Green and Clean Deliming Technology With Acetic Acid - Sodium Acetate Buffer For Removal Of Ammonia - Nitrogen From Leather Manufacturing Process

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Green and Clean Deliming Technology With Acetic Acid - Sodium Acetate Buffer For Removal Of Ammonia - Nitrogen From Leather

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Manufacturing Process

Abstract

The pollution of Pretanning operations of tanneries is of high concern. The search of technologies to reduce the consumption, time and cost of chemicals in leather manufacturing process can reduce the environmental impact. Deliming is an important step in beamhouse process sequence that follows the liming operation. During liming, the hides and skins are

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treated with calcium hydroxide (lime) and sodium sulphide to encourage the fibre swelling, plumping and unhairing, but along with this operation the system is reached in a high pH (typically above 12.5) region. The regular deliming process with Ammonium salts tries to minimize this high alkalinity slowly and steadily, bringing the pH down to a more neutral range suitable for following operations like bating and pickling. The consequence of conventional deliming operation is

the production of ammoniacal nitrogen, which is toxic and dangerous for our environment. The application of a carefully selected buffering system, such as sodium acetate and acetic acid, is essential to control the pH and also reduce the pollutional load.

Keyword – Elimination of Ammonia – Nitrogen from Beamhouse, Sodium Acetate and Acetic Acid buffer

1. Introduction

The leather engineering process is an intricate series of chemical and mechanical procedures planned at transforming raw hides or skins into sustainable leather[2]. While crucial for producing high-quality leather, several stages in this process have significant environmental impacts, particularly deliming and pickling[1]. These operations involve the use of various chemicals that can generate environmental pollutants, contributing to ecological balance disturbance if not managed properly[2].

Deliming is a step after the liming process, where the excess and unreacted lime materials along with alkaline swelling agents is taken out of the hide and skin[2]. This process usually involves the use of ammonium (sulphate and chloride) salts together with buffers to eventually bring the pH to the right level or to the neutral range for enzymatic bating[3]. Nevertheless, its effluent contains ammonia, calcium, nitrogen and residual organic matter in higher concentrations. If they are not treated properly, such effluent can be detrimental to the water quality and they would also raise the biochemical oxygen demand (BOD) in the water[3]. The most important, even though undesired, environmental concern is related to ammonia emission damaging the aquatic life with its eutrophication and toxicity[3], respectively.

The deliming process, that is the preparation of the pickling operation, further deposits onto the environment substances such as sulfuric acid and sodium chloride[5], which are used in the pickling process. The main purpose of pickling is a decrease in pH level and so an increase in tanning agents' permeability[10]. Nevertheless, pickling

effluents with a high concentration of salt, acidity, and sulfate are the most common pollutants when they are released into water bodies[5], which can thus change the osmotic balance of the aquatic organisms, and thus

soil and water salinity is one of the consequences[4]. This is a threat to the biodiversity and the agriculture productivity[8].

Pretanning steps like deliming and pickling are linked with the environmental concern, so it is important to measure and reduce their pollutional impacts[7]. This research work proposes the new technology to reduce the operational cost with elimination of the pickling operation. By progressing our understanding of these effects, the research pursues to inform the expansion of more sustainable practices in leather making, contributing to ecological safety and regulatory compliance.

In the deliming steps of leather manufacturing, the sodium acetate and acetic acid buffer system plays a crucial role in cautiously controlling the pH and removal of free and bound lime from the leather matrix to confirm effective deliming without damaging the leather structure. The main purpose of this buffer is to maintain and regulate the pH in neutral region or slightly acidic range.

pH Control : The sodium acetate and acetic acid buffer system supports to regulate the pH within a controlled range i.e., pH 5.34 (in this case). By using a weak acid (acetic acid) and its conjugate base (sodium acetate), the buffer resists drastic changes in pH.

The buffer system safeguards a slow pH reduction from the highly alkaline condition (pH > 12) to around pH 5-6. This gradual pH modification is vital to prevent acid swelling, a condition where collagen fibres swell extremely and become spoiled if exposed to a sudden drop in pH.

2. Materials and Methods

2.1. Materials

Raw Materials: Raw goat skins were collected. Each skin was cut from butt portion to ensure uniformity in experimental and control procedures.

Chemicals: Acetic acid (glacial 100%, sp. gr. 1.05, analytical grade, Merck) and sodium acetate (Merck Lab grade) and normal distilled water were used to prepare the pH 5.34 buffer solution. Conventional deliming chemicals such as ammonium chloride and sulphate were used for comparison. BCS powder (from Bayer AG) was taken for chrome tanning purpose. All chemicals were collected from authorised suppliers to maintain consistency and reliability in experimental results.

Equipment: pH meter (WTW, calibrated with pH 4,7 and 10 buffer for accurate readings), mechanical steel drum (Ronald) for the mechanical process, analytical balance (Metrohm India Private Ltd.).

2.2. Experimental Design

The experiment aimed to test the efficacy of a sodium acetate and acetic acid buffer (pH 5.5) in the deliming process and its effect on both leather quality and environmental pollution. The experiment was designed into two main groups: the test group (using sodium acetate and acetic acid buffer system) and the control group (using conventional ammonium- salt based deliming system).

2.3. Preparation of Buffer Solution

The acetic acid and sodium acetate buffer solution was prepared by using the Henderson-Hasselbalch equation.

= 4.74

pH = 4.74 + 0.6 = 5.34

Acetic acid was gradually added to the sodium acetate solution while monitoring the pH with a WTW pH meter until a stable pH of 5.34 was achieved.

The prepared buffer solution was stored in a sealed container and used for the deliming treatment.

2.4. Deliming Procedure

In this research goat skins are taken for both conventional and new technique. In both cases same conventional steps are followed up to fleshing operation. Then pelt weights are taken and treated with two different technology.

Sample Treatment: Small parts of limed (after fleshing) goat pelts were weighed and put in to deliming bath in a laboratory-scale in sample steel drums. The test group was treated with the acetic acid and sodium acetate buffer solution (pH 5.34), while the control group was delimed using a conventional ammonium chloride and ammonium sulphate solution in separate sample steel drum.

Application Parameters for test samples:

Volume of deliming solution for test materials: 100 ml buffer solution based on the weight of the goat skins.

Temperature: Room temperature condition.

Duration: The deliming process was carried out for 3 hrs, with constant monitoring of the pH and mechanical agitation to ensure uniform penetration of the chemicals.

Process – Acetic acid + Sodium acetate deliming Raw materials used – Goat skin All % are based on raw skin weight (Conventional process)

Unit operation Chemicals % Time and pH Remarks

Soaking Raw Goat Skin Water - 200% Wetting agent - 0.5% Preservative - 0.5%

Check softness.

4 to 5 hours pH – 7.0

Drain Wash

Liming Raw Goat skin Water - 200% Calcium hydroxide – 6% Sodium sulphide – 3%

Check pH and Unhairing

12 to 14 hrs pH – 12.5

Then Drain Wash

Hand Fleshing done with blunt knife and then take the pelt weight then wash it with water. Now All % are based on pelt weight

Prepared a buffer solution with sodium acetate, acetic acid and water using Henderson–Hasselbalch equation. The percentages are as follows: Water - 100 ml Sodium acetate - 8.3 g (i.e., 8.3%) Acetic acid - 1.44 ml (M= 60.05 g/mol, 1L= 1.05 kg) Checked the pH of this buffer solution is 5.34 and start deliming with this solution

Deliming 100 ml Buffer solution 4% NaCl salt

3 hrs pH – 5.34

Complete deliming Drain the bath Chrome Tanning No float

Run over night

6% BCS powder

Basification Sodium sulphite

Next day complete penetration of chromium in cross-section of skins, colour is little dark blue unlike normal process and then determine shrinkage temperature.

Deliming Efficacy

Deliming efficacy was confirmed by checking the cross section of the pelt by addition of phenolphthalein indicator solution and the absence of pink colour indicates the complete deliming process.

3. Chemical reaction

For complete deliming in leather manufacturing process, calcium ions ($Ca^{2}z$) from the calcium hydroxide used in the liming step needs to be removed from the skin matrix. The acetic acid and sodium acetate components of the buffer reacts with the calcium ions present in the skin protein matrix to form soluble calcium acetate, which can be effortlessly washed away from the system to obtain proper deliming results.

This solubilization supports in the effective removal of surplus lime and calcium compounds, reducing the risk of calcium carbonate deposition within the leather fibre.

$2CH3COONa + Ca(OH)2\ (CH3COO)2Ca + 2NaOH$

→

Calcium acetate is soluble in water.

Table 1: Results of physical testing

Parameter Testing sample 1

Testing sample 2

Testing sample 3

Control Minimum requirement Shrinkage temperature

92oC 93oC 91oC 100oC 70oC above

Table: 2 . Technical properties of the chrometanned leather (1 = Poor 2 = Fair 3 = Good 4 =

Very Good 5 = Excellent)

Parameter Testing sample 1 Testing sample 2 Testing sample 3

Hand feelings 4 4 4

Fullness 4 4 4

Roundness 4 5 4

Penetration 5 5 5

Colour Uniform 4 Uniform 4 Uniform 4

4. Conclusion

Ammonium salts are used in deliming during leather processing, which is a big environmental, health and safety concern for discharge of ammonium salt in the industry. The above problem has been solved by the emergence of ammonium salt free deliming process in leather processing which is developed using eco friendly materials like sodium acetate and acetic acid buffer solution.

However, the amount of water employed in the present ammonium salt free deliming system is similar to that of conventional process but pickling operation can be avoided which ultimately reduce the cost and overall water consumption.

Thus sodium acetate and acetic acid buffer solution could provide alternative solution to ammonium salt free deliming process, which is of great environmental and safety concern.

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