

GREEN SOLUTION FOR SALINITY IN TANNERY WASTEWATER: A STEP FORWARD IN LEATHER PROCESSING

by

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ABSTRACT

The conventional leather processing method contributes to high salinity in wastewater due to the discharge of enormous amount of salts used for preservation. Hence, an attempt has been made to replace the salt with polyethylene glycol (PEG) to reduce the salinity in tannery wastewater. The molecular weight (MW) and percentage offer of PEG were standardized based on the rate of dehydration of hide matrix during preservation and rehydration of preserved hide matrix. The determination of hydroxyproline in spent soak liquors at various time periods during storage showed that the preservation of hides using PEG MW 2000 was more effective than sodium chloride. The reduction in total salinity by 43% is possible in tannery wastewater through PEG based preservation of raw hides. Functional characteristics of the experimental crust leathers are shown to be on par with control crust leathers. The developed greener process appears to be technically viable and economically acceptable alternative for salt based preservation.

INTRODUCTION

Leather processing is presently evolving and adopting various cleaner, greener technologies.¹⁻⁵ One of the major issues faced by the industry is total dissolved solids (TDS). Salt is generally used for preservation of raw hides/skins. Raw hides and skins are easily attacked by microorganism due to the availability of rich leather making protein under favorable conditions.⁶ Hence, the leather making protein should be preserved between the time it is removed from the animal until it can be processed into a final product. The preservation or curing of hide or skin is to temporarily prevent the deterioration by the microorganisms.⁷ This can be achieved by bacteriostatic agent that prevents the growth of microorganism and bactericidal agent that kill the microorganisms.⁶ When bacteriostatic agent is used the growth of microorganism is limited by changing the favorable environmental condition in the raw hide or skin such as moisture, temperature and pH. Microorganisms can be easily killed by a variety of chemical poison. However, many of the best poisons for microbes are also poisonous to humans and therefore not good choice for treatment of hide or skin. Hence, bacteriostatic agent is most suitable for temporarily preserving the rawhide or skin.

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The moisture content of raw hide or skin is easily controlled or removed. Drying is an earliest form of preservation.⁸ Microorganism cannot digest a completely dried hide or skin. Drying is more rapid in a thin skin than in a thick hide and it can be done in areas that are consistently dry and warm. Hide or skin that dries too fast on the outside can leave moist areas in the interior that will decay during storage. It is difficult to preserve the hides by drying because of the length of time it takes for the moisture to diffuse out of the hide.⁷ The salt based preservation employs nearly 40-50% w/w sodium chloride on the raw weight of hide or skin. The applied salt is subsequently discharged during the soaking operation, which contributes to high salinity in tannery wastewater.⁸⁻⁹ It account for nearly 40% of salinity in tannery wastewater.⁹ Hence, the segregation of soak liquor for the recovery of salt and TDS reduction in wastewater through solar evaporation pan method has been developed.¹⁰ This method requires a high financial input and it creates a problem in reuse of recovered salt. This creates a major stumbling block to the tanners. Less salt and salt free methods have been evolved to reduce or eliminate the salinity in tannery wastewater. Less salt based preservation methods with and without anti-microbial agent have been explored.¹¹⁻¹⁷ However, these methods do not reduce the salinity significantly. Salt free methods such as chilling and irradiation based preservation methods have been developed.^{6,18-19} This methods are expensive, requires high financially input and difficult to adopt them in a tannery. Hence, no successful attempt has been made to completely replace the salt in preservation.

Polyethylene glycol (PEG) is an inert, water soluble, non-irritating linear chain polymer of oxy ethylene units with low toxicity.¹⁸ It is used as protein salting out agents and considered to be the most successful precipitant for protein crystallization.¹⁸ In the present work, the salt is completely replaced with PEG for preserving the cow hides to achieve the greener leather process. Different molecular weights and different percentage offer of PEG were employed. Rate of dehydration and rehydration studies were performed to standardize the preservation process. The effectiveness of preservation of cowhides has been assessed through the hydroxyproline content in the spent soak liquors at various time periods during the storage. Scanning electron microscopy analysis has been carried out for preserved cow hides. Spent soak liquors has been analyzed for biochemical oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solids (TDS) and chlorides (Cl⁻). Differential scanning calorimetry (DSC) and fourier transform infrared spectroscopy (FT-IR) studies have been carried out for preserved cow hides. Composite liquors from both control and experimental processes have been analyzed for environmental parameters. Strength characteristics and bulk properties of the processed leathers have also been evaluated.

MATERIALS AND METHODS

Materials

Raw cowhides with weight range of 15-20 kg were obtained from Perambur Slaughter House, Chennai, India. Hides were removed from the animal and transported through an ice packed container within 2 h. PEG (Molecular weight 2000 - 8000) and sodium chloride for preservation experiments were of laboratory grade. The chemicals used for bulk trial studies were of commercial grade. The chemicals used for the analysis of spent liquors were of analytical grade.

Selection of Molecular Weight of PEG for Preservation

Six raw cowhides were cut into two sides, further it trimmed and washed immediately. The washed sides were allowed to drain for 15 min and then fleshed. The fleshed sides were made into half sides by equally cutting across the backbone. Twelve half sides were numbered and weighed individually. Each experimental preservation trial was carried out using two half side. Different molecular weights (MW) of PEG MW 2000, MW 4000, MW 6000 and MW 8000 were applied on the fleshed side of each half side at an offer of 5% (w/w). Other four half sides were used for control preservation trial. Two half sides were preserved by conventional method of drying at room temperature and another two half side, were treated with sodium chloride 40% (w/w) for control preservation trials.⁸ Moisture content of the hide samples was determined at different intervals for a period of 24 h using the standard procedure.²⁰ The preserved cow sides were stored at room temperature.

Optimization of Percentage Offer of PEG MW 2000 for Preservation

Fourteen half sides were obtained as described above. Each half side were numbered and weighed. Concentration of PEG MW 2000 was varied as 1, 2, 3, 4 and 5% w/w of each half side weight. Two half sides were used for each concentration of PEG MW 2000. Other four half sides were used for control preservation trials as described above. Moisture content of the hide samples was determined at different intervals for a period 24 h using the standard procedure.²⁰ The preserved cow sides were stored at room temperature.

Rehydration Studies

Rehydration assays for the preserved samples were carried out in triplicate, by immersing the control and experimental preserved hide sample in water. Approximately, 10 g preserved sample was put in 100 mL distilled water at room temperature in a 250 mL beaker. At pre-determined sampling periods, the samples were removed from the beaker and gently blotted on the tissue paper to remove surface water and then weighed by an electronic balance with an accuracy of ± 0.0001 g. The preserved cowhides were evaluated for rehydration characteristics in respect of rehydration ratio, from the weight before and after the rehydration.

Scanning Electron Microscopy Analysis

The preserved control and experimental cow sides were cut from the official sampling position.²¹ The samples were kept in a desiccator for 48 h. Then the samples with uniform thickness were directly taken for analysis without any pre-treatment. Quanta 200 series scanning electron microscope was used for the analysis. The micrographs for the cross section were obtained by operating the SEM at low vacuum and an accelerating voltage of 12 KV with different magnification levels.

Differential Scanning Calorimetry and Fourier Transform Infrared Studies

The preserved control and experimental cow sides were cut from the official sampling position.²¹ The samples were kept in a desiccator for 48 h to attain uniform moisture content. The cross section of the preserved samples was scrapped to remove 1 mg using sharp knife. The scrapped samples were subjected to thermal denaturation (melting) using a Netzsch DSC 200 PC DSC at a heating rate of 10°C/min and IR spectra were obtained using a Perkin – Elmer RX1 FT-IR spectrometer.

Determination of Hydroxyproline

Approximately 25 g of control and experimental preserved samples were taken at various time periods up to 100 days of storage. The samples were soaked with 900% water for 8 h in water shaker and spent solution was collected. Hydroxyproline was determined using the method of Woessner, after acid hydrolysis of the sample.²² The amount of hydroxyproline was calculated by multiplying the concentration (mg/L) with volume of spent liquor (L) per kg of raw hides (dry weight basis).

Bulk Preservation Studies

Twenty half sides were obtained as described above. Each half side was weighed. Ten left sides and ten right sides were used for control and experimental trials, respectively. Experimental and control trials were performed using optimized amount of PEG MW 2000 (3% w/w) and sodium chloride (40% w/w), respectively. The method of application was followed as described above. Then the sides were kept undisturbed for 24 h at room temperature. Control and experimental preserved cow sides were folded and stored at room temperature.

Soaking Operation for Preserved Control and Experimental Cow Hides from Bulk Trials

Control cow hides were manually desalted and soaked in a pit employing three changes of 300% (w/w) water for a total period of 8 h. Experimental cow hides were directly taken for soaking employing the above method for a period of 6 h. Soaked control and experimental cow hides were separately converted in to shoe upper employing post soaking operations.

Input and Output Analysis

Input–output analysis for the raw materials, water and chemicals was carried out for control and experimental processes. The amount of salt removed during desalting was estimated for control preserved cowhides. The spent liquor from control soaking processes was analyzed for sodium chloride as per the standard procedure.²³ PEG was not analyzed in the spent soak liquor from experimental process since it is difficult to analyze in a mixed form.

Spent Soak Liquor and Composite Liquor Analysis

Spent liquors from soaking process were collected from control and experimental processes. The spent liquors were analysed for chloride (Cl⁻), BOD, COD and salinity as per the standard procedures.²³ Effluent loads were calculated by multiplying concentration (mg/L) with volume of spent soak liquor (L) from the soaking process for processing one ton of preserved raw hides. Composite liquors from conventional and experimental leather processing were collected from all unit operations up to post tanning and analyzed for BOD, COD, Cl⁻ and salinity (TDS) as per the standard procedures.²³ Emission loads were calculated by multiplying the concentration (mg/L) with volume of effluent (L) per tonne of raw hides processed.

Physical Testing and Hand Evaluation of Leathers

Samples for various physical tests from experimental and control crust leathers were obtained as per IUP method.²¹ Specimens were conditioned at 27 ± 2°C and 65 ± 2% relative humidity (R.H.) over a period of 48 h. Physical properties such as tensile strength, % elongation at break, tear strength and grain crack strength were examined as per the standard procedures. Experimental and control crust leathers were assessed for softness, fullness, grain smoothness, grain tightness (break) and general appearance by hand and visual examination. The leathers were rated on a scale of 0 – 10 points for each functional property by three experienced tanners, where higher points indicate better property.

RESULTS AND DISCUSSION

Underlying Principle for Selecting PEG for Preservation

PEG is an amphiphilic polymer, which is structurally soluble in water. The PEG–water interaction is truly remarkable, a minimum of ~2 – 3 water molecules per PEG monomer seems to be required to complete basic hydration.²⁴ In this work, PEG is used to remove water from the hide matrix through hydrostatic pressure. The water present in the hide matrix as free form can be displaced by PEG molecule, which is represented as dehydration process (Figure 1a). Hence, the favorable condition of the hide matrix for the growth of microorganism is altered. Further, the PEG molecules coat the individual fiber bundles thereby avoiding the fiber cohesion of the hide matrix. The PEG coated fiber bundles are quickly

rehydrated (wetted) when the matrix is subjected to rehydration process (soaking). During the rehydration process PEG molecules move out from the hide matrix and simultaneously water enters inside the matrix, which is represented as rehydration process (Figure 1b). This is mainly due to the presence of hydrophilic groups in PEG resulting in quick wetting process.¹⁶ Hence, the fiber bundles are again associated with water molecules, when the matrix is rehydrated.

Selection of MW of PEG for Preservation

Different MWs of PEG were employed to select the suitable molecular weight for preservation of hide matrix. The selection of molecular weight of PEG is based on the dehydration and rehydration rates of hide matrix. Dehydration and rehydration rate for control and experimentally preserved hide matrix are given in Figure 2a. It is expected that dehydration process is rapid for drying based preservation process. The dehydration rate of hide matrix is inversely proportional to the MW of PEG. However, the rate of dehydration of hide matrix by sodium chloride based preservation system lies in under the dehydration rate of hide matrix preserved with various molecular weight of PEG. The rate of rehydration of control and experimentally preserved hide matrix are given in Figure 4. It is known that the rehydration of hide matrix preserved by drying is difficult due to the fiber cohesion during the drying process.⁸ Hide matrix preserved with PEG MW 2000 provides faster rehydration of hide matrix compared to other MWs of PEG. Rate of dehydration and rehydration of hide matrix are faster for PEG MW 2000 compared to other MWs of PEG. This is primarily due to the molecular size of PEG. Further, the rehydration rate of hide matrix preserved with PEG MW 2000 matches with hide preserved by sodium chloride. Hence, PEG MW 2000 is chosen for further experimental trials.

Optimization of Percentage Offer of PEG MW 2000 for Preservation

Various percentages of PEG MW 2000 were employed to optimize the amount required to preserve the cow hides. It is observed from the Figure 3 that the dehydration rate of hide matrix preserved by 3, 4 and 5% offer of PEG MW 2000 is similar to salt preserved hide matrix. It is seen from Figure 4 that the rehydration rate of hide matrix preserved by varying percentages of offer of PEG MW 2000 is shows similar trend to hide matrix preserved by sodium chloride. Hence, an offer of PEG MW 2000 is optimized as 3% for bulk trials.

Scanning Electron Microscopy Analysis

Scanning electron micrographs of preserved hide samples from drying, salt and PEG based preservation method showing the cross section at a magnification ($\times 50$) is given in Figure 5. The preserved hide matrix sample from drying method shows more compact and closely packed fiber structure (Figure 5a) compared to sodium chloride (Figure 5b) and PEG MW 2000 (Figure 5c) based preservation. This is mainly due to the fiber cohesion of the hide matrix during the drying process. Salt

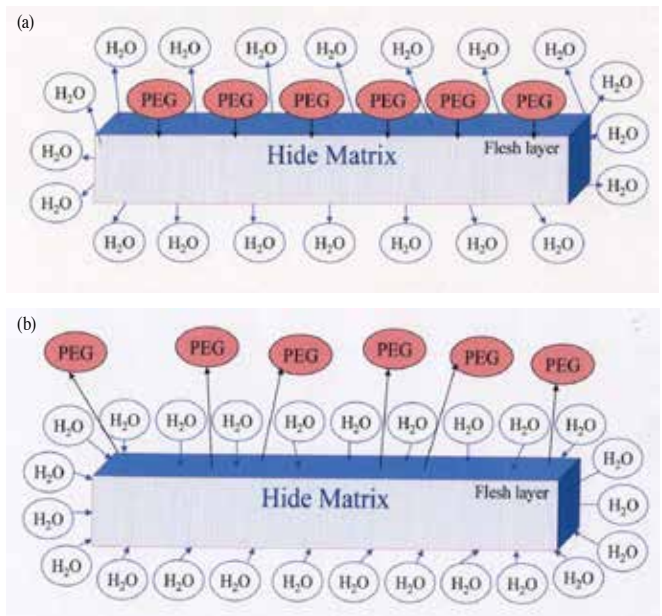
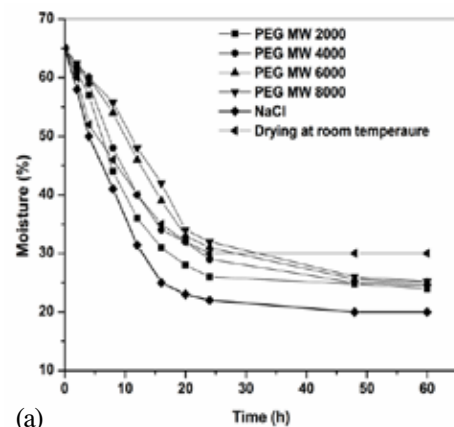
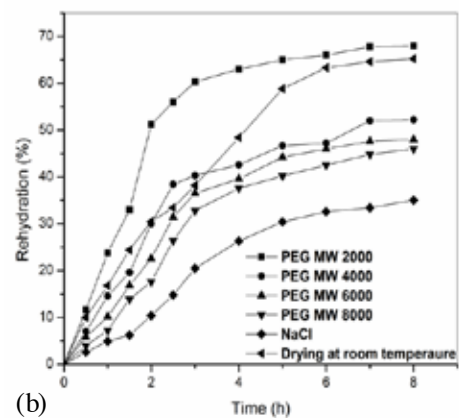


Figure 1. Schematic representation of (a) dehydration process of hide matrix by PEG (b) rehydration process of PEG treated hide matrix.



(a)



(b)

Figure 2. (a) Dehydration curves of raw hide during preservation of raw hide by PEG, NaCl and drying at room temperature, (b) Rehydration behaviors of raw hide preserved by PEG, NaCl and drying at room temperature.

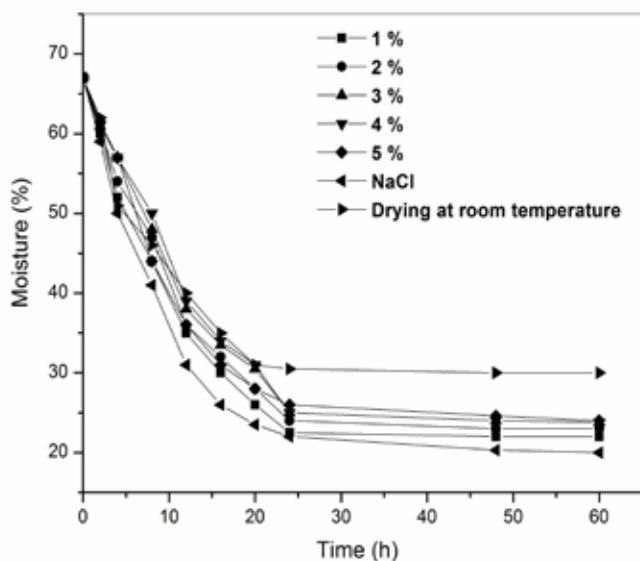


Figure 3. Dehydration curves of raw hide during preservation of raw hide by various percentage of PEG MW 2000, NaCl and drying at room temperature.

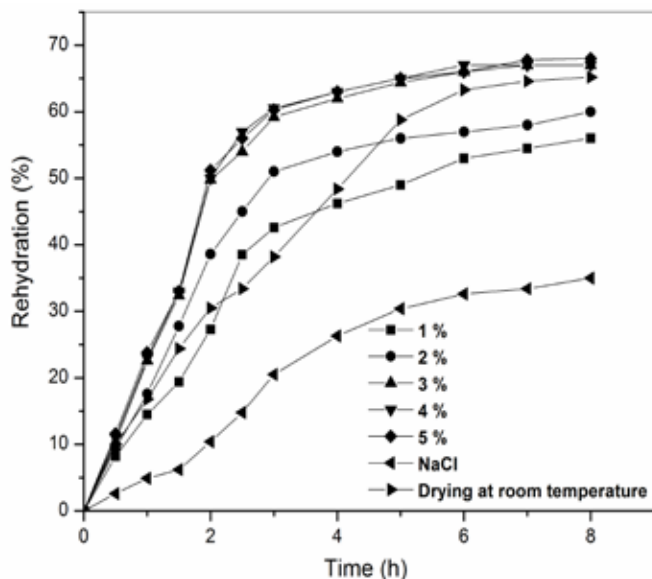


Figure 4. Rehydration behaviors of raw hide preserved by various percentage of PEG MW 2000, NaCl and drying at room temperature.

crystals are clearly seen in the hide matrix preserved using sodium chloride and it masks the arrangement of fiber bundles. However, hide sample preserved using PEG MW 2000 shows uniform and clear organization of fiber bundles. Further, the thickness of the PEG treated hide matrix sample is higher compared to control hides matrix samples. This is primarily due to the fiber coating nature of PEG, which retains the thickness of the hide during dehydration.

Differential Scanning Calorimetry and Fourier Transform Infrared Studies

The DSC thermograms of hide matrix preserved by PEG 2000, drying and sodium chloride are given in Figure 6. Endothermic peaks at 40°C is observed for hide matrix preserved using PEG 2000, which corresponds to melting temperature of PEG. Further, the peaks at 70 – 90°C show complete denaturation of the preserved hide matrix. This is in accordance with earlier literature.²⁴ The hide matrix preserved by drying and using sodium chloride shows endothermic peak at 215°C, which is the melting temperature of collagen/skin protein. Whereas the PEG 2000 treated hide matrix shows exothermic peak at 208°C. This could be due to the crystallization of PEG–protein. PEG not only coats the fiber, but also forms weak linkages with hide matrix.²⁶ Hence, the melting temperature of PEG treated hide matrix is slightly shifted to 230°C. FT–IR spectra for hide matrix preserved by PEG 2000, drying and sodium chloride are given in Figure 7. It is clearly seen that the PEG treated hide matrix exhibit peaks characteristic of both PEG and hide protein. The absorption band at 2931 cm^{-1} is attributed to the C–H stretching vibrations of the PEG alkane groups. Additional bands at finger print region such as 951 and 844 cm^{-1} shows bending of C–H linkages in peptide bond by CH_2 groups of the PEG. Further, it is evident from the literature that PEG forms linkages with peptide bonds and protein side chains.²⁷ All these signals indicate that the PEG is incorporated into the collagen/skin protein.

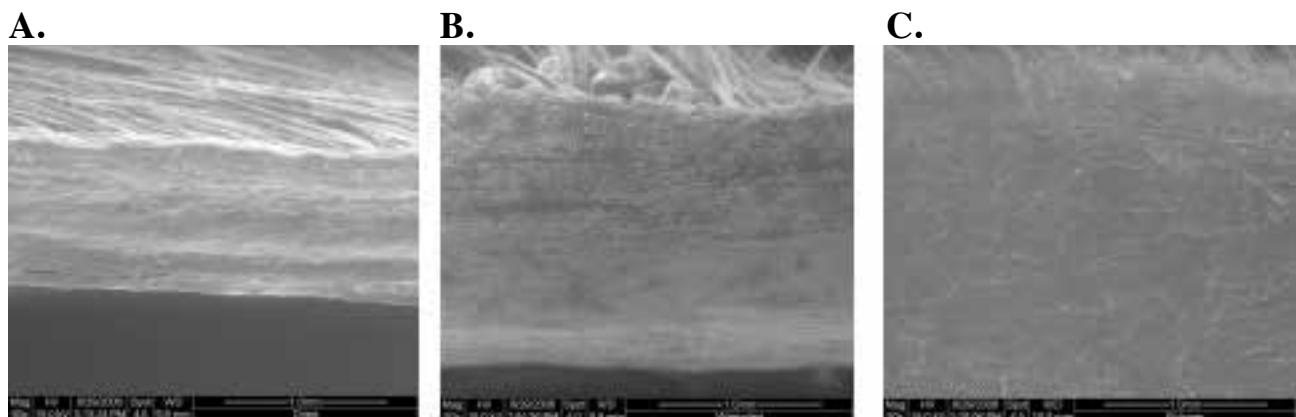


Figure 5. Scanning electron micrographs of preserved hide samples showing the cross section at a magnification of 50x from a) drying at room temperature b) sodium chloride and c) PEG MW 2000.

Comparison of the Effectiveness of Preservation

Method Based on PEG MW 2000 and Salt

Effectiveness of preservation process was assessed through the determination of loss of leather making protein during the storage of preserved hide samples for 90 days. It is known that estimation of hydroxyproline in spent soak liquor is used as a potential marker to identify the degradation of leather making protein.⁸ It is observed from Figure 8 that the hide sample preserved by drying shows significant degradation of hide matrix compared to sodium chloride and PEG MW 2000 based preservation. This is primarily due to improper removal of moisture during the drying process, which results in the degradation of inner layer of the hide matrix during the storage. It has been reported that drying method of preservation is difficult for hides due to their thickness.⁸ The degradation of hide matrix preserved by sodium chloride is slightly higher compared to the PEG MW 2000 based preservation of hide. Hence, PEG MW 2000 based preservation is found to be more efficient as compared to salt based preservation. The hide matrix preserved by drying method had difficulty in wetting back (soaking) and exhibited significant degradation during the initial storage condition, hence it has been omitted for bulk trial evaluations.

Bulk Trial Studies: An Appraisal Input and Output Analysis

The input and output of raw materials, chemicals and water were analyzed for both conventional and experimental preservation and soaking processes. The observed input and output values have been calculated for processing one ton (t) of raw cowhides and are given in Table I. The weight of the preserved hide from control is higher compared to experimentally preserved hides. This is mainly due to the use of 400 kg salt to displace 270 kg water. However, the experimental preservation employs only 30 kg PEG to displace 280 kg of water. The experimental process provides a reduction in chemical input by 92%. The excess amount of salt

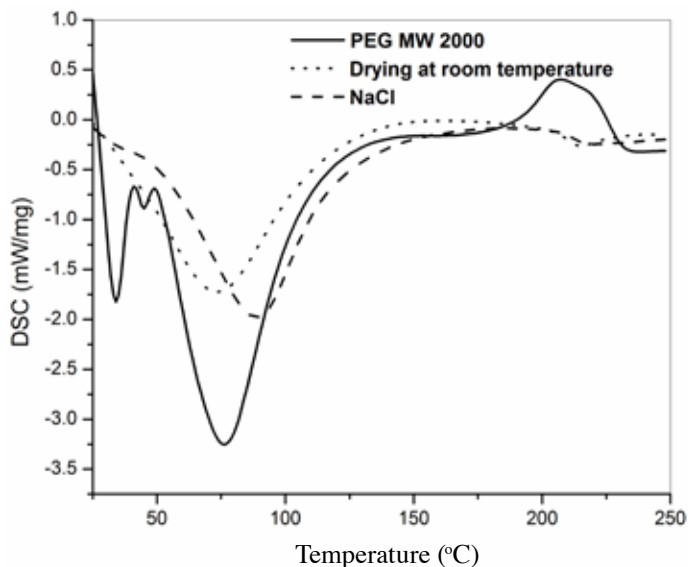


Figure 6. Differential scanning calorimetry (DSC) thermograms of hide samples.

used during preservation is removed before soaking through desalting operation. The desalting operation removes nearly 124 kg salt, which is a solid waste that causes a disposal problem.

Analysis of Soak Liquor and Composite Liquor

The spent soak liquors contain polluting matter and it contributes to high salinity (TDS). The emission loads of the pollutants are given in Table II. Pollutant loads from spent soak liquor of

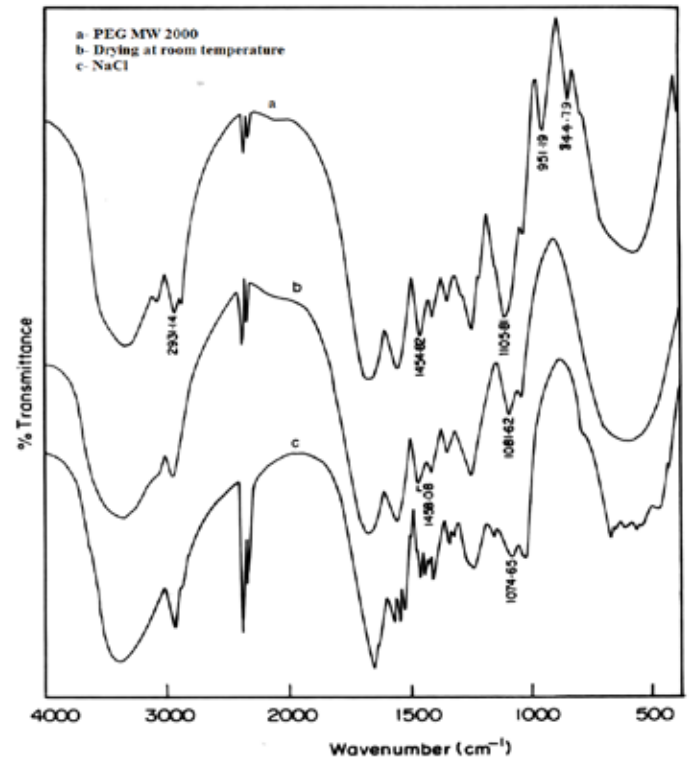


Figure 7. FT-IR spectra of hide samples.

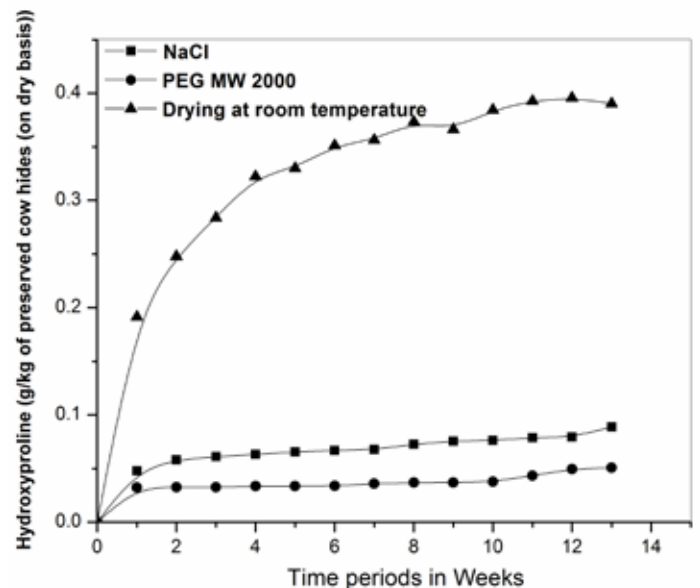


Figure 8. Effectiveness of preservation method by PEG MW 2000, NaCl and drying at room temperature.

experimental is lower compared to salt based preservation method. Generally, globular proteins such as albumin and globulin are removed from the hides during the soaking of hides preserved using sodium chloride, due to its salt solubility nature. Hence, the presence of these matter increases the BOD and COD loads in the spent soak liquor of cow hides preserved by sodium chloride. In the case of PEG MW 2000 based preservation, the globular proteins are removed during the subsequent operations such as liming, reliming, bating and pickling. Salt based preservation contributes to nearly 160 and 278 kg of Cl⁻ and TDS, respectively for soaking one-ton of preserved cow hides. This is primarily due to the removal of salt, which was used during the preservation process. This is one of the major problems faced by the tanners around the globe. The polymer based preservation contributes to 2 and 19.5 kg of Cl⁻ and TDS, respectively for soaking 1 t of preserved cow hides. Hence, the PEG MW 2000 based preservation method reduces the BOD, COD, Cl⁻ and TDS loads by 75, 28, 99 and 93%, respectively. The significant reduction in TDS and chloride loads helps in achieving cleaner and greener leather processing.

The composite liquors have been collected from control and experimental processes from soaking to post tanning and analyzed for their impact on environment. The calculated

emission loads of pollutants are given in Table II. There is no significant reduction in BOD and COD emission loads. However, the reduction in emission loads of Cl⁻ and salinity is about 63 and 43% compared to conventional leather processing. It is evident that the developed preservation method reduces the salinity of water significantly, which is a breakthrough in leather processing. This is primarily due to the PEG based preservation, which avoids the use of salt for preservation.

Physical and Hand Evaluation of Leathers

The strength properties such as tensile, tear and grain crack strength values were obtained by standard physical testing methods and are presented in Table III. It is seen that both control and experimental leathers exhibit comparable tensile, tear, grain crack and bursting strength values. Control and experimental crust leathers were evaluated for various organoleptic properties by hand evaluation. The average of the rating for the five leathers corresponding to each experiment was calculated for each functional property and is given in Figure 9. Higher numbers indicate better property. The experimental leathers exhibit better fullness compared to control leathers. Other properties such as softness, grain tightness and smoothness are comparable to that of conventionally processed leathers. In general, the appearance of experimental leathers is also similar to that of control leathers.

TABLE I
Input-output audit and cost analysis of conventional (C) and experimental (E) processes (for processing 1 t of raw cow hides)

Process	Chemicals/raw material	C		E		Cost (US\$/t of raw cow hides)		
		Input (kg)	Output (kg)	Input (kg)	Output (kg)	Parameter	C	E
Preservation	Raw cow hides	1000	1150	1000	730	Salt	24.17	-
	Salt	400	-	-	-	PEG 2000	-	31.45
	Water	-	270	-	280	Labor	4.03	4.03
	PEG 2000	-	-	30	N.E	Total	28.20	35.47
Desalting	Preserved hides	1150	1030	-	-			
	Salt	-	124	-	-			
Soaking	Desalted/Preserved hides	1030	1050	730	1070			
	Water	9000	8260	9000	7990			
	Salt	-	264	-	-			

N.E – Not Estimated

Note: all the costs are based on commercial value in India at the time of publication. The Indian rupee value was converted into US\$ for the convenience of global readers (1 US\$ = Rs. 55.00).

TABLE II
Analysis of pollution loads from control and experimental spent soak liquors and composite liquors.

Sample	BOD (ppm)	COD (ppm)	Cl ⁻ (ppm)	TDS (ppm)	Volume of spent soak liquor/ effluent (L/t of preserved hides)	Emission loads(kg/t of preserved hides soaked)			
						BOD (ppm)	COD ppm)	Cl ⁻ (ppm)	TDS (ppm)
Spent soak liquors analysis									
Control									
1 st soak	1282±12	5100±12	42904±22	75229±24	2480	3.17	12.64	106.40	186.56
2 nd soak	912±18	3400±8	16950±16	28517±18	2820	2.57	9.58	47.80	80.41
3 rd soak	794±8	2840±12	2130±18	3706±20	2960	2.35	8.40	6.30	10.96
Total						8.09	30.62	160.5	277.93
Experimental									
1 st soak	496±14	4280±10	221±12	3918±22	2350	1.16	10.05	0.52	9.20
2 nd soak	172±12	2824±12	262±16	2242±18	2780	0.47	7.85	0.72	6.23
3 rd soak	124±18	1246±8	234±22	1458±24	2860	0.35	3.56	0.66	4.16
Total						1.98	21.46	1.9	19.59
Composite liquor analysis									
C	1884±12	8204±32	12639±32	30378±48	18040	34	148	228	548
E	1745±16	7872±24	4726±32	17664±52	17780	31	140	84	314

^aComposite liquors were collected from all the unit operations from soaking to post tanning

^bAverage of three measurements

TABLE III
Physical testing data of control (C) and experimental (E) crust leathers

Sample	Tensile strength (kg/cm ²)	% Elongation at break	Tear strength (kg/cm)	Grain crack strength (average value ^b)	
	Average value ^a	Average value ^a	Average value ^a	Load (kg)	Distension (mm)
C	242±5	62±2	34±5	46±1	9.8±0.3
E	273±6	69±4	46±2	50±2	10.3±0.4

^aAverage of mean of five measurements of along and across backbone values

^bAverage of five measurements of load and distension values

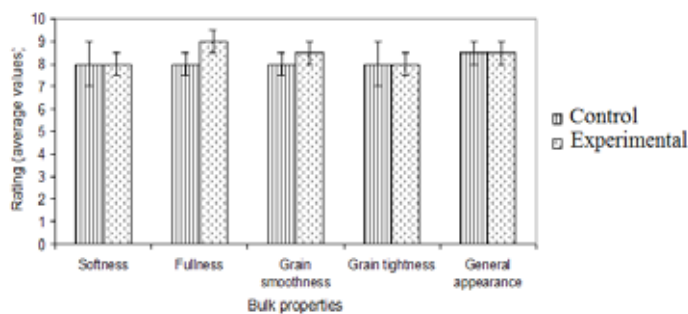


Figure 9. Bulk properties of control and experimental crust leathers.

Techno-economic Benefits

Techno-economic data for preservation of one ton of raw cow hides using PEG and sodium chloride is given in Table I. It is seen that the cost for PEG based preservation is slightly higher compared to salt based method. Further, the composite liquor from control and experimental process requires reverse osmosis treatment to meet the discharge norm prescribed by the pollution control boards.²⁸ The treatment cost of reverse osmosis depends on the salinity of the wastewater.²⁹⁻³⁰ The salinity is high for control compared to experimental wastewater. Hence, the experimental process reduces the treatment cost. This provides a benefit in saving of treatment cost. Besides, the disposal or reuse of salt removed during the desalting operation in control process is another major environmental constraint, which has been overcome successfully by using PEG for preservation.

CONCLUSIONS

The sustainability of global leather industry would depend on the development of an alternative system for leather making. The PEG molecular weight of 2000 at an offer of 3% has been standardized based on the dehydration and rehydration behavior of the preserved hide matrix. Scanning electron microscopy study reveals that the hide sample preserved by PEG shows well separated fibre bundles with uniform fibre structure compared to dried and salted hide matrix. Further, the grain surface of both the control and experimental crust leather samples seems to be clean and visible without any damage. The cross sectional view of the crust leather samples show uniform orientation of fibers. The presence of PEG in the hide matrix is confirmed through FT-IR spectrum. The degradation of hide matrix preserved by sodium chloride is slightly higher compared to the PEG based preservation of hides. Input-output analysis discloses that PEG based preservation process reduces the chemical input by 92%. PEG based preservation method reduces the BOD, COD, Cl⁻ and salinity loads by 75, 28, 99 and 93%, respectively. Further, the reduction in emission loads of Cl⁻ and salinity is about 63 and 43% compared to conventional leather processing in composite liquor. The functional properties of experimental leathers are

comparable to that of conventionally processed leathers. The cost analysis study showed that the developed preservation process is technically viable and economically acceptable alternative for salt based preservation.

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REFERENCES

1. Fathima, N.N., Saravanabhavan, S., Rao, J.R., Nair, B.U. ; An eco-benign tanning system using aluminum, tannic acid, and silica combination. *JALCA* **99**, 73-81, 2004.
2. Saravanabhavan, S., Fathima, N.N., Rao, J.R., Nair, B.U.; Combination of white minerals with natural tannins - Chrome-free tannage for garment leathers. *J. Soc. Leather Technol. Chem.* **88**, 76-81, 2004.
3. Thanikaivelan, P., Rao, J.R., Nair, B.U., Ramasami, T.; Progress and recent trends in biotechnological methods for leather processing. *Trends Biotechnol.* **22**, 181-188, 2004.
4. Nadiya, K., Punitha, V., Amsamani, S., Rao, J.R., Chandrasekaran, B., Thanikaivelan, P.; Eco-benign enzymatic dehairing of goat skins utilizing protease from *Pseudomonas fluorescens* species isolated from fish visceral wastes. *J. Clean. Prod.* **25**, 27-33, 2012.
5. Punitha, V., Kannan, P., Saravanabhavan, S., Thanikaivelan, P., Saravanan, P., Rao, J.R., Nair, B.U., Ramasami, T.; Enzymatic removal of melanin in enzyme based dehairing and fibre opening. *JALCA* **103**, 167-172, 2008.
6. Bailey, D.G. ; The preservation of hides and skins. *JALCA* **98**, 308-319, 2003.
7. Bienkiewicz, K.; Physical Chemistry of Leather Making; Krieger Publishing; Malabar, FL, 1983.
8. Heidemann, E.; Fundamentals of Leather Manufacture, Eduard Roether KG: Darmstadt, 1993.
9. Ramasami, T., Rao, J.R., Chandrababu, N.K., Parthasarathi, K., Rao, P.G., Saravanan, P., Gayathri, R., Sreeram, K.J.; Beamhouse and tanning operations: Process chemistry revisited. *J. Soc. Leather Technol. Chem.* **83**, 39-45, 1999.
10. CPCB. 2009. Recovery of better quality reusable salt from soak liquor of tanneries in solar evaporation pans, Central Pollution Control Board (CPCB) Ministry of Environment & Forests Control Of Urban Pollution Series: Cups, 2009-10.
11. Sundar, V.J., Muralidharan, C.; Eco-benign skin preservation through salt substitution - a low salt approach. *Desal. Water Treat.* **11**, 314-317, 2009
12. Didato, D., Steele, S., Stockman, G., Bailey, D.; Recent developments in the short term preservation of cattle hides. *JALCA* **103**, 383-392, 2008.

13. Kanagaraj, J., Chandrababu, N.K., Sadulla, S., Rajkumar, G.S., Visalakshi, V., Chandrakumar, N.; A new approach to less-salt preservation of raw skin/hide. *JALCA* **95**, 368, 2000.
14. Kanagaraj, J., Sastry, T.P., Rose, C.; Effective preservation of raw goatskins for the reduction of total dissolved solids. *J. Clean. Prod.* **13**, 959-964, 2005b
15. Kanagaraj, J., Sundar, V.J., Muralidharan, C., Sadulla, S.; Alternatives to sodium chloride in prevention of skin protein degradation - a case study. *J. Clean. Prod.* **13**, 825-831, 2005a.
16. Kannan, K.C., Kumar, M.P., Rao, J.R., Nair, B.U.; A novel approach towards preservation of skins. *JALCA* **105**, 360-368, 2010.
17. Ramos, M., Muir, Z.; Development of an alternative low salt bovine hide preservation using PEG and crude glycerol, Part 1: curing efficiency in terms of its dehydration and rehydration rate and chloride content. *JALCA*, Accepted September 2013.
18. Chin, J., Spear, S.K., Huddleston, J.G., Rogers, R.D.; Polyethylene glycol and solutions of polyethylene glycol as green reaction media. *Green Chem.* **7**, 64-82, 2005.
19. Saravanabhavan, S., Thanikaivelan, P., Raghava Rao, J., Nair, B.U.; A new leather making process for meeting eco-label standards: processing of goatskins. *JALCA* **101**, 192-205, 2006.
20. SLC 3, Détermination of moisture content in leather. 1966.
21. IUP 2. Sampling. *J. Soc. Leather Technol. Chem.* **84**, 303-309, 2000.
22. Woessner, J.F. Jr.; The determination of hydroxyproline in tissue and protein sample containing small proportions of this imino acid. *Arch. Biochem. Biophys.* **93**, 440-447, 1961.
23. Clesceri, L.S., Greenberg, A.E., Trussell, R.R., Eds.; In: Standard Methods for the Examination of Water and Wastewater, 17th ed.; American Public Health Association: Washington DC, 1989.
24. Ide, M., Yoshikawa, D., Maeda, Y., Kitano, H.; State of water inside and at the surface of polyethylene glycol films examined by FT-IR. *Langmuir* **15**, 926-929, 1999.
25. Fathima, N.N., Madhan, B., Rao, J.R., Nair, B.U.; Effect of zirconium(IV) complexes on the thermal and enzymatic stability of type I collagen. *J. Inorg. Biochem.* **97**, 47-54, 2003.
26. Sionkowska, A.; The influence of UV light on collagen/poly(ethylene glycol) blends. *Polym. Degrad. Stabil.* **91**, 305-312, 2006.
27. Zhou, S., Deng, X., Yang, H.; Biodegradable poly(ϵ -caprolactone)-poly(ethylene glycol) block copolymers: characterization and their use as drug carriers for a controlled delivery system. *Biomater.* **24**, 3563-3570, 2003.
28. Buljan, J.; Pollution limits for discharge of tannery effluent in water bodies and sewers. *World Leather*, November, 65-68, 1996
29. Scholz, W.G., Rouge, P., Bodalo, A., Leitz, U.; Desalination of mixed tannery effluent with membrane bioreactor and reverse osmosis treatment. *Environ. Sci. Technol.* **39**, 8505-8511, 2005.
30. Reddy, K.V., Ghaffour, N.; Overview of the cost of desalinated water and costing methodologies. *Desal.* **205**, 340-353, 2007.