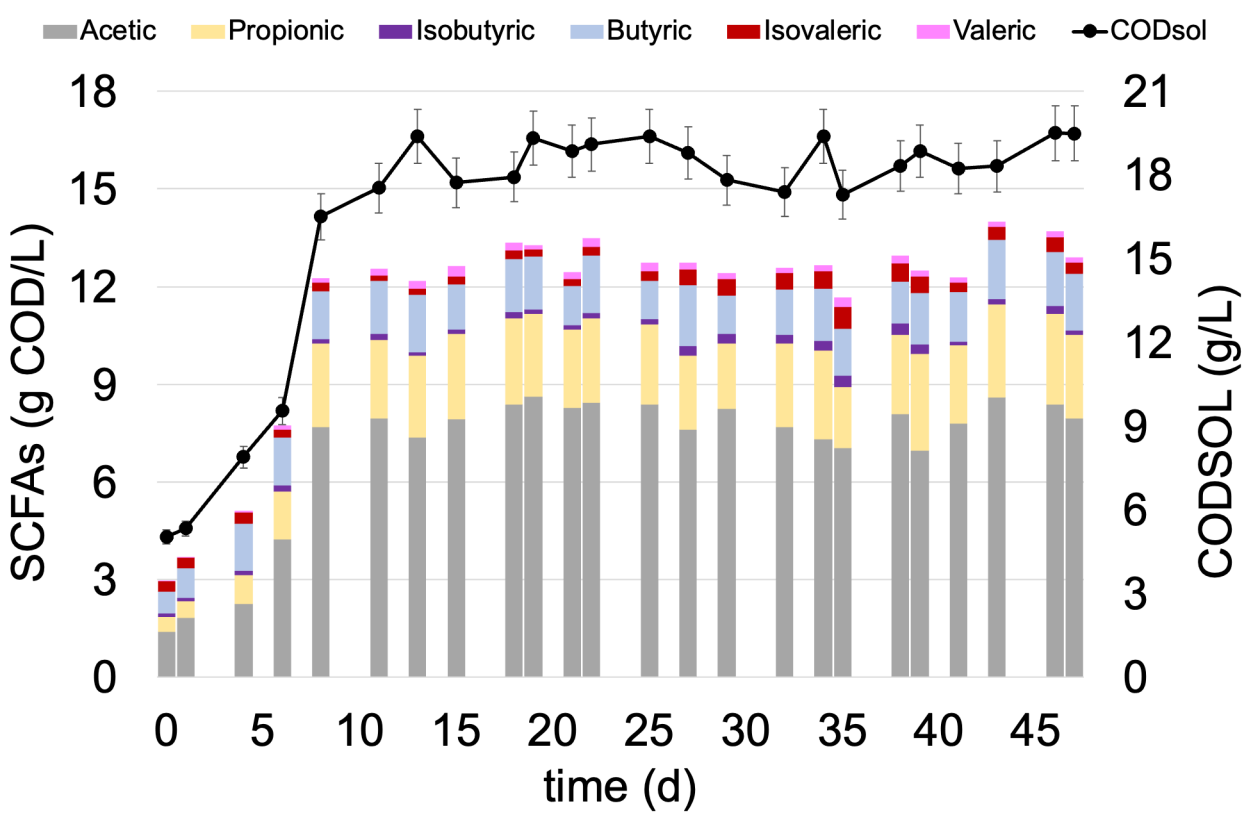
(3) Semi-continuous process sCSTR

Parameter	Run 1	Run 2
HRT (d)	4	8
OLR (g VS/L d)	17.5	8.4
H_2O_2 dosage (g/g TS)	0.4	0.4
Temperature (°C)	40	40
Monitored parameters		
SCFAs concentration (g COD/L)		
SCFAs/COD_{SOL} ratio (COD/COD)		
Y_{SCFAs} (g COD_{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

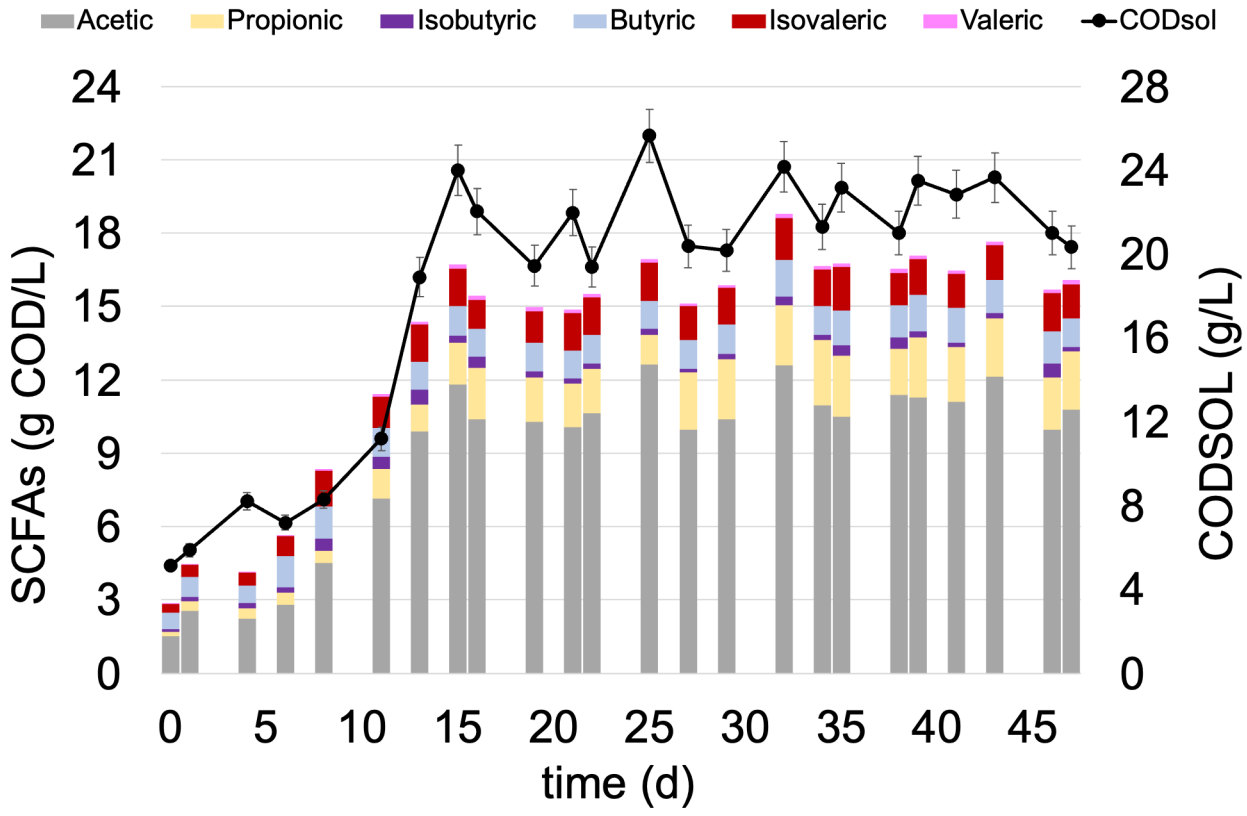
Run 1 (HRT 4.0 d)



COD_{SOL} : 18.2 ± 0.2 g/L
SCFAs : 12.8 ± 0.1 g COD_{SCFA}/L
Y_{SCFA}: 0.25 ± 0.01 g COD_{SCFA}/g VS

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

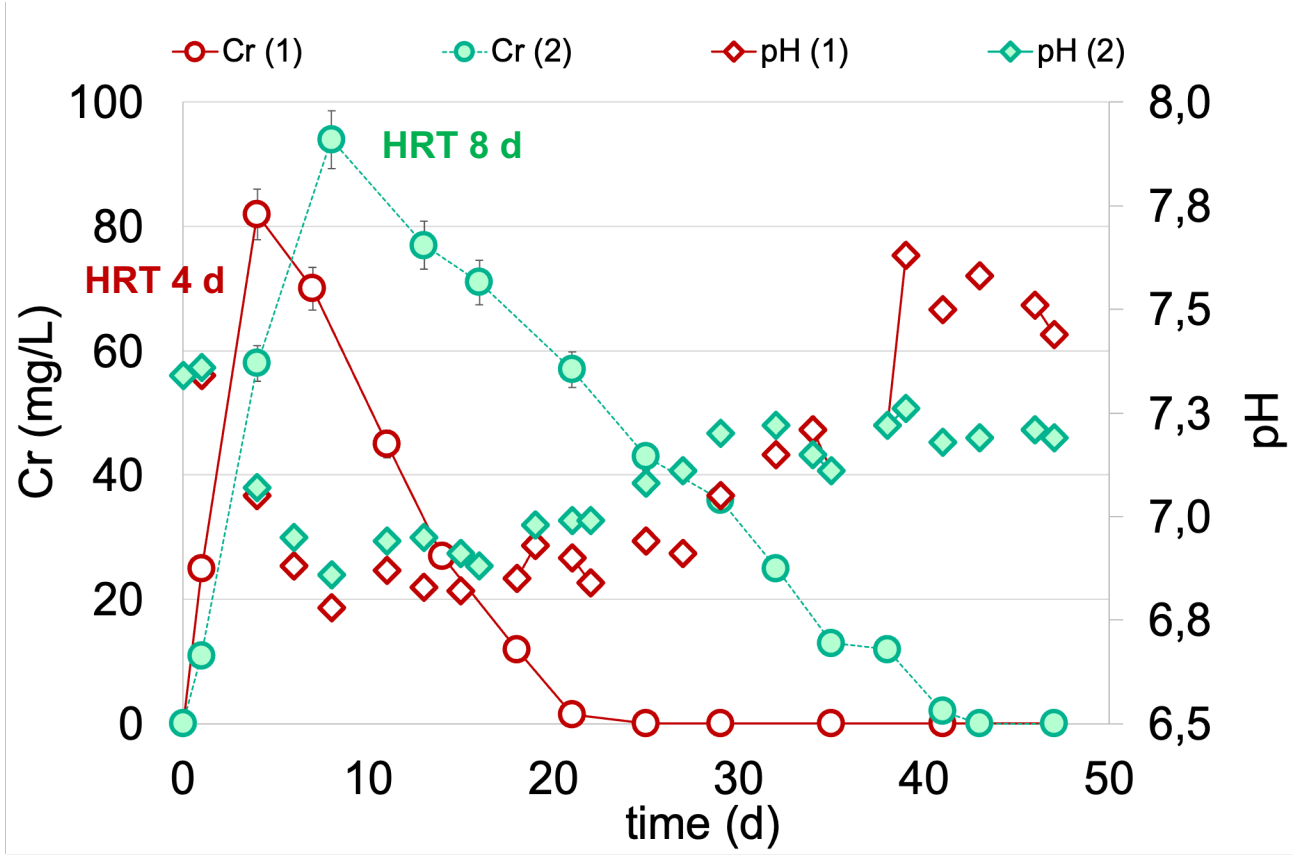
Run 2 (HRT 8.0 d)



COD_{SOL} : 21.8 ± 0.5 g/L
SCFAs: 16.0 ± 0.3 g COD_{SCFA}/L
Y_{SCFA}: 0.32 ± 0.01 g COD_{SCFA}/g VS

Acetic acid 67 % (COD basis);
Propionic acid 13.2 %

…. fate of the chromium

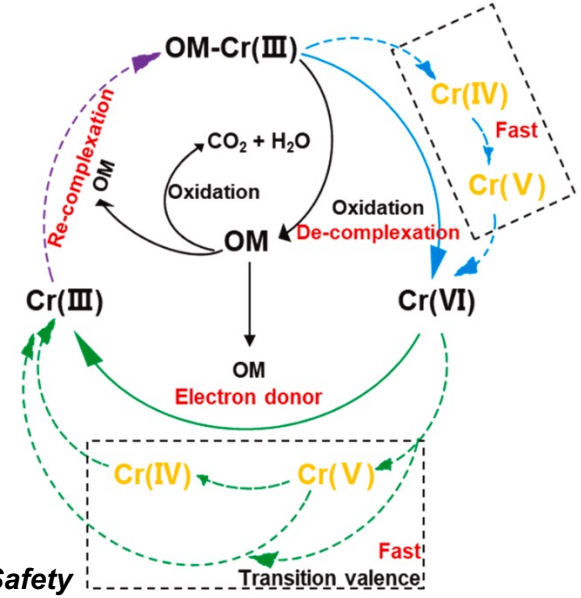


☞ Cr was partially released after the oxidative pre-treatment (**119 ± 11 mg Cr/L**)

☞ <u>Consequences:</u>

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

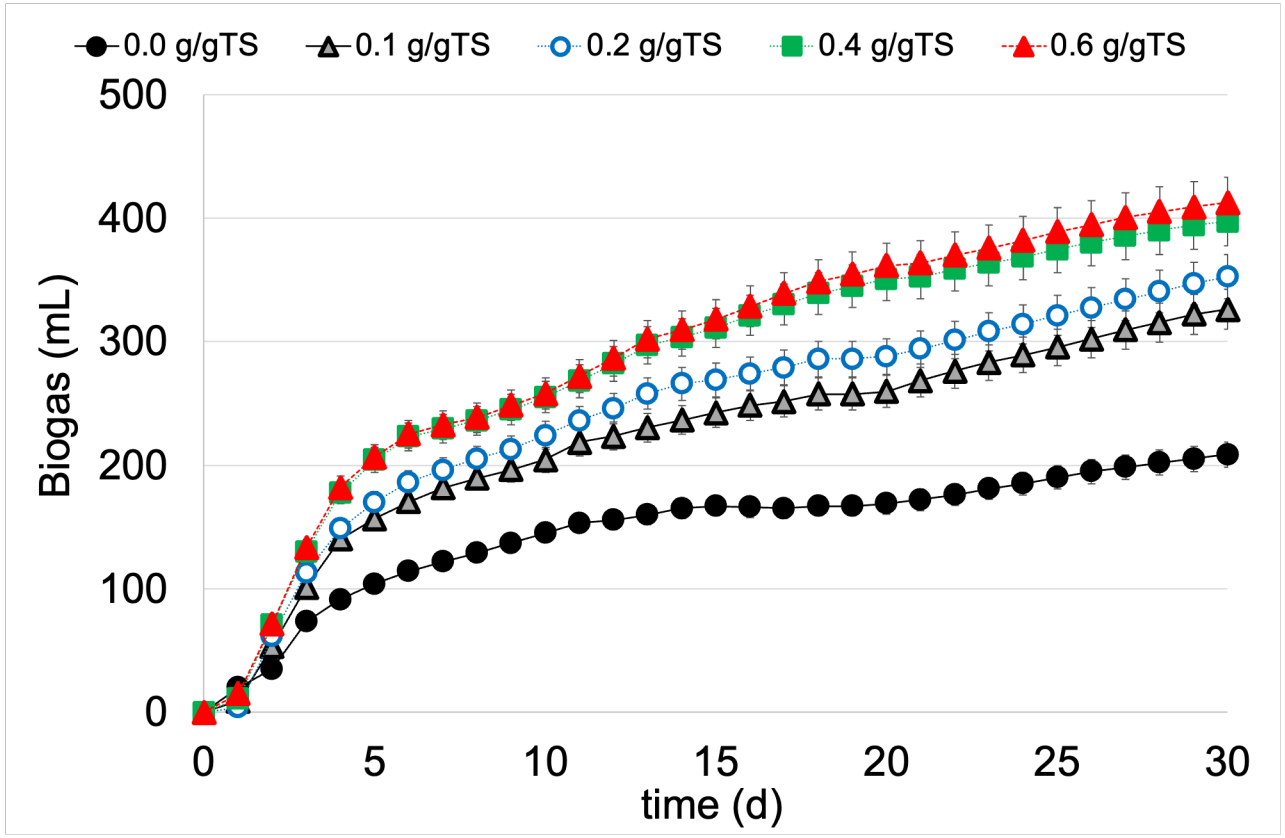
✓ SCFAs did not act as organic ligands, **no Cr presence in the liquid phase**

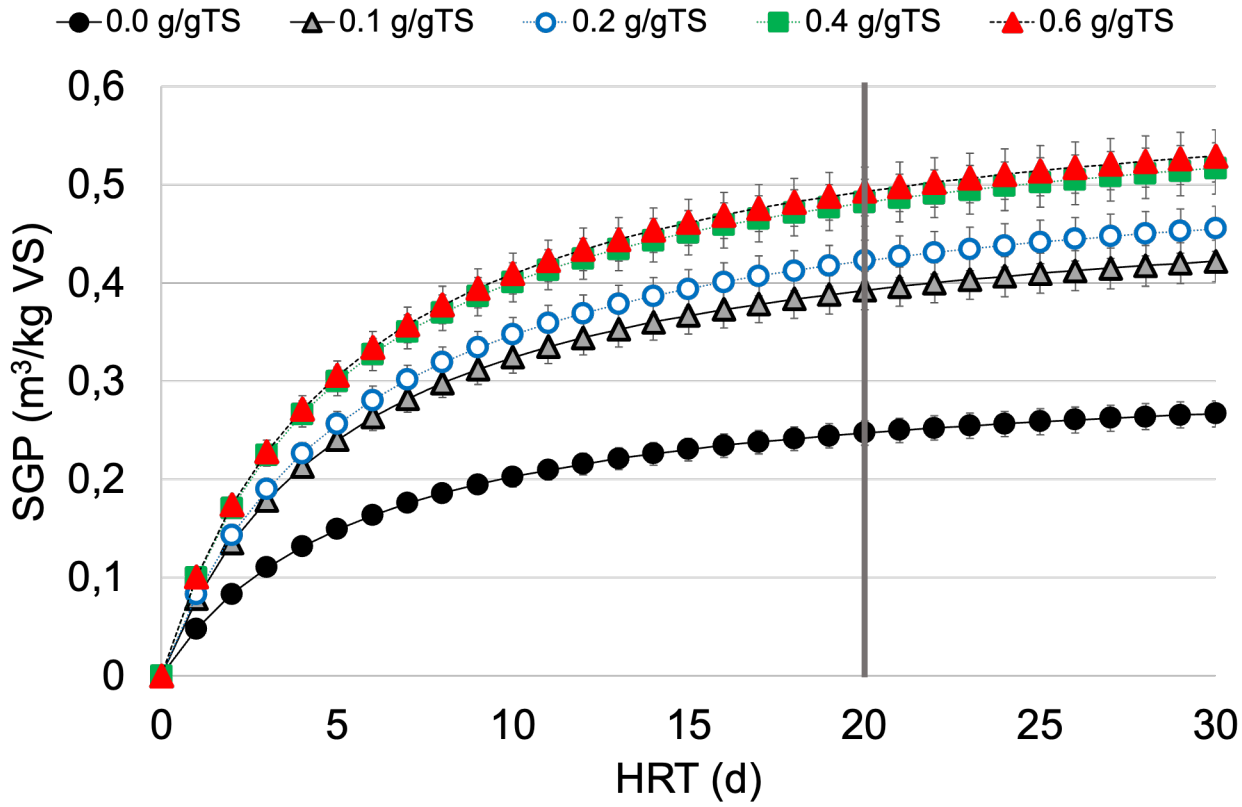


Hao et al., 2022. Ecotoxic. Env. Safety

(4) Biochemical Methane Potential (BMP)

solid-rich acidified residue





0.4 g H_2O_2/g TS **post-treatment**

SGP: 0.48 m^3 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 H_2O_2/g TS** improves the overall efficiency and production SCFAs (Y_{SCFA} 0.32 COD_{SCFA}/g VS) and biogas (SGP = 0.48 m^3/kg VS)

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

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Thank you!

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