From waste to values: hydrolysis and purification of tanning shavings for new circular materials chitosan-collagen hydrolysate based

A. Sarnataro*; C. Furbatto*; G. Calvanese*; C. Florio*

- Stazione Sperimentale per l'Industria delle Pelli e delle Materie Concianti srl, via Campi Flegrei 34, 80078 Pozzuoli, Napoli, Italy, a.sarnataro@ssip.it; c.florio@ssip.it.

Abstract

The tanning industry has long prioritized environmental sustainability and the principles of the circular economy, given its origins in repurposing waste from the food supply chain. Leather processing generates a variety of solid wastes; each associated with specific challenges depending on the production stage. Notably, post-tanning waste recovery becomes particularly complex, and currently, there are no well-established supply chains for its valorization.
This study focuses on recovering shavings from chrome-tanned leather through acid hydrolysis using 1.5 M HCl. This treatment enables the capture of chromium via zeolites, resulting in a protein hydrolysate for further research and a chromium-zeolite powder that allows for the safe recovery of the metal from the matrix.
In this work we explore the production of biodegradable polymer films by combining collagen hydrolysate with chitosan, a naturally abundant macromolecule known for its valuable properties in packaging, medical and food application, that can be derived agri-food industry waste. The aim is to develop a novel composite material with enhanced antimicrobial, antioxidant properties, characterized by high sustainability for use in packaging and potential future application in leather finishing.

🔷 Introduction

- The tanning industry generates significant amounts of **solid waste**.
- **Post-tanning residues** are difficult to recover and structured supply chains for their sustainable management are still lacking.
- However, these wastes have **strong potential for valorization** within a circular economy framework.
- In addition to **leather wastes, agri-food wastes** could be used to create innovative **bio-based composite materials** together with leather wastes.
- **Chitosan** is a biological macromolecule with well-known antimicrobial and filming properties that is possible to exploit in leather manufacturing.

🎯 Aim of the Study

•Develop a sustainable method for the recovery of chrome-tanned leather shavings.
•Apply **acid hydrolysis** using 1.5 M HCl to break down the protein matrix and obtain a soluble hydrolysate.
•Formation of bio-based composite films intended for applications in the packaging sector, and alternative finishing to the synthetic polymer finishes currently used for leather.
•Use **zeolites** to **capture chromium** in a stable form.
•Obtain two main products:

- a protein hydrolysate for use in the development of new biodegradable materials,
- a chromium-zeolite powder allowing safe and efficient metal recovery.

Materials and Methods

•Raw material: wet-blue shavings obtained immediately after the chrome tanning step.
•**Hydrolysis**:

- 20 g of wet-blue shavings were treated with 120 mL of 1.5 M HCl (solid-to-liquid ratio 1:6).
- The reaction was carried out at 80 °C for 2 hours under constant stirring.

•**Protein hydrolysate separation**:

- The hydrolyzed mixture was filtered, and the liquid phase was freeze-dried to obtain the protein hydrolysate.

•**Chitosan-hydrolyzed collagen film formation**:

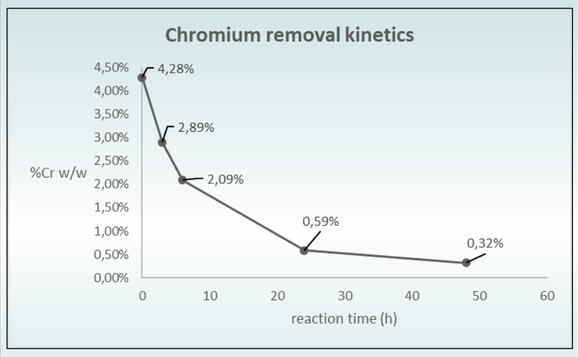
- Chitosan was dissolved in 1% acetic acid in order to obtain a chitosan solution of 1% m/v.
- 2 hours stirring.
- Addition of a mixture of 1% m/v of previously obtained hydrolysed collagen was added.
- Solvent removal by drying.

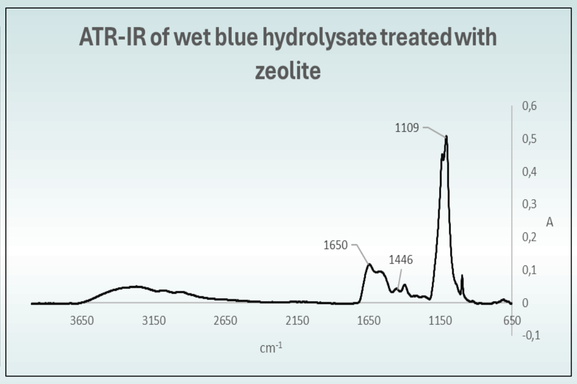
•**Chromium recovery**:

- 2 g of freeze-dried hydrolysate were dissolved in 200 mL of distilled water (initial pH ≈ 3.5).
- 8 g of Zeolite 4A (Si:Al = 1:1, Na^+ counterion) were added to the solution.
- After zeolite addition, pH increased to approximately 6.
- Aliquots of 15 mL were sampled at 3 h, 6 h, 24 h, and 48 h to monitor chromium removal via metal content analysis.

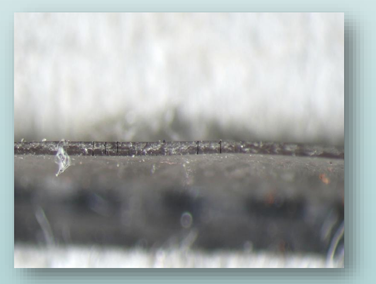
Initial hydrolysate

Hydrolysate after 2 days of treatment





Composite Film – front view



Composite Film – section view

Conclusions

❖ The acid hydrolysis process proved to be highly effective, achieving an impressive yield of approximately 96%.
❖ The chromium capture treatment using zeolite reduced chromium content from 4.28% to 0.32% w/w.
❖ First samples of chitosan-hydrolysate composite films have been successfully prepared. These will be subjected to comprehensive chemical-physical and biodegradability characterizations.

This study was carried out within the MICS (Made in Italy–Circular and Sustainable) Extended Partnership and received funding from the European Union Next-Generation EU (PIANO NAZIONALE DI RIPRESA E RESILIENZA (PNRR) – MISSIONE 4 COMPONENTE 2, INVESTIMENTO 1.3 –D.D. 1551.11-10-2022, PE00000004). This manuscript reflects only the authors' views and opinions, neither the European Union nor the European Commission can be considered responsible for them