MINUS SALT GOAT SKIN PRESERVATION: EXTREME CHLORIDE REDUCTION IN TANNERY WASTEWATER

M. A. Hashem[a], M. Hasan, M. A. Momen, S. Payel

Department of Leather Engineering, Khulna University of Engineering & Technology, Khulna-9203, Bangladesh

a) Corresponding author: mahashem96@yahoo.com, mahashem@kuet.ac.bd

Abstract. In the tannery, soaking is the first operation which emits a huge amount of chlorides in the water body during the processing of wet salted hide and skins. The increasing concern the chlorides encourage salt-free or less-salt methods for preservation of hides and skins. In this study, an alternative preservation 'minus salt' method has been developed. The S*phagneticola trilobata* leaf was applied on the flesh side of the goat skin and observed for 28 days. The comparison of the present minus salt method with the conventional method using common salt (NaCl) revealed that the method could be approached without any deterioration to the fibres and the physical properties of the produced leather. Moreover, the suggested method reduces the pollution load of chlorides, total dissolved solids, BOD and COD by 98.04%, 92.9%, 90.2% and 85.5% respectively. The overall assessment indicates that the salt-free method using S*phagneticola trilobata* leaf could be an attractive preservation system over the conventional wet salting method.

Keywords. S*phagneticola trilobata*, salt diminution, pollution load, soaking

1 Introduction

In spite of originating as a by-product industry, the leather industry has aspired with its growing demand of consumers worldwide. The existence of this industry starts with the raw hides and skins, coming from the meat industry. Being natural organic material, hides and skins tend to deteriorate with time after flaying which contradicts with the purpose of leather processing.

The term preservation or curing has been introduced as a solution to this degradation 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 hides and skins in an environmental-friendly process. Common salt, sodium chloride (NaCl) is the most popularly used curing agent due to its dual effect of dehydration and bacteriostatic effect on hides and skins at a very convenient price and availability. It is reported that approximately 6.5 million tons of hides and skins on the wet salted basis are processed globally per annum discharging 2.6 million tons of salt are in the soaking process alone (Kanagaraj et al. 2001; Kanagaraj et al. 2006). With the growing concerns of available fresh water, the chloride (Cl^-), total dissolved solids (TDS) and salinity added to fresh water from preservation and soaking of the leather industry are raising question and concern about the outcome in the near future.

Alternative several preservation techniques have been adopted by controlling moisture content like in sun drying (Roddy and Hermoso, 1943), controlled drying (Waters et al. 1981) or by controlling the action of microorganisms like using powder biocide or irradiation. Salt-free chemical preservation techniques have also been tried including boric acid (Hughes, 1974), sulphites (Vankar et al. 2009), bacteriocin compounds (Kanagaraj et al. 2014), sodium silicofluoride (Haines, 1973) in low salt skin preservation trials.

Some salt-less preservation system like cooling and chilling (Babu et al. 2012), vacuum (Gudro, 2014), dry ice (Sathis et al. 2013), aryl alcohols (Venkatachalam et al. 1982), potassium chloride (Aloy, 1998) has been adapted for laboratory and pilot scale. The limitations with these methods are that the preserving agents are hazardous itself or expensive to carry out or not practically

adaptable. Organic plant extract like *Moringa oleifera* (Hashem et al. 2018) has been applied as an alternative organic preservative. *Rumex abyssinicus* with salt have also been tried for preservation but it affects the strength and other properties of the final leather (Shegaw et al. 2016). Therefore, it has become a challenge to find out a suitable preserving agent that can preserve the skin in an environmentally safe condition, is available and inexpensive to use.

In this study, S*phagneticola trilobata* plant, locally known as "bhringraj", leaf paste has been tried without any salt as an attempt to meet the challenge of preserving the goat skin for 28 days. S*phagneticola trilobata* plant extract has been found to have antibacterial and antifungal activity (Toppo et al. 2013). The preservation process was evaluated by various parameters: moisture content, odour, hair slip, bacterial count, extractable nitrogen, and thermal stability in comparison to the conventional preservation method.

2 Materials and Methods

2.1 Materials

2.1.1 Skin and plant extract

Freshly flayed goat skins of average weight 1 kg per skin were purchased from a nearby local slaughterhouse, Khulna, Bangladesh. The S*phagneticola trilobata* leaf was collected from the university campus of Khulna University of Engineering & Technology, Khulna, Bangladesh and pasted using laboratory mortar for the experiment.

2.1.2 Salt and chemicals

Commercial NaCl and auxiliaries were used for preservation and pre-tanning and post-tanning processes for shoe upper leather and analytical grade chemicals were used for other experiments.

2.2 Experimental modelling and application

A preliminary experiment was conducted to define the minimal amount of leaf paste required for the preservation. Four (04) samples of size 30 cm × 30 cm was cut from the freshly flayed goat skin. The different combinations of curing materials were offered based on the raw skin weight and assessed periodically (fresh, 1^{st}, 2^{nd}, 4^{th}, 7^{th}, and 14^{th} day) to observe the changes like odour, hair slip, and moisture content, physical feel etc. Based on the preliminary result, the experimental sample was selected and compared with conventionally preserved skin by 50% NaCl, for further experiments.

2.3 Monitoring and evaluation

2.3.1 Moisture content

The Dean and Stark method (BIS, 1971) was followed to determine the moisture content based on the initial and final weight of the preserved skins.

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 in 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 was counted using a bacterial colony counter (Colony Counter, CC- 1, BOECO, Germany).

2.3.3 Extractable nitrogen content

The preserved skin samples of known weight (5 g) were treated with ten times (w/v) its weight of distilled water, shaken well in a bottle for 3 h at 30-35 rpm. The liquor was then filtered through a filter paper, digested and 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 (SATRA, ISO 3380, 2015) as a scale of determining hydrothermal stability where the temperature at which the specimen starts shrinking was noted as shrinkage temperature of the particular skin.

2.4 Characterization of leather

2.4.1 Physical strength and organoleptic properties

Both experimental and control sample were processed to produce shoe upper leather following conventional process and physical properties of the leather were assessed following ISO 3379 (SATRA, ISO 3379, 2015).

2.4.2 Scanning electron microscope (SEM)

Crust leathers both from the control and experimental goat skins were subjected to assess the effect of the proposed preservation method on the fibre structure of the leather. Firstly, leather samples from the same area have 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 1.0 kV with magnification 300X.

2.5 Pollution load

Different pollution load parameters, e.g., chlorides (Cl^-), biochemical oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solids (TDS), and total suspended solids (TSS) of the soaking liquor from experimental and control sample were measured following APHA standard methods (APHA, 2012).

3 Results and Discussion

3.1 Preliminary experiment

The preliminary experimental data, as shown in Table 1, indicates that only sample 01 showed little fungal growth but no hair slip. It indicates that the leaf paste acts as an antibacterial agent but due to lower pH or humidity fugal growth was visible. The other samples showed no fungal growth and only sample 04 and 05 were softer than the rest.

3.2 Optimizing percentage of plant leaf

Table 1 shows the four samples preserved in the preliminary experiment by various % (w/w) of leaf paste. Based on the physical feel and visual examination, 20% leaf paste (w/w) was found soft with no hair slip, odour and fungal growth. Therefore, 20% of leaf paste was considered as optimum and termed as the experimental sample.

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

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

3.3 Assessment of preservation method

3.3.1 Moisture content and total extractable nitrogen vs. time

Fig. 1 expresses the change in moisture content (a) and total extractable nitrogen (b) in the control and experimental sample with respect to the preservation period. It is clear that the moisture content decreased with time and on the 14th day the percentage of moisture content in both techniques was nearly the same. The moisture content was nearly constant from the 14th in both cases respectively. On the 28th day, the moisture content found in 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.

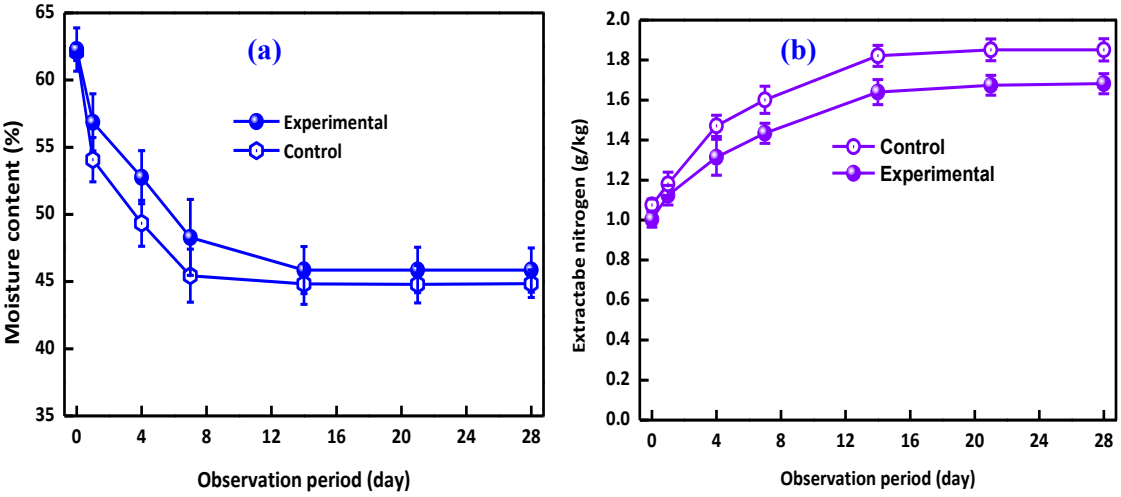

Fig. 1. Changes in moisture content (a) and total extractable nitrogen (b) with respect to the preservation period

With the reduction of moisture content, the bacterial action within the skin is restricted prohibiting the breakdown of protein. As a result, on the 21st day, the nitrogen content remains constant as the moisture content is unchanged. In comparison with the control sample, it can be seen that there are slight changes between the control and experimental sample. Since in control sample, NaCl initiates osmosis for moisture reduction, the reduction rate is faster. 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 14th day, both moisture content and nitrogen content reaches an equilibrium point. On the 28th day, the extractable nitrogen content for both in 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 goat skin.

3.3.2 Hydrothermal stability and total extractable nitrogen vs. time

Fig. 2 shows the relation of hydrothermal stability with changes in preservation time. 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 (Babu et al. 2012).

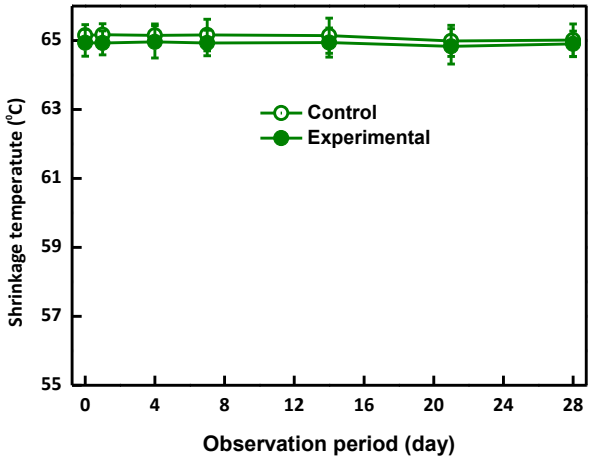

Fig. 2. Changes in hydrothermal stability with respect to preservation period

It 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 14th day as shown in Fig. 1 (b). 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 *Sphagneticola trilobata* leaf paste based preserving does not modify the stability of the collagen protein matrix in the goat skin.

3.3.3 Bacterial count

The bacterial count of the control and experiment preservation of the goat skins is shown in Table 2. Till on the 1st day, the bacterial count for control and experimental was 1×10^6/g and 1×10^6/g, respectively.

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

Preservation period	Experimental	Control
Fresh	1×10^6	1×10^6
1st	1×10^6	1×10^6
4th	1×10^6	2×10^6
7th	9×10^6	8×10^6
14th	6×10^6	5×10^6
21st	3×10^6	5×10^6
28th	3×10^6	5×10^6

The bacterial count in the experimental and control sample increased until on the 7th day and then slowly decreased. It became constant for both experimental and control on 21st and 14th day, respectively. It might be due to the reason is that the preservation method in the present approach (20% *Sphagneticola trilobata* leaf paste) have antibacterial effects, which inhibit the bacterial population. As a result, the experimental showed less bacterial growth than the control sample. There was also no hair slip, odour in the present approach preservation method by using 20% *Sphagneticola trilobata* leaf paste.

3.3.4 Pollution load comparison

Table 3 depicts the pollution parameters in soaking operation for both the control and experimental sample. It seems that the Cl^- and TDS load were greatly reduced by 98.04% and 92.9%, respectively with the present preservation method (20% leaf paste) in place of the conventional wet salting method. 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. The reduction in pollution makes the present preservation approach more attractive with its effectiveness.

Table 3. Pollution load generated in soaking operation

Parameters	Control Sample	Experimental Sample	Removal (%)
Cl^- (mg/L)	24942.3	488.9	98.04
TDS (mg/L)	4115	291	92.9
BOD_5 (mg/L)	1240	122	90.2
COD (mg/L)	4480	650	85.5

3.4 Inspection of leather quality

3.4.1 Determining the physical properties of leather

The crust leathers were assessed for softness, grain tightness, fullness, and smoothness and the physical properties are tabulated in Table 4 and compared with the required value for shoe upper leather.

Table 4. Physical properties of processed experimental and control leather

Parameters	Experimental	Control	Requirements (Kanagaraj et al. 2001)
Tensile strength (kg/cm^2)	213.4	226.3	200
Elongation at break (%)	51.08	59.02	40-65
Bursting strength:			
Distension at grain crack(mm)	7.2	8.3	7
Load at grain crack (kg)	27.3	25.1	20

The tensile strength (kg/cm^2), elongation at break (%), distension at grain crack (mm) and load at grain crack (kg) values fulfilled the required values for the experimental and control sample. It could be concluded that the present approach for preservation of the goat skin in 20% leaf paste is suitable for shoe upper leather.

3.4.2 SEM analysis of fibre structure

SEM photographs of the crust leather processed from the controlled and experimental salt preserved goat skin are illustrated in Fig. 3.

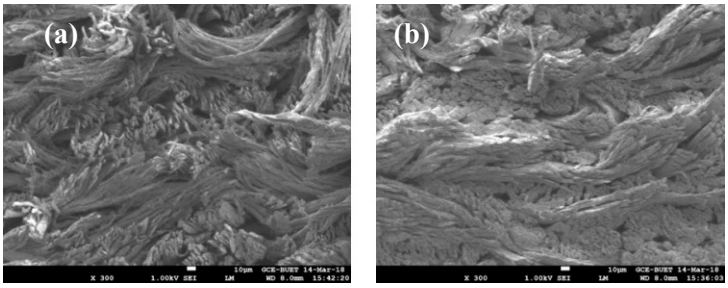

Fig. 3. SEM photographs of prepared crust leathers a) control (50% salt) and b) experimental (20% leaf paste) of the preserved skins

The fibre structure of the experimental goat skin is almost the same compared with the controlled goat skin. The texture and quality of the goat skin of the proposed leather and controlled preservation method also nearly similar to each other at crust condition. This supports that the proposed preservation method could be safely approached for goat skin preservation.

5 Conclusion

The present study concedes that *Sphagneticola trilobata* leaf paste could preserve the skin for a period of 28 days in an environmentally sound way without the addition of common salt. The comparison and assessment with the conventional wet salting method reveal the effectiveness of the method. This preservation 'minus salt' method reduces major pollution load parameters, Cl^-, TDS, BOD and COD in soaking operation by 98.04%, 92.9%, 90.2% and 85.5%, respectively. The physical properties of the produced leather fulfilled the requirement of shoe upper leather. The SEM analysis confirmed no deterioration in the fibre structure of the goat skin. Thus, the recommended preservation method could be a sustainable option to preserve goat skin, which would reduce the pollution load at a great extent during leather processing especially in soaking operation.

References

1. *Aloy M.: 'Cleaner tanning technologies in the beam house operation', Symp. Cleaner Tanning Technology., 6, 1998*
2. *APHA, American Public Health Association. Standard Methods for the Examination of Water and Wastewater, 2012*
3. *Babu N. K. C., Karthikeyan R., Swarna B., Ramesh R., Shanthi C., Sadulla S.: ' A systematic study on the role of chilling temperatures on the curing efficacy of hides and skins', J Am Leather Chem As., 107(11), 362–370, 2012*
4. *BIS, Bureau of Indian Standards, Chemical Testing of Leather, 2-80, 1971*
5. *Gudro I., Valeika V., Sirvaityte J.: 'Short Term Preservation of Hide Using Vacuum', PLOS ONE., 9(11), 1-9, 2014*
6. *Haines.:' Short term preservation with various preservatives', J. Soc. Leather Tech. Chem., 57, 356, 1973*
7. *Hashem M. A., Momen M. A., Hasan M.:' Leaf paste aided goat skin preservation: Significant chloride reduction in tannery', J. Environ. Chem. Eng, 6(4), 4423–4428, 2018*
8. *Hughes I. R.:' Temporary preservation of hides using boric acid', J Soc Leather Trade Chem, 58, 100–3, 1974*
9. *ISO 3379, Leather-Determination of distension and strength of surface (Ball burst method), 2015*
10. *ISO 3380, Leather-Physical and mechanical tests-Determination of shrinkage temperature up to 100°C, 2015*
11. *Kanagaraj J., Babu N. K. C., Sadulla S.: 'Cleaner techniques for the preservation of raw goat skins', J. Clean. Prod., 9, 261-268, 2001*
12. *Kanagaraj J., Tamil Selvi A., Senthilvelan T., Chandra Babu, N. K., Chandrasekar, B.:' Evaluation of New Bacteriocin as a Potential Short-Term Preservative for Goat Skin', Am. J. Microbiol. Res., 2(3), 86–93, 2014*
13. *Kanagaraj J., Velappan K. C., Babu N. K. C., Sadulla S.: 'Solid wastes generation in the leather industry and its utilization for cleaner environment-A review', J Sci Ind Res., 65, 541-548, 2006*
14. *Roddy W. T., Hermoso R. P.:' The coagulable protein of animal skin', J. Amer. Leather Chem. Assoc., 38, 96, 1943*
15. *Sathish M., Madhan B., Saravanan P., Rao J. R., Nair B. U.: 'Dry ice - an eco-friendly alternative for ammonium*

reduction in leather manufacturing', J. Clean. Prod., 54, 289-295, 2013

16. *Shegaw M. A., Balaraman M., Berhanu D. A. Brindha V., Alagumuthu T. S.: ' Rumex Abyssinicus (mekmeko) Ethiopian plant material for preservation of goat skins: Approach for cleaner leather manufacture', J. Clean. Prod. 133, 1043-1052, 2016*
17. *Toppo K. I., Gupta S., Karkun D., Agrwal S., Kumar A.: 'Antimicrobial activity of sphagneticola trilobata (l.) Pruski, against some human pathogenic bacteria and fungi', The Bisocan, 8(2), 695-700, 2013*
18. *Vankar P. S., Dwovedi A. K.:' Sulphates for skin preservation-A novel approach to reduce tannery effluent salinity hazards', J Hazard Mater, 163(1): 207-212, 2009*
19. *Venkatachalam P., Sadulla S., Duraiswamy B.:' Further experiments in salt-less curing', Leather Science, 29, 217-221, 1982*
20. *Waters P. J., Stephen L. J., Sunridge: 'Controlled drying', J. Soc. Leather Tech. Chem., 65, 41, 1981*