TOWARDS SUSTAINABLE LEATHER MANUFACTURING:

A ONE-STEP ENZYMATIC BEAMHOUSE WITH SIGNIFICANT ECONOMICAL AND ENVIRONMENTAL BENEFITS

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Outline

01. Introduction to Leather Manufacturing

02. Efforts in Green Leather Manufacturing

03. Enzyme-Based Leather Processing: A Sustainable Solution

04. Conlcusion and Outlook

01. Introduction to Leather Manufacturing

Tranditional (Chemical-based lime sulfide system (LSS))

These steps are necessary to transform raw animal hides into durable leathers.

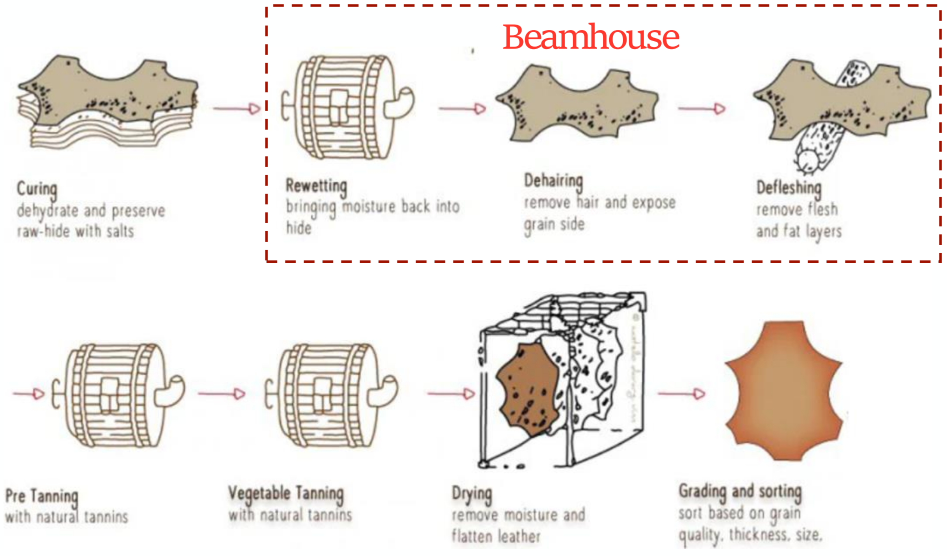

Fig. 1. The schematic diagram of traditional leather manufacturing.

- The beamhouse stage in traditional leather processes alone contributes 60-70% of the industry's total pollution load – high COD, ammonia, and solid waste.
- They also consume lots of water and energy.

With sustainability demands rising, we need cleaner methods.

- **Enzymatic technology is our green answer to these industry problems.**

02. Efforts in Green Leather Manufacturing

Sustainable

Advantages:

- Low Environmental Impact
- Reduced Energy Consumption
- High Efficiency

Drawback:

- Poor enzyme penetration can lead to over-hydrolysis of the surface, resulting in poor leather quality.

Enzymes

(*J. Cleaner Prod.*, 2020)

KCl-dispase synergistic system

potassium chloride-dispase

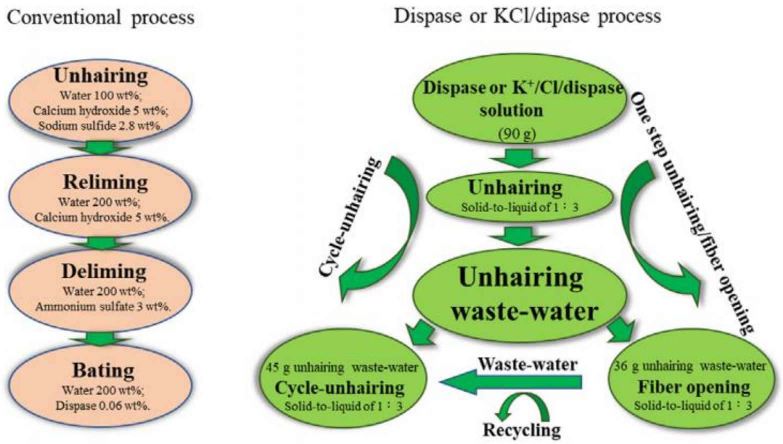

Fig. 2. Comparison between convention and KCl/dispase operation processes.

- Due to the Hofmeister series, K^+ and Cl^- were chosen to enhance dispase's binding to water molecules and substrate, allowing it to be recycled for up to 12 times.
- Also, they speed up enzyme penetration and protein hydrolysis, cutting unhairing/fiber opening process to 30 h.
- The results? Low pollution, well-dispersed collagen, and leathers with good physical and thermal properties.

02. Efforts in Green Production of Leather

(*J. Cleaner Prod.* 2023)

Effect of different ions in assisting protease

sodium sulfate (Na_2SO_4), disodium hydrogen phosphate (Na_2HPO_4), sodium chloride (NaCl), potassium chloride (KCl), ammonium chloride (NH_4Cl), and magnesium chloride ($MgCl_2$)

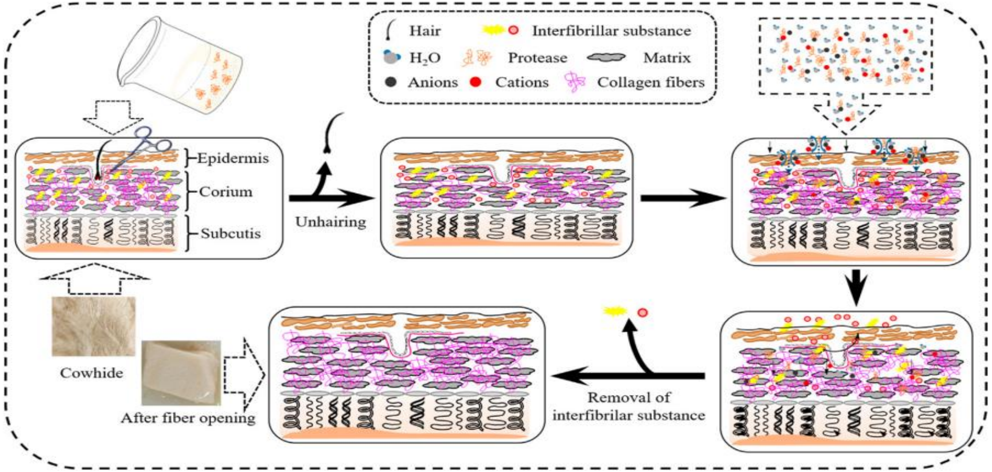

Fig. 3. The schematic diagrams of protease unhairing and ion-assisted protease for fiber bundle opening.

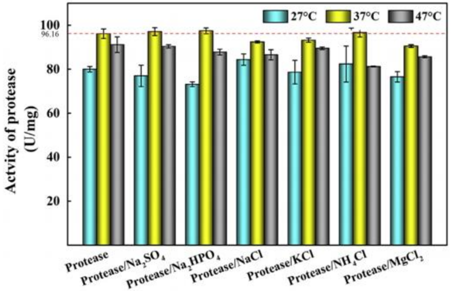

Fig. 4. Effect of different salt solutions on neutral protease activity at different temperature.

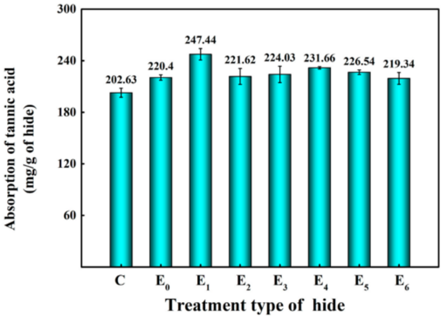

Fig. 5. Absorption of tannic acid by different processed hides.

- The ultilization of ions are effective in enhancing enzyme permeability and improving enzyme solubility and reaction activity.
- The magnesium ion (Mg^{+}) stand out, having the most remarkable effect on removing interfibrillar substances and opening collagen fiber bundles.

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(*Biochem. Eng. J.* 2024)

MgCl$_2$-assisted neutral protease for sustainable beamhouse

Optimization — reaction time, temperature, enzyme concentration

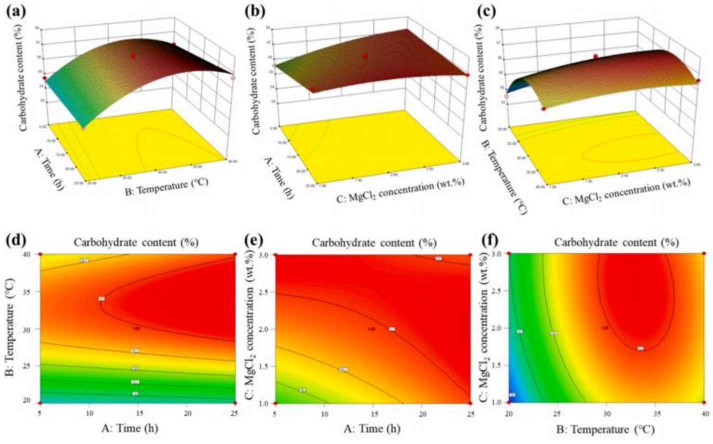

Fig. 6. RSM establishment of the samples.

- Response surface methodology (RSM) was utilized to optimize the experimental conditions for enhancing unhairing, fiber opening, and bating efficiency.
- It presents a promising alternative, aligning with the goal of achieving sustainable and environmental friendly leather production practices.

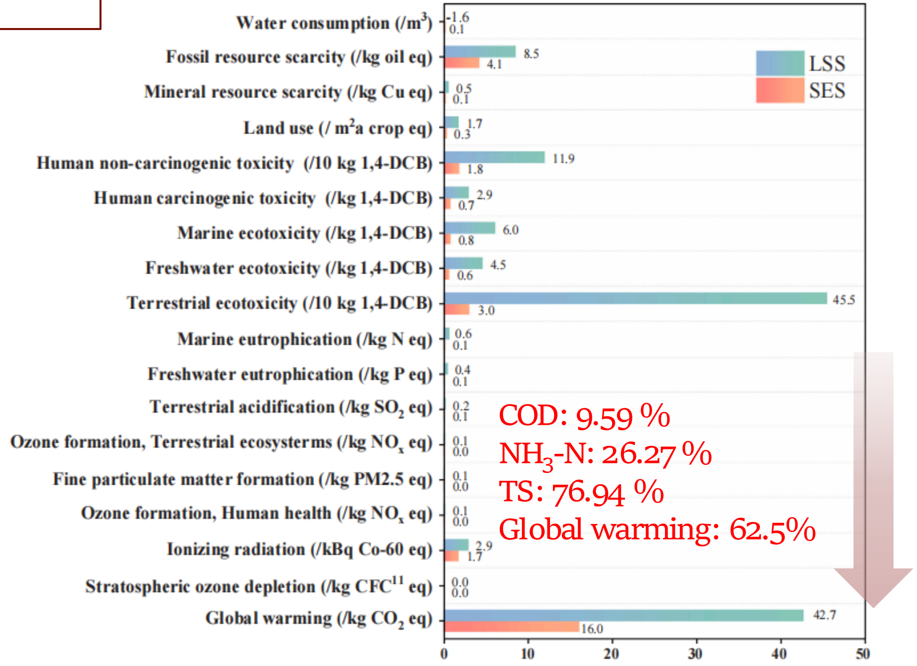

Fig. 7. Comparative analysis of environmental impact scores for producing 1 FU of cowhide using different methods.

03. Enzyme-Based Leather Processing: A Sustainable Solution

(*Green Chem.* 2024)

Sustainable (Enzyme-based α-amylase/neutral protease system (ANS))

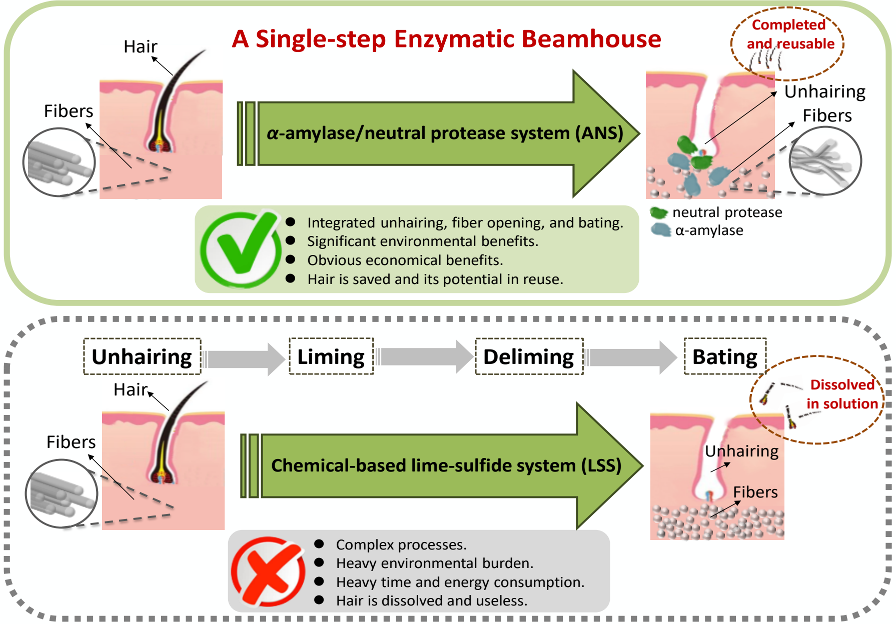

Fig. 8. The comparison of a single-step enzymatic beamhouse and tranditional one.

- Enzyme-only approach
- One-step beamhouse
- Both environmental and economical benefits
- Make hair saved and potentially resued.

➢ **Neutral protease** works by breaking down the protein substances between the hair shaft and hair follicle, as well as between the hair bulb and papilla, enabling effective unhairing.

➢ ***α*-amylase** breaks down the polysaccharides in the interfibrillar substances to facilitate fiber opening.

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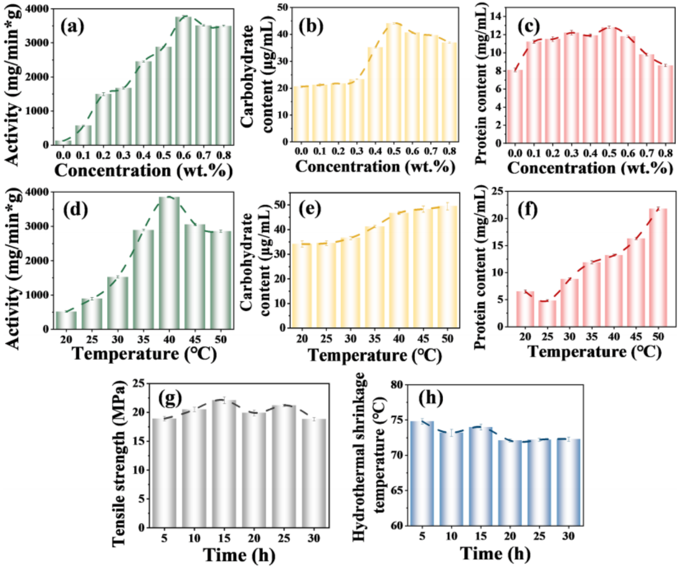

Fig. 9. The determination of pridominate parameters.

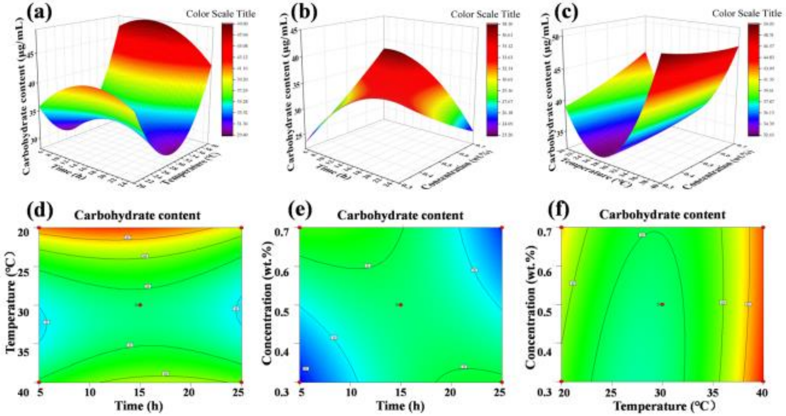

Fig. 10. The 3D response plots and 2D contour plots illustrating the impact of pridominate parameters.

Coded:

$$G = 33.76 - 0.24X_1 + 3.63X_2 + 0.92X_3 - 2.04X_1X_2 - 6.47X_1X_3 - 1.89X_2X_3 - 3.87X_1^2 + 11.21X_2^2 + 0.49X_3^2 \quad (4)$$

Actual:

$$g = 68.61 + 3.37x_1 - 5.59x_2 + 69.15x_3 - 0.02x_1x_2 - 3.24x_1x_3 - 0.94x_2x_3 - 0.04x_1^2 + 0.11x_2^2 + 12.28x_3^2$$

X1=0.16, 16.6h
X2=-0.16, 28.4℃
X3=-0.18, 0.5wt.% of neutral protease concentration

Optimization by RSM modelling

- The elliptical shape of the contours indicates a significant interaction.
- After calculation, the optimized conditions were obtained.

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Unhairing and fiber opening assessment

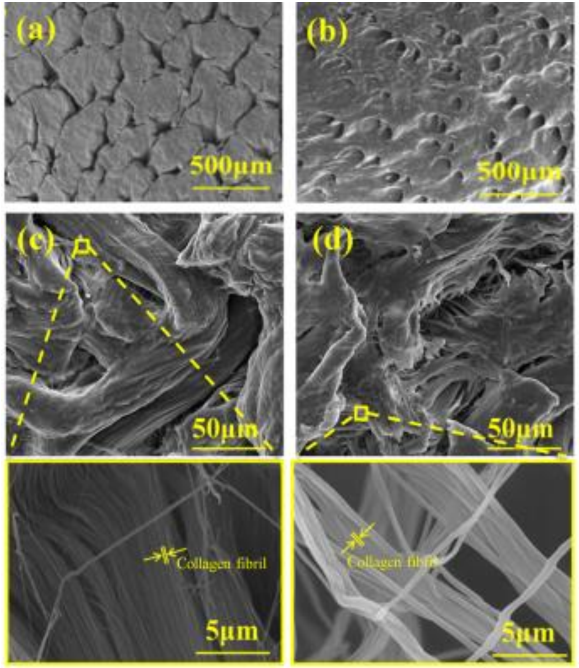
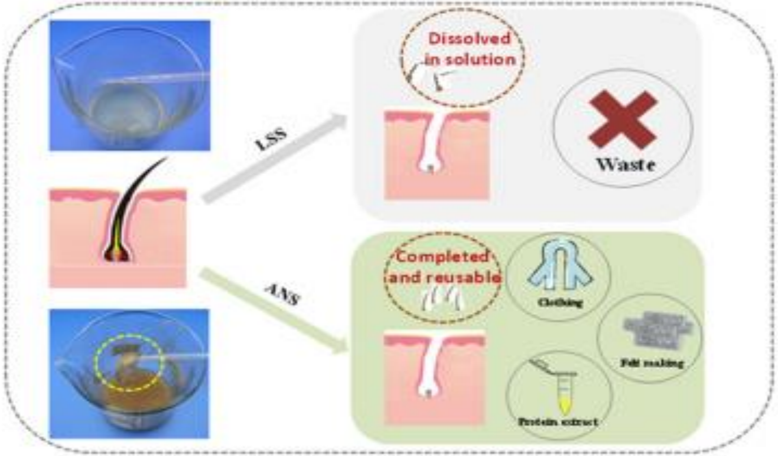


Fig. 11. The assessment of unhairing and fiber opening by SEM.



Unhairing and fiber opening assessment

- The optimized enzymatic method makes leather have smoother and denser surface pores compared to traditional methods.
- The structure of the hair after unhairing remains intact, making it possible to be recycled and reused.

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Bating assessment

collagen fibers

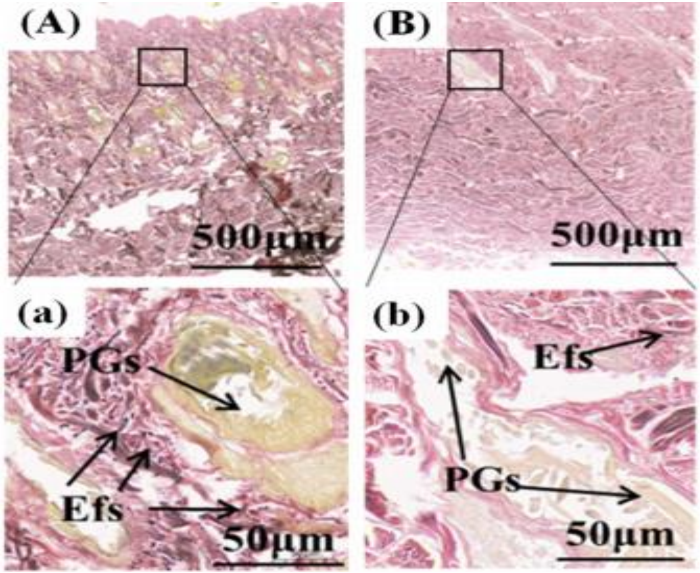

Fig. 12. The assessment of bating by Verhoeff's Van Gieson (EVG) staining: (A and a) the LSS and (B and b) the optimized ANS.

elastic fibers

proteoglycans, glycoproteins and other tissues

fiber interspaces or non-tissue regions

Bating assessment

- In LSS, the presence of dark and yellow regions is obvious, representing the elastic fibers and protein–polysaccharide, which were not removed.
- Conversely, in ANS, the dark and yellow regions have nearly disappeared, which could be evidence for the completeness of the hydrolysis reaction. The non-structural proteins and hair roots were completely removed, with the collagen fibers remained intact.

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Mechanical property assessment

Table 2. The Summary of leather properties: softness, tensile strength, elongation at break, and hydrothermal shrinkage temperature.

Samples	Softness (mm)	Tensile strength (MPa)	Elongation at break (%)	Hydrothermal shrinkage temperature (°C)
C	7.23±0.22	11.76±0.60	29.02±1.42	73.80±0.20
A/N	5.14±0.18	11.20±0.80	35.06±2.70	77.10±0.50

Unhairing, fiber opening, and bating assessment

- The leather produced via ANS method exhibited tensile strength (11.20 ± 0.80 MPa) similar to that of the conventional method treated leather (11.76 ± 0.60 MPa).
- Better softness of 5.14 (5.14 ± 0.18 mm) was observed, as well as an improved elongation at break from 29.02% to 35.06% and a hydrothermal shrinkage temperature from 73.80 °C to 77.10 °C.
- These improvements should be related to fiber opening, and adequate fiber opening can help expose more functional groups, such as hydroxyl groups, providing more binding sites for tanning.

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Environmental benefits

Life cycle assessment (LCA)

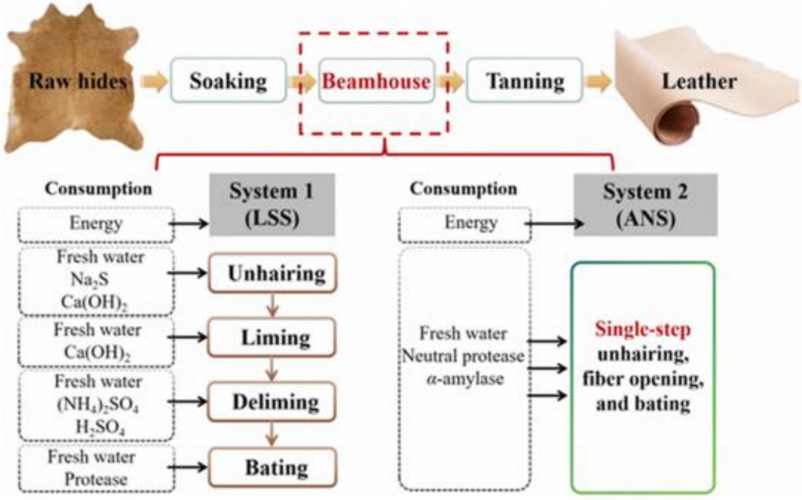

Fig. 13. The schematic diagram of the beamhouse process and its corresponding cost.

Table 3. Pollution loads in wastewater by different processes (kg/t).

Methods and processes		Pollution loads in wastewater: COD	NH_3-N	Cl^-	TS
C (kg/t)	Unhairing	1.64±0.11	-	5.83±0.32	33.25±0.00
	Reliming	1.02±0.20	-	0.65±0.25	9.40±0.00
	Deliming	0.27±0.42	0.37±0.10	4.56±0.17	7.18±0.00
	Total	2.93±0.73	0.37±0.10	11.04±0.74	49.83±0.00
A/N (kg/t)	Single-step Total	0.28±0.10	0.03±0.10	0.20±0.02	13.00±0.00
Pollution load reduction	-	90.44%	91.89%	98.19%	73.91%
Pollution load reduction of [1]	Enzyme unhairing NaOH-based fiber opening Pickle-less chrome tanning	43%			70%
Pollution load reduction of [2]	Three-step tanning process with biocatalyst assisted Pickle-less chrome tanning without basification	52%			74%
Pollution load reduction of [3]	Enzyme formulation with the activation of silicate salt for unhairing	53%			26%

[1] Thanikaivelan, P., Raghava, R.J., Unni, N.B., Ramasami, T. 2003. Biointervention makes leather processing greener: an integrated cleansing and tanning system. Environ Sci Technol. 37(11), 2609-2617.
[2] Saravanabhavan, S., Aravindhan, R., Thanikaivelan, P., Raghava, R.J., Unni, N.B, Ramasami, T., 2005. A source reduction approach: integrated bio-based tanning methods and role of enzymes in dehairing and fiber opening. Clean Technol Environ Policy. 7, 3-14.
[3] Saravanabhavan, S., Thanikaivelan, P., Rao, J.R., Unni, N.B., 2005. Silicate enhanced enzymatic dehairing: a new lime-sulfide-free process for cowhides. Environ Sci Technol. 39(10), 3776-3783.

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Economic benefits

Table 4. Cost estimation for processing per ton of raw soaked cowhide by LSS and ANS.

Methods	Processes	Consumption	Cost[f] ($)	Total cost[f] ($)
LSS	Unhairing	0.03 kg of Na_2S[a]	0.0101	3.97
		0.05 kg of $Ca(OH)_2$[a]	0.0049	
		1.00 kg of fresh water[b]	0.0008	
	Liming	0.05 kg of $Ca(OH)_2$[a]	0.0049	
		1.00 kg of fresh water[b]	0.0008	
	Deliming	0.03 kg of $(NH_4)_2SO_4$[a]	0.0076	
		0.01 kg of H_2SO_4[c]	0.0356	
		2.00 kg of fresh water[b]	0.0017	
	Bating	0.60 g of neutral protease[d]	0.0414	
		2.00 kg of fresh water[b]	0.0017	
	Energy	45 k W^{-1} h^{-1} of electricity[e]	3.8588	
ANS	Single-step	0.01 kg of α-amylase[d]	128.8	2.74
		3 g of neutral protease[d]	0.252	
		1 kg of fresh water[b]	0.0009	
	Energy	24.95 k W^{-1} h^{-1} of electricity[e]		

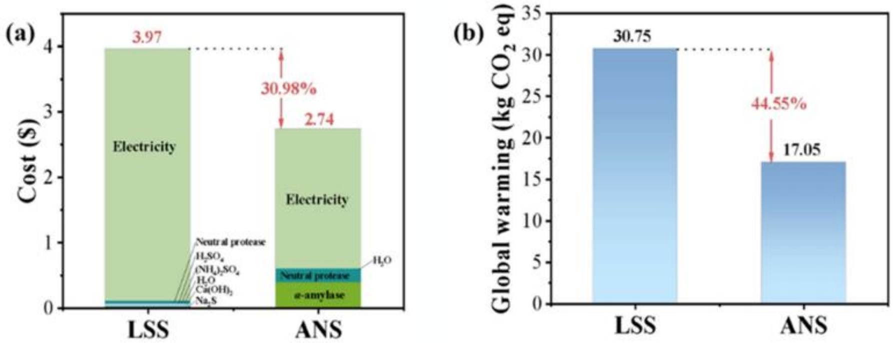

Fig. 14. (a) The cost estimation and (b) the global warming potential evaluation of the LSS and ANS.

Benefits assessment

- When producing 1 kg of cowhide, we achieved a remarkable cost reduction of 30.98% by transitioning from the traditional LSS to the ANS process.
- The global warming potentials (GWP, expressed in kg CO_2 equivalents) showed a 44.55% reduction in greenhouse gas emissions, aligning perfectly with the principles of green production.

04. Conclusion and Outlook

Conclusion

- The applications of enzymatic approach as a sustainable technology for leather manufacturing were comprehensively investigated.
- The significant environment and cost benefits were evaluated, showing how it can minimize pollution and reduce costs effectively.

Outlook

- In the pursuit of innovative materials and preparation processes, it is imperative to reassess and reform conventional manufacturing.
- Green technology has emerged as a captivating and pivotal frontier in 21st-century chemical technology and research. Biotechnology holds immense promise for promoting high-quality, low-pollution advancements within the leather industry with broad prospects for application.

05. Acknowledgements

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