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ALUMIMIUM-VEGETABLE COMBINATION TANNAGE FOR PRODUCTION OF SHOE UPPER LEATHERS

مزيج اللألمونيوم والنباتات للدباغة للإنتاج جلد الأحذية العلوية

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المستخلص

عملية الدباغة هي تحويل الجلد الخام القابل للتعفن الي جلد مدبوغ مفيد غير قابل للتعفن .ان تطوير تقنيات معالجة الجلود النظيفه الخاليه من التلوث البيئي ضروري لاستمرار صناعة الدباغه. في هذه الدراسه تم تطوير نظام الدباغه المختلطه باستعمال الحنا و الالمونيوم لانتاج جلود الوجه وقد استعمل مستخلص أوراق الحنا المتوفره في السودان لدراسة خصائصه الدابغه في نظام الدباغة المختلطه بالحنا و كبريتات الألمونيوم. وقد استعملت طريقتين للدباغة المختلطه. في هذه الدراسة تم تطبيق الدباغه بالحنا والالمونيوم، وكان تركيز كبريتات الالمونيوم (2% اوكسيد الالمونيوم). كل الخلطات أنتجت جلود ذات درجة انكماش فوق 90^oC. وقد كانت الجلود التي دبغت بالالمونيوم (2% اوكسيد الالمونيوم) و واتبعت بالدباغه بالحنا(20%) أنتجت جلود ذات درجة حرارة انكماش 95^oC - **اما** الجلود التي دبغت بالحنا (20%) و واتبعت بالدباغه بالالمونيوم (2% اوكسيد الالمونيوم) أنتجت جلود ذات درجة انكماش 97^oC **.** كمية الحنا الممتصه بواسطة الجلود في نظام الدباغه بالحنا (20%) المتبعة بالالمونيوم (2% اوكسيد الالمونيوم) كانت افضل من الالمونيوم المتبع بالحنا وكانت الجلود المنتجه تتميز بالياف متماسكه و متفتحه مما يدل بأن عملية الدباغه لا توثر علي تركيب الياف الجلد و كذلك قد ادي نظام الدباغه المختلطه لانخفاض في محتوي الكلي للمواد الصلبه الذائبه المطلقه في مخلفات المياه. وقد اعطي نظام الدباغه بالحنا المتبع بالالمونيوم جلود متميزه بخواص فيزيائيه جيده. في هذا البحث تم تاصيل أستعمال نظام الدباغه المختلطه بالحنا و الالمونيوم لنظام فعال ومواكب مع طرق الانتاج والتقنية النظيفة

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Abstract

Leather processing involves conversion of putrescible raw skins/ hides into useful material called leather by the process having common name 'tanning'. Development of cleaner leather processing technologies is imperative for the sustenance of the tanning industry. In the present study, a combination tanning system based on Henna–Aluminum tannage for the production of upper leathers as a cleaner alternative is presented. Extract from the leaves of widely distributed lawsonia inerims (Henna) from Sudan has been evaluated for its tanning characteristics in a combination tanning system based on Henna and Aluminum sulphate. Both tanning methodologies henna followed by Aluminum (Henna-Al) and Aluminum followed by Henna (Al-Henna) have been attempted at concentration of 2% Al_2O_3. All combinations tanning systems resulted in leathers with shrinkage temperature above 90^oC. However, Al-Henna leathers tanned using 2% Al_2O_3; followed by 20% henna resulted in shrinkage temperature of 95^oC, and Henna (20%) followed by Aluminum (2% Al_2O_3) resulted in leathers with shrinkage temperature of 97^oC. The uptake of henna in Henna-Al tanning system with Henna (20%) followed by Aluminum (2% Al_2O_3) has been found to be better than the tanning system of Al-Henna. These leathers showed opened up, split compact fibre structure, indicating that the tanning process did not bring about any major change or destruction on the fibre structure of the leathers. The combination system provides significant reduction in the discharge of total dissolved solids in tanneries wastewater. Henna-Al combination system resulted in leathers with good organoleptic and strength properties. The work presented in this paper established the use of henna aluminium combination tanning system as an effective alternative cleaner tanning methodology.

Key words: combination tanning, leather, aluminium

Introduction

Raw hides and skins are obtained as a co-product of the meat industry. Once hide or skin is removed from the animal it is treated with various chemicals at different stages for conversion into leather. The various processes involved in leather making are given in Fig. 1 (Suresh *et al*, 2001).

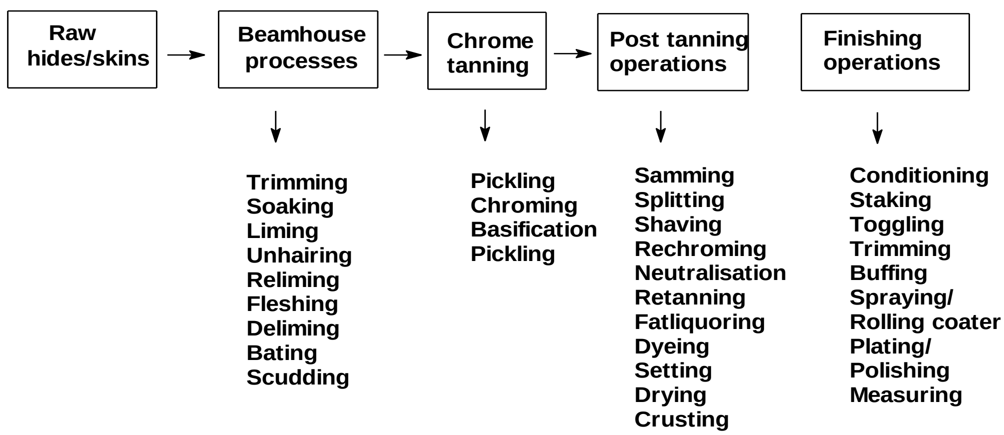


Fig. 1: Process flow sheet for conventional leather processing

Chrome tanning is the predominant tanning system employed in commercial practices, as they result in versatile leathers. Even though chrome tanned leathers have many significant advantages, they suffer from the serious disadvantage due to the constraints of its discharge norms of 2ppm (BIS, 1985). It is well established that hexavalent chromium is carcinogenic (Flora, et al 1990). It has also been shown that there is a possibility for the formation of chromium (VI) in leather during the processing conditions (Nickolauss. 1995; Font et al., 1999). Some reports suggest that at high levels and under certain ligand environments, chromium (III) is toxic (Vijayalakshmi, et al 2000). The problem is provoked by the fact that the conventional chrome tanning procedures results in an uptake of only 60-65% of the chromium offered to the leather and hence a substantial amount of chrome is discharged into the effluent (Chandrasekaran et al., 1999). As of now, there is no safe disposal method available for used chrome tanned leather products, which is another major concern. Hence to overcome the problems associated with chrome tanning, researchers throughout the world are looking for alternative tanning systems. In line with the resurgence of natural product dominance in the global manufacturing industry, leather industry is also re-looking at the possibility of increased use of organic materials. In this scenario, vegetable tanning could play a dominant role in the future of leather industry. The leathers processed through vegetable tanning have distinct advantages such as comfort, compatibility with human skin and high dimensional stability. Moreover, the tanning methodology adopted affords easy disposal of spent liquors (Thomas and Wayne, 1996). However, the problem with the vegetable tannage is its poor thermal stability. It is very difficult for a single tanning agent to match chromium tanning salt with respect to its hydrothermal stability. Hence one has to look for an additional (combination) tanning agent to be used along with vegetable tanning to improve the leather properties. Some of the vegetable based combination tanning systems viz., vegetable–oxozolidine (Happich et al, 1965; D'Aquino et al, 2004; Suparno et al, 2007**)**, vegetable-Aluminum (Chockalingam et al, 1981; Covington, 1998; Ding, 2007), vegetable–zinc (Morera, 1996) and vegetable-acrylic (Madhan et al , 2001) have produced encouraging results. In all these reports wattle had been the source for vegetable tannin as it is the primary vegetable tannin used by vegetable tanning industries. However, the resource of this single plant species will not be able to meet the requirements of tanning industry (Frendrup, 2000). Hence one has to look out for alternative vegetable tanning materials. Recently, Henna has been established as an alternative retanning material for wattle (Musa et al, 2008). Lawsonia inermis (Henna) is a shrub that is semi cultivated in the savannah region of West Africa. Leaves are commonly used as cosmetics for staining hands and feet in Sudan. Lawsonia inermis (Henna) is a member of the family Lythraceae. It is widely cultivated in tropical regions of Sudan, Egypt, China, and India (Leung, 1980). Extracts of henna had been shown to contain anti-fungal and anti-bacterial characteristics (Datta et al, 1989; Al Yahya, 1968). Henna finds use in traditional medicinal preparations and in textile industry for dyeing (Badri and Burkinshaw , 1993). However, there is no reported literature on the use of Henna as a tanning agent for the combination tanning. Rao and Nayudamma (1964) have extensively studied the vegetable–Aluminum combination tannage. In their studies, they have explored both the tanning options viz., addition of Aluminum salts before myrobalan and addition of Aluminum salts after myrobalan. Aluminum treatment followed by myrobalan exhibited a shrinkage temperature of 66-69^oC, and interestingly, pelts treated with myrobalan followed Aluminum resulted in shrinkage temperature of 110-114^oC. Whereas, in the case of wattle tannin Aluminum followed wattle (mimosa) results in better leather properties (Slabbert, 1981). Since Henna extract contain a mixture of several compounds with varied molecular weight including tannin (polyphenols), an attempt has been made in this study, to evaluate the combination tanning system with Aluminum sulphate.

Materials and Methods

Materials

Pickled goat skins were taken for the combination tanning trials. Henna leaves were sourced from Sudan (Aldamar area). Chemicals used for retannage were of commercial grade. Chemicals used for the analysis of spent liquor were of analytical reagent.

Extraction of Henna Leaves

Dry henna leaves were grounded into powder and known weight of powder was taken in water at the ratio 1:10 w/v of henna to water. The water bath containing henna powder was heated at 80^oC for an hour and then filtered through cotton cloth. The henna powder contains a total of 35% water solubles. For example, 1 kg of henna powder 10 liters of water needs to be added, after extraction, 350 grams of water soluble is obtained. The solution was further concentrated to 1 liter. The stock solution thus prepared contains 35% (w/v) solids and the same was used for combination tanning experiments.

Preparation of basic Aluminum sulphate solution

A known amount of Aluminum sulphate has been taken in a beaker and 150% of water (% based on the weight of Aluminum sulphate) has been added and the solution stirred for 15-20 minutes, subsequently required amount of ligand (sodium citrate and sodium tartrate) have been added and stirring has been continued for 45 min followed by slow addition of sodium carbonate until the pH has been raised to 3.5. For 0.5M of Aluminum sulphate 0.1M of ligand has been added.

Tanning Trials

Pickled goat skins have been used for combination tanning trials; Al-Henna tanning and Henna-Al tanning process are shown in Table 1 and 2 respectively. The amount of Aluminum sulphate used for the tanning trials has been 2% Al_2O_3 in both the experimental processes. A control tanning process has been carried out using Henna only as given in Table 3. The post tanning process as mentioned in Table 4 has been followed for experimental and control leathers.

Table 1: Formulation of the Henna–Aluminum combination tanning system for pickled goat skins

Process	**%**	**Product**	**Duration (min)**	**Remarks**
Adjustment of the pH	100	Water		
	0.75	Sodium bicarbonate	3× 15	pH 4.5 -4.7
Tanning	2	Basyntan P (phenolic syntan)	30	
	10	Henna extract	120	
	10	Henna extract	120	
	2	Al_2O_3 (prepared Aluminium sulphate solution))	90	

Basification	0.75	Sodium bicarbonate	3× 15	Check the pH to be 4. Drain the bath and pile overnight. Next day sammed and shaved to 1.2 mm. The shaved weight noted.

Measurement of shrinkage temperature:
The shrinkage temperature of both control and experimental leathers were determined using the Theis shrinkage tester (McLaughlin and Theis, 1945). A 2cm sample, cut out from the leather was clamped between the jaws of the clamp, which in turn was immersed in a solution of glycerol: water mixture (3:1). The solution was stirred using mechanical stirrer attached with the shrinkage tester. The temperature of the solution was gradually increased and the temperature at which the sample shrinks was noted. Triplicates were carried out for each sample and the average values are reported.

Table 2: Formulation of Aluminum-Henna combination tanning system for pickled goat skins

Process	**%**	**Product**	**Duration (min)**	**Remarks**
Pickled pelt	50	Pickled liquor		pH 2.8-3
Aluminum tanning	2	$Al_2 O_3$ (prepared Aluminum sulphate solution)	120	
Adjustment of pH	0.75	Sodium bicarbonate	3× 15	pH 4.5 -4.7
Henna tanning	2	Basyntan P (phenolic syntan)	30	

	10	Henna extract	90	
	10	Henna extract	90	
Fixing	0.5	Formic acid	3× 10 +30	Check the pH to be 3.5. Drain the bath and pile overnight. Next day sammed and shaved to 1.2 mm. The shaved weight noted.

Assessment of the crust leathers

Experimental and control crust leathers were assessed for softness, fullness, grain smoothness, grain tightness (break), general appearance and dye uniformity by hand and visual examination. Three experienced tanners rated the leathers on a scale of 0-10 points for each functional property, where higher points indicate better property.

Table 3: Formulation of control henna tanning process for goat pickled skins

Process	%	Product	Duration (min)	Remarks
Adjustment of the pH	100	Water		
	0.75	Sodium bicarbonate	3× 15	pH 4.5 -4.7
Tanning	2	Basyntan P (phenolic syntan)	30	
	10	Henna extract	120	
	10	Henna extract	120	
Fixing	0.25	Formic acid	3× 10 + 30	
Washing	300	Water	10	Check the pH to be 3.5. Drain the bath and pile overnight. Next day sammed and shaved to 1.2 mm. The shaved weight noted.

* - % chemical offer is based on pickled pelt weight of the goat skins

Physical properties

Samples for various physical tests from experimental and control crust leathers were obtained as per IULTCS methods (IUP 2, 2000). Specimens were conditioned at $20 \pm 2\,^{o}C$ and 65 ± 2 % R.H (Relative Humidity)over a period of 48 hrs. Physical properties such as tensile strength, percentage elongation at break (IUP 6, 2000), grain crack strength (SLP 9, 1996) and tear strength (IUP 8, 2000) were measured as per standard procedures. Each value reported is an average of four (2 along the backbone, 2 across the back bone) samples.

Table 4: Formulation of retanning process for control and experimental leathers

Process	**%**	**Product**	**Duration (min)**	**Remarks**
Washing	200	Water	10	
Neutralization	0.75	Sodium bicarbonate	3× 15	pH: 5-5.5
Pre-retannage	100	Water		
	2	Relugan RE (Acrylic syntan)	40	
Pre-fatliquor	2	Lipoderm liquor SAF (Synthetic fatliquor)	40	
	2	Basyntan DI	30	
Dyeing	3	Acid dye brown	30	
Fatliquoring	3	Lipoderm liquor SAF (Synthetic fatliquor)		
	4	LB II	40	
Retanning	3	Basyntan DI		
	4	Basyntan FB6(phenolic syntan)	40	
Fixing	1	Formic acid	3× 10 + 30	pH 3.5

* - % chemical offer is based on shaved weight of the tanned leather

Measurement of leather Softness

Softness measurement of experimental and control crust leather was carried out as per standard method.(IUP 36, 2000) Samples were conditioned at 20

$\pm 2\,^{o}C$ and $65 \pm 2\%$ R.H over a period of 48 hrs before the measurement. Circular aperture of diameter 35 mm is used for the softness measurement. Each value reported is an average of four measurements.

Scanning Electron Microscopic Analysis of Leather Samples

Samples from experimental and control crust leathers were cut from official sampling position. Samples were directly cut into specimens with uniform thickness without any pretreatment. All specimens were then coated with gold using Edwards E306 sputter coater. A Leica Cambridge Stereoscan 440 Scanning electron microscope was used for the analysis. The micrographs for the cross section were obtained by operating the SEM at an accelerating voltage of 20 KV with different lower and higher magnification levels.

Analysis of Henna Extract Exhaustion

Spent henna extract liquor from control and experimental tanning processing was collected and analyzed for the concentration using a spectrophotometric method by measuring the absorbance value at the λmax of the henna extract used, after suitably diluting the spent extract liquor using UV–visible spectrophotometer (Hitachi, Japan).

$$\% \text{ Henna extract exhaustion} = [(C_o - C_s)/C_o] \times 100$$

Where C_o is the concentration of henna extract offered and C_s is the concentration of henna extract in the spent liquor. Each value reported is an average of four measurements.

Analysis of spent liquors from tanning trials

The spent tannin liquor from control and experimental tanning processes have been collected, filtered and analyzed for chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), and total dissolve solids (TDS) as per standard procedures (Clesceri et al., 1989).

Results and Discussion

The tanning system using Henna and Aluminum are eco friendly, it is essential to study the properties of the leathers comparable with that of chrome tanning system. The thermal stability of chrome tanned leathers is known to be equal to $100^{o}C$. The shrinkage temperature data for various combinations of Henna and Aluminum combination tanning systems are given in Table 5. It is seen from the table that leathers treated with 2% Al_2O_3 exhibits higher shrinkage temperature. The shrinkage temperature of leathers obtained from combination tanning of Henna-Al is slightly higher than Al-Henna combination tanning systems. Both the combination tanning systems Henna-Al and Al-Henna resulted in leathers with shrinkage temperature above 95^{o}C, whereas control tanning using Henna alone resulted in a shrinkage temperature of 84^{o}C. From Table 5**,** it can be observed that Henna-Al combination tanning system resulted in enhancement of shrinkage temperature similar to that of wattle-Aluminum combination tanning system.

Gustavson (1956) proposed a mechanism for the increase in stability of alum-tanned leathers retanned with vegetable tannins. Interaction of tannins and non-tannins with Aluminum complexes results in increased fixation of vegetable tannins. However, tanning with the same combination but reversing the order (vegetable-tanned leather retanned with Aluminum), results in increasing the amount of irreversibly fixed tannins due to mordanting effect of the basic Aluminum salts on the uncombined tannins and non-tannins in leather (Official Methods of Analysis, 1965). The exhaustion of Henna for Al-Henna and Henna-Al and control (Henna tanning) are given in Table 5. It is observed that there is increase in the amount of Henna fixed in the presence of Aluminum and increased exhaustion of Henna is observed that can be related to increase in shrinkage temperature of combination tanning systems of Henna. As the shrinkage temperature and exhaustion have been better for the experimental leathers processed with 2% Al_2O_3, accordingly Al-Henna with 2% Al_2O_3 and 20% Henna combination tanning system has been optimized.

Performance of leathers

Bulk properties of leathers - hand evaluation of leathers

Crust leather from both control and experimental processes has been evaluated for various bulk properties by hand and visual evaluation. The average of the rating for the leathers corresponding to experiment has been calculated for each functional property and is given in Fig. 2. Higher numbers indicate better property. From the figure, it is observed that Henna-Al combination tanned experimental crust leathers exhibited good fullness compared to Henna control leathers. The organoleptic properties of the Henna-Al crust leathers are better compared to Al-Henna crust leathers. This is primarily due to improved penetration and fixation of Henna in the experimental process, compared to control process. Other properties such as softness, grain tightness, smoothness, dye uniformity and general appearance are comparable to that of conventionally processed leathers. The overall appearance of optimized experimental leathers is better than that of control and other experimental leathers.

Strength characteristics of experimental and control crust leathers

It is essential to study the influence of the tanning system on the strength properties of leathers. The physical strength measurements viz., tensile strength, elongation, tear strength, load at grain crack and distension at grain crack were carried out for the control and experimental crust leathers and the data is given in Table 6. It is observed that the tensile strength characteristics like tensile strength, elongation, tear strength of Henna-Al tanned crust leathers is found to be higher compared to that of the control and Al-Henna tanned crust leathers, whereas load at grain crack and distension at grain crack of both control and Al-Henna tanned leathers are found to be marginally lower.

Softness measurements of Henna-Al tanning system

Natural tannins from plant origin are known to produce hard leathers and generally employed for producing firm leathers. Hence, it is important to evaluate the extent of softness contributed by Henna on the final leathers. The softness values of leathers measured using softness tester are given in Table 6. The softness of the crust leathers measured in 35 mm diameter ring for Henna-Al is 5.3 mm compared to 3.4 mm for Henna tanned crust leathers. Higher values signify more softness of the leather. The experimental leathers exhibited better softness compared to the Henna control leathers, which is also in accordance with the observations made from visual assessment data shown in Fig. 2.

Scanning electron microscopic analysis of leather samples

Scanning electron micrograph of crust samples from control and experimental tanning process showing the cross section at magnification of X300 are shown in Fig. 3a-3c. The fibres of both control and experimental leathers appeared to be well separated and opened up as seen in the photomicrograph.

Environmental tolerability of Spent liquor

The spent tan liquor contains highly organic matter in both control and experimental process liquor and it contributes to exorbitantly high COD, dissolved and suspended solids. Hence, it is vital to assess the environmental impact from control and experimental tanning process. The COD, BOD_5, and TDS of the spent liquor for experimental and control trials have been determined and are given in Table 7. From the table, it is observed that the COD, BOD_5 and TDS of the spent liquor processed using both the experimental tanning system are lower than the spent liquor from Henna tanning (control). The BOD_5 and TDS of the spent liquor processed from Henna and aluminium combination tanning trials have significantly reduced compared to the spent liquor of control Henna tanning trial. This could be due to increased exhaustion of Henna during tanning which is also observed from the exhaustion data of Henna given in Table 5**.**

Table 5: Shrinkage temperature and % exhaustion of control and experimental tanning processes

Experiment	Shrinkage temperature (^oC)	Exhaustion %
Al- Henna (2% $Al_2 O_3$)	95±0.5	82±2
Henna-Al (2% $Al_2 O_3$)	97±1	86±2
Henna (Control)	84±0.5	75±2

* - % chemical offer is based on pickled pelt weight of the goat skins taken

* - 20% Henna used for all experiments

Table 6: Physical strength characteristics of experimental and control crust leathers

Parameter	Al- Henna	Henna - Al	Control (Henna)

Tensile strength (Kg/cm^2)	220±2	230±2	210±3
Elongation at break (%)	47±0.71	57±0.71	42±1.58
Tear strength (Kg/cm)	41±071	43±0.71	40±0.71
Load at grain crack (Kg)	22±0.71	21±0.71	25±0.71
Distention at grain crack (mm)	11±0.71	10±0.71	10±0.71
Softness	5.00±0.58	5.30±0.36	3.40±0.47

Table 7: Characteristic of spent liquor for experimental and control

Experiment	**COD (mg\l)**	**% reduction in COD**	**BOD$_5$(mg\l)**	**% reduction in BOD**	**TDS(mg\l)**	**% reduction in TDS**
Henna (Control)	117800±2950	-	24000±950	-	91140±1550	-
Al-Henna	104800±3000	11	15000±1200	37.5	42600±1050	53.3
Henna-Al	102320±2800	12	12000±550	50	40700±1000	55.3

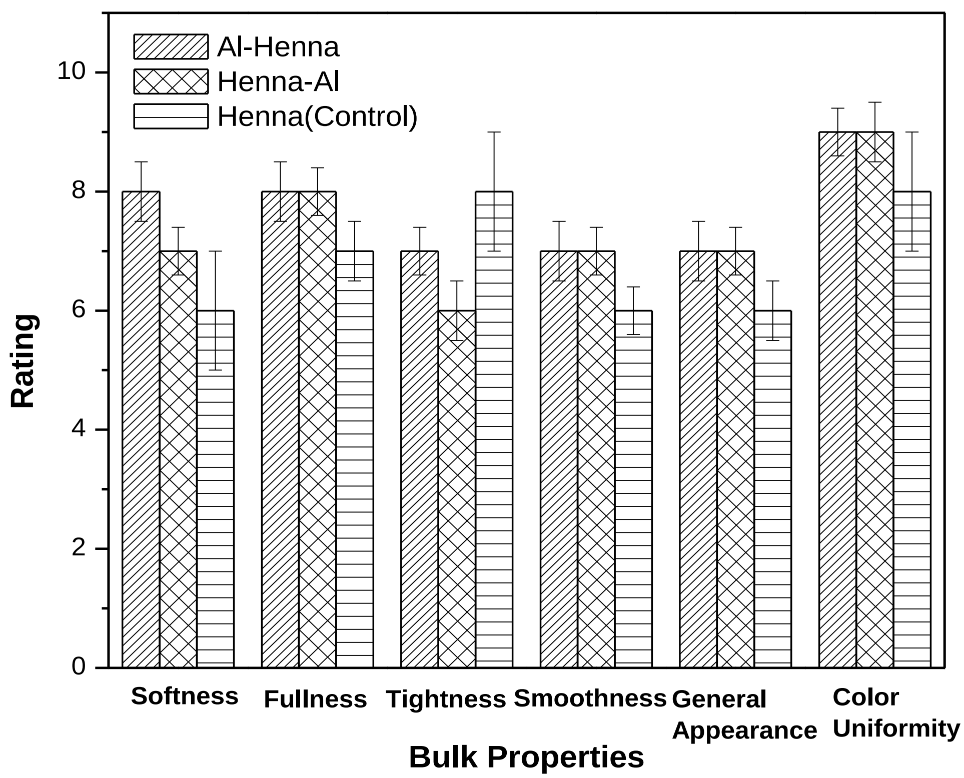
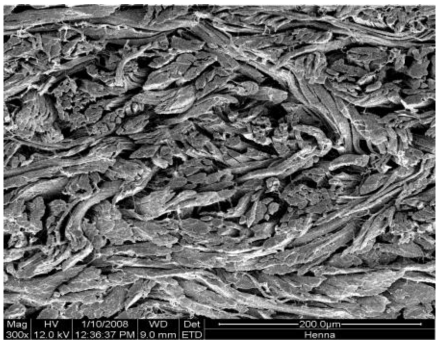
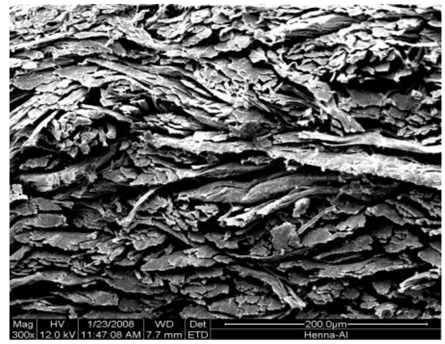
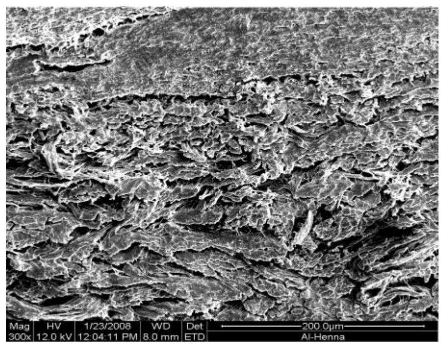

Al-Henna
Henna-Al
Henna(Control)
Rating
0
2
4
6
8
10
Softness
Fullness
Tightness
Smoothness
General Appearance
Color Uniformity
Bulk Properties

Fig. 2**:** Representation of organoleptic properties of the Experimental and control leathers





3a



3c

3b

Fig. 3: Scanning electron micrographs cross sectional(X300) view of crust leathers tanned from (a) control (henna), (b) Henna- Al and (c) Al-Henna.

Conclusions

In the present study, an attempt has been made to produce upper leathers using a new eco-friendly combination tanning process based on Henna and Aluminum. It is seen that combination tanning using Henna (20%) followed by Aluminum (2% Al_2O_3) resulted in leathers with shrinkage temperature of 97^oC, which is 13^oC more than the control (Henna tanned) leathers.

Aluminum followed by Henna tanning resulted in leathers with shrinkage temperature 95 ^{o}C. The exhaustion of Henna in this combination system was found to be greater than 80%. The physical and chemical characteristics of experimental leathers are comparable to control leathers. The experimental leathers are softer than the control leathers. Scanning electron microscopic analysis of both control and experimental leather samples show good separation of fiber bundles. The combination tanning using Henna and Aluminum appears to be an eco-friendlier option and results in leathers with good thermal stability and organoleptic properties that is important for commercial viability of the tanning system.

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