

# An integrated cleaner technology for minimization of pollution using enzymes and auxiliaries in leather manufacture



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- An **integrated non-ammonia bating, salt-free pickling and high exhaustion chrome-tanning technology** was designed and optimized.
- **Ammonia-nitrogen and chloride pollution** are almost eliminated by using salt-free pickling auxiliaries and acidic proteases.
- The **Cr utilization** ratio was increased to **94.9%** from 80.4% and the residual Cr concentration in the tanning liquor dropped to **294 mg/L** from 1134 mg/L.
- TN, TOC and COD were reduced by 75.7%, 37.1% and 45.2%, respectively.

## Introduction

- **Ammonium salts** are commonly used in enzymatic pelt **bating** and the previous **delimiting** processes to ensure the enzyme can achieve perfect bating performance.<sup>1-2</sup>
- **Sodium chloride** is necessary in the **pickle float** to avoid acidic swelling of collagen fiber in conventional chrome-tanning procedures.<sup>2</sup>
- Uptake ratio of **Cr** in the conventional chrome-tanning method is just about **60% - 80%**.<sup>3</sup>
- **Ammonia-nitrogen (NH<sub>3</sub>-N), chloride (Cl<sup>-</sup>) and Cr-containing wastewater from bating and chrome-tanning processes** is one of the major hazards restricting the **sustainable development** of the leather industry.
- **In this study, an integrated non-ammonia bating, salt-free pickling and high exhaustion chrome-tanning technology** was designed and optimized to minimize nitrogen, chloride and Cr pollution.

## Material and Methods

- Assay of caseinolytic and collagenolytic activity.<sup>4-5</sup>
- Bating pickling pelts with different acidic proteases.
- Bating delimiting pelts by conventional trypsin bating method.
- Test item of liquor and leather:
  - ✓ Soluble protein and hydroxyproline.
  - ✓ Histological analysis of elastin and collagen fiber.
  - ✓ Scanning electron microscopy.
  - ✓ Cr content and shrinkage temperature.
  - ✓ Physical and organoleptic properties.
  - ✓ NH<sub>3</sub>-N, Cl<sup>-</sup>, Cr, TN, TOC and COD.

## Results and Discussion

### ◆ Characteristics of acidic proteases

| Protease (pH 3.5, 40 °C)    | E1     | E2     | E3     |
|-----------------------------|--------|--------|--------|
| Caseinolytic activity (F)   | 222049 | 337956 | 745459 |
| Collagenolytic activity (H) | 20117  | 22585  | 57316  |
| H/F                         | 0.09   | 0.07   | 0.08   |

- All of the selected acidic proteases exhibited the maximum activities at pH 3.5.
- The collagenolytic activity per unit of caseinolytic activity was found to be approximately 0.08.

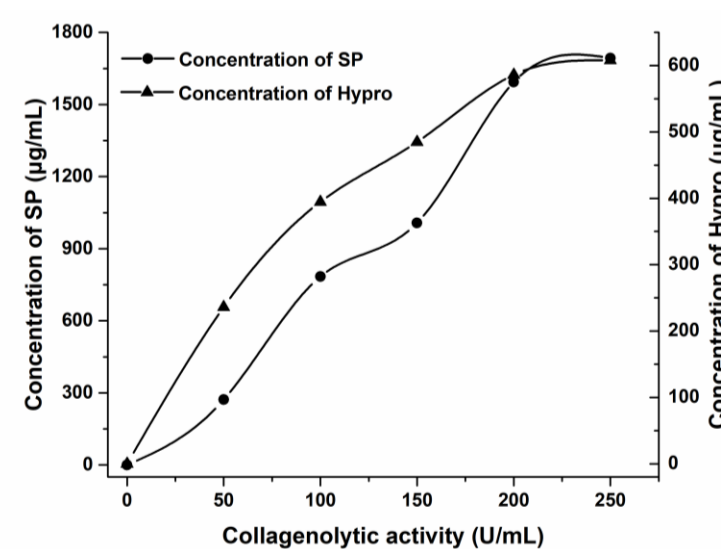
### ◆ Bating effectiveness of acidic protease

#### ➤ Bating performance of acidic proteases

| Proteases | Soluble protein (μg/mL) | Hypro (μg/mL) | Softness (mm) |
|-----------|-------------------------|---------------|---------------|
| E1        | 703                     | 329           | 8.2           |
| E2        | 782                     | 381           | 8.4           |
| E3        | 1024                    | 525           | 8.8           |

- ✓ Acidic protease E3 could significantly remove the inter-fibrillary substances in collagen fiber bundles along with improved softness and general appearance of the crust leather.

#### ➤ Optimizing of bating conditions

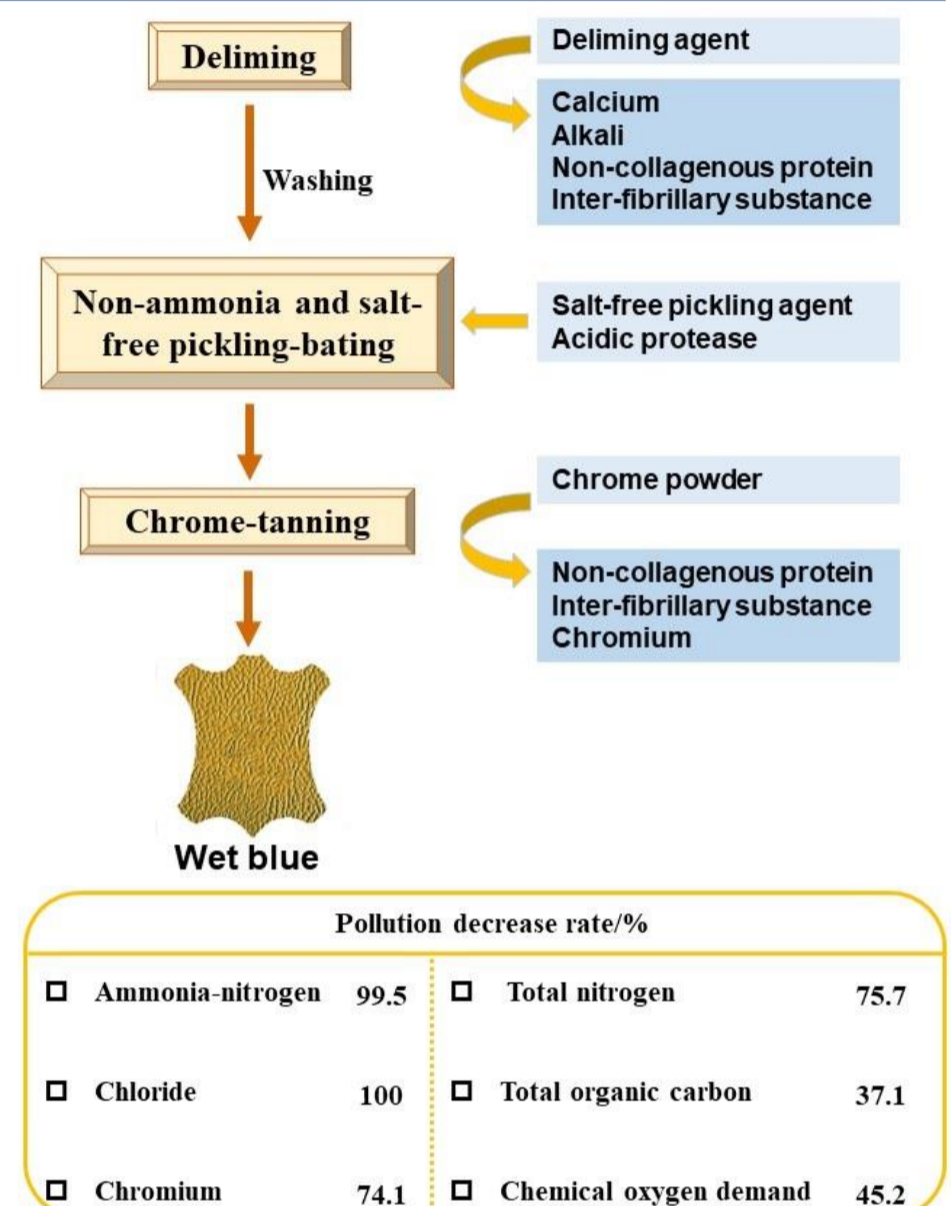


- ✓ **Optimum integrated salt-free pickling-bating technology:** pH 3.5, 150 U/mL of acidic protease E3 run for 3 h at 25 °C, and 12 h at pH 2.8.

### ◆ Comparison of the bating effectiveness and environmental benefits of the novel integrated salt-free pickling-bating method and conventional trypsin bating method

| Protease                | E3    | Trypsin |
|-------------------------|-------|---------|
| Dosage (%)              | 0.133 | 1.000   |
| Collagenolytic (U/mL)   | 150   | 103     |
| Elastinolytic (U/mL)    | 0.0   | 1.0     |
| Soluble protein (μg/mL) | 1583  | 1933    |
| Hypro (μg/mL)           | 514   | 68      |
| Desmosine (μg/mL)       | 0.0   | 0.4     |

## Results and Discussion



## Conclusions

- The novel integrated non-ammonia and salt-free pickling-bating technology almost eliminated the NH<sub>3</sub>-N and Cl<sup>-</sup> pollution from bating and pickling effluent, and reduced the chromium pollution in chrome tanning wastewater, by using salt-free pickling agent and 150 U/mL of acidic protease.
- The residual concentrations of TN, TOC and COD in wastewater were lower compared with the conventional leather manufacturing wastewater.
- The physical and organoleptic properties of the crust leathers were found to be comparable to and even better than that of the conventional method.

## References

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## Acknowledgements

The National Key Research and Development Program of China (2017YFB0308402)