Henna–Aluminum Combination Tannage: A Greener Alternative Tanning System

by

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Abstract

Development of cleaner technologies for leather manufacture is imperative for the sustenance of the tanning industry. In the present study, a combination tanning system based on a 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 sulfate. Aluminum-henna (Al-henna) leathers tanned using 2% Al_2O_3; followed by 20% henna resulted in shrinkage temperature above 95°C. 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 compact fibre structure, indicating that the tanning process did not bring about any major change or destruction on the fibre structure of the leathers. Surface colour values of henna-Al leathers resulted in darker shades with less red and more yellow components in the crust leathers. The combination tanning system provides significant reduction in the discharge of total dissolved solids in the wastewater. Henna-Al combination tanning system resulted in leathers with good organoleptic and strength properties. The work presented in this paper established the use of henna and aluminum combination tanning system as an effective alternative cleaner tanning methodology.

Resumen

El desarrollo de tecnologías más limpias para la fabricación de cuero es imprescindible para la sustentabilidad de la industria del curtido. En el presente estudio, un sistema combinado de curtido henna-aluminio para la producción de cueros de capellada como alternativa más limpia se presenta. Extracto de las hojas de *Lawsonia inerims* (Henna), ampliamente difundida en El Sudán, ha sido evaluado por sus características de curtido basado en Henna y Sulfato de Aluminio. Los cueros curtidos Aluminio-henna (Al-henna) empleando 2% Al_2O_3, seguido de 20% de henna resultan en temperaturas de contracción por encima de 95°C. La admisión de henna en el sistema de curtido henna-Al con henna (20%), seguido por el aluminio (2% Al_2O_3) se ha encontrado mejor que el sistema de curtido de Al-henna. Estos cueros mostraron una estructura compacta de fibra, lo que indica que el proceso de curtido no produjo ningún cambio importante o destrucción de la estructura de la fibra del cuero. Los valores del color de la superficie de cueros Al-henna resultaron en tonos más oscuros con menos componente rojo y más componente amarillo en los cueros semiterminados . El sistema de curtido combinado proporciona una reducción significativa en la descarga de sólidos totales disueltos en las aguas residuales. El sistema combinado de curtido de henna-Al resultó en cueros con buenas propiedades organolépticas y físicas. El trabajo presentado en este documento estableció el uso del sistema de combinación de curtido de henna y aluminio como una metodología alternativa efectiva de curtido más limpia.

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INTRODUCTION

Development of cleaner and greener processing methodologies is the need of hour for the sustenance of the tanning industry. 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.[1] It is well established that hexavalent chromium is carcinogenic.[2] It has also been shown that there is a possibility for the formation of chromium(VI) in leather during the processing conditions.[3,4] Some reports suggest that at higher levels and under certain ligand environments, chromium(III) also is toxic.[5] 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.[6] 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.[7] However, the problem with the vegetable tannage is its poor thermal stability. Vegetable tannins are not able to establish sufficient cross links within the fibres and fibrils of collagen which renders them a relatively weaker tanning system compared to chrome tanning system. 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,[8-10] vegetable-aluminum,[11-13] vegetable-zinc[14] and vegetable-acrylic[15] 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.[16] Hence one has to look out for alternative vegetable tanning materials.

Recently, henna has been established as an alternative retanning material for wattle.[17] The chemistry of the constituents of *Lawsonia inermis* has been of interest. Extracts of henna had been shown to contain anti-fungal and anti-bacterial characteristics.[19,20] Henna finds use in traditional medicinal preparations[20] and in textile industry for dyeing.[21] Recently we have reported the use of henna as a natural dyeing option in leather manufacture, and aluminum salts used as a mordant was found to improve the light fastness of henna dyed leathers[22]. Rao and Nayudamma[23] have extensively studied the vegetable-aluminum combination tannage. In their studies, they have explored both of 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°C, and interestingly, pelts treated with myrobalan followed aluminum resulted in shrinkage temperature of 110-114°C. Whereas, in the case of aluminum tanning followed by wattle (mimosa) tanning results in better leather properties.[24] 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 sulfate.

EXPERIMENTAL METHODS

Materials

Conventionally processed[25] pickled goat skins were employed for the tanning trials. Henna leaves sourced from Sudan were used for the study. Chemicals used for post tanning processes were of commercial grade. Chemicals used for the analysis of spent liquor were of analytical reagent procured from S.D. fine Chemicals, India. Aluminum sulfate (LR) used in the study was procured from S.D. Fine Chemicals, India.

Aqueous Extraction of Tannins from Henna Leaves

Aqueous extraction of henna leaves was carried out as reported elsewhere.[26] The required amounts of ground henna leaves from Sudan were soaked in water at 80°C (1:10 w/v) for an hour. The resultant solution was filtered through a cotton cloth and the supernatant was concentrated to 1/3rd of its volume and used for tanning studies. The solid content of the henna extract was determined to be 35±1%.

Preparation of Basic Aluminum Sulfate Solution

Aluminum salts are known to form highly labile complexes and hence may not form strong complexes with collagen. However, the presence of any ligands like sodium citrate and sodium tartrate are known to improve the complexation ability of aluminum.[27] Hence in the present study basic aluminum sulphate solution masked with sodium citrate and sodium tartrate ligands was prepared as per the following procedure. Aluminum sulfate (100 g) was taken in a beaker and 150 mL of water was added and the solution stirred using a magnetic stirrer for 15-20 minutes, subsequently calculated amount of sodium citrate and sodium tartrate (ligands) were added (for 0.5M of aluminum sulfate 0.1M of ligand was added) and stirring was continued for 45 min followed by slow addition of sodium carbonate until the pH raised to 3.5.

Henna and Aluminum Combination Tannage

Goat skins pickled using NaCl-H_2SO_4 system were employed for combination tanning trials; henna-Al and Al-henna tanning process are given in Table I and II, respectively. Four goat skins were used for each trial. The amount of aluminum sulfate used for the tanning trials was varied as 1% and 2% Al_2O_3 in both the experimental processes. A control tanning process was carried out using henna only as given in Table III. The post tanning process as mentioned in Table IV was followed for experimental and control leathers. All the tanning and post tanning experiments were carried out using smaller drums with a capacity to process five skins.

Measurement of Hydrothermal Stability of Leathers

The shrinkage temperature of control and experimental leathers was determined using Theis shrinkage tester.[28] Piece of tanned leather, cut from the official sampling position was clamped between the jaws of the clamp and immersed in solution containing 3:1 glycerol:water mixture. The solution was continuously stirred using mechanical stirrer attached to the shrinkage tester. The temperature of the solution was gradually increased and the temperature at which the sample shrinks was measured as the shrinkage temperature of the leathers.

Physical Testing and Hand Evaluation of Leathers

Samples for various physical tests from experimental and control crust leathers were obtained as per IULTCS methods.[29] Specimens were conditioned at 20°C±2°C and 65%±2% R.H

TABLE I
Formulation of the Henna–Aluminum combination tanning system for pickled goat skins

Process	%	Product	Duration (min)	Remarks
pH adjustment	100	Water		
	0.75	Sodium bicarbonate	3 x 15 + 30	pH 4.5 -4.7
Tanning	2	Basyntan P (phenolic syntan)	30	
	10	Henna extract	120	
	10	Henna extract	120	
	X	Al_2O_3 (prepared Aluminum sulphate solution)	90	X= 1%, 2% Al_2O_3
Basification	0.75	Sodium bicarbonate	3 x 15 + 30	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.

TABLE II
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	X	Al_2O_3 (prepared Aluminum sulphate solution)	120	X= 1%, 2% Al_2O_3
pH adjustment	0.75	Sodium bicarbonate	3 x 15 + 30	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 x 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.

TABLE III
Formulation of control henna tanning process for goat pickled skin

Process	%	Product	Duration (min)	Remarks
pH adjustment	100	Water		
	0.75	Sodium bicarbonate	3 x 15 + 30	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 x 10 + 30	Check the pH to be 3.5.
Washing	300	Water	10	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

TABLE IV
Formulation of post-tanning process for control and experimental leathers

Process	%	Product	Duration (min)	Remarks
Washing	200	Water	10	
Neutralization	0.75	Sodium bicarbonate	3 x 15 + 30	pH: 5.0-5.5; Drain/Wash
Pre-retannage	100	Water		
	2	Relugan RE (Acrylic syntan)	40	
Pre-fatliquor	2	Lipoderm liquor SAF (Synthetic fatliquor)	40	
	2	Basyntan DI (phenolic syntan)	30	
Dyeing	3	Acid dye brown	30	
Fatliquoring	3	Lipoderm liquor SAF (Synthetic fatliquor)		
	4	Lipoderm liquor 2 FB (Sulfited vegetable oil)	40	
Retanning	3	Basyntan DI (phenolic syntan)		
	4	Basyntan FB6 (Melamin resin)	40	
Fixing	1	Formic acid	3 x 10 + 30	pH 3.5

The leathers were piled overnight. Next day, sam, set, hook to dry, staked and trimmed.
* % chemical offer is based on shaved weight of the tanned leather

over a period of 48 hrs. Physical properties such as tensile strength, percentage elongation at break,[30] grain crack strength[31] and tear strength[32] were measured as per standard procedures. Each value reported is an average of four samples (2 values along the backbone and 2 values across the back bone). Experimental and control crust leathers were also 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 values indicate better property of leathers.

Measurement of Softness in Leathers

The leathers made from control and experimental henna-Al combination processes were taken for softness measurements and the samples (three) were cut from the official sampling position (IUP 2). The leather samples were conditioned at 20±2°C and 65±4% R.H. for 48 hours. The softness of the leathers was measured using ST 300D leather softness tester as per IUP 36 method.[33] The softness tester measures the deflection of leather by a fixed diameter plunger (35 mm) when a force (500 g) is applied to it.

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 have been 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 grain surface and cross section were obtained by operating the SEM at an accelerating voltage of 20 KV with different lower and higher magnification levels.

Analysis of Spent Liquors from Tanning Trials

The spent tannin liquor from control and experimental tanning processes were collected, filtered and analyzed for chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), and total dissolve solids (TDS) as per standard procedures.[34]

Analysis of Exhaustion of Tanning Spent Liquors

Spent henna liquor from control and experimental tanning processes was collected and analyzed for the tannin concentration using a spectrophotometric method by measuring the absorbance value at λ_{max} of the tannin used, after suitably diluting the spent tannin 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.

Color Measurements of Control and Experimental Leathers

The principle involves measuring the amount of light reflected from the surface of opaque specimen at a number of wavelengths throughout the visible spectrum as a fraction of that reflected by a white standard identically illuminated. This is known as reflectance factor. The white standard used is an absolute one i.e. it has a perfect reflecting diffuser as an absolute one, reflectance every wave length as 100%. The color of control and experimental leathers in this study was subjected to reflectance measurement using a Milton Roy Color Mate HDS instrument. Colour measurements viz. L, a, b, h and C were recorded for control and experiment leathers. 'L' represents whiteness on a scale of 0-100. Higher value means lighter shade. The total color difference (ΔE) and hue difference (Δh) were calculated using the following equations

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2}$$

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Where ΔE, over all color difference, ΔL lightness difference, Δa and Δb difference in a and b values where 'a' represents red and green axis, where 'a'>0 means red and 'a'<0 means green and 'b' represents yellow and blue axis, where 'b'>0 means yellow, where 'b'<0 means blue and 'C' represents the chromaticity of the color, which means the intensity. Change in lightness is represented as 'ΔL', which provides the depth of the shade. The positive value of 'ΔL' represent lighter shade, ΔH, hue difference, ΔC chromaticity difference. Other parameters such as ΔL, Δa, Δb and ΔC were calculated by subtracting the corresponding values for leather made from that of control leather.

Evaluation of Chemical Constituents in Leathers

The chemical constituents such as total ash content, % moisture, % oils and fats, % water soluble, % hide substance, % insoluble ash and degree of tannage have been carried out for control and experimental leathers according to standard procedures.[35]

RESULTS AND DISCUSSION

Optimization of Combination Tanning System using Henna and Aluminum

Combination tanning using henna and aluminum sulfate with variation of Al_2O_3 at a concentration of 1 or 2% at constant henna concentration of 20%, changing the order of addition has been carried out. Though, the tanning system using henna and aluminum are eco-friendlier, it is essential to study the properties of the leathers comparable to that of chrome tanning system. The thermal stability of chrome tanned leathers is well known to be greater than 100°C. The shrinkage temperature data for various combinations of henna and aluminum combination tanning systems are given in Table V. 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°C, whereas control tanning using henna alone resulted in a shrinkage temperature of 84°C. From Table V, 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.

TABLE V
Shrinkage temperature and % exhaustion of control and experimental tanning processes

Experiment	Shrinkage temperature (°C)	Exhaustion %
Al- Henna (1% Al_2O_3)	90±1	79±1
Al- Henna (2% Al_2O_3)	95±0.5	82±2
Henna-Al (1% Al_2O_3)	91±1	80±2
Henna-Al (2% Al_2O_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

Gustavson[36] 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. The exhaustion of henna for Al-henna and henna-Al and control (henna tanning) are given in Table V. 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

Organoleptic Properties of Leathers

Crust leather from both control and experimental processes has been evaluated for various organoleptic 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. 1. 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 are better than that of control.

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 VI. 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. The strength characteristics of combination tanned experimental leathers were also found to meet the Bureau of Indian Standard (BIS) requirement stipulated for full chrome upper leathers.[37]

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 VI. 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. 1.

Scanning Electron Microscopic Analysis of Leather Samples

Scanning electron micrograph analysis has been performed to investigate the grain characteristics and fibre structure of the tanned leathers. The scanning electron micrographs of crust samples from henna (control), henna-Al, and Al-henna are shown in Fig. 2a-c, respectively. It is seen that the grain

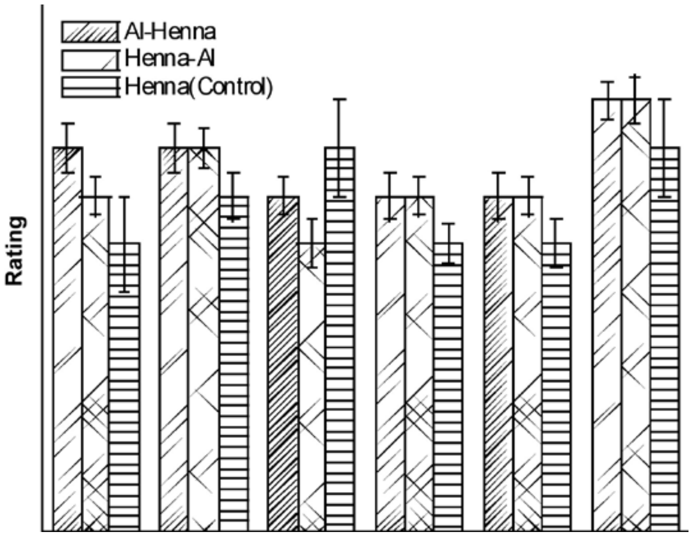

Figure 1: Graphical representation of organoleptic properties of the Experimental and control leather

surface of sample from experimental tanning process at magnification of X100 is clean and the pores are clearly visible without any surface deposition of tannins. This is comparable to that of control leathers. 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-c. The fibres of both control and experimental leathers appeared to be well separated and opened up as seen in the photomicrograph.

Reflectance Measurements — Effect of Surface Color on Control and Experimental Leathers

The colour measurement data for the control and experimental leathers are given in Table VII. It is seen from the table that the L value on treatment with henna-Al combination tanning is higher than the henna treated control and Al-henna tanned experimental leathers, which is clearly indicative of the lighter shade in the case of henna-Al leathers. The 'a' value of Al-henna is more than control and henna-Al treated leathers this indicates that the Al-henna treated leathers are reddish compared to control and henna-Al treated leathers. The 'b' value for Al-henna is found to decrease which is clearly indicative that the Al-henna treated leather is bluer than the

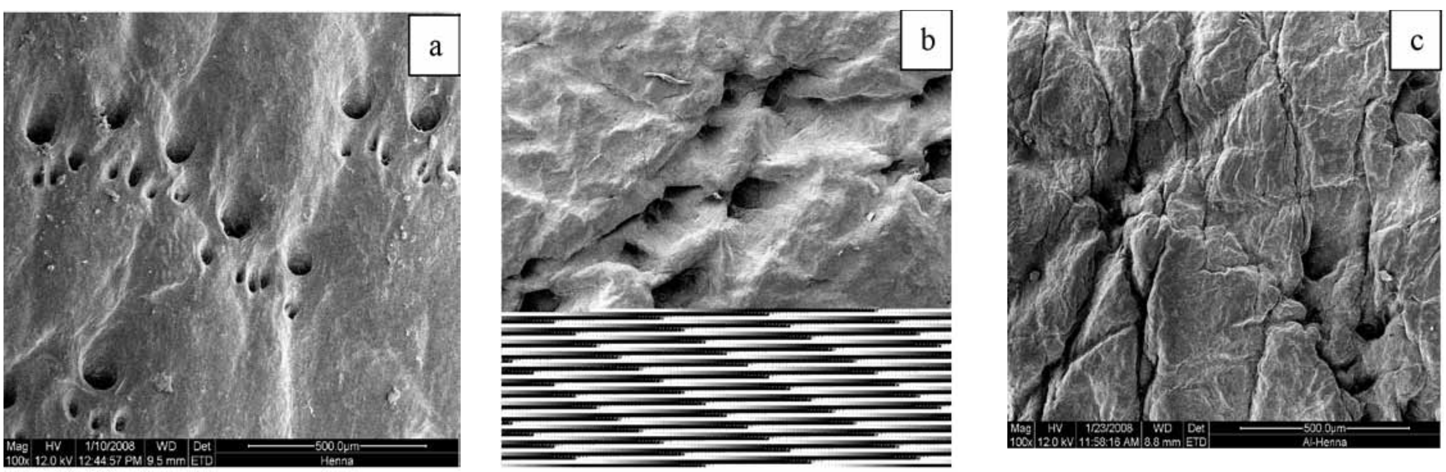

Figure 2: Scanning electron micrographs grain surface (X100) of crust leathers tanned from (a) control (henna), (b) Henna- Al and (c) Al-Henna.

TABLE VI
Physical strength characteristics of experimental and control crust leathers

Parameter	Al- Henna	Henna - Al	Control (Henna)	BIS Norms[37]
Tensile strength (Kg/cm^2)	220±2	230±2	210±3	200
Elongation at break (%)	47±0.71	57±0.71	42±1.58	40-75
Tear strength (Kg/cm)	41±071	43±0.71	40±0.71	25
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	7
Softness	5.00±0.58	5.30±0.36	3.40±0.47	—

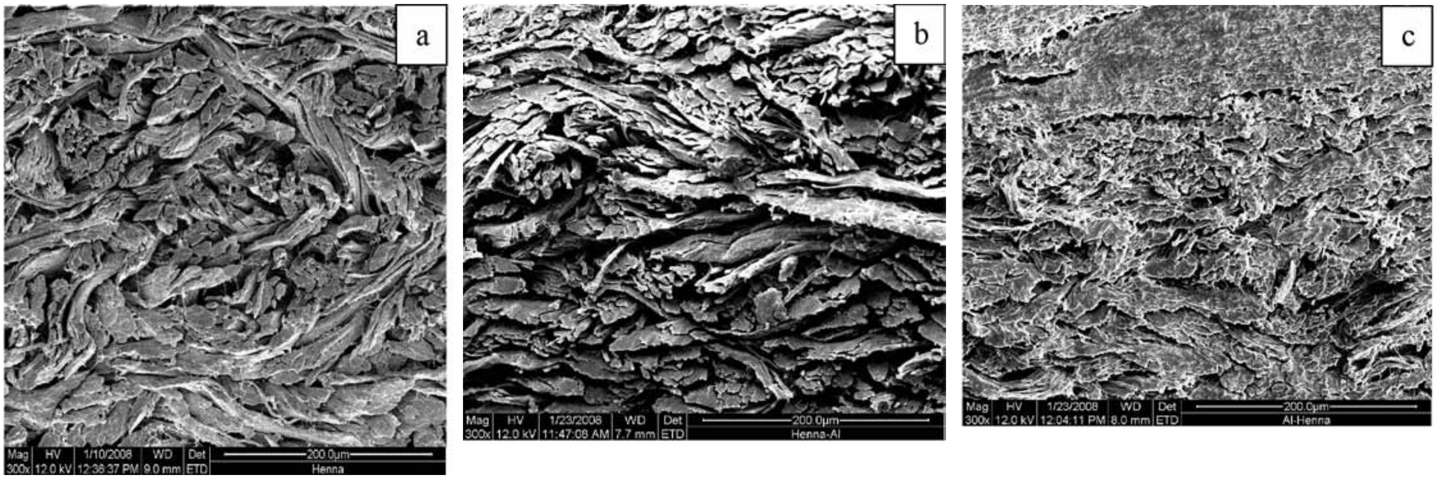

Figure 3: Scanning electron micrographs cross sectional(X300) view of crust leathers tanned from (a) control (henna), (b) Henna- Al and (c) Al-Henna.

TABLE VII
Color measurement data for control and experimental crust leathers

Sample		**L**	**A**	**B**	**C**	**H**
Control (Henna)		3.089	0.303	- 0.022	0.304	355.939
Al - Henna		9.276	1.092	- 4.310	4.446	284.212
Henna - Al		17.814	0.156	0.768	0.784	78.587
Sample	**ΔL**	**Δa**	**Δb**	**Δc**	**Δh**	**ΔE**
Al - Henna	6.186 Lighter	0.788 More red	-4.289 More blue	4.142 Stronger	-1.362 Decrease	7.569
Henna - Al	14.725 Lighter	-0.148 Less red	0.784 Yellower	0.480 Stronger	0.644 Increase	14.747

TABLE VIII
Chemical Analysis of crust leather of experimental and control

Parameter	**Henna (control)**	**Al-Henna**	**Henna-Al**
Moisture %	13.30	13.00	12.20
Total ash content %	2.70	2.20	2.60
Fats and oils %	3.60	3.10	2.90
Water soluble matter %	5.10	3.50	3.40
Hide substance %	52	51	53
Insoluble ash %	1.20	1.4	1.50
Degree of tannage %	47.70	54.90	51

Henna- 20%; Al_2O_3- 2%

TABLE IX
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

henna crust leather (control). The 'b' value of henna-Al is found to be more, indicating that the henna-aluminum treated leather (experimental) is yellower than the henna leather (control). The variations in the shade and intensity of color have been clearly observed from the L, a, b, h and C values obtained.

Chemical Analysis of the Crust Leather

The chemical analysis of crust leathers from control and experimental tanning trials are given in Table VIII. The chemical analysis data for the experimental leathers is comparable to the control leathers. However, the water soluble matter for the control leathers is more than the experimental leathers.

Environmental Tolerability — Spent Liquor Analysis

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 IX. 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 aluminum 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 V.

CONCLUSIONS

In the present study, an attempt has been made to produce upper leathers using a new eco-friendlier 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°C, which is 13°C more than the control (henna tanned) leathers. Aluminum followed by henna tanning resulted in leathers with shrinkage temperature 95°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 clean grain surface devoid of any foreign particles and 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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