

## 2025 IULTCS Young Leather Scientist Grant

Identification: YLSG\_2025\_applicantname

COMPLETE APPLICATION FORM (click application area)

☒ Basic Research ☐ Environmental/Sustainability ☐ Machinery/Testing

### 1) Applicant Information

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### Advisor Information

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By submitting this application, I commit to develop the project as outlined in the attached Research Project Plan and to complete a written report by February 28, 2026 with the following items:

- 1) Introduction
- 2) Materials and Methods
- 3) Results and Discussion
- 4) Conclusion
- 5) Suggestion for Future Work
- 6) References

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## **2) Research Project Plan outline – Maximum 3 pages**

### **Alkaline Hydrolysis of Zeolite and Chrome Shavings: Investigating the fate of their hydrolysate and Undigested Materials**

**Introduction:** Zeolite-based tanning agents have emerged as a chrome-free alternative in sustainable leather production. Zeolites are aluminosilicate materials with highly ordered, three-dimensional porous structures composed of interconnected cavities.<sup>1,2</sup> This framework makes them versatile, and their environmentally benign nature, along with low toxicity, makes them suitable for various applications, including those involving human and veterinary use. Chromium(III) salts are used in approximately 80% of global leather tanning, effectively stabilizing collagen fibres and producing leather with superior handling qualities and high hydrothermal stability.<sup>3</sup> However, disposal of chrome-tanned leather shavings (CTLS) is both environmentally challenging and economically burdensome. Chromium(III) can potentially oxidize into a toxic hexavalent form, chromium(VI), with landfilling costs in New Zealand reaching approximately \$1.5 million annually. The strong chromium-collagen bonds in CTLS present challenges as dechroming is costly and time-consuming. Thus, the increasing shift towards chrome-free tanning alternatives in response to environmental and consumer pressures.

Multiple studies have extensively explored the use of CTLS hydrolysates, but achieving chromium removal efficiencies exceeding 95% has proven to be difficult.<sup>4,5,6</sup> This limits the potential applications of the CTLS hydrolysates as the persistence of residual chrome poses environmental and health concerns. Similarly, wet white leathers tanned with agents such as glutaraldehyde, tetrakis(hydroxymethyl)phosphonium sulfate (THPS), and triazine compounds present challenges in complete removal of these tanning agents during hydrolysis, restricting the usability of the resulting hydrolysates. In contrast, zeolite-based tanning agents offer a significant advantage, as their inorganic nature and structural properties facilitate more straightforward separation from collagenous materials during hydrolysis, enhancing the purity of the hydrolysate and expanding their applicability across industries, while also supporting environmental sustainability objectives.

While the incomplete removal of chromium in hydrolysates from CTLS is documented, the behavior of zeolites during the hydrolysis of zeolite-tanned leather shavings (ZTLS) remains largely underexplored. Given the distinct binding characteristics and particle sizes of zeolites, their interactions with collagen during tanning and subsequent hydrolysis may differ significantly from those of chromium. Investigating the fate of zeolites in this context is essential for assessing the feasibility of producing high-purity collagen hydrolysates and, by extension, determining their utility.

The optimization of hydrolysis conditions for CTLS and ZTLS enables a detailed investigation into their breakdown behavior and the characteristics of the resulting collagen hydrolysates. A comparative analysis of digested versus undigested fractions will provide insight into the purity of the hydrolysates, particularly in terms of organic and inorganic content. Furthermore, studying the fate of chrome and zeolites during hydrolysis will reveal the extent to which these tanning agents remain bound to the collagen matrix or are released. These analyses are essential for understanding the

potential of zeolite-based tanning as a sustainable alternative and for assessing the implications of tanning agents on the hydrolysis process.

**Objectives:** The aim of this project is to investigate the properties of ZTLS in comparison to CTLS by optimizing a hydrolysis process that facilitates complete breakdown, allowing for the analysis of digested versus undigested materials.

Detailed objectives are outlined below:

- Optimisation of an alkaline-based hydrolysis method widely used on CTLS for ZTLS.
- Quantify the amount of tanning agents in the hydrolysate and undigested material following hydrolysis.
- Determine the purity of the collagen hydrolysates produced from both shavings to assess their applicability across industries.

### **Methods:**

**Local:** This research will be performed at New Zealand Leather and Shoe Research (LASRA)

**Source of Substrate:** De-limed hide, ZTLS, and CTLS, will be sourced from Tasman Tanning, NZ.

**Hydrolysis Optimization:** Leather shavings will undergo an alkaline-based hydrolysis process to facilitate the breakdown of collagen and tanning agents. This will be optimized and kept the same for both ZTLS and CTLS. The digestion process will involve incubating the leather shavings in an alkaline solution at specific temperatures and times, followed by filtration to separate the hydrolysate from undigested material. The purity of the collagen hydrolysates will be assessed based on the content of organic and inorganic components.

**Assessing Hydrolysis Efficiency:** Size-exclusion chromatography (SEC) will be used to analyze the molecular weight distribution of collagen hydrolysates obtained from the hydrolysis of CTLS and ZTLS. The resulting elution profiles will reveal the extent of collagen breakdown, highlighting differences in molecular weight and distribution. By comparing these profiles with those from delimed hides, it will be possible to infer whether tanning agents remain bound to the hydrolysates, providing deeper insight into how these agents interact with collagen during hydrolysis.

**Profiling of inorganic Materials:** FTIR spectroscopy will be employed to analyze and compare the inorganic content of undigested samples from CTLS and ZTLS. Characteristic peaks associated with the tanning agents—chromium compounds in CTLS and aluminosilicate structures in ZTLS—will serve as key indicators. These spectral fingerprints will offer insights into the distribution of inorganic residues between digested and undigested fractions. By evaluating these differences, the retention or release patterns of the tanning agents during hydrolysis can be inferred, shedding light on their behavior within the collagen matrix.

**Quantification of Tanning Agents:** The tanning agents retained in the hydrolysates and undigested materials will be quantified using ICP-MS and AAS. This will allow for the

respective elemental quantification, in order to determine the distribution of zeolites and chromium across the hydrolysis fractions.

**Collagen Content Analysis of Hydrolysates:** After hydrolysis, collagen hydrolysates will be analyzed by determining the content of collagenous material. The amino acid profile will be assessed using liquid chromatography, where collagen concentration will be quantified based on its hydroxyproline content. The results will help evaluate the suitability of the hydrolysates for future industrial applications.

**Hypothesis/Expected Results:** The optimized alkaline hydrolysis process is expected to effectively break down collagen in both CTLS and ZTLS, with SEC revealing molecular weight distributions that reflect differences in hydrolysis efficiency and tanning agent interactions. FTIR analysis of undigested residues is anticipated to show characteristic peaks for chromium and aluminosilicates, offering insights into the retention and separation patterns of the tanning agents. Quantification through ICP-MS and AAS is expected to confirm the greater ease of separation for zeolites compared to chromium. These findings will enhance our understanding of how tanning agents interact with the collagen matrix during hydrolysis and demonstrate the potential of a modified alkaline-based method to produce high-purity collagen hydrolysates from ZTLS, supporting future applications across various industries.

**Research benefit for the local or global leather industry (one sentence only):**

This research aims to explore ZTLS as a sustainable alternative to CTLS, with zeolite-based tanning agents offering a viable solution to mitigate the environmental impact of chrome and align with circular economy principles by enabling easier separation and reuse during hydrolysis

**Literature:**

1. Wise, W. R., Davis, S. J., Hendriksen, W. E., von Behr, D. J., Prabakar, S., & Zhang, Y. (2023). Zeolites as sustainable alternatives to traditional tanning chemistries. *Green Chemistry*.
2. Shriver, D. F., Atkins, P. W., & Langford, C. H. (1995). *Inorganic Chemistry* (2nd rev. ed.). Oxford University Press.
3. Covington, A. D. (2009). *Tanning Chemistry: The Science of Leather* (1st ed., Chapter 11, pp. 204–258). Cambridge University Press.
4. Scopel, B., Baldasso, C., Dettmer, A., & Santana, R. (2018). Hydrolysis of chromium-tanned leather waste: Turning waste into valuable materials—a review. *Journal of the American Leather Chemists Association*, 113.
5. Kassem, S. T., & El-Shemy, K. A. (2023). Extracting chromium-free protein hydrolysate from leather tanning wastes. *International Journal of Environment, Agriculture and Biotechnology*, 8(6).
6. Codreanu, A. M. N., Stefan, D. S., Kim, L., & Stefan, M. (2024). Depollution of polymeric leather waste by applying the most current methods of chromium extraction. *Polymers*, 16(11), 1546.