PILOT SCALE STUDY OF SULFIDE FREE ENZYMATIC UNHAIRING FOR ETHIOPIAN RAW MATERIALS: TOWARDS SUSTAINABLE AND CIRCULAR ECONOMY PATHWAY

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ABSTRACT

Enzymatic unhairing is an alternative to traditional sulfide-based unhairing processes in leather manufacture to achieve sustainable and cleaner methods. The leather manufacturers poised forward-thinking strategy to replace conventional methods. However, there are a series of challenges due to the sulfide-based unhairing methods, such as hair burning and emission of toxic gas. Introducing enzymes for unhairing process is the vision pursued by researchers for decades during leather production that eliminates sulfide use. Our recent project work on ***The Green Tannery Initiative: Enzymatic Unhairing and Sustainable Waste Utilization in Ethiopia's Leather Sector*** under Sustainable Manufacturing Environmental Pollution (SMEP) programme, commercial unhairing enzymes have been screened and chosen to standardize the enzymatic unhairing processes for Ethiopian raw materials.

Pilot-scale trials were carried out using drum method for cattle hides and paste and drum methods for sheep skins. The trials achieved complete hair recovery, enabling valorization of hair and fleshing waste into high-value by-products. The enzymatic process led to 100% elimination of sulfide, significant reduction in COD and TSS, with enhanced grain quality. The optimized enzymatic unhairing was completed within 12 hours, demonstrating both environmental and operational feasibility.

This paper will detail the optimized parameters for enzymatic unhairing of Ethiopian raw materials, compare the results with the conventional lime-sulfide process, and highlight the techno-commercial and environmental benefits of adopting enzyme-based systems as a sustainable pathway for leather production in Ethiopia.

Keywords: Enzyme; Unhairing; Protease; Sulfide-Free; Ethiopian Raw Material.

1. Introduction

The Ethiopian leather industry plays a vital role in the nation's economy, providing employment opportunities and contributing significantly to export earnings (Yimam 2025). However, the sector faces critical environmental challenges arising from the extensive use of hazardous chemicals, particularly sodium sulfide during conventional leather processing, coupled with inadequate waste management practices. These factors contribute to substantial water pollution, unpleasant odors, occupational health hazards, and environmental degradation (Thanikaivelan 2004).

In response, sustainable leather processing technologies have gained attention worldwide, particularly sulfide-free enzymatic unhairing, which eliminates or reduces hazardous chemicals in beamhouse operations (Kanth 2009). This study aims to investigate the feasibility, operational performance, and environmental benefits of enzymatic unhairing under Ethiopian conditions. By integrating waste valorization techniques, specifically the utilization of hair and fleshing by-products, the project seeks to support Ethiopia's transition towards a sustainable and circular leather industry.

2. Materials and Methods

2.1. Enzyme Selection

Commercially available proteolytic enzymes {Commercial Enzymes-A (CEA), Commercial Enzymes-B (CEB) and Commercial Enzymes-C (CEC)} were evaluated for their unhairing efficiency, compatibility with Ethiopian hides and skins, and environmental performance.

2.2. Processing Trials

Pilot-scale sulfide-free enzymatic unhairing trials were conducted on Ethiopian wet-salted sheep skins (Table 1 & 2) and cattle hides (Table 3) using both drum and paste application methods. Each enzymatic process was benchmarked against conventional sulfide-lime unhairing. The aim was to compare performance, optimize enzyme dosages, and record process modifications required for efficient hair removal under local conditions.

Table 1. Sulfide-free enzymatic unhairing trials of sheep skin using drum method

Enzyme Used	Chemical Offer (%)	Application Notes
CEA	0.75% Enzyme + 3% Lime	After 1 h of enzyme treatment, lime was added in three feeds with an interval of 1 h
CEB	1.5% Enzyme + 3% Lime	After 1 h of enzyme treatment, lime was added in three feeds with an interval of 1 h

CEC	0.2% Enzyme + 3% Lime	Following 30 min pretreatment with 5% (w/w) activator, enzyme was applied. After 3 h enzyme treatment, lime was added in three feeds with an interval of 1 h

Table 2. Sulfide-free enzymatic unhairing trials of sheep skin using paste method

Enzyme Used	Chemical Offer (%)	Application Notes
CEA	0.75% Enzyme + 3% Lime + 10% Water	Enzyme-based paste application for hair removal.
CEB	1.5% Enzyme + 3% Lime + 10% Water	Enzyme-based paste application for hair removal.

Table 3. Sulfide-free enzymatic unhairing trials of cattle hide using drum method

Enzyme Used	Chemical Offer (%)	Application Notes
CEA	0.75% Enzyme + 4% Lime	After 1 h of enzyme treatment, lime was added in four feeds with an interval of 1 h
CEB	1.5% Enzyme + 4% Lime	After 1 h of enzyme treatment, lime was added in four feeds with an interval of 1 h
CEC	0.2% Enzyme + 4% Lime	Following 30 min pretreatment with 5% (w/w) activator, enzyme was offered. After 3 h of enzyme treatment, lime was added in four feeds with an interval of 1 h

2.3. Environmental Assessment

The reduction of chemical oxygen demand (COD), total suspended solids (TSS), and sulfide levels in wastewater was measured. Effluent samples were analyzed according to Best Available Techniques (BAT) guidelines for tanning.

2.4. Quality Evaluation

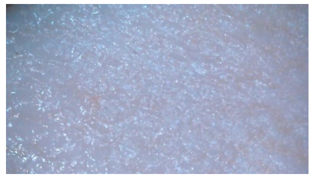
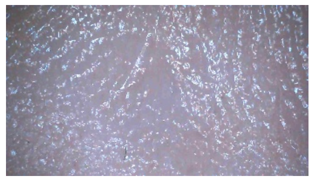
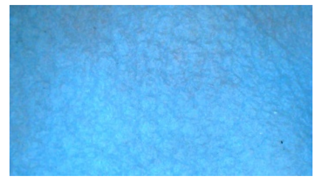
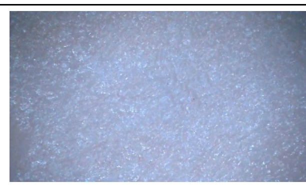
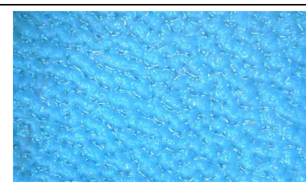
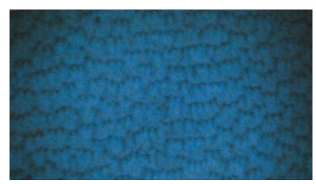
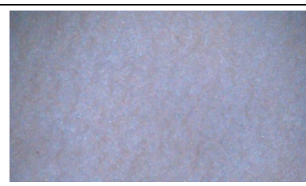
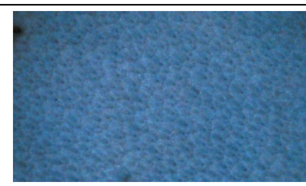
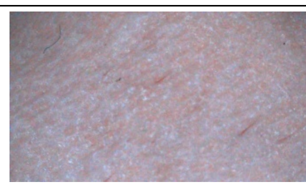
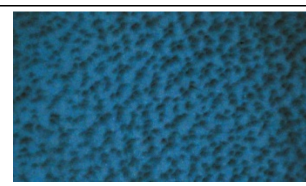
Leather quality was assessed through tensile strength, tear load, and aesthetic characteristics. The results were compared with UNIDO Acceptable Quality Standards for chromium-tanned garment leathers (IS 12718:1989).

3. Results and Discussion

3.1. Enzyme performance

The three enzymes evaluated: Commercial Enzymes-A (CEA), Commercial Enzymes-B (CEB) and Commercial Enzymes-C (CEC) demonstrated distinct operational characteristics, making them suitable for different processing conditions and raw material types.

Table 4. Microscopic images of the experimental pelt and leather

Enzyme	Material	Method	Enzymatically Unhaired Pelt	Enzymatically Unhaired Wet Blue Leathers
CEA	Sheep	Paste		
	Sheep	Drum		
CEB	Sheep	Paste		
	Sheep	Drum		
CEC	Sheep	Drum		
	Cow	Drum		

CEA trials showed specific suitability for skins in pasting applications**,** requiring a minimum of 16–20 hours processing time to achieve complete unhairing. For hides, the optimum enzyme dosage was 0.5–0.75%**,** while pasting applications for skins required 0.75–0.85%**.** One operational advantage of CEA is that it does not require pH adjustment of the soak liquor, potentially simplifying the process and reducing chemical inputs. In drum method trials, a minimum of 12 h was required for effective unhairing, indicating that CEA trials operate at a slower reaction rate compared to CEB trials but may offer gentler fiber treatment.

CEB was effective for both pasting and drum applications, though results indicated it may be more suitable for pasting applications in skins. The recommended enzyme dosage for pasting applications was 1.5–1.75%**,** higher than that for CEA and CEC trials, but this was compensated by superior fiber opening and swelling observed during trials. This enhanced fiber opening can contribute to better penetration of tanning agents and potentially improve softness and handle in the finished leather. However, in the case of short-haired skins, CEB trials required drum scudding followed by mild bating operations**,** adding an extra mechanical step to achieve optimal unhairing results.

CEC trials proved to be versatile, being suitable for both hides and skins**.** But it can be used for drum based enzymatic unhairing methods. The manufacturer recommends pH adjustment prior to enzyme addition**,** ensuring the optimal activity range is achieved. Processing temperatures between 25–35 °C were identified as ideal for maintaining enzymatic efficiency. The optimum dosage was relatively low, with 0.1–0.15% for hides and 0.15–0.2% for skins**.** This lower application rate, combined with its compatibility with both raw material types, suggests CEC trials could offer cost-effective operation with reduced enzyme consumption.

3.2. Environmental Impact Reduction

3.2.1. Wet salted sheep skins

3.2.1.1. COD (Chemical Oxygen Demand) Analysis

Chemical Oxygen Demand (COD) measures the total quantity of oxygen required to chemically oxidize organic matter in wastewater. High COD values indicate higher organic pollution load, which directly affects water quality and increases the cost of effluent treatment.

Table 5. Chemical oxygen demand analysis for the enzymatic experimental trial of sheep skin

Enzymatic trials	COD (g/skin)
CEA (D)	77.28
CEB (D)	60.35
CEC (D)	58.54
CEA (P)	85.29
CEB (P)	55.72

In the enzymatic unhairing trials, COD values ranged between 55.72 and 85.29 g/skin, depending on the enzyme used and the method of application (drum or paste).

For comparison, the IUE 6 reference for conventional unhairing/liming processes (soaking to bating stage) is 250–600 g/skin (Table 5). This means enzymatic methods achieved an average COD reduction of about 72% compared to standard chemical processing. This significant decrease demonstrates the environmental advantage of replacing sodium sulfide-based unhairing with enzymatic methods.

3.2.2. Wet salted Cattle hides

Table 6. Effluent analysis for the enzymatic experimental trial of cattle hides using CEC system

Parameter	Enzymatic Trials	Conventional Technology*	% Reduction
S^{2-} kg/ton	0	2-9	100.00
COD kg/ton	34.85	130	73.19
TSS kg/ton	36.17	93	61.11

The enzymatic trials have the complete elimination of sulfide in wastewater (0) compared to 2–9 kg/ton in conventional processes (Table 6). This represents a 100% reduction in one of the most hazardous pollutants from tanneries, which is responsible for toxic gas emissions (H_2S), bad odor and high aquatic toxicity.

For cattle hides, COD values in enzymatic processing averaged 34.85 kg/ton, while conventional sulfide-liming produced 130 kg/ton. This equates to a 73.19% reduction (Table 6). When compared to IUE 6 BAT values (120–160 kg/ton), enzymatic COD levels are substantially lower, showing performance well beyond the “good practice” benchmark. TSS values in enzymatic processing were 36.17 kg/ton, compared to 93 kg/ton for conventional processes a 61.11% reduction. The IUE 6 BAT range for TSS (70–120 kg/ton) is again much higher than the enzymatic results, indicating cleaner effluent with less particulate matter (Table 6).

3.3. Strength Performance of Sheep Garment Leather from Enzymatic Unhairing Trials

Two key mechanical properties were evaluated and are given in the Table 7.

- Tensile Strength (N/mm^2): a measure of the leather’s resistance to breaking under tension, reflecting the integrity of collagen fibers.
- Double-Edge Tear Load (N/mm): an indicator of the leather’s resistance to tearing, important for garment durability during use.

Average tensile strength of 14.88 N/mm^2 when expressed as given in the trials, The Standard Requirement: 13–17 kg/mm^2 (IS 12718:1989). Most enzymatic trials fall within or near the recommended range, showing adequate fiber strength for garment applications. Highest value: CEA at 19.8 N/mm^2 – exceeds the upper limit of the reference range, indicating very strong fiber structure. Lowest value: CEB at 10.4 N/mm² – below the standard, suggesting possible localized fiber weakening (likely due to raw material variability or processing inconsistencies).

Tear Load: UNIDO Recommendation is ~15 N/mm. It is observed that all enzymatic leathers exceed this benchmark. This implies that tear resistance is significantly higher than the minimum acceptable value, indicating excellent structural cohesion and durability in all samples. Even the lowest tear load (36.5 N/mm) is well above the recommended minimum.

Table 7. Strength characteristics of the enzymatically unhaired sheep garment leather

S. No.	Enzymatic Trial	Tensile Strength (N/mm²)	Tear Load (N/mm)
1.	CEA-Drum	16.9	42.5
2.	CEB-Drum	10.4	42.0
3.	CEC-Drum	11.2	53.1
4.	CEA-Paste	19.8	46.9
5.	CEB-Paste	15.5	36.5

These results indicate that enzymatic unhairing can produce leather meeting or surpassing standard strength requirements for garment use. The higher-than-required tear loads demonstrate that the process maintains fiber integrity, while avoiding the over-degradation sometimes associated with aggressive chemical treatments. From an industrial perspective, these mechanical property results strengthen the case for enzymatic unhairing as a sustainable, high-quality alternative to sulfide-based processing.

3.4. Solid Waste Generation in Enzymatic Unhairing Trials

Enzymatic unhairing differs from conventional sulfide-based processing in that it allows hair to be removed intact rather than dissolved into the effluent. This shift transforms hair from a pollutant into a recoverable by-product, opening opportunities for waste valorization. Similarly, fleshing waste, the fatty and connective tissue removed from hides and skins, can be recovered for further processing rather than contributing to wastewater solids.

Table 8. Percentage of hair waste generation from the enzymatically unhaired hides/skins

Enzyme	Raw Material	Method	Hair (kg/t, 0% moisture)
CEC	cattle	Drum	13.21

CEC	sheep	Drum	463.66
CEA	sheep	Drum	377.54
CEB	sheep	Drum	406.36
CEA	sheep	Paste	273.87
CEB	sheep	Paste	307.27

From the table it is observed that cattle hides yield much lower hair mass (13.21 kg/t) than sheep skins because short cattle hair. For sheep skins, the highest hair recovery was 463.66 kg/t (CEC: drum method) and the lowest was 273.87 kg/t (CEA: paste method) (Table 8). Drum method consistently yielded more hair mass than paste method, indicating hair detachment efficiency. These intact hair wastes are suitable for further use, such as in fertilizer production, amino acid extraction, keratin recovery, or as raw material in brush and felt manufacturing, offering potential economic value.

Table 9. Percentage of fleshing waste generation from the enzymatically unhaired hides/skins

Enzyme	Raw Material	Method	Flesh (kg/t, 0% moisture)
CEC	Cattle	Drum	61.42
CEC	Sheep	Drum	22.44
CEA	Sheep	Drum	33.3
CEB	Sheep	Drum	46.97
CEA	Sheep	Paste	7.75
CEB	Sheep	Paste	10.21

Cattle hides produce the highest fleshing waste (61.42 kg/t) due to thicker dermal layers and subcutaneous fat content (Table 9). Among sheep skins, drum method trials generated more fleshing waste than paste method. These fleshing wastes, being free from heavy chemical contamination in enzymatic processes, are more suitable for animal feed supplements, gelatin/collagen production, biofuel feedstock, or organic fertilizer.

4. Conclusions

The pilot-scale trials demonstrate that sulfide-free enzymatic unhairing is a viable alternative to conventional chemical methods in Ethiopia’s leather industry. The process significantly reduces environmental pollution, particularly COD, TSS, and sulfide loads, while maintaining leather quality. Furthermore, the recovery of solid wastes for valorization supports sustainable and circular production models. Wider adoption could yield substantial environmental, economic, and occupational health benefits for the Ethiopian leather sector.

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