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GOATSKIN PRESERVATION WITH AEGLE MARMELOS LEAF PASTE TO REDUCE POLLUTION IN TANNERY

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Abstract- *In Bangladesh, the most common wet salting method is used for the preservation of animal skins due to its simplicity of application and cost-effectiveness. The use of common salt (sodium chloride) increases the salinity as well as total dissolved solids (TDS) of the discharged tannery wastewater. In this present study, low-salt goatskin preservation in combination with Aegle marmelos leaf paste was applied on the flesh goatskin and monitored for 28 days. The samples were collected on fresh,1st, 4th, 8th, 16th, 23rd, and 28th day and assessed for shrinkage temperature, hair slip, moisture content, extractable nitrogen content, bacterial count, putrefaction, odour, etc. Results indicate that 10% leaf paste in combination with 4% salt preserved the goatskin for 28 days without deterioration. The produced leather had better physical property compare to conventionally preserved goatskin. The preservation method reduces pollution load in soaking operation e.g., chloride and TDS by 71% and 38%, respectively. This method could be a suitable alternative to preserve goatskin.*

Keywords: *Aegle marmelos*, Chloride, Pollution load and Total dissolved solids

1. INTRODUCTION

Raw animal skin is used as basic raw material for the leather industry, its preservation and processing need lots of chemical and mechanical operation which produces a huge amount of waste that pollutes the environment. Therefore, preservation and processing of raw animal skin have always been a challenge for the leather manufacturers [1]. Due to the metabolic defense of an animal containing bacteria in the skin living animal remain in control. About 60-70% of water and 25-30% of protein remain in rawhide/skin [2]. Animal skin is a natural protein substance and its deterioration starts within 5-6 hours after flaying [3]. Within 8-12 hours bacteria may enter into the corium section of the rawhide/skin and start to break down the protein matrix [4]. Hence, it is necessary to preserve the raw hide/skin immediately after flaying.

There are several physical and chemical methods for preserving raw hide/skin. The physical methods have proposed the preservation of animal skin e.g., controlled drying in a drying chamber [5], radiation curing by using gamma rays and electron beam [6], cooling [7] are used for animal skin preservation. The chemical methods included the using of sodium sulphate [8], sodium metabisulphite with acetic acid [9], silica gel [10], potassium chloride [11], boric acid [12], neem (*Azadirachta Indica*) oil with sodium chloride [13], soda ash [2], and formaldehyde [14] are proposed to preserve the animal skin.

But the most conventional process for preserving raw hide/skin is adding 40-50% salt (NaCl) on the flesh side of the skins on the basis of skin weight. The NaCl is a popular preserving agent because of its availability, low cost, dehydrating ability and bacteriostatic effects [15]. Daniels [16] reported that during leather processing annually 3 million tons of salts are discharged if the hide/skin preserved with NaCl. These untreated salt help to increase the salinity of the soil and contributes about 40% total dissolved solids (TDS) in the tannery effluent after soaking operation [3]. Therefore, the researcher is trying to find out an alternative way that can preserve the raw hide/skin and also reduce the pollution load. Hashem et al. [17] reported that *Moringa oleifera* leaf paste can preserve the raw hide/skin and also reduce the pollution load as well. It was found that *Moringa oleifera* could preserve the goatskin for 28 days and reduce chlorine, total dissolved solids, biological oxygen demand, and chemical oxygen demand in soaking operation by 46%, 39%, 46%, and 48%, respectively. Kanagaraj et.al [9] reported that goat skins preserved with sodium meta-bisulfite could reduce TDS in tannery effluent.

In the present research, an attempt was made to preserve goatskin with *Aegle marmelos* leaf paste and in combination with the lower sodium chloride. The performance of the preservation process was accessed for 28 days investigating different parameters: extractable nitrogen content, moisture content, hair slip, bacterial count and compare with the conventional preservation method. Also, compare the physical as well as organoleptic properties of the produced crust leathers.

2. MATERIALS AND METHODS

2.1 Goatskin

Freshly flayed goatskin was collected from a nearby slaughterhouse at Khulna, Bangladesh. The average weight of the goatskin was 1 kg per skin.

2.1 *Aegle marmelos* (Bael) leaf

Aegle marmelos (Bael) leaf paste which was used for this study was collected from the campus of Khulna University of Engineering & Technology, Khulna, Bangladesh.

2.3 Chemicals

Analytical grade reagents were used in all experiments and commercial grade chemicals were used in leather processing. All the chemicals were purchased from a local scientific store, Khulna, Bangladesh.

2.4 Method

To optimize the quantity of leaf paste in combination with NaCl is required for preservation, a freshly flayed goatskin was cut equally into four pieces and different percentage of paste in combination with NaCl were applied on the four pieces based on raw goatskin weight which is presents in Table 1. The samples were stored in the laboratory at the surrounding temperature (28±2°C) and assessed periodically for hair slip, odour, and physical feel.

Table 1: Leaf paste optimization study (14 days)

No.	% of curing agents	Hair slip	Odour	Physical feel
01.	5% leaf paste + 4% NaCl	No	No	Soft
02.	10% leaf paste + 4% NaCl	No	No	Soft and flexible
03.	15% leaf paste + 4% NaCl	No	No	Moderate soft
04.	20% leaf paste + 4% NaCl	No	No	Moderate soft

Preliminary experimental results showed that 10% leaf paste with 4% NaCl salt was satisfied with the optimization parameters and it was taken as an optimum concentration of paste for the preservation of skins. To compare the experimental preservation method with conventional preservation method a freshly flayed goatskin was cut equally into two pieces along the backbone line. For control, 50% NaCl was applied on the flesh side of the skin and 10% leaf paste with 4% NaCl was applied onto the flesh side of another half and stored them both at surrounding temperature (28±2°C) for 28 days. The preservation method was observed by determining shrinkage temperature, bacterial count, moisture content, total extractable nitrogen content, hair slip, odor, etc. at a different time interval (fresh, 1st, 4th, 8th, 16th, 23rd, and 28th day) by cutting a small piece of goatskin from preserved samples.

2.5 Monitoring different preservation parameters

2.5.1 Determination of Moisture Content

Moisture content in the samples was determined by following standard procedures [18]. About 3g of preserved sample skins were taken for optimum and control. Samples were weighted in analytical balance and placed it in an oven at 105±1°C for 3 hours. After heating the samples were cooled down in a desiccator and again weighted the samples. Each experiment was performed for three times for accuracy.

2.5.2 Determination of Extractable Nitrogen Content

Total extractable nitrogen content was determined by taking 8g of preserved skins (both experiment and control) which was further cut into three pieces. The pieces were placed into a conical flask and added 80 mL of distilled water. Each flask was placed onto a shaker and stirred for 30 min. The stirred samples were then filtered and 50 mL sample was used for the determination of extractable nitrogen in the aqueous sample according to the Kjeldahl procedure [19]. Amount of nitrogen was expressed as g from 1 kg of absolutely dry skin mass.

2.5.3 Determination of Bacterial Count

A volume of 1ml filtrate sample (similarly collected as nitrogen content) was taken into a vial added 9 mL of sterile distilled water and shaken for preparing a uniform suspension media for bacteria. Then molten nutrient agar (40°C) was poured in a sterile petri dish and 0.1 ml of the diluted solution was taken by micropipette then poured into the agar media. The petri dish was shaken gently for uniform distribution of the diluted sample and kept in an incubator at 37°C for 48 h. The number of colonies formed on the agar media was counted by a bacteria colony counter (Colony Counter CC-1, BOECO, Germany).

2.5.4 Determination of Shrinkage Temperature

Shrinkage temperature of the preserved goatskin was determined in a shrinkage tester (SATRA TD 114, UK) according to the ISO 3380 [20] standard. Each experiment was performed for three times for accuracy.

2.5.5 Leather Processing

After 28 days of preservation, both experimental and control samples were processed in conventional leather making process and manufactured into crust shoe upper leather following the standard leather manufacturing process.

2.5.6 Pollution Load Determination during Leather Processing

Pollution load during leather-making was determined by collecting wastewater both for experimental and control from soaking operation. Then the samples were analyzed for biochemical oxygen demand (BOD), chemical oxygen demand (COD), chlorides (Cl-), and TDS following the standard methods [19]. Each experiment was performed three times for accuracy.

2.5.7 Determination of Physical Strength of Leather

For determination of physical strength of produced crust leather, samples were taken according to standard sampling location from skins and the tests were carried out under temperature 20 ± 2°C and relative humidity 65 ± 2% for 48 h. Physical properties like tensile strength (TS), elongation at break (EB), bursting strength (BS) were assessed under ISO 3376 [21] and ISO 3379 [22].

3. RESULTS AND DISCUSSION

3.1 Moisture content

In raw animal skin, moisture content plays a vital role in the growth of bacteria. One of the main functions of the preservation is to reduce the moisture content of the raw skin up to a certain limit. Fig.1 represents the moisture content in the experimental (10% leaf paste with 4% NaCl) in comparison with the conventional (50% NaCl) preservation methods during the period of 28 days.

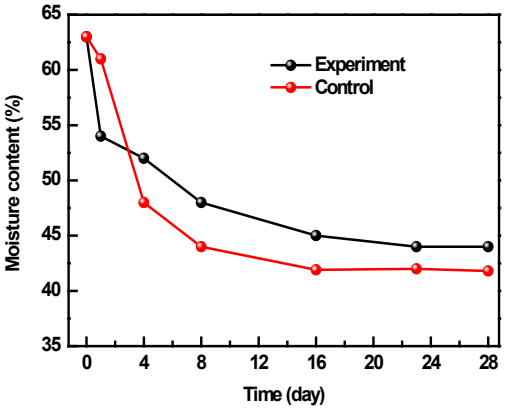

Fig. 1: Moisture content in control (50% NaCl) and experimental (10% leaf paste with 4% NaCl) of the preserved goatskin

At the initial stage, the moisture content in the experimental sample was lower than the control sample. With the increase of the time moisture content was gradually decrease for both the control and experimental sample. On the 28th day moisture content was 41.8% for control and 44% for the experimental sample which is below the critical moisture content and there was no sign of putrefaction.

3.2 Total extractable nitrogen

Total extractable nitrogen content plays an important role in assessing the efficiency of curing skins. Nitrogen content in the soaking liquor is increased due to the breakdown of the polypeptide chain of the skin to the level of amino acids and ammonia these kinds of things only happened when the skin undergoes putrefaction. The extractable nitrogen content (experimental & control) in preserved skins is presented in Fig. 2. Up to 4 days the amount of nitrogen release from both control and the experimental sample was almost the same level but from the day 5 the skin preserved with 10% leaf paste with 4% salt (experimental) generates a lower level of extractable nitrogen compared to the control (40% NaCl) sample (Fig.1). Though the amount of nitrogen release was increasing with the increase of time there was no hair slip and bad odour up to 28 days for experimental sample. This can be explained that some nitrogen source may present in the leaf paste.

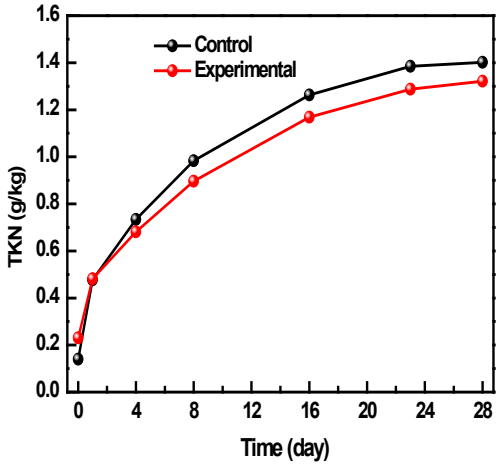

Fig. 2: Extractable nitrogen content in control (50% NaCl) and experimental (10 % leaf paste and 4% NaCl) of preserved skin

On the 23rd day and 28th day, extractable nitrogen contents were in control (1.385 g/kg and 1.402 g/kg) and experimental (1.287 g/kg and 1.321 g/kg) goat skins. It seems that the extractable nitrogen content at 23th day and 28th were lower for the experimental sample than the control sample which indicates that goatskin can be preserved with the combination of 10% leaf paste and 4% NaCl for 28 days.

3.3 Bacterial count

One of the most important symptoms of putrefaction of the preserved skins is the presence of the bacterium. The bacterial count of the control and experiment preservation of the goat skins is shown in Table 2.

Table 2: Bacterial count (CFU/g) in preserved goatskin

Preservation period	Control	Experimental
Fresh	1×10^6	2×10^6
1st	2×10^6	2×10^6
4th	3×10^6	4×10^6
8th	2×10^6	6×10^6
16th	5×10^6	5×10^6
23th	3×10^6	3×10^6
28th	3×10^6	2×10^6

On the 1stday, the bacterial count was the same (2×10^6 CFU/g) for both control and experimental. On the 4th day and 8th day, bacterial count in the experimental was (4×10^6 CFU/g, 6×10^6 CFU/g) greater than the control (3×10^6 CFU/g, 2×10^6 CFU/g) preserved goatskin. It may

be the reason that at the initial stage leaf paste activity was a little bit slower. On the day 16th, 23rd, and 28th day bacterial counts were gradually decreased both in the control (5×10^6 CFU/g, 3×10^6 CFU/g, and 3×10^6 CFU/g) and experimental (5×10^6 CFU/g, 3×10^6 CFU/g, and 2×10^6 CFU/g) preserved goat skins.

According to the test results, the bacterial count was decreased after 28th days but according to the extractable nitrogen content test results, values of nitrogen content was increased these are the two opposite phenomena. But in this study, only putrefactive bacteria were not determined here the presence of all kinds of bacteria was determined. This may be due to the presence of non-nitrogenous bacteria in the skin. In this study, the bacterial count was reduced after 28th days and one of the previous study Hashem et al. [23] found the nearly same results which support this study.

3.4 Shrinkage temperature

Shrinkage temperature is the measurement of the breakdown of protein cross-linkages and collagen matrix structure [24]. Shrinkage temperature is an important property for preservation which indicates structural degradation of skin protein. Fig.3 illustrates the shrinkage temperature in control (50% salt) in comparison with experimental (10% leaf paste with 4% NaCl) from fresh to 28 days

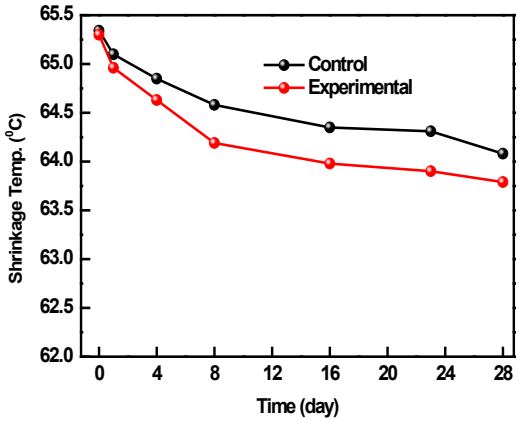

Fig. 3: Shrinkage temperature in control (50% NaCl) and experimental (10% leaf paste with 4% NaCl) of the preserved skins

From the graph, it can be said that from fresh up to 4 days shrinkage temperature was almost the same both for control and experimental methods. On the 28th day shrinkage, temperature reduced slightly in the experimental and control. This may be due to the breakdown of some cross-linkages in the collagen matrix which may reduce the shrinkage temperature. According to the test results, as the shrinkage temperature was dropped after 23rd days the skin cannot be preserved more than 28th days and skin should be tanned after 23rd days. But according to[23] goatskin could be preserved with *Clerodendrum viscosum* leaf paste can preserve goat skin up to 30 days which is a better option than *Aegle marmelos* leaf paste.

3.5 Pollution load in soaking operation

Table 3 depicts the pollution load during the soaking operation of the preserved goat skins for both control and experimental samples.

Table 3: Pollution load produced in the soaking operation of preserved goatskin

Parameters	Control	Experimental	Standard [23]
Cl^- (mg/L)	15420±156	11048±11	9980±14
TDS (mg/L)	28091±37	10810±28	21215±45
BOD (mg/L)	1324±44	736±21	1360±11
COD (mg/L)	6400±41	3213±37	5644±23

It is clear from table 3 that the chloride value was lower with the present preservation (10% leaf paste with 4% common salt) compare to the control method (50% NaCl). According to Hashem et al. [23] chlorides and TDS were reduced by 45% and 50% but in this study chlorides reduction value was increased to72% but TDS value was decreased to 38%. The BOD and COD value was also lower in the experimental soaking wastewater compared to the control of soaking wastewater. Thus, showing *Aegle marmelos* leaf paste not only preserves the skin effectively but also reduces the pollution load in soaking wastewater.

3.6 Physical properties of leather

The produced leather from conventional and experimental preservation was taken for physical test. The physical strength of crust leather such as tensile strength, percentage elongation at break, ball burst strength is presented in table 4.

Table 4: Physical properties of processed experimental and control leather

Parameters	Experimental	Control	Standard [3]
TS (kg/cm^2)	215.93	226.66	200
EB (%)	46.22	52.38	40-65
BS (kg/cm)	34.38	33.46	20

The results showed that leather produced from the skins preserved with 10% leaf paste with 4% NaCl possessed better result than the requirements which indicates that *Aegle marmelos* leaf paste along with low salt is suitable for skin preservation.

4. CONCLUSION

The present preservation method of the goatskin using 10% leaf paste in combination with 4% NaCl allows storage for a period of 28 days without putrefaction. Leather produced from the preserved goatskin has good physical properties which fulfilled the requirement of shoe upper leather. This less-salt preservation method reduced the pollution load, e.g., chlorides and TDS in the soaking operation by 71% and 38%, respectively. The present study shows the evidence that *Aegle marmelos* could preserve the goatskin and also reduce the pollution load in leather processing.

5. REFERENCES

[1] I. Gudro, V. Valeika, and J. Sirvaitytė, "Short term preservation of hide using vacuum: Influence on properties of hide and of processed leather", doi:10.1371/journal.pone.0112783

[2] B. R. Rao, and R. L. Henrickson, "Preservation of hides with soda ash", Journal of the American Leather Chemists Association, vol. 78, pp. 48-53, 1983.

[3] J. Kanagaraj, and N. K. B. Chandra, "Alternatives to salt curing techniques-A review", Journal of Scientific and Industrial Research, vol. 61, pp. 339-348, 2002.

[4] F. J. Unango, R. Duraisamy, and K. Ramasamy, "A review of eco-friendly preservative and bio-tannin materials using powdered barks of local plants for the processing of goatskin", International Research Journal of Science and Technology vol. 1, no. 1 pp.13-20, 2019.

[5] P. J. Waters, L. J. Stephen, and S. Sunridge, "Controlled drying", Journal of the Society of Leather Technologies and Chemists, vol. 65, pp. 32-35, 1997.

[6] D. G. Bailey, "Evergreen hide market-ready", Leather Manufacture, vol. 115, pp. 22-6, 1997.

[7] K. Vijayalakshmi, R. Judith, and S. Rajakumar, "Novelplant based formulation for short term preservation of animal skins", Journal of Scientific and Industrial Research, vol. 68, pp. 699-707, 2009.

[8] P. S. Vankar, and A. K. Dwivedi, "Raw skin preservation through sodium salts- A comparative analysis", Desalination, vol. 249, pp. 158-162, 2009.

[9] J. Kanagaraj, T. P. Sastry, and C. Rose, "Effective preservation of raw goatskins for the reduction of total dissolved solids", Journal of Cleaner Production, vol.13, pp. 959-964, 2005b.

[10] J. Kanagaraj, N. K. C. Babu, S. Sadulla, G. S. Rajkakumar, V. Visalakshi, and N. C. Kumar, "Cleaner techniques for the preservation of raw goatskins", Journal of Cleaner Production, vol. 9, pp. 261-268, 2001.

[11] D. G. Bailey, and J. A. Gosselin, "The preservation of animal hides and skins with potassium chloride", Journal of the American Leather Chemists Association, vol. 91, pp. 317-333, 1996.

[12] I. R. Hughes, "Temporary preservation of hides using boric acid", Journal of the Society of Leather Technologies and Chemists, vol. 58, pp. 100-103, 1974.

[13] M. S. U. Khan, M. M. Rahman, M. A. Samad, M. M. Khatun, and M. M. Rahman, "Efficiency of neem oil in pre-tanning operations to control green hide deterioration", Journal of Biosciences, vol. 5, no. 2, pp. 181-185, 2005.

[14] J. H Sharphouse, and G. Kinweri, "Formaldehyde preservation of raw hides and skins", Journal of the Society of Leather Technologies and Chemists, vol. 62, pp. 119-23, 1978.

[15] V. Sivabalan, and A. Jayanthi, "A study to reduce salt usage in the preservation of skins and hides with alternate use of plant extract", ARPN Journal of Agricultural and Biological Science, vol. 4, no. 6, pp. 43, 2009.

[16] R. Daniels, "Overview: Avoiding Salts", World Leather, vol. 10, no. 2-7, pp. 41-45, 1997.

[17] M. A. Hashem, M. A. Momen, and M. Hasan, "Leaf paste aided goat skin preservation: Significant chloride reduction in tannery", Journal of Environmental Chemical Engineering, vol. 6, pp. 4423-4428, 2018.

[18] Bureau of Indian Standards Chemical Testing of Leather, 1971.

[19] APHA, Standard Methods for the Examination of Water and Waste Water. 22nd Edition, American Public Health Association, American Water Works Association, Water Environment Federation, 2012.

[20] ISO 3380, Leather-physical and mechanical test-Determination of shrinkage temperature up to 100°C, 2015.

[21] ISO 3376, Leather-Physical and Mechanical Tests-Determination of tensile strength and percentage extension, 2011.

[22] ISO 3379, Leather-Determination of distension and strength of surface (Ball burst method), 2015.

[23] M. A. Hashem, M. N. Arman, M. H. R. Sheikh, and M. M. Islam, "Sodium Chloride Substitute for Lower Salt Goat Skin Preservation: A Novel Approach", Journal of the American Leather Chemists Association, vol. 112, 2017.

[24] N. K. C. Babu, R. Karthikeyan, B. Swarna, R. Ramesh, C. Shanthi, and S. Sadulla, " A systematic study on the role of chilling temperatures on the curing efficacy of hides and skins", Journal of the American Leather Chemists Association, vol. 107, pp. 363–370, 2012.