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# Green Preservation of Goatskin to Deplete Chloride from Tannery Wastewater

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#### Abstract

Globally, in wet-salting preservation, common salt (sodium chloride, NaCl) is generally used for the raw animal skin, which emits a huge amount of chloride-containing wastewater, affecting groundwater quality and human and plant life. Chlorides in tannery wastewater encourage salt-free or less-salt preservation methods of raw skin. In this study, an alternative salt-free "green method" has been described for goatskin preservation with rapidly growing obnoxious weeds like *Sphagneticola trilobata* leaf. The 'green leaf paste' was applied on the flesh side of the raw goatskin and compared with the conventional wet-salting (50% NaCl) method for 28 days. Different parameters of both samples, like moisture, nitrogen, hydrothermal stability, and bacterial growth, were periodically assessed and compared. Shoe upper leather was produced from both preserved goatskins. After comparing with standards, the physical properties like tensile strength, elongation at break, and bursting strength satisfied the standard requirements. SEM images showed no deterioration to the fiber structure of both samples. Moreover, the suggested method reduces the pollution loads: chloride, total dissolved solids, biochemical oxygen demand, and chemical oxygen demand by 98.04%, 92.9%, 90.2%, and 85.5%, respectively. The overall assessment recommends that the salt-free 'green method' utilizing *S. trilobata* leaf paste could be an attractive system over the conventional wet-salting method.

Keywords: Sphagneticola Trilobata; Salt Diminution; Pollution Load; Soaking; Leaf Paste.

# **1. Introduction**

Hide/skin, a byproduct of the meat industry, is the natural raw material for the tanning industry. The existence of this industry began with the raw hide/skin, received from the meat industry. Being a natural organic material, hide/skin tends to deteriorate with time after flaying, which contradicts the purpose of leather processing. The raw hide/skin is susceptible to the invasion of microbes, which begins within 5-6 h following the mortality of the animal [1]. In order to produce quality leather, raw hide/skin needs to be preserved immediately after flaying to prevent bacterial deterioration.

The term "preservation" or "curing" has been introduced as a solution to stop the degradation of raw animal skin with the purpose of storing and safe transportation. The ideal preservation method, whether physical, chemical, or other, is expected to be reversible to the original raw condition of the hide/skin in an environmental-friendly process. Common salt, sodium chloride (NaCl), is the most popularly used curing agent [2, 3] due to its dual effect of dehydration and bacteriostatic effect on hide/skin at a very convenient price and availability. It is reported that

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approximately 6.5 million tons of hide/skin on a wet salted basis are processed globally per annum, discharging 2.6 million tons of salt in the soaking process alone [4, 5]. With growing concerns about available freshwater, the chloride (Cl<sup>-</sup>), total dissolved solids (TDS), and salinity added to freshwater from the conventional wet salting preservation of raw hide/skin as well as the soaking of the leather industry are raising questions. Moreover, halophilic bacteria that thrive in high salt concentration can cause red spots on the flesh side of the salt-cured hide/skin and produce red heat damage on the final leather [6].

Alternatives to several preservation techniques have been adopted by controlling moisture content, viz. in sundrying [7], controlled drying [8], or by controlling the action of microorganisms like using powder biocide or irradiation. These techniques are either cheap and affect the quality of the leather or expensive to apply in the industry. Salt-free chemical preservation techniques have also been tried, including ozone [9], sulfites [10], bacteriocin compounds [11], and silicate [12] in low salt skin preservation trials. However, the resultant soaking liquor after the preservation raised concern about the increasing chemicals in the wastewater.

Some salt-less preservation systems, like cooling and chilling [13], vacuum [14], dry ice [15], boric acid [9], silica gel [16] have been adapted for laboratory and pilot scale. The limitations with these methods are that the preserving agents are hazardous themselves, expensive to carry out, or not practically adaptable. Organic plant extracts like *Moringa oleifera* [17] have been applied as an alternative organic preservative. Utilization of *Citrus limon* leaf extract [18] and extracted oil from *Aphanamixis polystachya* seed [19] for preservation is a recent and well developed approach, but the preparation of the leaf and oil extract requires extra attention. *Rumex abyssinicus* with salt has also been tried for preservation, but it affects the strength and other properties of the final leather [20]. Therefore, it has become a challenge to find a suitable preserving agent that can preserve the skin in an environmentally safe condition, is available, and is inexpensive to use.

*Sphagneticola trilobata* plant, locally known *as "bhringraj"*, is sometimes grown as an ornamental herb in the garden but grows rapidly into the surrounding region vegetatively. It quickly forms a dense cover on the ground and prevents other plants from regenerating. It is considered a noxious weed that grows abundantly on agricultural land, on roadside urban waste dumping grounds, and in other disturbed areas. This weed invades along canals, streams, and the borders of mangrove marshland and coastal vegetation. The IUCN has listed *S. trilobata* as one of the world's 100 worst invasive species [21].

In this study, *S. trilobata* plant leaf paste has been applied to preserve the goatskin without any salt (common salt). The proposed work speculated that applying green leaf paste as a salt-free curing agent to preserve goatskin for short term. The qualitative and quantitative analysis of the investigation verified the conjecture. The plant extract has been found to have antibacterial and antifungal activity [22]. The preservation process was evaluated by various parameters: moisture content, odor, hair slip, bacterial count, extractable nitrogen, thermal stability, and leather quality in comparison to the conventional preservation method for 28 days. The parameters of pollution load were assessed and compared with the standard limits.

# 2. Materials and Methodology

#### 2.1. Materials

### 2.1.1. Skin and Plant Extract Collection

Freshly flayed goatskins of the average weight of 1 kg per goatskin were purchased from a nearby local slaughterhouse, Khulna, Bangladesh. The *S. trilobata* leaf was collected from the university campus of Khulna University of Engineering & Technology, Khulna, Bangladesh, and pasted using laboratory mortar for the experiment (Figure 1). The freshly prepared leaf paste was applied on the fresh side of the goatskin.



Figure 1. (a) Sphagnetcola triloata leaf and (b) leaf paste

#### 2.1.2. Salt and Chemicals

Commercial sodium chloride (NaCl) and auxiliaries were used for the preservation process. The pre-tanning and post-tanning processes for the shoe upper leather were conducted with industrially used chemicals. Analytical grade chemicals were used for testing and other experiments.

#### 2.2. Experimental Modelling and Applications

Figure 2 shows applied goatskin for the preliminary experiment. The preliminary experiment was conducted to define the minimal amount of leaf paste required for the preservation. Five (5) samples of an average area of 900 cm<sup>2</sup> cut from the freshly flayed goatskin. The leaf paste materials were offered 10, 15, 20, 25, and 30%, based on raw goatskin weight (w/w).



Control (50% Common salt) Experimental (20% Green leaf paste)

Figure 2. Preliminary experiment with green leaf paste

Figure 3. Comparison between experimental and control sample

Periodically, preserved goatskin was assessed for different intervals: fresh (raw), 1<sup>st</sup>, 2<sup>nd</sup>, 4<sup>th</sup>, 7<sup>th</sup>, and 14<sup>th</sup> day of changes viz. odor, hair slip, and moisture content, physical feel, etc. The assessment offered the least amount of leaf paste required to achieve the targeted results. Based on the preliminary results, the experimental sample was selected and compared with conventionally preserved skin by 50% NaCl (Figure 3). The experimental and control sample was monitored at a previously determined interval and evaluated for quantitative information for further comparison.

## 2.3. Monitoring and Evaluation

#### 2.3.1. Moisture Content

The Dean and Stark method [23] was followed to determine the moisture content based on the initial and final weight of the preserved goatskins. A pre-weighed sample from both experimental and control skin was collected at different curing interval. The skins were dried in an oven at  $105^{\circ}\pm1^{\circ}$ C for 3 h. After that, they were placed in a desiccator cooled and weighed again. The operation was replicated repeated until a constant mass was obtained (with  $\pm 0.1$  mg variation).

The Equation 1 was pursued for determination of moisture content:

Moisture content (%) = 
$$\frac{\text{Initial weight} - \text{Final weight}}{\text{Initial weight}} \times 100$$
 (1)

#### 2.3.2. Bacterial Count

A 5 g preserved skin per piece was taken and shaken in 50 mL sterile water at 200 rpm for 30 min. After 10 times dilution, a volume of 0.1 mL of the respective diluted solution was taken on the sterile Petri plates and molten nutrient agar at 40°C was poured and uniformly distributed by gentle motion. After 48 h incubation at 37°C, the number of colonies on the agar medium (CFU or colony-forming unit) was counted using a bacterial colony counter (Colony Counter, CC- 1, BOECO, Germany) Equation 2.

$$CFU(/g) = \frac{\text{No. of colony} \times \text{Dilution factor}}{0.1 \times 5}$$
(2)

#### 2.3.3. Extractable Nitrogen Content

The preserved goatskin samples of known weight (5 g) were treated with distilled water in an orbital shaker for 3 h at 30-35 rpm. The liquor was then filtered through a filter paper (Whatman No. 1) to extract the soluble nitrogen content and then digested with sulphuric acid, potassium sulfate, and copper sulfate in a Kjeldahl flask providing

temperature 375-385°C for effective digestion. The amount of nitrogen was determined using the Kjeldahl method of extraction.

#### 2.3.4. Hydrothermal Stability

A shrinkage tester (SATRA STD 114, UK) was used to measure shrinkage temperature following ISO 3380 standard [24] as a scale of determining hydrothermal stability to measure the breakdown of stabilizing linkages existing in the collagen matrix. For measuring the shrinkage temperature, the test samples of dimension  $80 \times 10$  mm were taken and hooked in the tester. The samples were immersed in a glycerine-water solution (70:30). The temperature at which the specimen starts shrinking was noted as the shrinkage temperature of the particular specimen.

#### 2.4. Characterization of Leather

#### 2.4.1. Physical Strength and Organoleptic Properties

Both experimental and control samples were processed to produce shoe upper leather following the conventional process. To assess the physical properties of the leather, at first, they were conditioned at  $20\pm2^{\circ}C$  temperature and  $65\pm2\%$  relative air humidity for 48 hours. In this environment, the leather is conditioned up to a certain predetermined degree and ready for measuring strength properties. The samples were collected from the official sampling position (OSP) of the leather and then the physical strength properties were assessed following ISO 3376 [25] and ISO 3379 [26].

#### 2.4.2. Scanning Electron Microscope (SEM)

Crust leathers both from the control and experimental goatskins were subjected to assess the effect of the proposed preservation method on the fiber structure of the leather. Firstly, leather samples from the same area have been placed on conducting carbon tape. After preparing, the samples were analyzed to an SEM (JEOL JSM-7600F, USA). The photographs were obtained by operating the SEM at an accelerating voltage of 1.0 kV with magnification 300X.

#### 2.5. Pollution Load

Pollution loads: chlorides (Cl<sup>-</sup>), biochemical oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solids (TDS) of the soaking liquor from experimental and control sample were measured following the APHA standard methods [27]. The complete flowchart is presented in Figure 4.



Figure 4. Flow chart of the proposed method

# **3. Results and Discussion**

#### 3.1 Preliminary Experiment

The preliminary experimental data was carried out to explore the optimum percentage of leaf paste. Here, to reduce the consumption of leaf paste several percentages of leaf paste based on the raw goatskin weight were taken for preservation. All the samples were assessed for hair slip, odor, physical fell, and fungal growth, which are tabulated in Table 1. Table 1 indicates that only sample 01 (10% leaf paste) showed little fungal growth but no hair slip. The hair was intact for other four samples and there was no odor. It shows that the leaf paste acts as an antibacterial agent [17], which prevents the putrefaction of the hair root and inhibit hair fall. The possible reason of fungal growth could be the low pH or humidity. The other samples showed no fungal growth and only samples 04 (25% leaf paste) and 05 (30% leaf paste) were softer than the rest.

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 No.	% of leaf paste (w/w)	Hair slip	Odor	Physical feel	Fungal growth
 01	10	No	No	Hard	Little growth
02	15	No	No	Moderately soft	No growth
03	20	No	No	Soft	No growth
04	25	No	No	Soft	No growth
 05	30	No	No	Soft	No growth

 Table 1. Leaf paste optimization in this study (14 days)

Based on the physical feel and visual examination, a 20% leaf paste was found soft with no hair slip, odor, and fungal growth. Therefore, 20% of leaf paste was considered optimum and termed as the experimental sample.

#### 3.2. Assessment of Preservation Method

#### 3.2.1. Moisture Content and Total Extractable Nitrogen vs. Time

The moisture content is an important indicator for the evaluation of preservation method, as bacteria require moisture for their survival. Raw skin contains about 60-70% moisture which is a favourable condition for bacterial growth. The salt curing system is considered to be one of the better systems because of the dual effect of salt: dehumidification and bacteriostatic action are exploited in skin preservation. Conventional salt curing produces better leather quality because in this process the salt is diffused into hide/skin by osmotic pressure. As a result, the moisture content is reduced substantially to yield better preservation [28].

Figure 5 expresses the change in moisture content (a) and total extractable nitrogen (b) in the control and experimental sample for the preservation period. It is clear that the moisture content was decreased with time for both experimental and control sample. On the 14<sup>th</sup> day the percentage of moisture content in both techniques became nearly the same. After that, the moisture content was nearly constant in both cases. On the 28<sup>th</sup> day, the moisture content found in the experimental and control sample was 45.9% and 44.8%, respectively. It ensures no skin degradation, which is confirmed by the changes in nitrogen content.



Figure 5. Changes in moisture content (a) and total extractable nitrogen (b) with preservation period

With the reduction of moisture content, the bacterial action within the skin is restricted. Consequently, the breakdown of the protein inside the skin is prohibited. It is seen that after the 21<sup>st</sup> day, the nitrogen content remains constant for both samples. It can be correlated with the change in moisture content. Since, the moisture content is also unchanged from the 21<sup>st</sup> day; bacteria cannot grow in the lower moisture condition. Since the protein inside the skin is intact, the nitrogen content from the protein is also stable at this stage. However, in comparison with the control sample, it can be seen that there are slight changes between the control and experimental sample. Since in the control sample, NaCl initiates osmosis for moisture reduction, the reduction rate is faster than the experimental sample. Whereas, the control sample cannot resist the bacterial attack as well as the experimental sample shows.

The extractable nitrogen data is also consistent with moisture content. On the 14<sup>th</sup> day, both moisture content and nitrogen content reach an equilibrium point. On the 28<sup>th</sup> day, the extractable nitrogen content found for both the experimental and control sample was 1.7 and 1.9 g/kg, respectively, which indicates higher total extractable nitrogen in the control sample. It ensures the antibacterial action of the leaf paste as well as the preservation of the goatskin.

#### 3.2.2 Hydrothermal Stability and Total Extractable Nitrogen vs. Time

Figure 6 shows the relation of hydrothermal stability with changes in preservation time. The hydrothermal stability indicates the effect of wet heat on the integrity of the material, especially in terms of denaturation transition [28]. It is expressed by shrinkage temperature. The shrinkage temperature is the measurement of the breakdown of stabilizing linkages and the bases for the type of interactions existing in the collagen matrix [13].



Figure 6. Changes in hydrothermal stability for preservation period

Figure 6 indicates that during the preservation period the shrinkage temperatures were almost the same for both the experimental and control methods. Although the nitrogen content increases up to the  $14^{th}$  day as shown in Fig. 4 (b) indicating slight breakdown of protein, the shrinkage temperature is not affected. The reason might be because the increase of nitrogen content is due to the breakdown of non-structural protein but not collagen protein. Therefore, it can be said that *S. trilobata* leaf paste based preserving does not modify the stability of the collagen protein matrix in the goatskin.

#### **3.2.3. Bacterial Count**

The bacterial count of the control and experiment preservation of the goatskins is shown in Table 2. On the 1<sup>st</sup> day, the bacterial count for control and experimental were  $1 \times 10^6$  CFU/g and  $1 \times 10^6$  CFU/g, respectively.

Observation (day)	Experimental	Control
Fresh	1×10 <sup>6</sup>	1×10 <sup>6</sup>
1	$1 \times 10^{6}$	$1 \times 10^{6}$
4	1×10 <sup>6</sup>	2×10 <sup>6</sup>
7	9×10 <sup>6</sup>	$8 \times 10^{6}$
14	6×10 <sup>6</sup>	5×10 <sup>6</sup>
21	3×10 <sup>6</sup>	5×10 <sup>6</sup>
28	3×10 <sup>6</sup>	5×10 <sup>6</sup>

Table 2. Bacterial count (CFU/g) in preserved goat skins

The bacterial count in experimental and control samples increased until the 7<sup>th</sup> day and then slowly decreased. It became constant for both experimental and control on the 21<sup>st</sup> and 14<sup>th</sup> day, respectively. It might be due to the reason that the preservation method in the present approach (20% *S. trilobata* leaf paste) has antibacterial effects [22], which inhibit the bacterial population. As a result, the experiment showed less bacterial growth than the control sample. Besides, there was no hair slip, odor in the present approach preservation method by using 20% *S. trilobata* leaf paste. Selvi et al. 2020 [18] also presented similar data where the bacterial count decreases after 8<sup>th</sup> days, which indicates antibacterial activity of the leaf paste. The result is consistent with moisture content.

#### 3.2.4. Pollution Load Comparison

Table 3 depicts the pollution parameters in soaking operations for both the control and experimental sample. It seems that the Cl<sup>-</sup> and TDS load were greatly reduced by 98.04% and 92.9%, respectively, with the present preservation method in place of the conventional wet salting method. Since TDS is responsible as one of the most polluting parameters foe lowering the soil and water quality near the tanning industry, replacing the salt utilized in the preservation process can prevent these problems. Although the chloride content of soaking liquor in the experimental sample is not fully reduced. This is because some salt is utilized during soaking operation separately and there is no

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presence of salt in the preserved sample to remove the hyaluronic acid in hide/skin [28]. The BOD and COD were also reduced at the levels of 90.2% and 85.5%, respectively in the experimental soaking wastewater compared to the control method. The reduction of pollution makes the present preservation approach more attractive to its effectiveness.

			e		
	Parameters	Unit	Control Sample	Experimental Sample	Depletion (%)
	Cl-	mg/L	$24942.3\pm0.02$	$488.9\pm0.03$	98.04
	TDS	mg/L	$4115\pm0.5$	$291\pm0.3$	92.9
	BOD <sub>5</sub>	mg/L	$1240\pm0.01$	$122\pm0.03$	90.2
	COD	mg/L	$4480\pm0.06$	$650\pm0.5$	85.5

Table 3. Pollution load generated in soaking operation

#### 3.3. Inspection of Leather Quality

#### 3.3.1. Determining the Physical Properties of Leather

The crust leathers were assessed for softness, grain tightness, fullness, and smoothness, and the physical properties which are tabulated in Table 4. The ascertained data are compared with the required value for shoe upper leather to find out the eligibility of the leather in the final product according to the proposed preservation.

Table 4. Physical properties of processed experimental and control leather

Parameters	Experimental	Control	Requirements [5]
Tensile strength (kg/cm <sup>2</sup> )	$213.4\pm0.6$	$226.3\pm0.8$	200
Elongation at break (%)	$51.08\pm0.05$	$59.02\pm0.03$	40-65
Bursting strength:			
Distension at grain crack (mm)	$7.2\pm0.03$	$8.3\pm0.05$	7
Load at grain crack (kg)	$27.3\pm0.02$	$25.1\pm0.01$	20

The tensile strength (kg/cm<sup>2</sup>), elongation at break (%), distension at grain crack (mm), and load at grain crack (kg) were 213.4, 51.08, 7.2, 27.3 and 226.3, 59.02, 8.3, 25.1 for the experimental and control sample, respectively. All the values of experimental and control leather fulfilled the requirement for shoe upper leather. It could be concluded that the present approach for preservation of the goatskin in 20% leaf paste is suitable for shoe upper leather.

#### 3.3.2. SEM Analysis of Fiber Structure

SEM photographs of the crust leather processed from the controlled and experimental salt-preserved goatskin are illustrated in Figure 7. The fiber structure of the experimental goatskin is almost the same compared with the controlled goatskin. The texture and quality of the goatskin of the proposed leather and controlled preservation method are also nearly similar to each other at crust conditions. There is no visible change in the quality of the fiber structure. SEMs of leather from the goatskin cured with experimental composition exhibit properly arranged bundle arrays as it is in the control sample which absorb the dye properly in the further processing of the skin; giving a well lustrous grain to leather [10]. This supports that the proposed preservation method could be safely approached for goatskin preservation.



Figure 7. SEM photographs of prepared crust leathers a) control (50% salt) and b) experimental (20% leaf paste) of the preserved skins

#### 4. Conclusion

The present study confirms the effectiveness of *S. trilobata* leaf paste to preserve the goatskin for 28 days in an environmentally sound way without the addition of common salt. S. trilobata is an obnoxious weed that grows extremely well in any open space, such as: roadside, agricultural land, dumping ground, etc. The proposed method involves a novel way to convert this weed into a valuable product, which reduces water pollution. The comparison and assessment of the experimental proposed solution with the conventional wet salting method reveals that in the case of moisture content, hydrothermal stability, and bacterial count, there were insignificant differences in both samples. The physical properties of the produced experimental leather, e.g., tensile strength, elongation at break, and bursting strength, fulfilled the requirements of shoe upper leather. The SEM image confirmed the utility and compatibility of *S. trilobata* leaf paste as a curing agent because it enhances bundling and striation of fibers, which is a necessary requirement for tannage acceptance. Moreover, no deterioration was observed in the fiber structure of the goatskin. This 'green' preservation method reduces major pollution load parameters like Cl<sup>-</sup>, TDS, BOD, and COD in soaking operations by 98.04, 92.9, 90.2, and 85.5%, respectively. The original aspect of this study was to propose a preservation method that would be able to replace the NaCl and reduce the pollution load substantially. Thus, it can be said that the recommended preservation method could be a sustainable option to preserve goatskin, which would reduce the pollution load to a great extent during leather processing, especially during soaking operations.

#### **5. Declarations**

#### 5.1. Author Contributions

Md.A.H. and S.P. analysed and interpreted the data and are major contributors in writing and revising the manuscript. M.H. and Md.A.M. carried out some section of the methodology part and helped in writing. Md.S.S. collected the sample and helped during preservation. All authors read and approved the final manuscript.

#### 5.2. Data Availability Statement

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

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#### 5.4. Institutional Review Board Statement

Not applicable.

#### 5.5. Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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