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A cleaner goatskin preservation with leaf paste and powder: An approach for salinity remediation in tannery wastewater

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ABSTRACT

In this study, a new skin preservation method using *Clerodendrum viscosum* leaf has been explored to find out an efficient alternative to the most popular salted preservation in leather processing. The effectiveness of the preservation systems was evaluated on a regular interval by measuring parameters like organoleptic properties, moisture content, bacterial count, and hydrothermal stability of preserved skins. After preservation, the goatskins were processed into crust leather and compared with different strength properties of corresponding conventionally preserved skins. The cross-sectional fiber structure was found undamaged by assessing scanning electron microscopy images. The salt-free preservation method in this study could reduce the total dissolved solids and chloride in the soaking liquor by 74% and 98% respectively. In contrast, the less-salt preservation method could reduce the total dissolved solids and chloride by 57% and 59%respectively. The overall results of this study revealed that the leaf of *Clerodendrum viscosum* plant can be used to preserve skin. The strength properties of the produced leathers also fulfilled the requirements of shoe upper leather. The proposed Eco-friendly preservation techniques are found comparable to a great extent with the traditional salt curing approaches. So, these can be used as viable alternative options for skin preservation in the leather processing industries.

1. Introduction

The leather sector provides praiseworthy contributions to the overall economic growth of Bangladesh. The exported quality leathers from Bangladesh have a worldwide reputation mainly because of their fine-textured skins (Paul et al., 2013). Because of the production of a large number of quality hides and skins as well as cheap labor cost, Bangladesh achieves more export earnings every year. Bangladeshi leather industries satisfy nearly 10% 0f the overall requirements of leather around the world (Akter and Mahfuz, 2018). In accordance with the statement of the government, every year approximately 11.2 million native animals like cows, goats, etc. are slaughtered in Bangladesh during the Eid festival (Tribune Desk, 2019, p. 8). For various limitations and unfavorable conditions, this vast number of raw skins cannot be equipped for production. Moreover, if left untreated, putrefaction will occur. So, the skins need to be persevered to promote continuous supply and time-worthy production of leather with high profit.

Salt curing i.e., using different salts, mostly sodium chloride, is the most traditional acceptable method, which is regularly practiced in most of the tanneries for hides/skin preservation. Salt takes out nearly 20% water and approximately 13–17% salt is fixed into the hide. As the rest unabsorbed salts flow out into nearby rivers, it increases salinity which in turn affects aquatic life. (Hides and Skins Improvement Handbook: Trainer's Manual, n.d.). Salt is a strong dehydrating agent with excellent bacteriostatic property. For this reason, it is so popular and widely used for the preservation of skins in most tanneries. The optimum percentage of NaCl for efficient skin preservation is around 40–50% (w/w). The higher the consumption of salt in this stage, the higher the load of chlorides, total dissolved solids in tannery effluent and this isn't at all expected as it adversely affects the aquatic environment (Sharma et al.,

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1996; Vankar and Dwivedi, 2009). Salts in large amounts coming from preservation and beam house operations in tanneries are flown out into rivers every day. Consequently, the excess salt disposal during de-salting and soaking originates acute environmental constraints (Mottalib et al., 2017). The problem of salinity is especially pronounced in arid areas. It affects the quality of water used for irrigation. Sodium chloride is well known for its solubility and stability. So, the treatment of wastewater having sodium chloride isn't so easy. High TDS load in water creates changes in osmotic conditions for aquatic organisms. On the other hand, salinity changes the ionic composition of water which causes loss of biodiversity in rivers (S.C. Bhatia, 2001). Affiang et al. (2018) and Srivastava et al. (2008) revealed that if saline water is used for irrigation purposes may increase surface salinity when evaporated naturally which may end up causing lesser crop yield. Besides, the chlorides may be flushed from the soil by rain and re-enter the ecosystem, which may ultimately end up in the groundwater.

The primary pollutants in tannery effluents are chlorides, sulfides, and TDS, which enhance the pollution load of tannery effluent (Wibowo et al., 2018; Wu et al., 2017). Owing to the negative impacts of salt on the environment, researchers are now searching for an efficient alternative to the traditional skin curing method. Various chemical-based alternative preservation methods have been noted. 5% cetyl trimethyl ammonium bromide solution was found effective for preservation of skins (Babu et al., 2009). 1% sodium hexafluorosilicate with only 5% salt allowed storage for 14 days without putrefaction (Valeika et al., 2017). The use of bacteriocin also have been noted by (Kanagaraj et al., 2015). However, most of the chemical methods are expensive and may not be environment-friendly.

Some skin preservation techniques using various plant formulations have already been investigated. Selvi et al., (2015) used *Tamarindus indica*. It was observed that 15% *Tamarindus indica* with 10% salt and 10% salt added with 15% *Tamarindus indica* showed effective preservation systems. Iyappan et al. (2013) investigated the potential of *Semecarpus anacardium* nut extract. The extract could preserve skins for more than a month. The dehydrating ability of acetone added with the extract played a vital role (Vinodhkumar et al., 2016). described the effects of *Cassia fistula and Psidium guajava* leaf extract on skin preservation. The experiment was conducted for 21 days. The physical properties of the processed leather were found comparable to the conventionally preserved skins. A minus salt preservation attempt was made by M. A. Hashem et al. (2019). The leaf paste was applied on the flesh side of the goat skins and observed for 28 days. No sign of hair slip, bad odor was found. The suggested method reduced chlorides and total dissolved solids by 98. 04% and 92.9% respectively. Mohammed et al. (2016) assessed the efficacy of *Rumex abyssinicus* roots for preservation. The curing system using 10% root powder with 15% salt was found efficient in preserving raw ides and skins. *Citrus limon* leaf paste was also found effective in skin and hide preservation (Tamil Selvi et al., 2020).

Clerodendrum viscosum (Synonym: *Clerodendrum infortunatum linn.*) is usually found in both tropical and subtropical areas of the world, mostly in Asian countries (Nandi and Lyndem, 2016). It is very much available along the roadsides and unused lands in Bangladesh which is locally known as 'Vat' (Nandi and Lyndem, 2016). The plant contains important phytochemicals like phenols, flavonoids, alkaloids, sugar, gallic acids, stearic acids, protein, etc. (Ghani, 2003; Swargiary et al., 2016). These compounds are known to have biological activities. Traditionally, the plant has been used as medicine in homeopathy for the treatment of skin diseases (Nandi and Lyndem, 2016). The leaves, roots, and other parts of the plant *Clerodendrum viscosum Vent. (Verbenaceae)* showed significant antimicrobial activity against a variety of proteolytic bacteria and fungi which are reported to cause proteolysis (Lobo et al., 2010; Oly, 2011; Waliullah et al., 2014). Researchers have investigated various plants for goatskin preservation. *Clerodendrum viscosum* is more available especially in this region than in any other plants previously studied. So, it has a higher potential to be used for skin and hide preservation. There are two types of application system in preservation for using plant leaf. One is extract application in combination with less salt or without salt and other one is paste or powder application with less salt or without salt. Extract application with salt may provide better performance than paste or powder formulations but in industrial scale the extract application process will be very costly and inadequate for preservation of skins. In paste formulation the concentration of leaf extract will be lower than using direct extract formulation. But in the meantime, leaf paste or powder application system will be more preferable for its easier application in industrial scale. So, the potential of this methods should be investigated.

In this study, due to wide availability, antimicrobial properties, and well-known traditional medicinal uses of the plant, various formulations using *Clerodendrum viscosum* leaf paste and powder with less or no salt have been implemented to assess it's potential for skin preservation in Leather processing. The study attempts to find out cleaner skin preservation technique that will contribute largely to the TDS and salinity reduction in tannery wastewater. In addition, the study revealed the comparative benefits of both using less salt and salt-free mixtures of leaf formulations on skins during storage. A new skin preservation method using *Clerodendrum viscosum* leaf has been explored to find out an efficient alternative to the most popular salted preservation in leather processing.

2. Materials and methods

The efficacy of *Clerodendrum viscosum* leaf for goatskin preservation was investigated. A large goatskin was collected from a meet shop located in the local Hazaribagh market, Dhaka, Bangladesh. The skin was split into two sides (left and right). Both two sides were further divided into six pieces for the preliminary experiment. Six different combinations (% based on raw skin weight) of leaf paste, powder with less or no salt were made and then smeared by hand on the flesh side of each skin separately for observation. The leaf was collected from local areas in Dhaka, Bangladesh. First, about 1 kg leaves were pasted using laboratory mortar. Another 1 kg of the green leaves was dried under the sun and the dried leaves were made into a fine powder and used for preservation. 10% leaf paste on skin weight was found minimal for proper distribution on the whole surface of each side goatskin. Similarly, the required percentage of leaf powder was considered 5% based on skin weight. Using 5% of leaf powder as the curing agent, it was easily possible to provide uniform distribution of curing agents on the skin surfaces. After observation, the two best possible methods for preservation were noted as experiment 1 and experiment 2. Optimization is necessary to find out the minimal quantity of leaf paste or powder required for preservation. Moreover, the impact of mixing less salt or no salt with the plant-based formulations should be visualized. Again, freshly flayed two goat skins were collected. The left side of each skin was used for the two optimized experiments respectively and the right sides were for corresponding controls. The preservation experiments were conducted in the rainy season (From June to August). The condition was tough and unfavorable for preservation as the atmosphere was very much humid than other months of the year. The average relative humidity in Dhaka, Bangladesh, in July is around 81 percent. July, like June, is a hot summer month in Dhaka, Bangladesh, with average temperatures ranging from 32.6 °C (90.7 °F) to 26.8 °C (80.2 °F). For the

Table 1
Different combinations of curing agents (% based on raw skin weight).

Sample ID	Percent (w/w) of curing agents used
1	10% leaf paste
2	10% leaf paste + 10% salt
3	20% leaf paste
4	20% leaf paste + 10% salt
5	5% powder
6	5% powder + 5% salt

assessment of biochemical and other pollution parameters, chemicals of analytical grades were used. The effectiveness of all curing methods as in Table 1, was periodically assessed by determining bacterial count, moisture content, hydrothermal stability (shrinkage temperature), organoleptic properties like hair slip, bad odor, physical feel, etc. For this analysis, a small portion of skins cut from every skin was collected on the 1st, 7th, 15th, and 30th day of preservation.

Priority was given not only to the results of various parameters like bacterial count, hydrothermal stability, moisture content but also to the physical feel of skins, treatment cost, etc. was considered for optimization. Two of the above treatments (10% paste, 10% paste + 10% salt) were chosen for experimentation. The powdered skins became very hard during storage. So, it will difficult to wet back the skins in beam house operations and other chemical consumption will be higher for these. Moreover, skins treated with a higher amount of paste also showed significant hardness after preservation. The two experiments were carried out for a preservation period of 15 days with corresponding controls and then the preserved skins were taken into the industry for final leather processing.

2.1. Monitoring preservation method

2.1.1. Moisture content

About 5 gm of skins were cut at regular intervals from the preserved skins for measuring the moisture content. The samples were weighed and then placed in the oven at 105 °C for 3 h. When the drying was completed, the skins were cooled down into a desiccator and then weighted. The procedure was repeated for obtaining a constant mass. The measurement and method were followed according to the given standard (IS582, 1971).

2.1.2. Hydrothermal stability

Hydrothermal stability for the preserved skins, shrinkage temperature was determined by SATRA STD 114 apparatus in accordance with the method described in the standard (ISO3380, 2015).

2.1.3. Total bacterial count

About 5g of skins were cut and taken into stomacher bags and about nine times sterilized distilled water was added into the bags. The bag was placed into a stomacher machine and shaken for 30 seconds at 230 rpm. Then 0.1 mL (100 μl) of the corresponding diluted sample solutions were spread onto the Petri plates containing tryptic soy agar and then incubated at 37 °C for 48 h (Cruickshank, 1965). The colonies were calculated by colony counter.

2.1.4. Extractable nitrogen

About 5 gm of skin from each sample was taken into a conical flask and ten times distilled water was added and then shaken well for 30 min at 200 rpm to extract the soluble nitrogenous compounds. The extracted liquid was filtered through a filter paper (Whatman No. 1).

The filtrate was digested with Sulphuric acid, potassium sulfate, and copper sulfate in a Kjeldahl flask providing temperatures 375–385 °C for effective digestion. The amount of nitrogen was determined in accordance with the standard of APHA (Eaton et al., 2005). Leather Quality and Pollution Load during the soaking process for the preparation of leather, the conventional leather processing method was adopted.

2.1.5. TDS and salinity load generated from soaking liquor

After 15 days of preservation, all the goat skins in both experiments and controls were processed to make shoe-upper leathers. The physical properties like tensile strength, elongation percentage at the break, cracking strength of grain were measured and the fiber conditions of the leather were also assessed and visualized by scanning electron microscope (SEM).

The wastewater generated from each soaking operation was collected and investigated for Cl^-, TDS followed by the standard methods of APHA (Eaton et al., 2005).

2.2. Physical characterization of processed leather

The produced leathers were conditioned at 20 ± 1 °C and 65 ± 3% relative humidity for 48h. Then specimens were cut from leather samples following standard procedures (ISO2418, 2017). Tensile strength and percentage of elongation at break (IULTCS, 2000), load at grain crack (IULTCS, 1960), and stitch tear strength tests (DIN, 1980) were performed following the standards described by IULTCS.

2.3. Microscope image analysis

The SEM images of the processed shoe upper leathers made from both experimental and corresponding control skins were evaluated. The cross-section of the shoe upper leather samples was examined. The photographs were obtained by operating the SEM at an accelerating voltage of 20 kV with 250x magnification.

3. Results and discussion

3.1. Preliminary preservations

Preliminary Preservations The quality of the preserved skin was evaluated by observing the physical feel and the appearance of a bad odor or any hair slip. The skin may be easily prone to deterioration due to the presence of hair slip, bad odor, or mucous surface of the skin.

Table 3showed that there was no sign of putrefaction like odor, hair slip even on the 30th day of preservation although the physical feel of the skins varied significantly. Almost all the salt-free leaf paste applied skins became hard early on the 7th day of preservation.

Significant hardness was observed for the skins treated in salt-free approaches while the skins treated with less salt showed medium hardness during storage. In addition, skins treated with leaf powder both with salt or without salt became harder than others.

3.1.1. Bacterial count

Table 4 represents the number of bacterial colonies on the preliminary experimental skins at various time intervals during the preservation period of 30 days. Due to the bactericidal effect of the plant, the bacterial load on all the preserved skins decreased significantly on the 7th and 15th day of preservation as in Fig. 1.

On the 7th day of preservation, the bacterial count for 10% paste, 10% paste+10% salt, 20% paste, 20% paste+10% salt, 5% powder and 5% powder+5% salt-treated skins were 7×10^9, 3×10^9, 1.2×10^9, 9×10^9, 3.5×10^9 and 5×10^9 respectively whereas on the 15th day of preservation, the respective values were 14×10^7, 6×10^7,11×10^7, 14×10^7, 10×10^7, and 3×10^7 CFU/gm which represents the reduction scenario of bacterial population on skins under treatments. Even on the 30th day of preservation, a reduced amount of bacterial load was found for skin samples preserved with less salt approaches. However, the skins treated with leaf paste only on flesh surfaces showed little bacterial growth on the 30th day of preservation. Therefore, it was assumed that the antibacterial performance of leaf paste will not be available for a longer time of preservation. On 28th day, the bacterial count was 1.3×10^6 CFU/gm according to (Hashem et al., 2018) while in this study the bacterial count reduced from 6.2×10^9 to 4×10^6 CFU/gm on the 30th day. Researchers need to focus on percentage reduction of bacteria with time. The reduction percentage is found much higher than the other study. Bacterial count depends on many factors. We have found many other studies where the bacterial load was higher than present study. This actually varies from season to season, countries to countries and this plant formulation inhibits bacterial activity more than the *Moringa oleifera* as the initial bacterial load was higher than the other study. It may be revealed that the bacteriostatic property of this plant is playing the major role. The initial bacterial load also need to be considered.

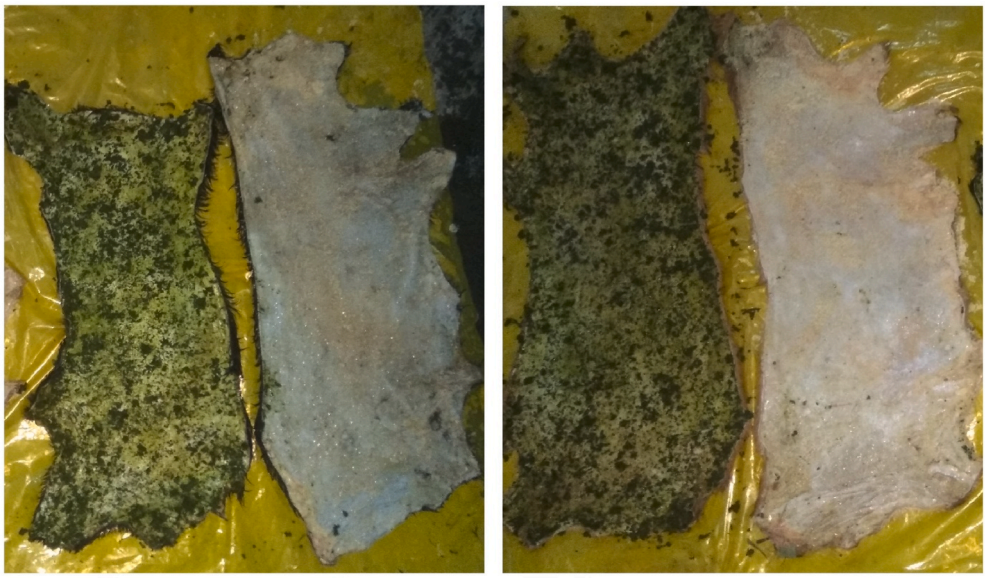

Fig. 1. Experimental and Control goatskins during preservation (a) Expt. 1 (10% paste); (b) Cont. 1 (50% salt); (c) Expt. 2 (10% paste+10% salt) and (d) Cont. 2 (50% salt).

Prior to treatment, on 1st day, the bacterial load on skin of this study was much higher than Hashem et al. (2018). Moreover, the fat content in raw goat skin also differ from region to region which also can contribute to this high load of bacteria.

Although the load of bacteria for all the experimental skins was high, there was no presence of putrefaction like hair slip, bad odor, etc. The high load of bacteria on skins may be for various environmental factors. Most importantly, for all the experimental skins, there was an increase in the number of bacteria and the number was continuously decreasing until the 15th day of preservation as showed in Fig. 2. Therefore, it may be said that the plant-based treatments inhibited bacterial actions (proliferation, enzyme secretion, etc.) and have the potency to preserve skins).

3.1.2. Moisture content

Moisture content percentage is an important indicator to measure the effectiveness of the skins under preservation for leather processing. Fig. 3 depicts the moisture percentage of all the preliminary experimental skins.

Among the experimental skin samples, less salt-treated skins had more moisture than the salt-free skins due to the hygroscopic character of salt. Salt absorbs moisture from the environment. Almost every skin showed a gradual decrease in moisture content up to the 30 days of curing. On the 30th day, the moisture decreased to less than 20% for all the skins.

For the favorable actions of enzymes and bacteria and for the development of molds that secrete proteolytic enzymes, the hides and skins need to have higher moisture content.

3.1.3. Hydrothermal stability

To determine the hydrothermal stability, shrinkage temperature of all the treated skins was tested and presented in Fig. 4. No major difference was found between them. All of the experimental skins showed a shrinkage temperature between 60 °C to 70 °C. On the 7th, 15th, and 30th day of preservation except for the leaf powder-applied samples. The powder-treated skin samples overall showed shrinkage above 70 °C. It was assumed that there might be some tanning actions that in the case of the powder-applied skins. As there was no much variation observed at shrinkage for all of the experimental skins during storage, it can be concluded that there was no significant denaturation or breakdown of linkages of protein happened due to the above treatments of preservation.

3.2. Optimization of skin curing agent

To find out the optimized minimal preservation of goatskin, a various combination of leaf paste percentages with or without salt was investigated and presented in Table 2. It can be declared from Table 3 that the preserved goatskins treated with all the different formulations of curing agents were more or less suitable for leather processing as the physical feels were different.

However, the skin with leaf powder was very hard and difficult to bend. It was supposed that the wet back of these skins would be difficult. Therefore, two combinations were considered as the optimum curing agents and further continued for the experiment simultaneously, named as ‘Expt. 1’ for 10% leaf paste and ‘Expt. 2’ for 10% leaf paste+10% salt with corresponding controls (‘Cont. 1’ and ‘Cont. 2’) respectively.

3.3. Assessment of comparative effects of the optimized methods

3.3.1. Moisture content (experiment vs. control)

As it is already discussed that the moisture content is one of the important indications to measure the effectiveness of the preservation method. The analysis of the amount of moisture on the experimental and control skins during the preservation of 15 days is displayed in Fig. 5. Gradual decreases in moisture in the experimental skins were noted until the curing period of 15 days. On the 15th day moisture percentage of the Expt. 1 skin was 27.56% which was slightly lower than that of Cont. 1 skin. Besides, the moisture on the Expt. 2 skin was 25.19%, which was approximately 8% lower than the corresponding salt-treated skin. At the end of 15 days of preservation, the moisture gradually declined to less than 26% for both the experimental skins whereas it was above 30% for the corresponding conventional salt-treated skins. So, it can be reported that the leaf has shown some bacteriostatic properties on skins.

3.3.2. Hydrothermal stability (experiment vs. control)

Fig. 6 showed shrinkage temperature of preserved skins at various times during storage. The shrinkage temperatures of treated goatskins did not show any significant changes between experimental and conventional salt curing techniques. As there are very little changes in the

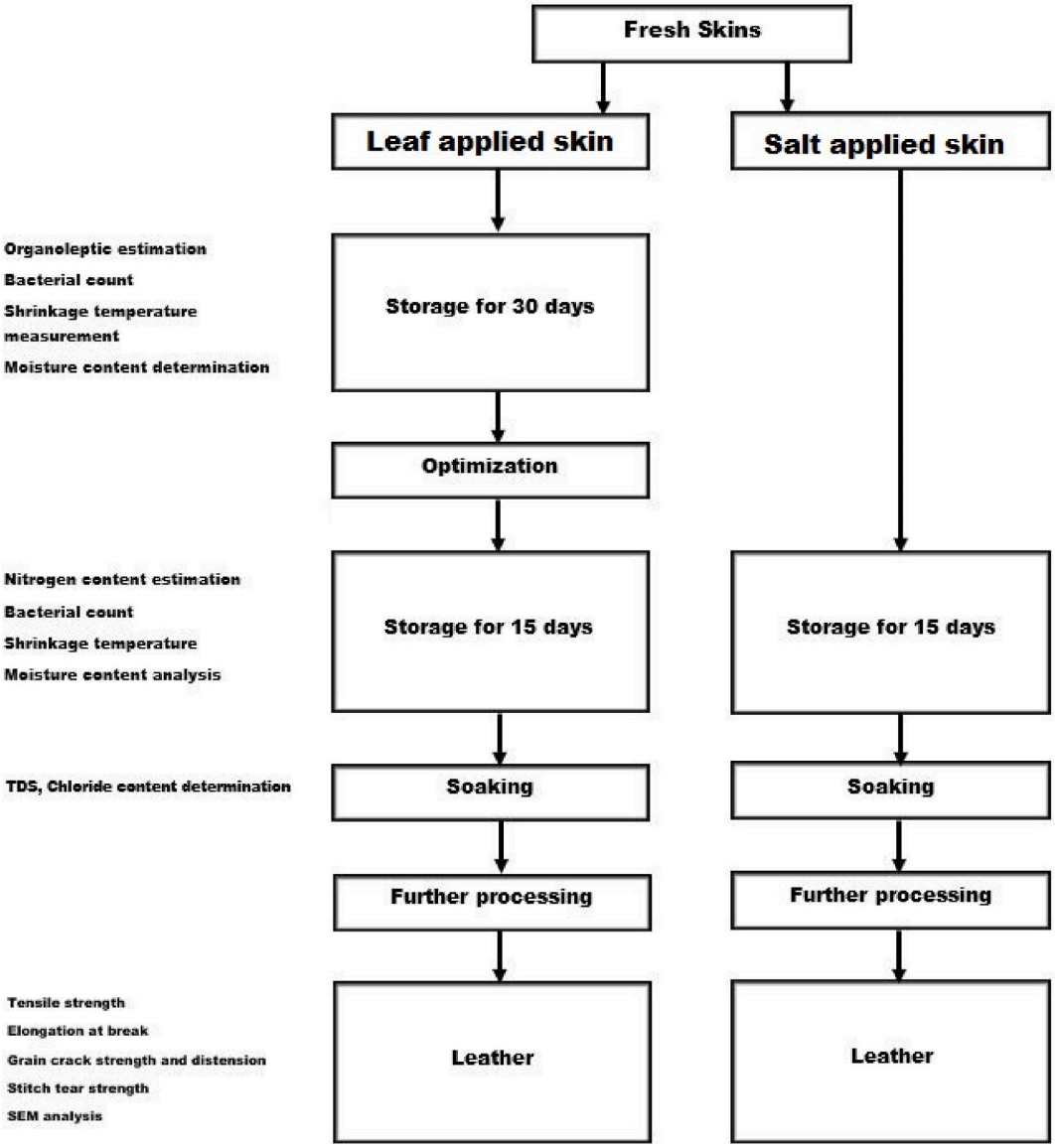

Fig. 2. Working flow diagram

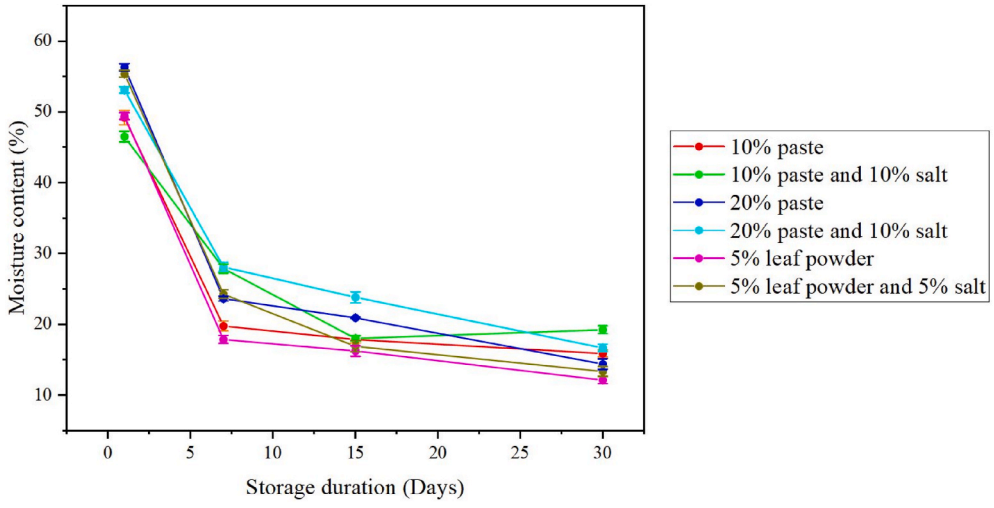

Fig. 3. Moisture content (%) of preserved skins during preliminary storage.

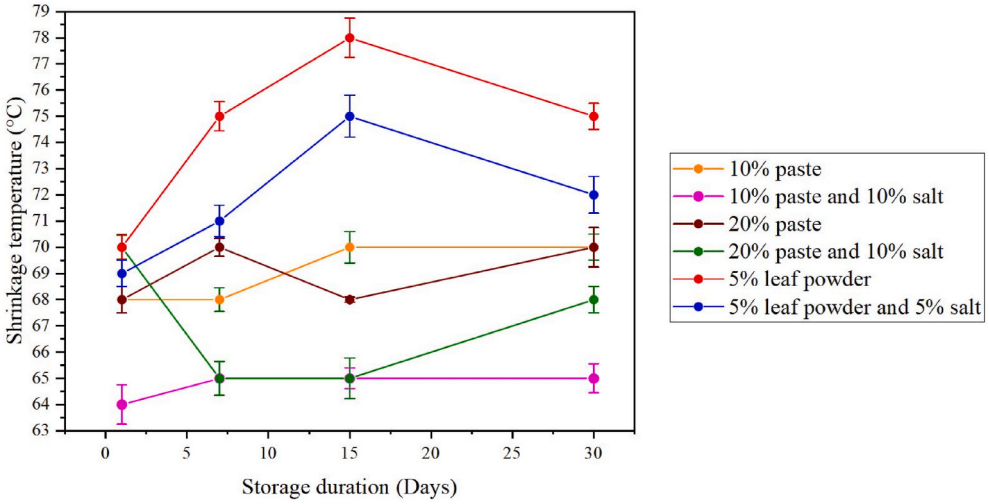

Fig. 4. Shrinkage temperature (°C) of preserved skins during preliminary storage.

Table 2
Optimized combinations with corresponding controls.

Experiment Code		Percent (w/w) of preservation materials used
Preservation Method 1	Expt. 1	10% paste
	Cont. 1	50% salt
Preservation Method 2	Expt. 2	10% paste +10% salt
	Cont. 2	50% salt

Table 3
Organoleptic properties of skin during preliminary trials.

Combination	Duration (days)	Odor	Hair Slip	Physical Feel
10% paste	7th	No	No	Medium Hard
	15th	No	No	Hard
	30th	No	No	Hard
10% paste + 10% salt	7th	No	No	Soft and flexible
	15th	No	No	Soft and flexible
	30th	No	No	Soft and flexible
20% paste	7th	No	No	Hard
	15th	No	No	Hard
	30th	No	No	Hard
20% paste + 10% salt	7th	No	No	Hard
	15th	No	No	Hard
	30th	No	No	Hard
5% powder	7th	No	No	Hard
	15th	No	No	Hard
	30th	No	No	Hard
5% powder + 5% salt	7th	No	No	Medium hard
	15th	No	No	Hard
	30th	No	No	Hard

shrinkage temperature during the curing period for the experimental skins, this may be an excellent indication of the hydrothermal stability of the preserved skins. Therefore, it can be easily understood that *Clerodendrum viscosum* leaf pastes itself or in combination with a reduced amount of salt do not affect the stability of the collagen protein matrix of the goatskin.

Hashem et al. (2018) applied 10% leaf paste of *Moringa oleifera* in preliminary experiment of 14 days for organoleptic evaluation only. No bacterial count, shrinkage temperature or other information was found in this case. However, for 10% paste in combination with 10% salt the shrinkage temperature on 28th day was 65–67 °C whereas on 30th day in this study the shrinkage temperature was 72 °C for 10% leaf paste application with no salt.

3.3.3. Bacterial count (experiment vs. control)

The bacterial load on all of the control and experimental preserved goat skins is presented in Table 5. On the very first day, the bacterial population for Expt. 1, Cont. 1, Expt. 2 and Cont. 2 was found to be 2.6×10^9, 4×10^7, 2.2×10^9, and 2.4×10^9 CFU/gm simultaneously. From Table 4, it is clear that the bacterial load for all the mentioned skins was decreased significantly on the 7th and 15th days accordingly. It may due to the reason that the two approaches have bactericidal activity, which inhibits bacterial growth.

Both the leaf paste applied skins showed a lower bacterial count than the corresponding controls on the 15th day of preservation. Therefore, this microbial study revealed that the given experimental conditions were able to inhibit multiplication or bacterial growth.

3.3.4. Extractable nitrogen content (experiment vs. control)

Goatskin preservation with the present approaches in comparison with the conventional methods is shown in Fig. 7. Total extractable nitrogen is the best indicator of whether bacteria has degraded the animal skins or not. It was calculated by the amount of nitrogen extracted in the aqueous phase.

The putrefaction of skin proteins causes release of nitrogenous components, which leads to the emission of putrefactive odor and hair slip. It was found that there was no sign of odor, hair slip for any skin during storage of 15 days. On the very 1st day extractable nitrogen contents in expt. 1 and cont. 1 skins were 2.2 g/kg and 1.6 g/kg, and for expt. 2 and cont. 2 skins the values were 2.4 g/kg and 1.7 g/kg. At the end of the 15 days, the extractable nitrogen content of the expt. 1 and expt. 2 skins were 5.2 g/kg and 5.5 g/kg while for cont. 1 and cont. 2, those were 6.1 g/kg and 6.2 g/kg. It seems that the amount of extractable nitrogen was almost similar between experimental and corresponding control skins. It can be declared that the leaf paste has the potency to preserve skin.

In experimental skin, the extractable nitrogen content was found 3.7 g/kg on 14th day of preservation in Hashem et al. (2018) whereas for the similar type (10% paste+ 10% salt) of mixture, we found higher amount of extractable nitrogen on 15th day. This may due to the presence of high initial load of bacteria on the first day prior to treatment.

3.4. Pollution load generated during the soaking process

The pollution load was determined after the soaking operation and the results were depicted in Table 6. The wastewater from soaking operations was collected and investigated for chlorides and TDS followed by the standard methods of APHA (Eaton et al., 2005). It can be noted that the chlorides and TDS load were significantly reduced with the

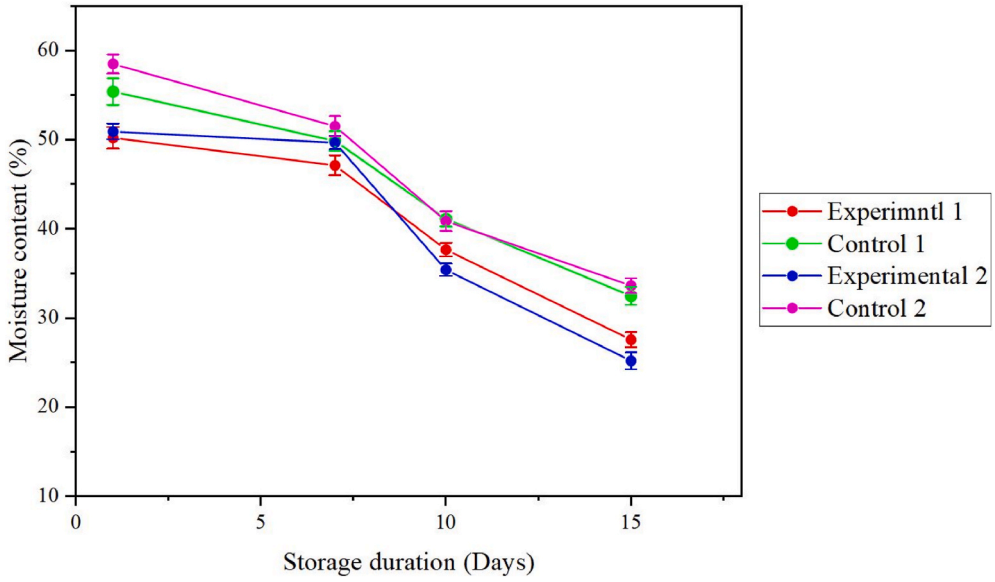

Fig. 5. Moisture content of preserved experimental and control skins during storage.

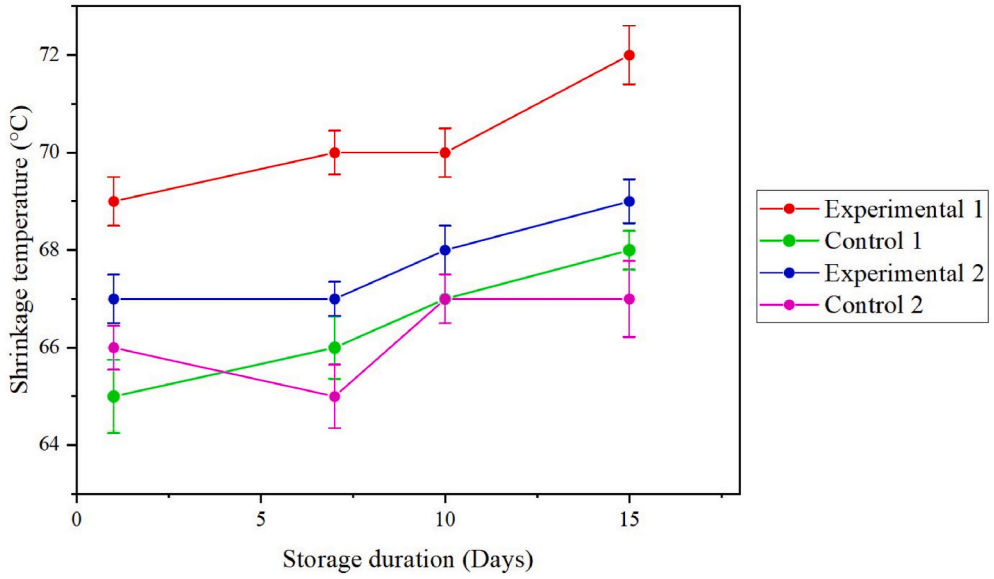

Fig. 6. Shrinkage temperature of preserved experimental and control skins at various intervals during storage.

Table 4
Bacterial population (CFU/gm) on the preserved skins during preliminary trials.

DayDuring Storage	10% paste	10% paste and 10% salt	20% paste	20% paste and 10% salt	5% leaf powder	5% powder and 5% salt
1	8×10^9	6.2×10^9	4.5×10^9	11×10^9	6×10^9	7.5×10^9
7	7×10^9	3×10^9	1.2×10^9	9×10^9	3.5×10^9	5×10^9
15	14×10^7	6×10^7	11×10^7	14×10^7	10×10^7	3×10^7
30	12×10^8	4×10^6	16×10^7	13×10^6	14×10^8	7×10^7

present preservation approaches (10% salt and 10% leaf paste+10% salt) in comparison with the control methods (50% salt). The Cl- and TDS load were reduced to 98.28% and 73.98% respectively for Expt. 1

Table 5
Bacterial population (CFU/gm) on the preserved skins during preservation experiments.

Storage Duration (day)	Experiment 1 (10% paste)	Control 1 (50% salt)	Experiment 1 (10% paste and 10% salt)	Control 2 (50% salt)
1	2.60×10^9	4.0×10^7	2.20×10^9	2.4×10^9
7	9.0×10^7	5.0×10^6	5.90×10^6	6.2×10^6
10	5.4×10^6	1.87×10^6	3.7×10^6	1.5×10^6
15	1.7×10^6	8.0×10^5	4.0×10^6	7.2×10^6

while for Expt. 2, the Cl- and TDS load in soaking liquor were reduced to 58.51% and 57.14% respectively.

Minus salt method using *Sphagneticola trilobata* leaf paste was used by Hashem et al. (2019) where 98.04% salt reduction was noted. Another plant *Rumex abyssinicus* (mekmeko) roots which were shade dried at room temperature and powdered was investigated for its effectiveness in

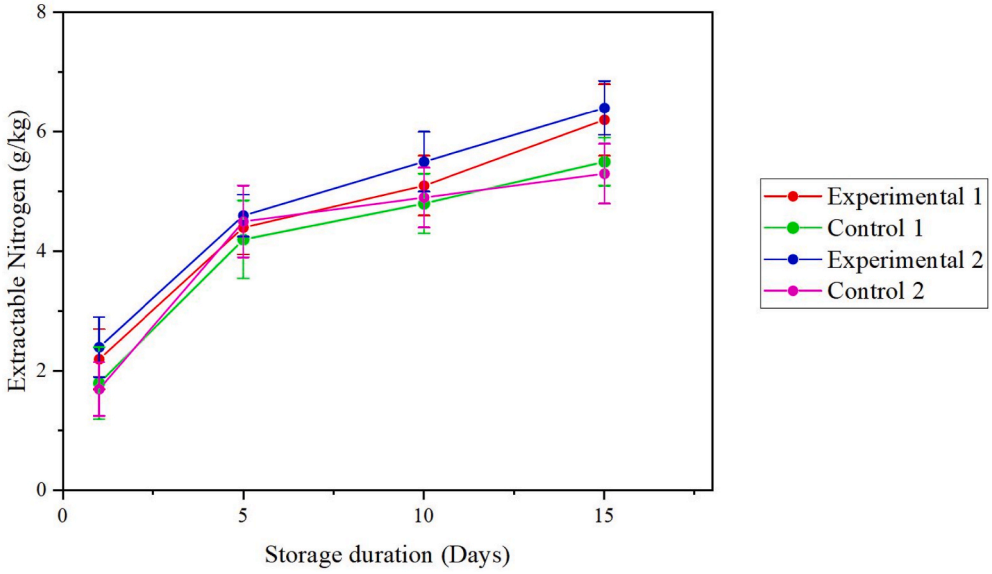

Fig. 7. Extractable nitrogen content of preserved skin during storage.

Table 6
Pollution loads (TDS, Chlorides) generated in the soaking process for the preserved skin samples.

Parameters	Experiment 1	Control 1	Removal (%)	Experiment 2	Control 2	Removal (%)
Cl^- (mg/l)	359 ± 54	20,846 ± 115	98.28	8294 ± 86	19,988 ± 105	58.51
TDS (mg/l)	9980 ± 48	38,355 ± 67	73.98	17,263 ± 35	40,279 ± 74	57.14

the preservation of goat skins (Mohammed et al., 2016). The leaf of the plant wasn't used for treatment. With that, 70% chloride reduction was observed.

3.5. Physical properties of leather

The physical tests like tensile strength, percentage of elongation at break, load at grain crack, distension and stitch tear strength for both the processed experimental and control crust shoe upper leathers were performed and presented in Table 7. The physical tests like tensile strength, elongation percentage at the break, load at grain crack, distension and stitch tear strength for both the processed experimental and control crust shoe upper leathers were performed and presented in Table 7. The tabulated physical properties indicated that the physical strengths of expt. 1 and expt. 2 skins were comparable with that of the corresponding control samples. It was found that the values meet the standard requirements of shoe upper leather. So, the present approach for the preservation of the goatskin with expt. 1 and expt. 2 can be two effective replacements for conventional salt curing systems.

3.6. SEM analysis of processed leather

The SEM images of the produced shoe upper crust leathers are represented in Fig. 8. The cross-section of both the experimental and corresponding control shoe upper leathers was examined at 250x magnification and it is confirmed that the fiber structure of the experimental samples seems to be comparable to that of the corresponding control samples.

4. Conclusion

In this study, cleaner skin preservation techniques using the leaf paste and powder from *Cledrodendrum viscosum* plant without salt and in combination with the reduced amount of salt were investigated. The results of the study showed that the leaf has the potency to preserve goat skins. The high load of bacteria reduced sufficiently after treatment. Even in tough and humid condition this plant has provided sufficient antimicrobial effects even without salt. There is the novelty of this research. There is no other study where both the leaf paste with salt and without salt have been used as final experiments. Another novelty of this research is that, not only leaf paste but also powder formulations also have been investigated. Moreover, the effects of salt application with paste will be visible to everyone. Previous two other studies used *Salicornia brachatia, seuviam* (Kannan et al., 2009) *portulascastrum* (Kanth et al., 2009) leaf paste without mixing with salt where the results were good enough but those plants are still not being used in large scale production due to low availability. Further Investigation on other plants also need to be considered for this reason. With this point of view, *Clerodendrum viscosum* will be a good alternative option. More research is required to find out the best plant for using as an effective and

Table 7
Physical properties of processed leather.

Parameters	Experiment 1	Control 1	Experiment 2	Control 2	Requirement for shoe upper leather (Kanagaraj et al., 2001)
Tensile strength (kg/cm^2)	218.8 ± 3.17	240.8 ± 4.75	230.36 ± 3.18	235.5 ± 3.78	200
Elongation at break (%)	63.54 ± 5.56	56.19 ± 3.50	48.56 ± 2.14	51.23 ± 3.15	40–65
Load at grain crack (kg)	25 ± 3.53	32 ± 3.45	30 ± 2.51	35 ± 4.01	20
Distension (mm)	7.6 ± 0.64	8.3 ± 0.85	8.5 ± 0.71	8 ± 0.46	7
Stitch tear strength (kg/cm)	86.17 ± 5.8	89.28 ± 4.18	94.36 ± 3.86	96.81 ± 5.11	80–100

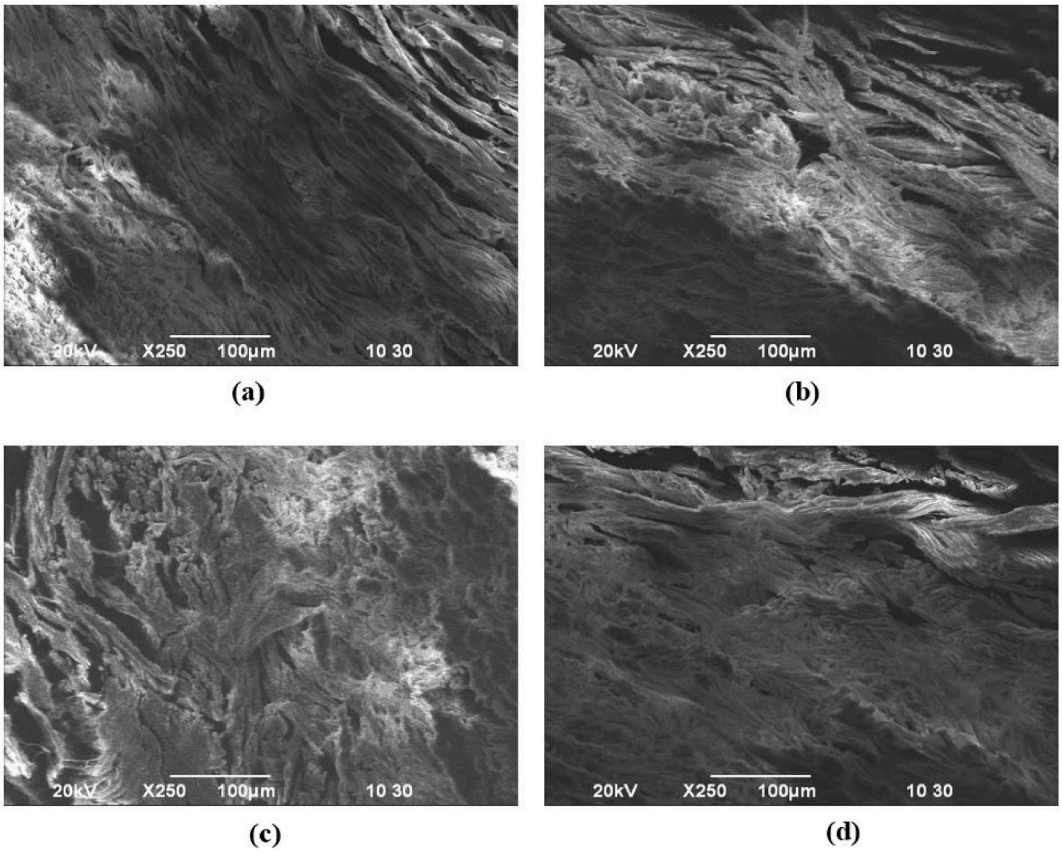

Fig. 8. SEM images at 250x magnification cross section of experimental and control crust leathers (a)Expt. 1; 10% paste (b) Cont. 1; 50% salt (c) Expt. 2; 10% paste +10% salt and (d) Cont. 2; 50% salt.

available alternative of sodium chloride salt. As the availability of plants vary from country to country, it is necessary to study more plants. This salt-free preservation method with 10% leaf paste reduces chlorides and TDS by 98% and 74% respectively in wastewater from soaking operation while the lower salt preservation system with 10% leaf paste +10% salt reduced the chlorides and TDS by 59% and 57% respectively. The physical properties of the processed leathers from experimental skins fulfilled the minimum requirements of shoe upper leather. The studied methods could be sustainable options to preserve the goatskin and to reduce the TDS and salinity load that occurred during leather processing.

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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