Recovery, Purification and Reuse of Contaminated Sodium Chloride Obtained from Tanneries for Raw Goat Skin Preservation

by

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Abstract

Large quantity of sodium chloride is used for raw skin preservation. Significant amount of salt is removed from raw skin through a mechanical process before taking for further processing in tanneries. This recovered salt is contaminated with various dirt, proteinous materials and microorganisms and gets accumulated, which creates a serious waste disposal problem for tanneries. In this study the recovered contaminated waste salt was purified and reused for skin preservation. The recovered contaminated salt from tannery was dissolved in water, filtered, treated with activated charcoal to remove the undesired components and subjected to ozone treatment for the removal of microbial contamination. The ozonized solution was subjected to solar evaporation. Improved evaporation techniques were employed to facilitate evaporation of salt solution. Dried purified salt obtained was checked for microbial contamination. Then the dry salt was used for the preservation of a fresh batch of animal skin. After a minimum storage period of 21 days, the skins were processed into leather as per the usual procedure and compared with the leathers obtained by conventional fresh salt preserved skins. The physical tests, chemical analysis and organoletic properties of experimental leathers show that the quality of leather obtained from animal skins preserved using purified salt was comparable to leathers obtained from conventional pure salt preserved skins. The approach minimizes salinity concerns of tanning by providing simple and practical solution.

Introduction

Animal skin performs many physiological functions such as protection from injury or infection, maintenance of body temperature, etc. The main constituents of raw skin are: 60-70% moisture, 19.2-32.75% proteins, 0.36-0.5% mineral matter and 1.5-12.25% fatty substances.[1] Animal hides and skins are the byproduct of the meat industry and common salt (sodium chloride) is conventionally used for raw skin preservation. In India, nearly 2000 tons of hides and skins are processed per day. Leathers produced from properly cured hides and skins find wide applications. Curing is a process of short term preservation of animal skins carried out immediately after slaughtering so that skin degradation can be prevented. Large quantity of salt is being used for animal skin preservation because it is the cheapest and plentiful. The principle underlying salt based-curing methods are the reduction of moisture from hides and skins. Moisture content above 35% helps the growth of bacteria and subsequent putrification.[2] Preservation of skins and hides is performed to enable raw skins and hides to reach tanneries in the acceptable conditions. In the tanning process, animal hides and skins are treated with chemicals to remove hair and non-structural proteins and fats, leaving an essentially a stabilized pure collagen matrix. The salted hides/skins when transported from collection centers to tanneries for processing, a small portion of salt is lost during transportation and handling of salted hides and skins. However, significant quantity is recovered as contaminated salt and the rest of the unrecovered salt goes into solution in water during soaking process in tanneries. The recovered salt from tanneries cannot be used for any other purpose due to the presence of insoluble impurities such as dirt, dung, animal hair and sand particles as well as soluble impurities such as soluble proteins and microbial contaminants.

The amount of salt used for preservation of skin generally is 40% or more on skin's weight.[3] This 40% or more of salt is applied in two steps. In the first step, 10% of salt is applied on the skin. As soon as 10% salt is applied, water start oozing from the skin along with the applied salt. In the second step, 30% or more of the salt is applied on the skin and it is stored till it reaches tanneries. Some quantity of this salt is recovered (8-15%) and this recovered salt contains salt tolerant microorganisms and other impurities like dirt, dung, animal hair, blood stains, etc. Hence, used salt obtained from

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Manuscript, revised, received April 18, 2015, accepted for publication September 30, 2015.

raw skin may not find application for preservation of fresh batch of raw hides and skins without any treatment. This contaminated salt causes environmental pollution, especially during monsoon season because these salts could wash-off and goes into land and makes the land saline. Some attempts have been made in the past on reuse of used salt as such and also after treatment. Curing trials on hides show that repeated use of salt for preparing wet salted hides is not recommended.[4] Use of recovered salt along with new salt also causes lowering of hide quality and therefore concluded that only new clean salt or used salt after washing and treating with an antiseptic can be recommended for preparing wet salted or green salted hides.[5] Investigation on the use of purified salt obtained by a sedimentation process followed by addition of trichlorphenate for the curing of skins had comparable results as that of new salt.[6]

In view of this, a detailed study has been made to recover the used salt from salted skins, purify by physio-chemical methods and use it again for the preservation of fresh batch of raw skins and process the skins into finished leather for evaluation and testing.

Experimental

Material and Methods

The outline of this experimental study is as follows: Waste salt recovered from preserved skin was dissolved in water to get saturated salt solution. This salt solution was filtered using filter cloth. During filtration the insoluble impurities are removed. The filtered solution was brown in color due to blood, dirt and other impurities. This undesired color was removed by treating the filtered solution with activated charcoal as it is a good color removal agent. Ozone is a powerful oxidizing agent and it is used for the removal of bacterial contamination. Hence this activated charcoal treated solution was ozonized in order to remove the microbial contaminants present in the solution. Then the solution was evaporated under direct sunlight to obtain dried purified salt and this salt was used for the preservation of a fresh batch of raw skins.

Determination of Moisture Content in Salt

Depending upon the initial moisture content of the raw hides/skins the moisture content of contaminated salt varies significantly. So it is necessary to measure the initial moisture content of contaminated salt for subsequent purification process. To determine the moisture content of the salt, 100 grams of salt (W1) was taken in a petri-dish and kept in an oven for about 2 hours at 110°C for moisture removal and then cooled in desiccator and weighed (W2). The moisture content is calculated as per the formula[7] (W1-W2)x100/W1.

Preparation of Salt Solution

One kilogram of waste contaminated salt recovered from cured skins was dissolved in three kilogram of water to get 25% (w/w) solution.

Filtration

This salt solution was filtered using a filter cloth. The amount of insoluble solids (residue) was determined by keeping the residue in an oven for about 2 hours at 110°C and the residue was quantified.

Activated Charcoal Treatment

Activated charcoal is a form of carbon processed to be riddled with small, low volume of pores that increases the area for adsorption.[8] Activated carbon is most widely used in industries to remove odor compounds and dyestuff in waste water. The pellets are also used for air cleaning and deodorization.[9] Activated charcoal used has methylene blue value of 180. The filter paper used was Whatmann having a pore size of 11µm. The filtered charcoal consists of dissolved salts in it, which can be removed by washing of the charcoal.

Ozonation

Ozonation is a disinfection process that destroys microorganisms through an infusion of ozone.[10] The activated charcoal treated filtered solution was then ozonized by passing ozone containing oxygen gas at a rate of 15 lpm for a period of 15 minutes. As the ozone gas passes through the solution, it inactivates and destroys all the microorganisms, odor, undesired color, etc. The ozonated salt solution is taken for solar evaporation under direct sunlight.[11]

Evaporation

Evaporation under sunlight takes a long time. So to increase evaporation different experiments were conducted in five different trays having same dimensions for three days and the amount evaporated in each tray was monitored periodically. Five white plastic trays (each 28 cm x 40 cm) were taken and four of them were wrapped with black plastic, paper (polyethylene plastic sheet, Thickness: color value: L*-39.54, a*-0.942, b*-0.502) one tray was left as such and in the rest 3 trays 1,2,3 floating plastic sheet covered with black cloth (wrap 34, weft 36, color factor-13.8) were placed to facilitate salt solution evaporation. Five different trays in which purified saturated salt solution kept for evaporation are the following: a) White tray, b) Black tray covered with black plastic cover, c) Black tray covered with black plastic cover with one floating disc (25 cm*12 cm) covered with black cloth, d) Black tray covered with black plastic cover with two floating discs (each 25 cm* 12 cm) covered with black cloth, e) Black tray covered with black plastic cover with three floating discs (each 25 cm* 12 cm) covered with black cloth. The weight loss in each tray was measured periodically and after evaporation of entire solution the purified salt was recovered and weighed.

Studies on Microbial Load in Contaminated and Purified Salt

Salt used for curing is always contaminated with some microorganisms present in skin. Hence the following method was used for quantifying the microorganisms present in contaminated salt and purified salt.

Total Bacterial Load

A total of 2.8 g of Nutrient Agar (NA) was dissolved in 100 mL of distilled water. Then it was sterilized by autoclaving at 15 lbs pressure (121°C) for 15 minutes. Ten gram of waste contaminated salt and purified salt were taken in separate conical flask were suspended in 90 mL of sterile distilled water and kept in the shaker for 30 minutes. From the respective tubes 1mL of solution was serial diluted up to 10^{-3} dilution. The autoclaved Nutrient Agar was poured in different sterile petri plates and allowed to reach 25°C. To this media 100 µL of the three dilutions were spread using sterile L-glass rod and incubated for 48 hours at 37°C. The number of viable bacterial colonies were counted and recorded.

Total Fungal Load

Potato Dextrose Agar (PDA) of 3.9 g was dissolved in 100 mL of distilled water and autoclaved (15 lbs for 15 min at 121°C). The treated and untreated salt sample (ten grams of sample suspended in 90 mL of sterile distilled water) were serial diluted up to 10^{-3} dilution. The autoclaved Potato Dextrose Agar was poured in different sterile petri plates and allowed to reach 25°C. To these plates, 100 µL of the three dilutions were spread using sterile L-glass rod and incubated for five days at 25°C. The number of viable fungal colonies were counted and recorded.

Preservation Trials

Two sets of salt preservation experiments were conducted using conventional salt and purified recovered salt on twelve fresh goat skins. A total amount of 40% salt on skin weight was used and it was applied in two installments. After a storage period of 21 days both set of skins were taken and processed into full chrome goat upper leathers. In both cases same process steps and chemicals were used and finally the leathers were subjected to physical tests, chemical analysis and organoleptic properties.

Strength Tests and Chemical Analysis of Leathers

The leathers produced from conventional salt preserved skins and purified salt preserved skins were tested for tensile, tear strength, chrome content and oils and fats as per official test methods.

Organoleptic Properties of Leathers

The leathers produced from conventional salt preserved skin and purified salt preserved skin were subjected to organoleptic assessment for softness, fullness, grain smoothness and general appearance by hand and visual examination by three experts.

RESULTS AND DISCUSSION

Experiments were conducted thrice and the average values presented here. The moisture content of the contaminated salt was 7%. The insoluble impurities present in the used salt were found to be 3.0% (w/w) after filtration using filter cloth. Amount of charcoal needed was 0.35g of activated charcoal for 100g of salt solution. The charcoal treatment has removed dirt and other color components of salt solution and the amount of charcoal recovered was found to be 96.5%. The amount of ozone consumed is 0.55 mg/L during ozonation process. The color of saturated salt solution has improved significantly after ozonation process.

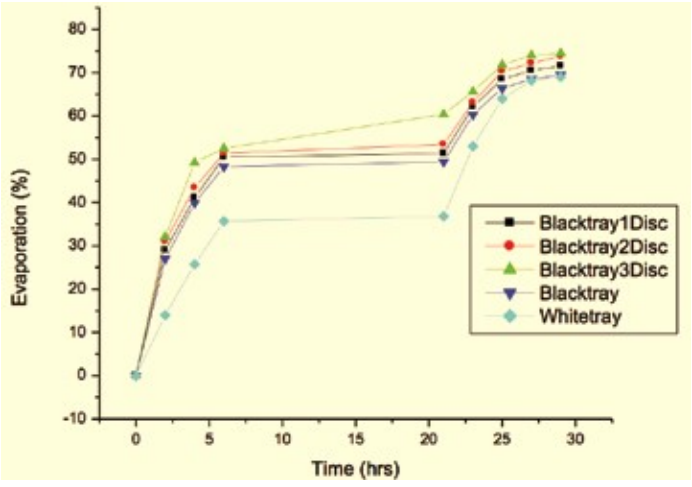

Figure 1. Effect of time on evaporation of saturated salt solution in different trays.

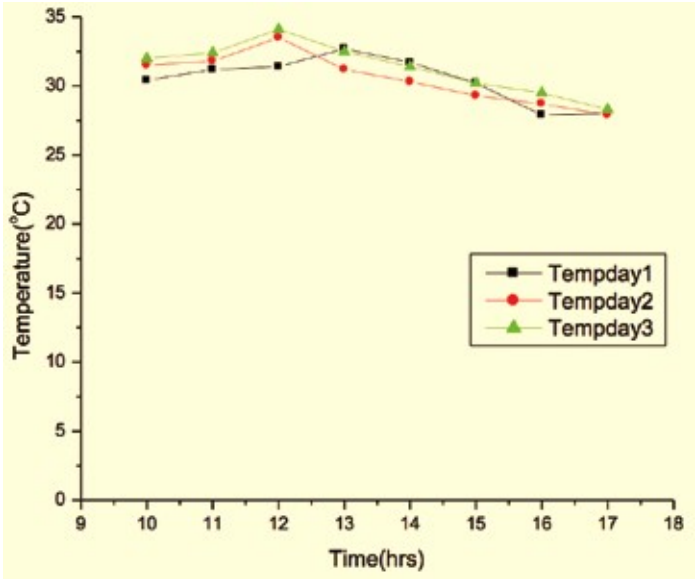

Figure 2. Change in ambient temperature with time during the period of evaporation.

Figure 1 shows the effect of time on evaporation of saturated salt solution in different trays under direct sunlight. As expected, the amount of evaporation was low in case of the white tray compared to white tray covered with black plastic sheets due to increased heat absorption of black tray. To facilitate evaporation, when plastic discs are covered with black cloth and floated on salt solution, an increased evaporation was observed. The rate of evaporation increased when the number of floating discs is increased. Figure 2 shows the ambient temperature with time for three days during evaporation of salt solution where the temperature was between 27-33°C.

Figure3 (a) shows sample of contaminated salt from the leather industry containing insoluble impurities such as dung, animal hair etc. Figure 3 (b), purified salt by the present process and Figure 3 (c) commercially used salt for skin preservation. Study on bacterial and fungal load in untreated and treated salt reveals the following. The number of bacterial colonies was very high as shown in Figure 4 (a), and in untreated salt compared to purified salt as shown in Figure 4 (b). This treatment method, especially ozonation has helped to bring down the microbial load significantly as shown in Table I, before and after treatment. Study on bacterial and fungal load in untreated and treated salt reveals the following. The number of viable bacterial colonies was very low as shown in Figure 4 (b), in purified salt compared to contaminated salt as shown in Figure 4 (a).

TABLE I
Number of viable bacterial colonies observed in serial diluted Nutrient Agar plates.

Salt sample	Dilution (CFU/ mL)		
	10^{-1}	10^{-2}	10^{-3}
Contaminated salt	TNTC	TNTC	TNTC
Purified salt	57	3	0

TNTC: Too numerous to count (above 300 number of viable bacterial colonies).

TABLE II
Number of viable Fungal colonies observed in serial diluted Potato Dextrose Agar plates.

Salt sample	Dilution (CFU/ mL)		
	10^{-1}	10^{-2}	10^{-3}
Contaminated salt	TNTC	TNTC	TNTC
Purified salt	64	0	0

TNTC: Too numerous to count (above 300 number of viable bacterial colonies).

Figure 3 (a). Contaminated salt from the tannery.

Figure 3 (b). Purified salt after the present process.

Figure 3 (c). Commercial salt used for skin preservation.

The number of viable fungal colonies in purified salt sample was very low compared with contaminated salt sample as shown in Figure 5 (a) and Figure 5 (b). This treatment method, especially ozonation has helped to bring down the microbial load significantly as shown in Table I and Table II before and after treatment. The purified salt was used for the preservation of a fresh batch of raw animal skin. The cured skins were kept for 21 days and checked for hair slip, odor, and growth of microorganisms on the surface of the skin and hides. It was found that both cured skins are equally good and there was neither hair slip nor odor.

TABLE III
Physical testing results of experimental leathers.

Experimental leathers	Tensile strength (kg/cm^2)	Tear strength (N)
Leather produced from conventional salt preserved skin	203±5	28±1
Leather produced from purified salt preserved skin	204±5	29±1
Average value of three experiments		

The tensile and tear strength analysis results are shown in Table III. Results show that leathers produced from conventional salt preserved skins and purified salt preserved skins were almost similar in strength characteristics. The chemical analysis of leathers produced from conventional salt preserved skins and leathers produced from purified salt preserved skins are shown in Table IV reveals that the chrome content, oils and fats content were almost same. The leathers were subjected to organoleptic assessment for softness, fullness, grain smoothness and general appearance by hand and visual examination by experts. The rating was based on a scale of 1-10 grade points and the results are tabulated in Table V. The higher grade point indicates a better property of leather. Evaluation of leather produced from conventional salt preserved skin and purified salt preserved skin showed that both leathers were having almost similar organoleptic

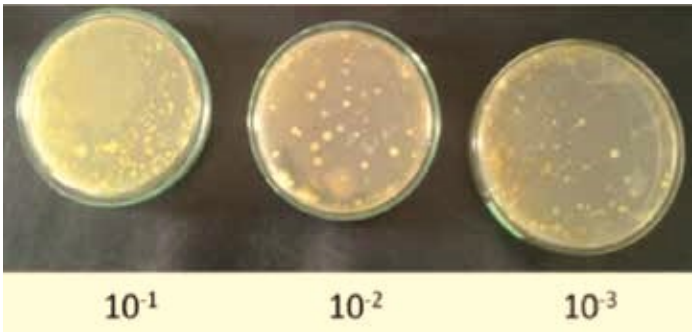

Figure 4 (a). Reduced Bacterial load in serial diluted Nutrient Agar plates of untreated salt (recovered contaminated salt) sample.

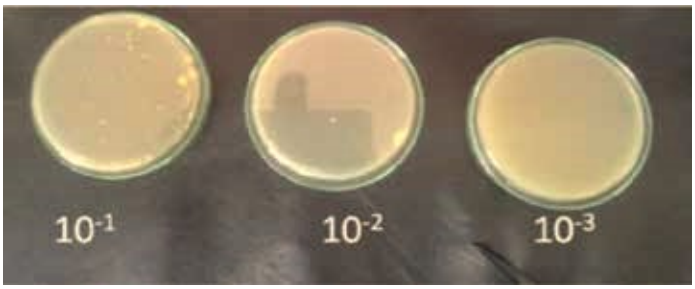

Figure 4 (b). Reduced Bacterial load in serial diluted Nutrient Agar plates of purified salt sample.

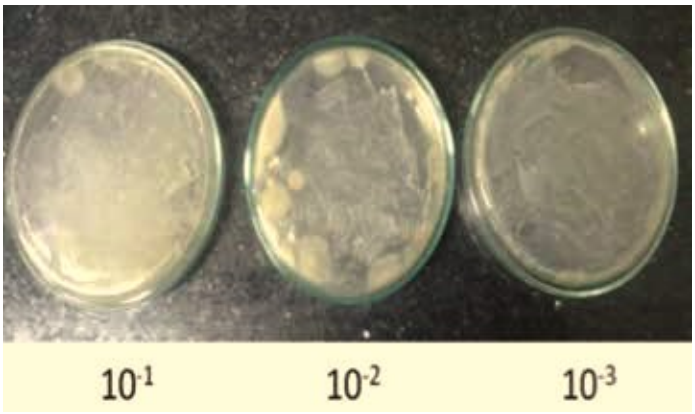

Figure 5 (a). Reduced Fungal load in serial diluted Potato Dextrose Agar plates of untreated salt (recovered contaminated salt) sample.

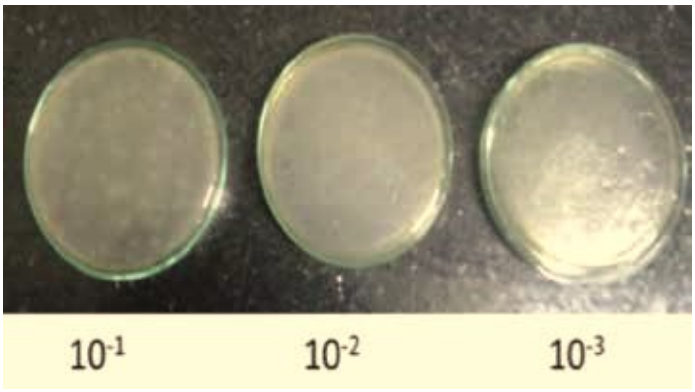

Figure 5 (b) Reduced Fungal load in serial diluted Potato Dextrose Agar plates of purified salt sample.

TABLE IV
Chemical analysis of experimental leathers.

Experimental leathers	Moisture content (%)	Chrome content (as % Cr_2O_3)	Oils and fats (%)
Leather produced from conventional salt preserved skin	14.6±0.2	3.61±0.1	4.8±0.1
Leather produced from purified salt preserved skin	14.5±0.2	3.65±0.1	4.9±0.1

Average value of three experiments

TABLE V
Organoleptic properties of leathers.

Experimental leathers	Softness	Fullness	Grain smoothness	General appearance
Leather produced from conventional salt preserved skin	8±1	7±1	8±1	8±1
Leather produced from purified salt preserved skin	7±1	8±1	8±1	8±1

Scale 1-Poor, 10-Excellent

properties. Physical and chemical tests of both leathers showed that the quality of leathers obtained from animal skins preserved using purified salt was comparable to leathers obtained from conventional pure salt preserved skins.

CONCLUSION

This study demonstrated a simple recovery and purification method for reuse of contaminated salt for raw skin preservation. Salinity associated with leather processing is a major environmental concern. There is no viable treatment system for addressing this technological challenge. Avoidance and reuse are the prudent tools for any environmentally friendly process development. The present study has opened up a possibility for overcoming a major problem, as currently no other widely acceptable preservation system without salt is available. Hence, this method of recovery, purification and reuse of contaminated sodium chloride, if adopted on large scale- environmental pollution due to contaminated salt from tanneries can be minimized.

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