STUDIES ON THE DEVELOPMENT OF PICKLE-LESS VEGETABLE TANNING

by

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ABSTRACT

Pickle-less vegetable tanning is becoming vital to the tanners due to environmental problems. In this investigation an attempt has been made to tan goatskins using commercially available vegetable tanning agent (wattle) at pH 8.0-8.5. In order to have a comparative study, partial pickling to pH 4.5 has also been performed as a control. There is no surface deposition of vegetable tannin in the experimental leathers although vegetable tanning has been carried out at higher pH. This has been substantiated through scanning electron microscopic analysis. The exhaustion of vegetable tannin is higher in the case of the experimental process. The experimentally processed leather shows slight improvement in hydrothermal stability compared to conventionally processed leather. Performance of the leathers is shown to be on par with conventionally tanned leathers through physical and tactile evaluation. Color measurement studies show that the variation in color or shade between control and experimental leather is negligible. The process also enjoys reduction in total solids, chloride and chemical oxygen demand (COD) loads by 73, 97 and 19 %, respectively from the identified streams.

INTRODUCTION

Leather making is a craft and trade of great antiquity and records exist relating to its operation in Mediterranean regions dating back to 5000 BC.[1] Man has used vegetable tannins to convert animal hides to leather for many thousands of years. The invention of chrome tanning in 1858 AD ousted vegetable tanning slowly.[2] Leather making with vegetable tannins remains because; it offers naturality compared to other tanning agents. During the past few decades, the awareness of environmental problems has increased considerably. This is because of the increased environmental and health legislations in the industrialized countries on the one hand, and the increased realization of environmental objectives through market forces on the other. Conventional methods employed in leather processing subject the skin or hide to wide variations in pH.[3] Such pH changes demand the use of acids and alkalis, which lead to the generation of salts and this results in a net increase in total dissolved solids (TDS) comprising chlorides, sulfates and other minerals in tannery wastewater.[4,5] Conventional vegetable tanning process requires partial pickling of the delimed/bated skins/hides since the vegetable tannins possess optimal particle size for penetration into the matrix at pH 4.5-5.0.[6,7] Spent pickle liquor from vegetable tanning process has more amount of dissolved solid content and considerable amount of COD, since this partial pickling involves the use of 4-5% sodium chloride salt along with required quantity of sulfuric acid.[3] Salt, usually sodium chloride, is added to restrict the swelling of the collagen in the acidic medium. The recovery and reuse of water and salt are necessary to contain the problem of dissolved solids in composite tannery wastewater. Hence, there is a need for better strategic practices leading to improved products and process alternatives to decrease the total dissolved solids in the wastewater.

Conventional effluent treatment plants comprise primary, secondary and in some cases tertiary treatment which offer the possibility of reduction in contaminants including undissolved solids, sulfides, ammonia, bio-chemical oxygen demand (BOD), and COD. Dissolved salts, however, will pass through each of these effluent treatment processes and remain relatively unaffected in the final discharge. A range of process technologies is available commercially to permit the separation of salts from water. These include electrodialysis, reverse osmosis, and thermal distillation; however the techno-economic feasibility of these methods is limited. As the discharge norms for TDS is 2100 ppm in India,[8] it becomes necessary to control the amount of neutral salts

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being used in leather processing. Various options towards the reduction of TDS are salt-less curing,[9] lime-free opening up,[10] pickle-less chrome tanning,[11,12] leather processing in a narrow pH profile[5] and use of syntans and fatliquors with minimum salt content. Although pickle-less chrome tanning system has been evolved, it is important to investigate such a process using vegetable tannins since it is known that the process mechanisms are different.[3] In the present approach, pickle-less vegetable tanning with commercial vegetable tannin agent (wattle) at a starting pH of 8.0-8.5 has been attempted. The primary objective of this work is to decrease TDS and chlorides using pickle-less vegetable tanning by avoiding the use of salt and acid in the process. The approach does not employ synthetic tanning agents or acids prior to tanning. The uptake of vegetable tannin, shrinkage temperature of the leathers, COD, TS, chlorides and characteristics of leathers have been compared with control process.

EXPERIMENTAL

Wet salted goatskins were chosen as raw material. Goatskins with more compact structure and of larger area (4-6 sq. ft.) were chosen. All the chemicals used for leather processing were of commercial grade and the chemicals used for the analysis of spent tan liquors were of analytical grade. Relugan RE, Basyntan DI, Basyntan FB6 and Lipoderm liquor SLW were procured from M/s BASF Ltd, Vernaminol liquor ASN and Vernol liquor SS were acquired from M/s Colour Chem Ltd.

Optimization of Wattle Offer for Pickle-Less Tanning

Preliminary trials have been carried out to find out the suitable percentage of wattle to use in main tanning. Therefore five halves of delimed skins were taken. One half skin was used for each trial. Five different percentages of wattle were used viz., 10, 15, 20, 25 and 30% with 100% water (percentages based on pelt weight). Drum was run for 4 hrs after which complete penetration of tanning agent was ascertained. The pH of the pelts was adjusted to 3.5 - 3.7 using 0.2% formic acid. Then the pelts were piled for 24 hrs. A control trial was carried out as given below using one skin for comparison. Next day, hydrothermal stability of leathers was measured using a shrinkage tester.[13] The leathers were then sammed and shaved to 1.0-1.1 mm thickness. The leathers were converted into crust upper leathers using conventional post-tanning recipe and were assessed by an experienced tanner.

Control Vs Experimental Vegetable Tanning

a) Control Tanning Process

The tanning experiments were carried out on delimed goatskins. Five delimed goat pelts were taken for the control process.

To the delimed pelts,

add:	Water	-	100%	
	NaCl	-	5%	run for 10 min
	H_2SO_4	-	0.75%	3 feeds @15 min interval + 30 min; pH of the cut section was 4.5 - 4.7; Then 50% float was drained.
add:	Basyntan P	-	2%	run for 1 hr
	Wattle	-	10%	run for 1 hr
add:	Wattle	-	10%	run for 3 hr, then complete penetration of vegetable tannin was ascertained.
add:	Formic acid	-	0.1%	run for 45 min, final pH was found to be 3.5-3.7.

b) Experimental Tanning Process

The tanning experiments were carried out on delimed goatskins. Five delimed goat pelts were taken for experimental process.

To the delimed pelts,

add:	Water	-	100%	
add:	Wattle	-	10%	run for 1 hr
add:	Wattle	-	10%	run for 3 hr, then complete penetration of vegetable tannin was ascertained.
add:	Formic acid	-	0.2%	run for 45 min, final pH was found to be 3.5-3.7.

The leathers from control and experimental processes were piled overnight. The leathers were then sammed, split and shaved to uniform thickness (1.0-1.1 mm). Subsequently, the control and experimental leathers were taken for post tanning operation.

Post Tanning Process for Control and Experimental Leathers

The following post-tanning process sequence was adopted in order to convert the tanned leathers into crust upper leathers.

add:	Water	-	100%	
add:	Borax	-	0.5%	run for 30 min.
add:	Sodium sulfite	-	0.5%	run for 30 min. drain/wash/drain
add:	Water	-	100%	
add:	Oxalic acid	-	0.5%	run for 45min, drain/wash/drain
add:	Water	-	80%	
add:	Acrylic syntan (Relugan RE)	-	2%	run for 20 min.
add:	Phenolic syntan (Basyntan DI)	-	3%	run for 30 min.
add:	Urea formaldehyde (Basyntan FB6)	-	3%	run for 30 min.
add:	Synthetic fatliquor (Lipoderm liquor SLW)	-	3%	emulsified with water run for 45 min.
add:	Dye	-	2%	run for 30 min.
add:	Semi synthetic fatliquor (Vernol liquor SS)	-	3%	run for 30 min.
add:	Synthetic fatliquor (Vernol liquor ASN)	-	3%	run for 30 min.
add:	Formic acid	-	1.5%	3 feeds @10min interval + 30min, drain/wash/ drain

Physical Methods

Determination of Shrinkage Temperature

The shrinkage temperature, which is a measure of hydrothermal stability of leather, was measured using a Theis shrinkage meter.[13] The Shrinkage temperature measurements were carried out for both control and experimental leathers at tanned stage.

Physical Testing and Hand Evaluation of Leathers

Samples for various physical tests from experimental and control crust leathers were obtained as per IUP method.[14] Specimens were conditioned at 80 ± 4°F and 65 ± 2% R.H. over a period of 48 hrs. Physical properties such as tensile strength, % elongation at break, tear strength and grain crack strength were examined as per the standard procedures.[15-17] Experimental and control crust leathers were assessed for softness, fullness, grain flatness, 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 experienced tanners, where higher points indicate better property.

Objective Assessment of Softness through Compressibility Measurements

Softness of leathers can be numerically measured based on their compressibility.[18] Circular leather pieces (2 cm^2 area) from experimental and control crust leathers were obtained as per IUP method[14] and conditioned at 80 ± 4°F and 65 ± 2% R.H. over a period of 48 hrs. The samples were spread uniformly over the solid base of the C & R (compressibility and resilience) tester. The initial load acting on the grain surface was 100 g. The thickness at this load was measured 60 sec after the load was applied. Subsequent loads were added and the change in thickness was recorded one minute after the addition of each load. Logarithm of leather thickness (Y axis) was plotted against logarithm of load (X axis).

Reflectance Measurements

The principle involves measuring the amount of light reflected from the surface of opaque specimen at wavelengths throughout the visible spectrum as a fraction of that reflected by a white standard identically illuminated. It is known as the reflectance factor. The white standard used should be an absolute one i.e., it should be a perfect reflecting diffuser whose reflectance at every wavelength is 100%. The control and experimental crust leathers made in this study were subjected to reflectance measurements using a Mitton Roy Colour Mate HDS instrument.

Color Measurements

Colour measurement parameters viz., *L, a, b, h* and *C* were recorded using a Milton Roy Color Mate HDS instrument for control and experimental crust leathers. The total color difference (ΔE) and hue difference (ΔH) were calculated using the following equations:

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \quad (1)$$

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

where ΔL, lightness difference; Δa and Δb, difference in '*a*' and '*b*' values, where 'a' represents red and green axis and '*b*' represents yellow and blue axis; *H*, hue difference; ΔC, chromaticity difference. ΔL, Δa, Δb and ΔC were calculated by subtracting the corresponding values for experimental leathers from that of control leathers.

Fastness to Artificial Light

The samples were cut from the official sampling position.[14] The leather specimens were conditioned at 80 ± 4°F and 65 ± 4 % R.H. for 48 hours. The resistance of the color of the experimental and control leathers to an artificial light source, Xenon lamp, was measured using IS 6191-1971 (LF: 4) method.[19] A side of the leather was exposed to light from a Xenon arc under prescribed conditions for 20 hrs, along with eight dyed Blue wool standards having increasing levels of fastness. Black panel temperature was maintained at 63 ± 1°C and the relative humidity was 30 ± 5%. Fastness was assessed by comparing the fading of crust leathers with that of the standards, from standard 1 (very low light fastness) to standard 8 (very high light fastness), where each standard being approximately twice as fast as that preceding one. Rating was given on a scale of 1-5 points, where higher points indicate better fastness. The same methodology was repeated for control and experimental leathers aged for 6 months.

Analysis of Spent Tan Liquor

Spent tan liquors from both control and experimental leather processing were collected and analyzed for %

uptake of vegetable tannin, COD, TS (dried at 103-105°C for 1 hr) and chlorides (Cl^-) as per the standard procedures.[20,21] The liquors were also analyzed for spectral characterization from 250-400 nm using Perkin-Elmer Lambda 35 UV-visible spectrophotometer after proper dilution.

Scanning Electron Microscopic Analysis

Samples from control and experimental tanned leathers were cut from the official sampling position after normal drying. 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.

Results and Discussion

The approach of this study is based on the fact that the vegetable tannin can penetrate rapidly at higher pH. It has been reported from the fixation profile of vegetable tannin at various pH values that penetration is facilitated at higher pH while fixation is promoted at lower pH and maximum fixation of vegetable tannins on collagen occurs at pH around 3.5.[22] Since the pH of the aqueous solution of vegetable tannin is around 4.0 - 4.2, the penetration of vegetable tannins is facilitated at this pH.[23] On the application of vegetable tannins on delimed pelt, penetration of vegetable tannins can be achieved by two factors namely high concentration and pH. The acidity of vegetable tannins will make the pH of the residual float in the drum to around 5.0. Further, the pH of the inner cross-section of the pelt cannot be less than 5.0. This prevents the surface fixation on the skins and aids proper penetration of vegetable tannins. Finally, the pH is adjusted to 3.5 - 3.7 using minimum amount of formic acid to fix the penetrated vegetable tannins.

Optimization of Pickle-Less Vegetable Tanning

Various percentages of wattle ranging from 10-30% have been chosen in order to optimize the amount of wattle required for achieving good quality leather with higher shrinkage temperature. The percentages of wattle employed and the respective shrinkage temperatures are given Table I. It is seen that there is no significant increase in the shrinkage temperature beyond 20% of wattle offer. Hence, the amount of wattle has been optimized as 20% and employed for the subsequent experimental tanning process. Further, the leather obtained from 20% wattle offer shows better bulk properties. It is seen that at similar offer (20%) experimental tanning process provides improved shrinkage temperature compared to the control vegetable tanning process. This could be due to the improved uptake of vegetable tannins at higher pH values.

TABLE I
Shrinkage Temperature of the Leathers Tanned With Various Percentage of Wattle

Wattle (%)	Shrinkage temperature, Ts (°C)
Control, 20	82 ± 2
10	80 ± 1
15	81 ± 2
20	85 ± 1
25	85 ± 1
30	85 ± 1

Conventional vs Pickle-Less Vegetable Tanning

Bulk Properties of the Leathers

It is known that the results of hand and visual evaluation method are not objective but subjective, which varies from person to person. Yet it could be taken as reliable, if carried out by experienced person. The hand and visual evaluation has been done for both tanned and crust leathers. The tanned stage assessment values are shown in Table II. It is seen that the experimental leathers have good bulk properties which are comparable to that of control leather. Vegetable tannin patches and case hardening have not been observed for both control and experimental leathers. Grain smoothness is good for both control and experimental leathers.

TABLE II
Hand and Visual Assessment Data for Control (C) and Experimental (E) Leathers After Tanning

Parameters	Control	Experiment
Tannin patches	Nil	Nil
Grain smoothness	8 ± 0.5	8 ± 1.0
Case hardening	Nil	Nil
Color of leather	8 ± 1.0	7.5 ± 0.5
Fullness	8 ± 0.5	8 ± 0.5
General appearance	8 ± 1.0	8 ± 1.0

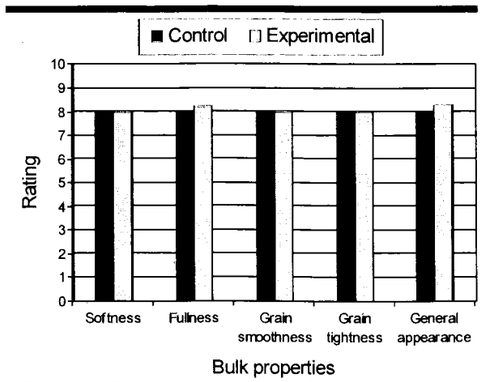

Figure 1. - Graphical representation of organoleptic properties of the control and experimental leathers

TABLE III
Strength Characteristics of Control (C) and Experimental (E) Leathers

Sample	Tensile Strength (kg/cm²)	%Extension at Break	Tear Strength (kg/cm)	Grain Crack Strength Load (kg)	Grain Crack Strength Distension (mm)
C	205 ± 5	54 ± 2	48 ± 3	32 ± 1	12.5 ± 0.2
E	202 ± 10	62 ± 2	36 ± 3	28 ± 2	13.4 ± 0.3

Note: The values are mean ± S.D of four leathers

TABLE IV
Colour Measurements Data between the Control and Experimental Leathers

Sample	*L*	*a*	*b*	*C*	*H*
Control	55.034	14.187	35.848	38.553	68.409
Experiment	57.044	14.540	39.088	41.705	69.596
	Δ*L*	**Δ*a***	**Δ*b***	**Δ*C***	**Δ*H***
	2.010	0.354	3.241	3.152	0.830
Δ*E*				1.830	

(Δ*E*, overall color difference; Δ*L*, lightness difference; Δ*a* and Δ*b*, difference in *a* and *b* values, where *a* represents red and green axis and *b* represents yellow and blue axis; Δ*H*, hue difference; Δ*C*, chromaticity difference)

Crust leather from both control and experimental processes were evaluated for various bulk properties by hand and visual evaluation. The average of the rating for the five leathers corresponding to each experiment was calculated for each functional property and is given in Fig 1. Higher numbers indicate better property. The experimental leathers exhibit better fullness compared to control leathers. This is primarily due to increased penetration and fixation of vegetable tannins in the experimental process, compared to control process. Other properties such as softness, grain tightness and smoothness are comparable to that of conventionally processed leathers. The overall appearance of both control and experimental leathers is also comparable.

Strength Properties

Tensile and tear strength tests were carried out for all the control and experimental crust leathers both along and across the backbone line. The mean of the values corresponding to along and across backbone was calculated. The grain crack strength for all the control and experimental crust leathers was measured. The average values are given in Table III. It is seen that both control and experimental leathers exhibit comparable tensile, tear and grain crack strength values.

Softness Measurements

The pickle-less vegetable tanning system employs vegetable tannins at pH of 8.0-8.5, which may result in deposition of vegetable tannins and subsequent grain coarsening. Hence, it is important to evaluate the extent of softness on the final leather. Quantitative assessment of softness for both control and experimental leathers has been made through compressibility measurements. The logarithm of thickness was plotted against logarithm of load for the control and experimental leathers, which exhibits a linear fit.[18] The plots are shown in Figs 2a and 2b. The corresponding equation of the line was obtained. The negative slope angles were calculated and the values are 8.66° and 8.49° for the control and experimental leathers. Higher values imply more softness in the leather. It is apparent that the experimental leather (E) exhibits comparable negative slope angle (compressibility index, CI) with that of control leather (C).

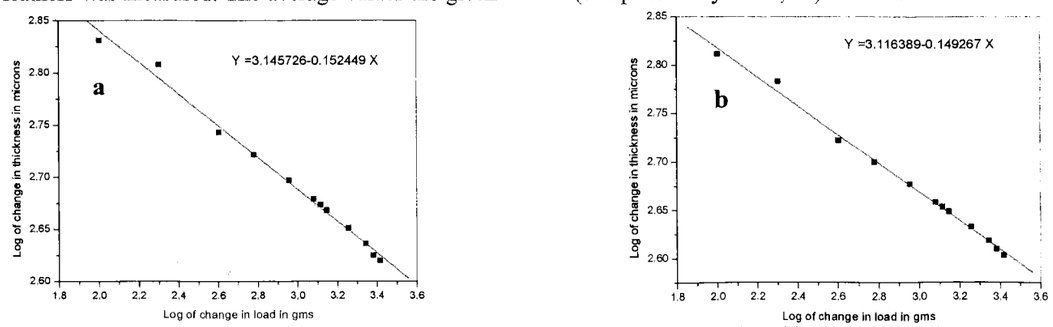

Figure 2. - Plot of log of change in load vs log of change in thickness for (a) control and (b) experimental leathers

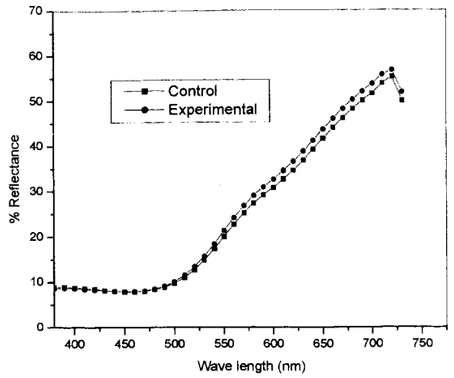

Figure 3. - Plot of percentage reflectance vs wavelength for control and experimental leathers

This shows that the experimental leather offers comparable softness to that of the control leathers.

Color Difference Studies

Figure 3 shows the reflectance measurement data vs visible wavelength for both control and experimental crust leathers. The absorbance maxima is around 450 nm for both control and experimental leathers. An absorbance maximum is the wavelength at which the reflectance is minimum. Since the absorbance maxima is similar for both control and experimental leathers, it can be concluded that there is no significant variation in the color or shade between control and experimental leathers.

The L, a, b, C, H values of control and experimental leathers and the color differences are given in Table IV. It is observed that the experimental samples show total color difference (ΔE) of 1.830 compared to control leather, which means the overall color difference is negligible. The values of 'ΔL', 'Δa', 'Δb', 'ΔC' and 'ΔH' are 2.01, 0.354, 3.241, 3.152 and 0.830, respectively. The values indicate that the experimental leather possesses negligible difference in the color measurement parameters with that of control leather. These results are similar to that observed in the visual assessment.

Light Fastness

The fastness property of both control and experimental crust leathers under artificial light (Xenon lamp) was studied and is given in Table V. The leathers from both control and experimental processes show moderately good light fastness, which is equivalent to the Blue wool standards 5 (given in parenthesis in Table V). The effect of ageing of crust leathers for six months on the fastness properties was also studied and the values are given in Table V. It is observed that both the samples do not show appreciable change in the fastness properties upon ageing.

TABLE V
Light Fastness Characteristics of Control (C) and Experimental (E) Leathers

Sample	Before Aging Light Fastness	After Aging Light Fastness
C	3 (5)	3 (4)
E	3 (5)	3 (4)

values in parenthesis indicate the corresponding Blue wool standard

Scanning Electron Micrograph Analysis

Scanning electron micrograph analysis has been performed to investigate the grain characteristics and fiber structure of the tanned leathers, since the pickle-less vegetable tanning process is carried out at pH 8.5 against the conventional pH levels of 4.5-4.7. The scanning electron micrographs of tanned samples from control and experimental vegetable tanning processes showing the grain surface at a magnification of x50 are given in Figs 4a and 4b, respectively. It is seen that the grain structure of the sample from experimental tanning process is clean without any foreign particles and comparable to the control sample. The hair pores are clearly visible without any surface deposition of vegetable tannins. The scanning electron micrographs of tanned samples from control and experimental tanning processes showing the cross section at a magnification of x200 are given in Figs 4c and 4d, respectively. Both the samples show a compact fiber structure, which is characteristic of vegetable tanned leather. This means that the elimination of conventional partial pickling process does not provide any change in the fiber structure of the leathers.

Environmental Tolerability

The spent vegetable tan liquor contains highly polluting matter and it contributes to an exorbitantly high BOD, COD, dissolved and suspended solids. Hence, it is vital to assess the environmental impact from both pickle and pickle-less vegetable tanning process. Composite liquor was prepared by mixing spent liquors from pickling and vegetable tanning processes. It should be noted that the experimental vegetable tanning process does not have a pickling process and hence spent vegetable tan liquor alone was considered as composite. COD, TS, chlorides and % up take of vegetable tannin are the parameters that have been chosen for analyzing the environmental impact. A direct correlation of the observed COD/TS values with the environment may not give proper consequences. Hence, the COD/TS values have been converted into emission loads by multiplying COD/TS values (mg/lit) with volume of effluent (lit) per metric ton of raw skins processed. The COD and TS values and the calculated emission loads are given in Table VI. One of the major problems faced by the tanner is the huge

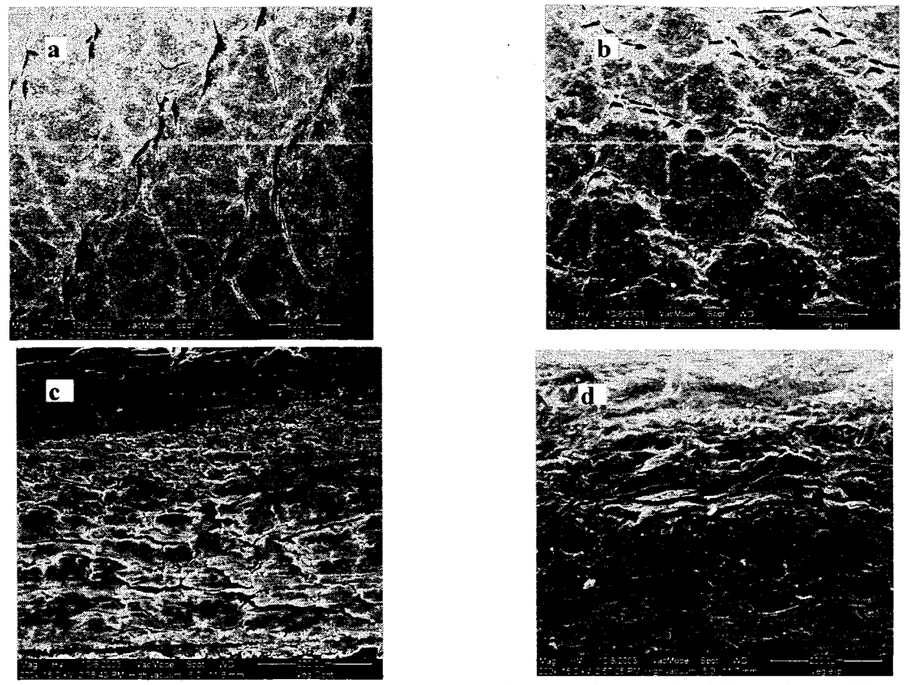

Figure 4. - Scanning electron micrograph of tanned sample showing the grain surface of (a) control and (b) experiment at X50 magnification and cross section of (c) control and (d) experiment at X200 magnification

TABLE VI
Environmental Impact of Control (C) and Experimental (E) Processes

Parameters	C[a]	E[b]
% Uptake of tannin	84 ± 2	91 ± 1
COD (ppm)	20256 ± 24	16785 ± 32
TS (ppm)	85217 ± 58	23571 ± 46
Chlorides (ppm)	23625 ± 28	780 ± 16
Volume of effluent (L/metric ton of raw skins)	575	560
Emission load (Kg/metric ton of raw skins)		
COD	11.6	9.4
TS	49	13.2
Chlorides	13.6	0.44

[a]Composite of spent pickle and tan liquor
[b]Spent tan liquor alone considered as composite

emission of total dissolved solids. It is seen that the COD, TS and chlorides values of experimental spent tan liquor are lower than that of control. Partial pickling and vegetable tanning processes contribute nearly 49 kg of TS for processing 1 metric ton of raw skins conventionally. It is evident that the pickle-less vegetable tanning method reduces the COD, TS and Cl^- loads by 19, 73 and 97%, respectively. The reduction in COD, TS and chloride loads helps in achieving cleaner vegetable tanning. Especially the reduction of chlorides by 97% is a significant achievement in avoiding pollution due to chlorides.

The uptake of vegetable tannin in experimental process is higher than control process. This is primarily due to increased penetration of tannins at higher pH followed by fixation at lower pH value of 3.5 - 3.7. It is also in agreement with the increase in hydrothermal stability of experimental leather compared to control leather as evident from

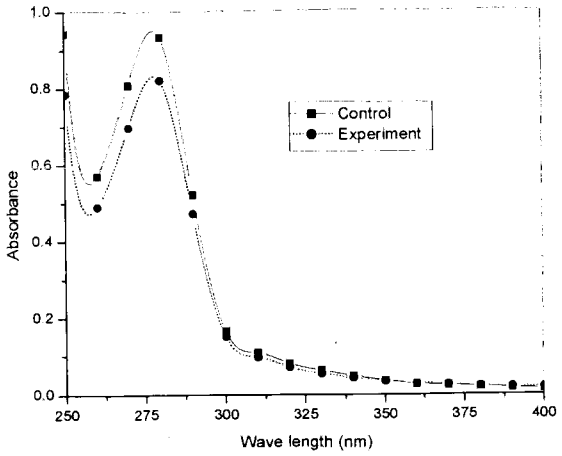

Figure 5. - Plot of absorbance vs wavelength for control and experimental spent vegetable tan liquors

Table I. Fig 5 shows the spectral characteristics of spent liquor from control and experimental vegetable tanning process. It is seen that the absorbance maximum is 287 nm. The absorbance value of experimental spent tan liquor at 287 nm is lower compared to control spent tan liquor at constant dilution. Hence, the reduction in COD and higher uptake of tannin is evident from the spectrum. The adoption of pickle-less vegetable tanning method could bring significant change in the tanning industry by making it environmentally sustainable in the context of cleaner production.

Conclusions

In the present study, an attempt has been made to develop a method for tanning skins using vegetable tannins at the pH range of 8.0-8.5 without pickling. The hand and visual assessment of leathers at tanned and crust stage indicate that there is no significant variation in the properties compared to the conventional vegetable tanned leathers. SEM analysis shows that there is no physical deposition of vegetable tannins at higher pH values. Color measurement studies show that there is no significant variation in color or shade between control and experimental leathers. The leathers from both control and experimental process exhibits similar light fastness character. The experimentally processed leather exhibits higher hydrothermal stability compared to conventionally processed leather. The reductions in TS, Cl^- and COD loads are 73, 97 and 19 % compared to control process, apart from achieving better uptake of vegetable tannin. In general, this approach provides an ample scope for decreasing the pollution load. Analyzing various results from the experiments, it is viewed that the partial pickling process is not essential for vegetable tanning. However, pickling can be used in occasions where the pelts need to be preserved for long without tanning.

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