

TOWARDS SUSTAINABLE LEATHER MANUFACTURING:

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

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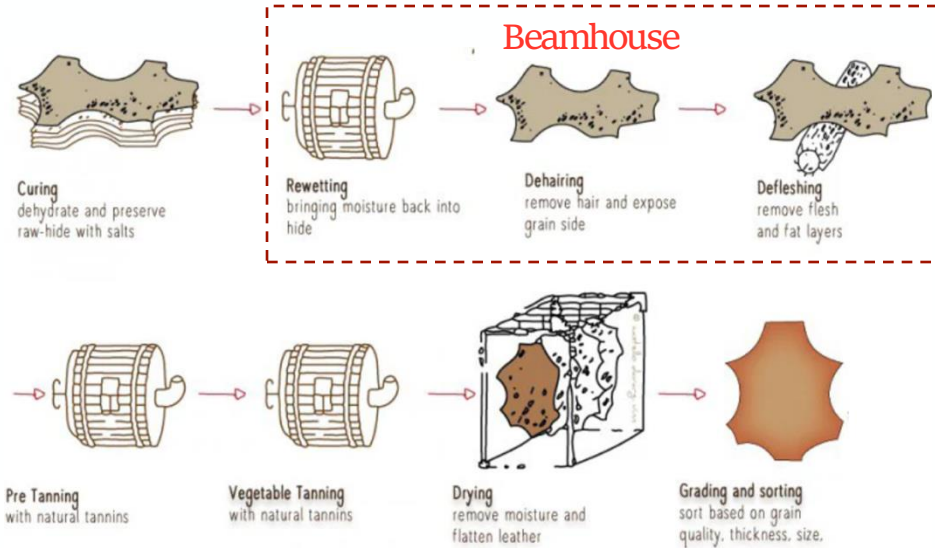


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01. Introduction to Leather Manufacturing

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

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



- 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.

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

02. Efforts in Green Leather Manufacturing

(J. Cleaner Prod., 2020)

Sustainable

KCl-dispase synergistic system

potassium chloride-dispase

Advantages:

- Low environmental impact
- Low Energy Use
- High Efficiency

Drawbacks:

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

Enzymes

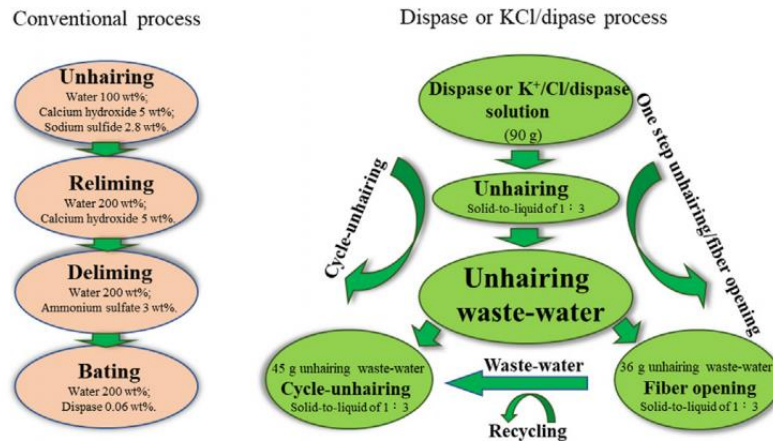


Fig. 2. Comparison between convention and KCl/dispose operation processes.

- 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

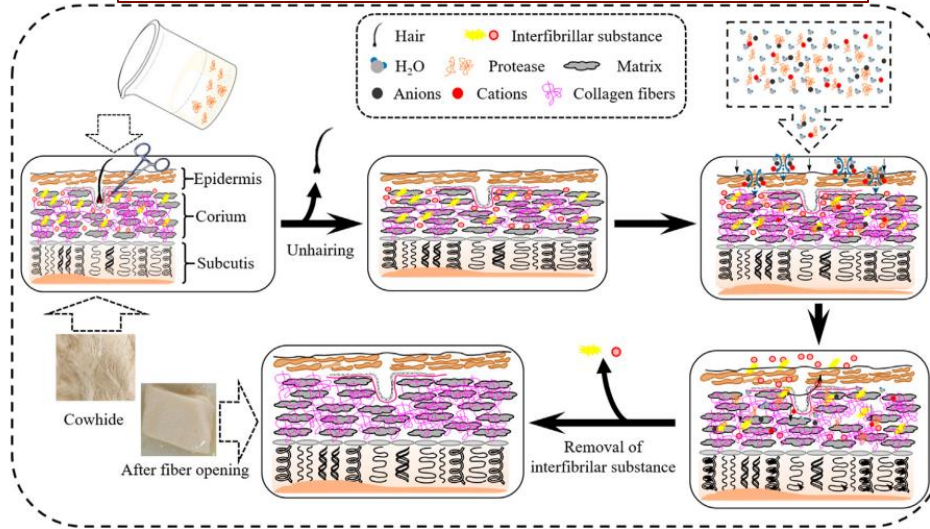


Fig. 3. The schematic diagrams of protease unhairing and ion-assisted protease for fiber bundle opening.

- The utilization of ions are effective in enhancing enzyme permeability and improving enzyme solubility and reaction activity.
- The **magnesium ion (Mg²⁺)** demonstrated most significant effect on the interfibrillar substance removal and fiber bundle opening.

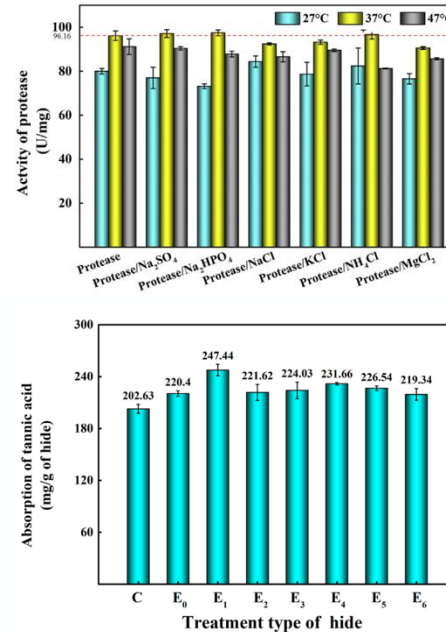


Fig. 4. Effect of different salt solutions on neutral protease activity at different temperature.

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

02. Efforts in Green Production of Leather

(Biochem. Eng. J. 2024)

MgCl₂-assisted neutral protease for sustainable beamhouse

Optimization

reaction time, temperature, enzyme concentration

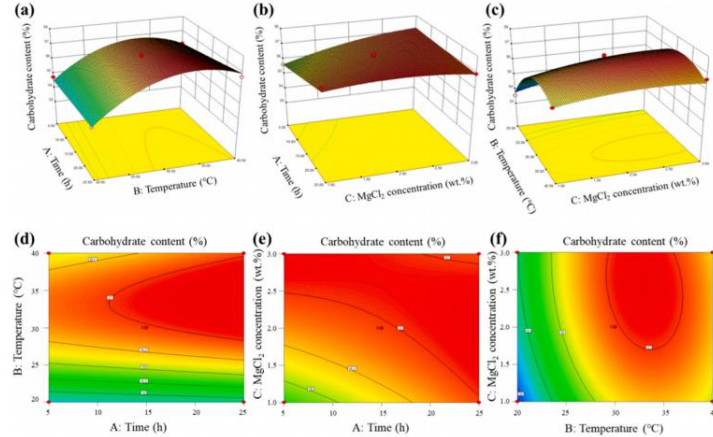


Fig. 6. RSM establishment of the samples.

- By carefully examining the interactions between key variables, we successfully streamlined the beamhouse process into a single step and identified the optimized conditions.
- This not only mitigates environmental impact but also offers impressive reductions in pollution.

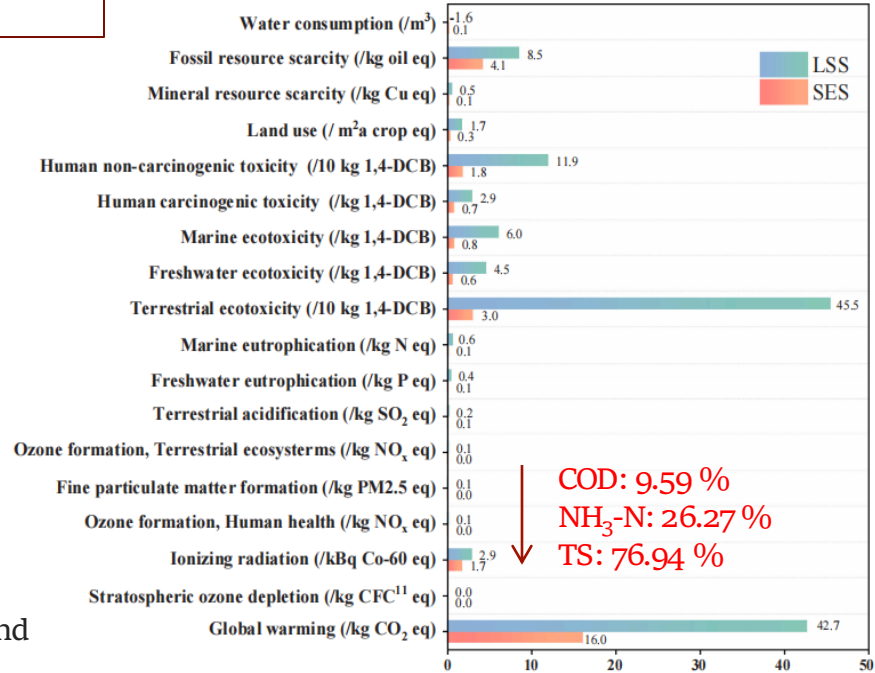
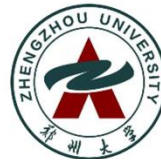


Fig. 7. Comparative analysis of environmental impact scores for producing 1 FU of cowhide using different methods.

03. Enzyme-Based Leather Processing: A Sustainable Solution

(Green Chem. 2024)

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

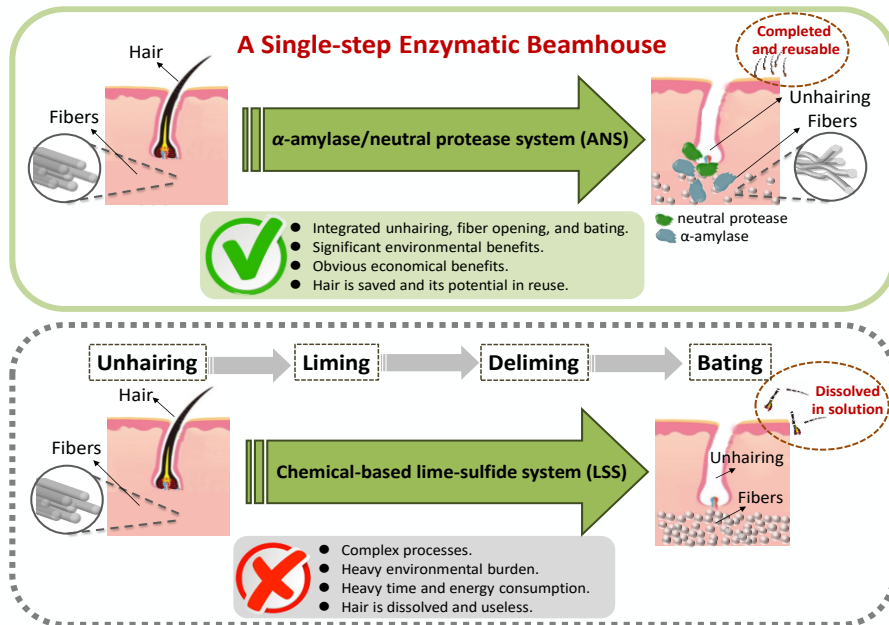


Fig. 8. The comparison of a single-step enzymatic beamhouse and traditional one.

- **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.

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

03. Enzyme-Based Leather Processing: A Sustainable Solution

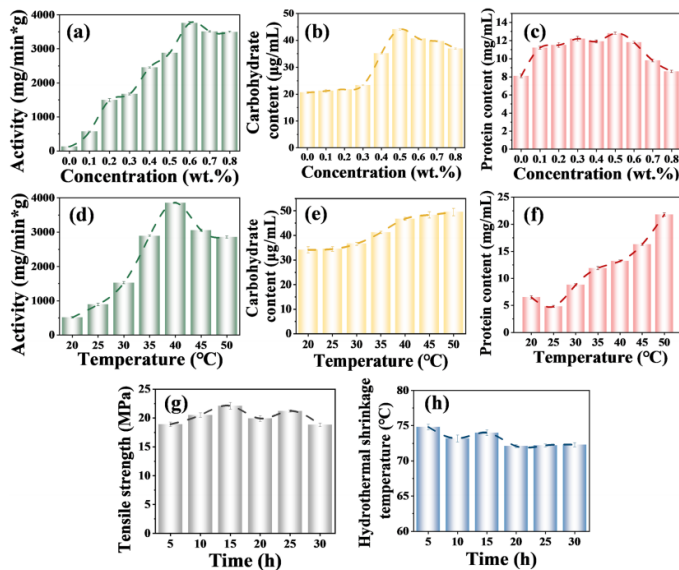


Fig. 9. The determination of predominant parameters.

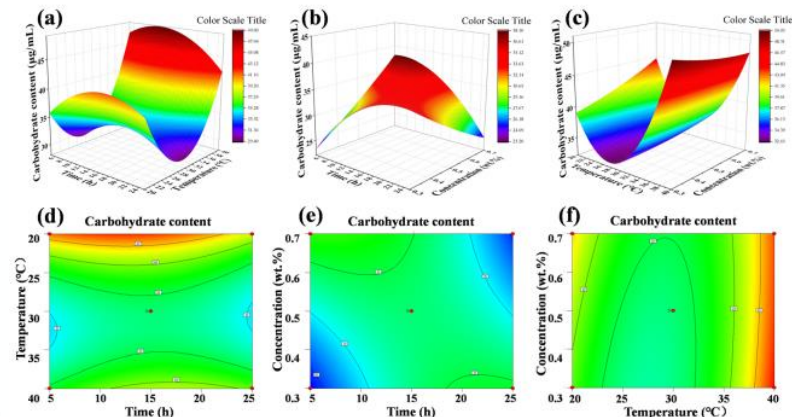


Fig. 10. The 3D response plots and 2D contour plots illustrating the impact of predominant parameters.

Optimization by RSM modelling

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

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:

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



$X_1=0.16$, **16.6h**
 $X_2=-0.16$, **28.4°C**
 $X_3=-0.18$, **0.5wt.% of neutral protein concentration**

03. Enzyme-Based Leather Processing: A Sustainable Solution

Unhairing and fiber opening assessment

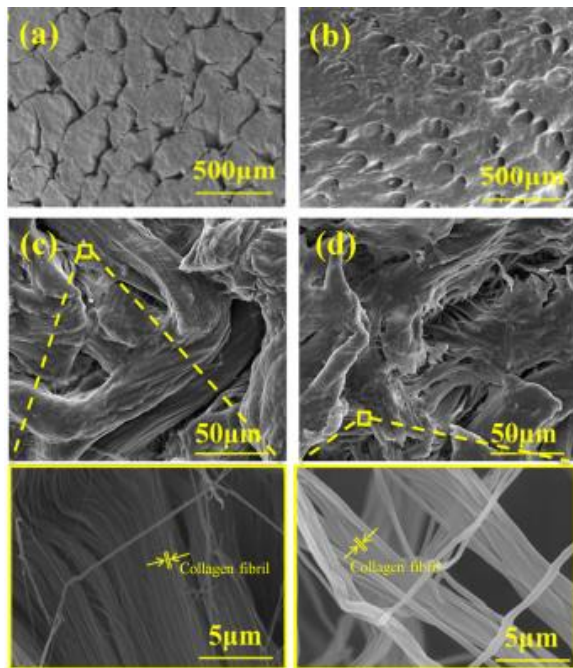
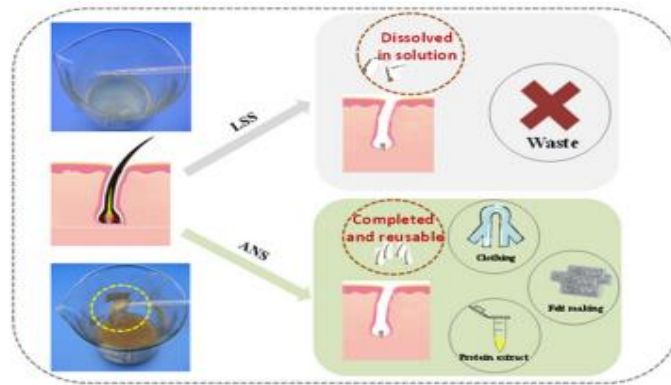


Fig. 11. The assessment of unhairing and fiber opening by SEM.



Unhairing and fiber opening assessment

- The optimized enzymatic method produced leather with 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.

03. Enzyme-Based Leather Processing: A Sustainable Solution

Bating assessment

collagen fibers

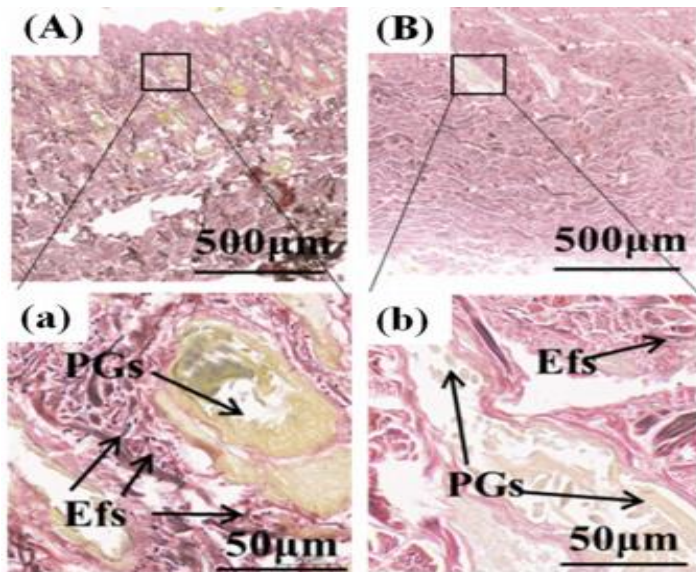


Fig. 12. The assessment of bating by Verhoeff's Van Gieson (EVG) staining: (A and a) the LSS and (B and b) the optimized ANS.

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.

03. Enzyme-Based Leather Processing: A Sustainable Solution



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 with the optimized enzymatic 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.

03. Enzyme-Based Leather Processing: A Sustainable Solution

Environmental benefits

Life cycle assessment (LCA)

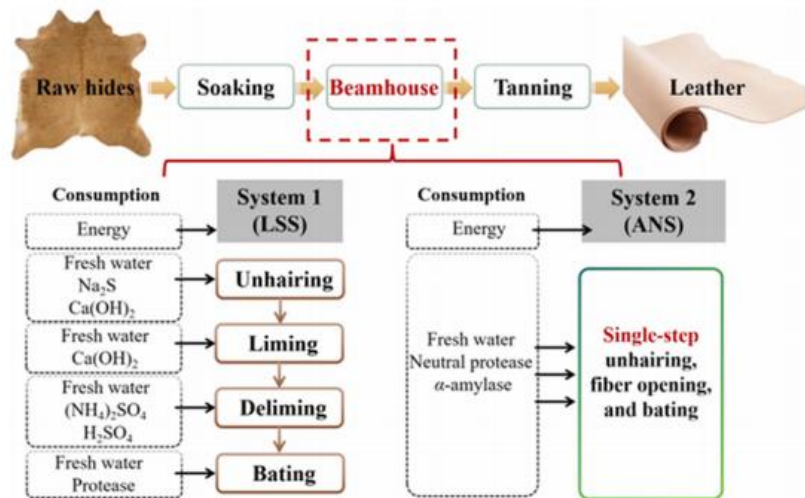


Table 3. Pollution loads in wastewater by different processes (kg/t).

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	0.28±0.10	0.03±0.10	0.20±0.02
	Total				
Pollution load reduction	-	90.44%	91.89%	98.19%	73.91%
Pollution load reduction of [1]	Enzyme unhairing NaOH-based fiber opening	43%			70%
Pollution load reduction of [2]	Pickle-less chrome tanning 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 chrome and fiber opening	53%			26%

[1] Thanikaivelan, P., Raghava, R.J., Unni, N.B., Ramasami, T. 2003. Biointervention makes leather processing greener: an integrated chrome and fiber opening 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: integrating 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 ₂ S ^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) ₂ SO ₄ ^a	0.0076	
		0.01 kg of H ₂ SO 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	
ANS	Energy	45 k W ⁻¹ h ⁻¹ of electricity ^e	3.8588	2.74
		0.01 kg of α-amylase ^d	128.8	
		3 g of neutral protease ^d	0.252	
	Single-step	1 kg of fresh water ^b	0.0009	
		24.95 k W ⁻¹ h ⁻¹ of electricity ^e		

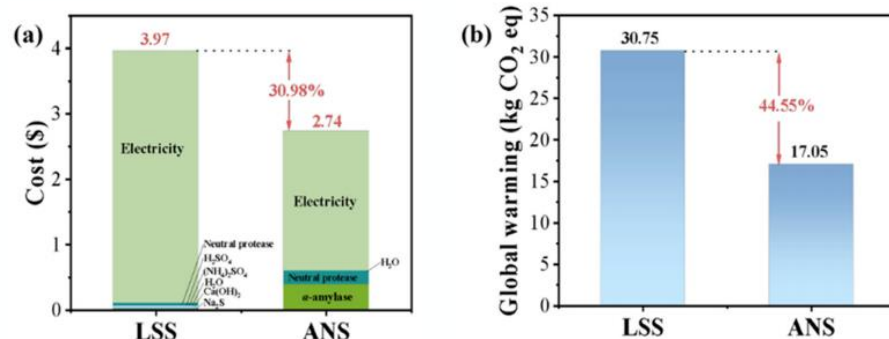


Fig. 14. (a) The cost estimation and (b) the global warming potential evaluation of the LSS and ANS.

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 CO₂ 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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