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ORIGINAL PAPER

# Cleaner tanning process for the manufacture of upper leathers

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**Abstract** There is a growing need for eco-benign tanning systems owing to stringent environmental regulations. In this study, a combination tanning process based on henna and tetrakis hydroxymethyl phosphonium sulphate (THPS) for the production of upper leathers as a cleaner alternative is presented. Extract from the leaves of *Lawsonia inermis* (henna) has been evaluated for its tanning characteristics in a combination tanning system based on henna and THPS. Both tanning methodologies, henna followed by THPS (henna–THPS) and THPS followed by henna (THPS–henna), have been attempted. It has been observed that THPS–henna combination tanning, employing 20% henna and 1.5% THPS, provides a shrinkage temperature of 96°C. The characteristics of the leathers indicate that the THPS–henna combination system provides leathers with good organoleptic properties and comparable strength properties. The combination system provides significant reduction in the discharge of total dissolved solids in the wastewater. These leathers showed opened up, split compact fiber structure, indicating that the tanning process did not bring about any major change or destruction on the fiber structure of the leathers. The leathers have been further characterized for chemical analysis and scanning electron microscopy. The leathers obtained from the combination system are lighter in color compared to control leathers. Possibility of making upper leathers from THPS–henna combination system as an effective alternative cleaner tanning methodology is established in this work.

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## Introduction

Despite the many advantages offered by chrome tanning and its widespread use for the production of almost all types of leather, there is a worldwide interest in containing the chrome wastes. Prerequisites of any chrome-free tannage are that it must impart at least equivalent properties to those of chrome-tanned leather (Covington 1999; Lu et al. 2003). In recent years, environmental impact has become a worldwide concern for manufacturing process. This environmental concern, combined with consumer preference, particularly in European market, for chromium-free leather is now driving researchers into the development of reduced chrome and chrome-free tanning methods. Chrome-tanned leathers are stable in the presence of heat and moisture. The characteristic shrinkage temperature ($T_s$) of at least 100°C is a standard to which leathers tanned by other processes are compared. Considerable research has shown that the tanning effects of minerals other than chromium (Al, Zr, Ti, or Fe) are enhanced when they are used in combination with vegetable tannins, aldehydes, or other organic molecules (Sundarrajan et al. 2003; Fathima et al. 2005). Leathers tanned with these combinations had $T_s$ of near 100°C and physical-mechanical properties adequate for variety of applications. Nevertheless, these combination tannages have not been widely adopted.

The vegetable tanning has advantages such as comfort, compatibility with skin, high-dimensional stability and ease of disposal. The drawbacks of vegetable tanned leather are

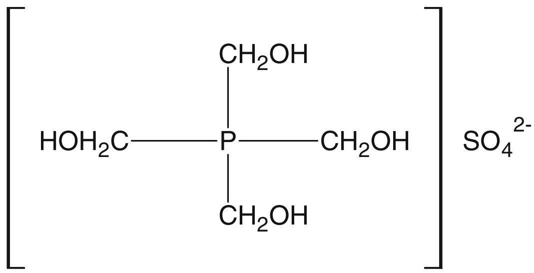


**Fig. 1** Structure of THPS

that they lack softness as they are very hard and firm and lack the affinity for anionic fat liquors. The vegetable tanned leathers also lack the degree of hydrothermal stability required. Studies on combination of vegetable–oxazolidine (Covington and Shi 1998) and vegetable–zinc (Morera et al.1996) produced good results.

Tetrakis hydroxymethyl phosphonium sulphate (Fig. 1) has been widely used as textile flame retardants, as oil field and commercial waste water treatment agents to control bacterial growth and as tanning agents for leather and also as disinfectants in other fields (D'Aquino et al. 2004). It has been reported that THPS could be used as a chrome-free tanning agents (Collins et al. 2003) and improved hydrothermal stability was observed when THPS was used in combination with other tanning agents (Das Gupta 1991, 1998; Fathima et al. 2006). THPS's benefits include low toxicity, low recommended treatment level, rapid breakdown in the environment and bioaccumulation (Fathima et al. 2005). Combination of THPS and vegetable-tannin had been an effective tanning system (Das Gupta 1998; Fathima et al. 2006). Leathers that are used in shoe upper construction for footwear industry have the largest share in the total leather production. Hence, in this work, an attempt has been made to develop upper leather using an eco-benign tanning system based on henna and THPS. Recently, henna (*Lawsonia inermis*) has been established as an alternative retanning material for wattle (Musa et al. 2008). *L. inermis* is a member of the family Lythraceae widely spread in tropical regions with relatively few species in temperate region (Jones and Luchainger 1979). *L. inermis* has been well investigated phytochemically by various researchers. The occurrence of $\beta$-sitosterol glucoside (Mahmoud et al. 1980), flavonoids (Afzal et al. 1980), quinoids (Nakhala et al. 1980), naphthalene derivatives (Afzal et al. 1984), gallic acid (Nakhala et al. 1980), coumarins (Dzhuraev et al. 1982), and xanthones (Bhardwaj et al. 1978) in Lawsonia leaves have been reported.

## Experimental

### Materials

Conventionally processed pickled goat skins (Sharphouse 1995) were taken for tanning trials. henna leaves sourced from Sudan have been used for the study. Tetrakis hydroxymethyl phosphonium sulphate (THPS) liquid formulation (Albrite® AD75E, 75% w/w concentrated THPS) was procured from Rhodia Consumer Specialties Ltd., UK. Chemicals used for post-tanning processes were of commercial grade. Chemicals used for the analysis of spent solution were of analytical grade.

### Aqueous extraction of tannins from henna leaves

Ground henna leaves of known quantity was soaked in water (1:10 w/v) at a temperature of 80 ± 2°C in water bath for 1 h, filtered through a piece of cotton cloth and concentrated and used in combination tanning.

### Henna–THPS combination tannage

Pickled goat skins were used for combination tanning trials; THPS–henna tanning and henna–THPS tanning process are given in Tables 1 and 2, respectively. The

**Table 1** Formulation of THPS–Henna combination tanning process for pickled goat skins

| Process | % | Product | Duration (min) | Remarks |
|---|---|---|---|---|
| Pickled pelt | 50 | Water pickled liquor | | |
| | 4 | Salt (Sodium chloride) | 10 | pH 2.8–3 |
| Tanning | 1.5 | THPS | 60 | |
| 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 | 120 | |
| | 10 | Henna extract | 120 | |
| 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 |

**Table 2** Formulation of Henna–THPS combination tanning process 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 | |
| | 1.5 | THPS | 90 | |
| Basification | 0.75 | Sodium bicarbonate | 3 × 15 | pH 4 |
| Washing | 300 | Water | 10 | 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 3** Formulation of Henna tanning process 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 | |
| Fixing | 0.5 | Formic acid | 3 × 10 + 30 | pH 3.5 |
| 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 |

**Table 4** Formulation of post-tanning process for making upper crusts from experimental (combination) and control tanning trials

| 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-fat liquor | 2 | Lipoderm liquor SAF (Synthetic fatliquor) | 40 | |
| | 2 | Basyntan DI | 30 | |
| Dyeing | 3 | Acid dye brown | 30 | |
| Fat liquoring | 3 | Lipoderm liquor SAF (Synthetic fatliquor) | | |
| | 4 | Balmol BL II | 40 | |
| Retanning | 3 | Basyntan DI | | |
| | 4 | Basyntan FB6 | 40 | |
| Fixing | 1 | Formic acid | 3 × 10 + 30 | pH 3.5 |

amount of THPS used for the tanning trials was 1.5% 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 for making upper crust leathers as mentioned in Table 4 was followed for experimental and control leathers.

## Measurement of hydrothermal stability of leathers

The shrinkage temperature of control and experimental leathers was determined using Theis shrinkage tester (McLaughlin and Thesis 1945). A 2 × 0.5 $cm^2$ piece of tanned leather cut from the official sampling position was clamped between the jaws of the clamp, which was 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 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 (IUP2 2000). Specimens were conditioned at 20 ± 2°C and 65 ± 2% RH over a period of 48 h. Physical properties such as tensile strength, percentage elongation at break (IUP6 2000), grain crack strength [SLP9 (IUP9) 1996] and tear strength (IUP8 2000) 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 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–THPS combination processes were taken for softness measurements and the samples (three) were cut from the official sampling position (IUP2 2000). The leather samples were conditioned at 20 ± 2°C and 65 ± 4% RH for 48 h. The softness of the leathers was measured using ST 300D leather softness tester as per IUP 36 method (IUP36 2000). 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 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 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 was collected, filtered and analyzed for chemical oxygen demand (COD), biochemical oxygen demand ($BOD_5$), and total dissolved solids (TDS) as per standard procedures (Clesceri et al. 1989).

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 $\lambda_{max}$ 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, which has a perfect reflecting diffuser whose reflectance at every wave length is 100%. The color of control and experimental leathers in this study has been subjected to reflectance measurement using a Milton Roy Color Mate HDS instrument. Color 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 ($\Delta E$) and hue difference ($\Delta h$) were calculated using the following equations:

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

$$\Delta H = \sqrt{\Delta E^2 - \Delta L^2 - \Delta C^2}$$

where $\Delta E$, overall color difference, $\Delta L$ lightness difference, $\Delta a$ and $\Delta b$ 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 '$\Delta L$', which provides the depth of the shade. The positive value of '$\Delta L$' represents lighter shade, $\Delta H$ hue difference, $\Delta C$ chromaticity difference. Other parameters such as $\Delta L$,

$\Delta a$, $\Delta b$ and $\Delta C$ have been calculated by subtracting the corresponding values for leather made from that of control leather.

### Chemical analysis of leathers

Total ash content, % moisture, % oils and fats, % water soluble, % hide substance, % insoluble ash and degree of tannage were carried out for control and experimental leathers according to standard procedures (Official Methods of Analysis 1965).

## Results and discussion

Combination tanning using henna–THPS with a THPS offer of 1.5%, keeping the offer of henna constant at 20%, and changing the order of addition was carried out. Though the tanning system using henna and THPS are eco-friendlier, it is essential to study the properties of the leathers whether it is 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 are given in Table 5. It is seen from the table that just by the use of 1.5% of THPS in combination with henna exhibited more than 10°C increase in shrinkage temperature compared to henna control leathers. The henna–THPS combination tanning provides shrinkage temperature of 97°C compared to 84°C for control. The exhaustion of henna for THPS–henna and henna–THPS and control (henna tanning) are given in Table 5. It is observed that there is an increase in the amount of henna fixed in the presence of THPS and increased exhaustion of henna observed can be semi-quantitatively related to the increase in shrinkage temperature of combination tanning systems of henna.

### Bulk properties of leathers—hand evaluation of leathers

Upper crust leathers from control and experimental processes have been evaluated for various bulk properties by hand and visual evaluation. The average rating for the leathers 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 THPS–henna tanning experimental crust leathers exhibited good softness, fullness, smoothness, general appearance and dye uniformity compared to control leathers from henna tannage. The organoleptic properties of the THPS–henna crust leathers are better compared to henna–THPS crust leathers.

**Table 5** Shrinkage temperature of leathers from experimental and control tanning trials

| Experiment | Shrinkage temperature, $T_s$ (°C) | Henna exhaustion (%) |
|---|---|---|
| THPS–henna crust leather (Exp) | 96 ± 0.5 | 88 ± 3 |
| Henna–THPS crust leather (Exp) | 97 ± 1 | 83 ± 2 |
| Henna crust leather (Control) | 84 ± 0.5 | 75 ± 2 |

### Strength and softness 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 at break, tear strength, load at grain crack and distension at grain crack were carried out for the control and experimental upper crust leathers and the data are given in Table 6. The strength characteristics of both experimental and control leathers are observed to be comparable. Natural tannins from plant origin are known to produce hard leathers and are 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 for THPS–henna is 4.50 mm compared to 3.4 mm for henna tanned crust leathers. Higher values signify more softness of the leather. Henna–THPS resulted in value of 4.0. The experimental leathers especially THPS–henna exhibited better softness compared to the henna control leathers and henna–THPS experimental leathers. The trend in the object assessment of softness values are in accordance with the observations made from visual assessment data shown in Fig. 2.

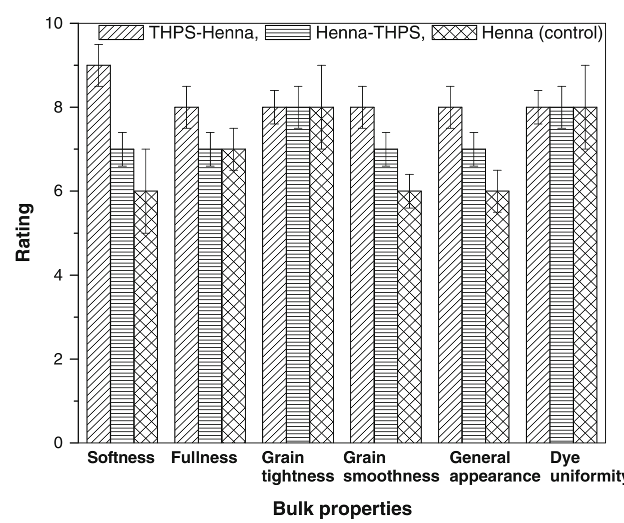


**Fig. 2** Graphical representation of organoleptic properties of the experimental and control crust leathers

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

| Parameter | THPS/Henna | Henna/THPS | Henna (control) |
|---|---|---|---|
| Tensile strength (kg/cm$^2$) | 220 ± 3 | 230 ± 2 | 210 ± 2 |
| Elongation at break (%) | 51 ± 1.41 | 55 ± 1.58 | 56 ± 1.58 |
| Tear strength (kg/cm) | 42 ± 1.50 | 47 ± 1.50 | 47 ± 0.71 |
| Load at grain crack (kg) | 39 ± 0.71 | 24 ± 0.71 | 25 ± 0.71 |
| Distention at grain crack (mm) | 11.5 ± 1.58 | 11 ± 0.71 | 10 ± 071 |
| Softness | 4.50 ± 0.81 | 4.00 ± 0.70 | 3.40 ± 0.47 |

## Scanning electron microscopic analysis of leather samples

Scanning electron microscopic analysis has been performed to investigate the grain characteristics and fiber structure of the tanned leathers. The scanning electron micrographs of crust samples from henna (control), THPS–henna, and henna–THPS are shown in Fig. 3a–c, respectively. It is seen that the grain surface of sample from experimental tanning process at magnification of 100× is clean without any damage and foreign particle. This is comparable to that of control leathers. Scanning electron micrograph of crust samples from control and experimental tanning processes showing the cross section at magnification of 300× are shown in Fig. 4a–c. The fibers of both control and experimental leathers appeared to be well separated and opened as seen in the photomicrographs.

## Reflectance measurements—effect of surface color on control and experimental leathers

The color measurement data for the control and experimental leathers are given in Table 7. It is seen from the table that the *L* value on treatment with THPS–henna

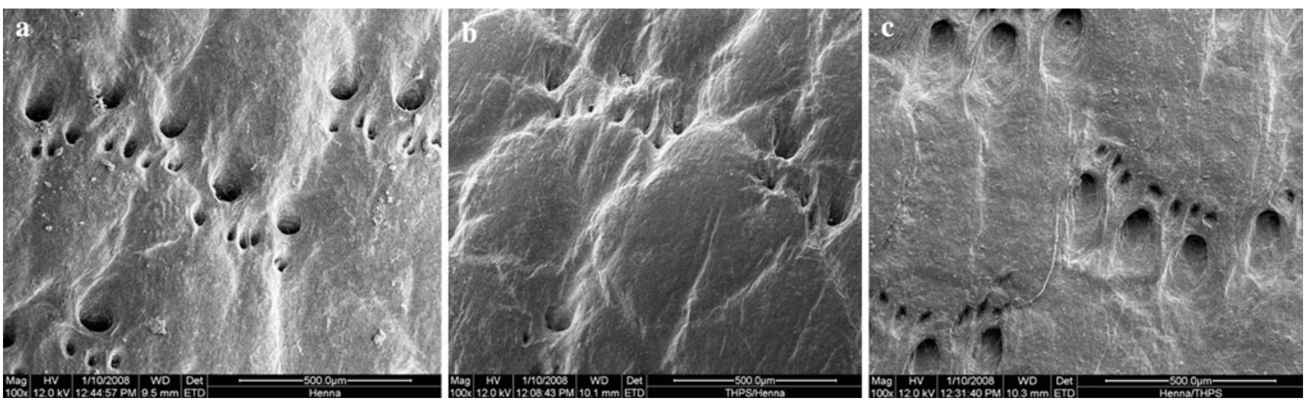


**Fig. 3** Scanning electron micrographs of **a** henna (control), **b** THPS–Henna (experimental) and **c** Henna–THPS (experimental) samples showing the grain surface at magnification of ×100 after tanning

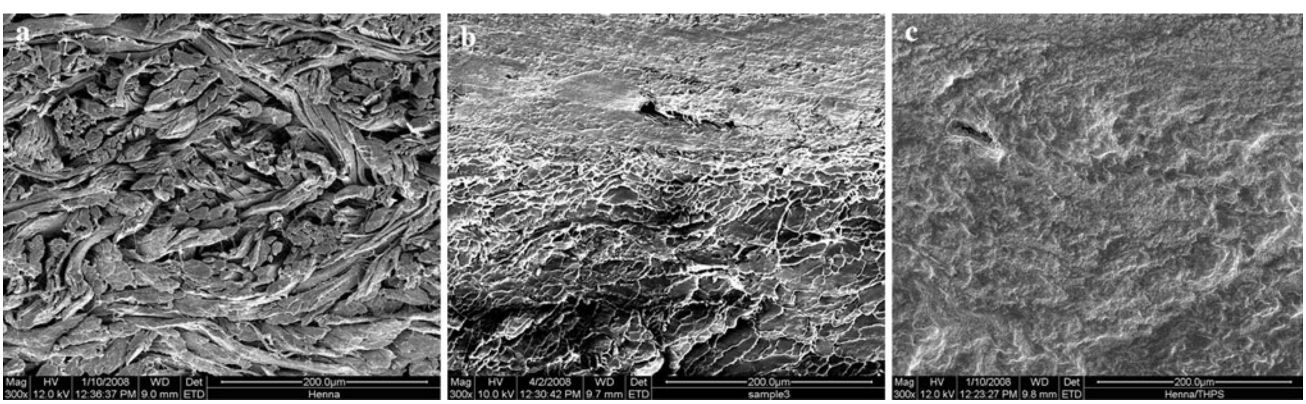


**Fig. 4** Scanning electron micrographs of **a** control (henna), **b** THPS–Henna (experimental) and **c** Henna–THPS (experimental) samples showing the cross section at magnification of ×300 after tanning

combination tanning is higher than the Henna treated control and Henna–THPS tanned experimental leathers which is clearly indicative of the lightness of the leathers. The '*a*' value on treatment with THPS–Henna is less than control and Henna–THPS treated leathers, this indicates that the THPS–Henna treated leathers (experimental) are greener as compared to control and Henna–THPS treated leathers. The '*a*' value on treatment with Henna–THPS is slightly less than control, this indicates that the Henna–THPS treated leathers (experimental) are less red as compared to control. The '*b*' value on treatment with THPS–Henna is found increased which is clearly indicative that the THPS–Henna treated leather is yellower than the Henna crust leather (control). The '*b*' value on treatment with Henna–THPS is found to decrease, indicating that the Henna–THPS treated leather (experimental) is bluer than the Henna leather (control) and THPS–Henna treated leathers. 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 8. The chemical analysis data for the experimental leathers are comparable to the control leathers. However, the water soluble matter for the control leathers is more than that for the experimental leathers.

### Environmental tolerability—spent liquor analysis

The spent tan liquor in both control and experimental process contains high organic matter which could lead to the contribution of high COD, dissolved and suspended solids. Hence, it is vital to assess the environmental impact from control and experimental tanning processes. The COD, $BOD_5$, and TDS of the spent liquor for experimental and control trials have been determined and are given in Table 9. From the table, it is observed that the COD, $BOD_5$ and TDS of the spent liquor processed using both the experimental tanning systems are lower than that for the spent liquor from Henna tanning (control). The $BOD_5$ and TDS of the spent liquor processed from Henna and THPS combination tanning trials have significantly reduced values compared to the spent liquor of Henna control 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 8** Chemical analysis of crust leathers from experimental and control

| Parameter | Henna (control) | THPS/Henna | Henna/THPS |
|---|---|---|---|
| Moisture (%) | 13.30 | 12.30 | 12.50 |
| Total ash content (%) | 2.70 | 2.60 | 2.50 |
| Fats and oils (%) | 3.60 | 3.50 | 3.40 |
| Water soluble matter (%) | 5.10 | 5.00 | 4.50 |
| Hide substance (%) | 52 | 51 | 50 |
| Insoluble ash (%) | 1.20 | 1.00 | 1.10 |
| Degree of tannage (%) | 47.70 | 53.33 | 57 |

## 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 THPS. It is seen that combination tanning using Henna (20%) followed by THPS resulted in leathers with shrinkage temperature of 97°C, which is 13°C more than the control (Henna tanned) leathers. THPS followed by Henna tanning resulted in leathers with shrinkage temperature 96°C. The exhaustion of Henna in the 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 shows clean grain surface devoid of any foreign particles and good separation of fiber bundles. The combination tanning using

**Table 7** 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 |
| THPS/Henna | 11.465 | −0.787 | 0.993 | 1.267 | 128.385 |
| Henna/THPS | 4.664 | 0.146 | −0.177 | 0.230 | 309.416 |

| Sample | $\Delta L$ | $\Delta a$ | $\Delta b$ | $\Delta c$ | $\Delta h$ | $\Delta E$ |
|---|---|---|---|---|---|---|
| THPS/Henna | 8.375 lighter | −1.090 greener | 1.015 yellower | 0.963 stronger | 1.136 increase | 8.507 |
| Henna/THPS | 1.574 lighter | −0.157 Less red | −0.156 More blue | −0.074 weaker | −0.209 decrease | 1.577 |

**Table 9** Characteristics of spent tan liquor from experimental and control processing

| Experiment | COD (mg/l) | Reduction in COD (%) | $BOD_5$ (mg/l) | Reduction in BOD (%) | TDS (mg/l) | Reduction in TDS (%) |
|---|---|---|---|---|---|---|
| Henna (control) | 117,800 ± 2950 | – | 24,000 ± 950 | – | 91,140 ± 1,550 | – |
| THPS–Henna | 105,200 ± 3000 | 11 | 16,000 ± 1,100 | 33 | 75,500 ± 1,150 | 17 |
| Henna–THPS | 97,000 ± 1500 | 18 | 13,000 ± 900 | 46 | 62,300 ± 1,700 | 32 |

Henna and THPS 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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