

# TOWARDS SUSTAINABLE LEATHER PRODUCTION: VEGETABLE TANNING IN NON-AQUEOUS MEDIUM

by

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## ABSTRACT

The process of stabilizing the skin collagen against denaturation under heat, enzymes, stress etc. – popularly described as tanning is carried out either using metal ions (predominantly Cr(III)) or vegetable tannins derived from plant sources rich in polyphenols. Conventional leather processing is carried out in aqueous medium and hence the tannins have been extracted into water, sulfited to increase water solubility and then sold as spray dried extracts. Classical drawbacks include the low resistance of the extracts to bacteria and fungi, copious quantities of water required for extraction and tanning etc. In an attempt to make the leather processing sustainable, taking cue from other economically viable methods for tannin extraction, this paper looks at paradigm shift from water extraction of tannins to solvent based extraction, followed by leather processing in solvent. The results presented with ethanol as the green solvent highlights the significance of the developed method, in not only enhancing tannin to non-tannin ratio (T/NT), but also improving thermal stability of the tanned collagen at microscopic rat tail tendon (RTT) and macroscopic leather level.

## INTRODUCTION

One noticeable aspect of the leather industry is the liquid emission from the process, such as 30-35 L of wastewater being generated for every kilogram of raw hide/skin processed, containing heavy metal ions like Cr(III), dissolved solids, suspended protein impurities etc.<sup>1</sup> While the possibility of replacing leather products such as footwear with synthetic alternatives have been widely considered, the need for a visco-elastic material that would adopt to the needs of the growing feet of children, that could ease the pain in higher levels of diabetes, adjust to the needs of flat feet etc. puts leather in a non-replaceable advantageous position.<sup>2</sup> The sustainability of leather processing activity through adoption of in-plant cleaner and greener technologies is thus a strong need.

Wattle (*Acacia mearnsii*) is one such vegetable tanning material of the condensed tannin variety.<sup>3</sup> In addition to its use in leather processing, it also finds applications in areas such as precipitant for clay suspensions, manufacture of adhesives, surface coating of wood, mud thinning for oil-well drilling etc.<sup>4</sup> The process of vegetable tanning has changed over a period of time, from one that took over 45 days to complete, essentially due to poor kinetics of tannin extraction into leather processing vessels to rapid processes based on pre-extracted, sulfited extracts.

In an endeavor to look at sustainable methods of leather production, we have embarked on a time bound project to explore the possibility of carrying out leather processing in non-aqueous media. Wei (1987) had carried out an extensive survey of the literature relating to leather processing in solvent medium and highlighted the challenges such as fire risk, cost of recovery and water miscibility.<sup>5</sup> While addressing to the issue of water miscible / immiscible solvent for leather processing, Silvestre et al., demonstrated that trichlorotrifluoro ethane or perchloroethylene provided for advantages such as complete exhaustion of tanning bath and higher chromium binding even at pilot scale levels.<sup>6</sup> However, literature was devoid of applications involving vegetable tanning materials and also a scientific outlook towards selection of solvents. For this, a complete analysis of the GSK Solvent Guide was carried out. One of the primary conditions laid for selection was the miscibility of the chosen solvent in water, as hide/skin would naturally come with at least 30% water on its weight. Ethanol figured mostly under the green category with a score of 8 -9 in a scale of 10, in aspects such as environmental impact, health, toxicity, polarity, stability and life cycle score.<sup>7</sup> Aspects that could be considered negative for ethanol were vapor pressure and flammability. However, based on the availability, miscibility with water and environmental impact, ethanol was chosen for this study.

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Conventional extraction of wattle requires large quantities of water and a high temperature of close to 90°C for beneficial extraction. For this work, wattle was extracted in ethanol at a temperature just below 70°C and its properties evaluated vis-à-vis those extracted using water. Anti-fungal property of the ethanol-extracted wattle was compared with that of conventional. The wattle extract was also evaluated for vegetable tanning process carried out in an ethanolic medium. Negative influence if any in the use of ethanol for tanning was evaluated at the rat-tail tendon level.

## EXPERIMENTAL

### Materials and Methods

Wattle barks were dried under sunlight and crushed to obtain a semi-milled powder. A Soxhlet extraction procedure as detailed in Figure 1 was employed for obtaining the wattle extract. Briefly, the semi-milled powder was taken in a thimble, and extracted at 70°C for ethanol and 90°C for water. The extraction process was considered complete when the solvent in the Soxhlet carried no traces of color characteristic of wattle. In the case of ethanolic extraction, the solvent was recovered by distillation, leaving the wattle extract in a semi-solid powder form.

### Tanning and Post Tanning

Wet salted goatskins with good compact structure and area of 4 – 6 sq.ft were chosen for the experiments. Commercial grade chemicals were employed for post tanning processes. The authors do not recommend any single product and product names used, if any, are only for representative purpose. The process employed up to delimiting was conventional and tanning trials were carried out employing five delimited pelts as per the procedure detailed in Table I. Standard procedures for determination of moisture content, oils etc. were employed to characterize the leathers.

### Characterization of wattle extract

#### Functional Groups

FT-IR studies are carried out for wattle extracted from water and ethanol using an FTIR spectrophotometer (Jasco 6200, Japan). All spectra are recorded by absorption mode at 2 cm<sup>-1</sup> interval and in the wavelength range of 4000–600 cm<sup>-1</sup> wave numbers.

#### Size and Stability

The number average diameter and the zeta potential of the extracted wattle was evaluated by dynamic light scattering (DLS) method on a Malvern Zeta sizer nanoZS carrying a He-Ne laser (633 nm) at a scattering angle of 173°. All experiments were carried out in triplicates by dispersing the sample in the respective solvent medium.

#### Tannin/Non-tannin Content

Determined using IUC 32 as per specified procedures in both extracts and spent liquors after tanning for both ethanol and water based tanning. Absorptivity was calculated as a difference between offered to that present in spent liquor.

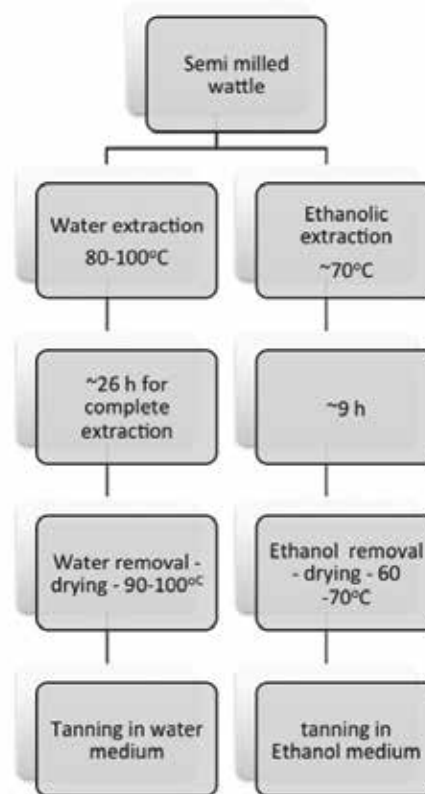


Figure 1. Scheme for extraction of wattle using ethanol and water.

**TABLE I**  
**Tanning methodology adopted for ethanolic and water extracts in ethanol and water medium respectively.**

Chemicals	%	Time	Remarks
Delimiting			
Ammonium chloride	1.5	120 min	Completion of delimiting confirmed by pink to colorless with phenolphthalein indicator
Bate	0.5	30 min	
Washing		10 min	
Acetic acid	0.5	60 min	Check pH 5.0 (drain the float)
Ethanol/ Water	100	10 min	
Wattle extract	15	240 min	Check penetration, adjust the pH to 3.5
			Drain, wash, rinse, pile

### **Thermal Stability of Rat Tail Tendon**

#### **Treated with Extracted Wattle**

Differential scanning calorimeter (Q series 200, TA instruments, USA) was used to determine peak temperature  $T_p$  (in °C) and the enthalpy changes  $H$  (in J/g of wet weight) associated with the phase change for the shrinkage process was studied. For this rat-tail tendon equilibrated for 24 h in ethanolic / water extracted wattle liquor was employed. After the tanning, the tendons were blotted uniformly and hermetically encapsulated in aluminum pans. The samples were fused in a differential scanning calorimetric cell of a TA Differential Scanning Calorimeter. The temperature was calibrated effectively using indium as standard. The heating rate is maintained constant at 5°C/min.

#### **Evaluation of Developed Leathers**

Samples from control (water extracted wattle) and experimental (ethanolic wattle extract) tanned leathers were cut from the official sampling position of the crust leather (as per IUP 1, 2 and 3). For morphological evaluation, the samples were first washed in water and then dehydrated gradually using 90:10 to 0:100 water- ethanol mixtures. A Quanta 200 series 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 5 kV at different magnification levels.

#### **Shrinkage Temperature**

Employing the Theis shrinkage tester and standard protocols, the  $T_s$  of both control and experimental leathers were evaluated.<sup>8</sup>

#### **Physical Parameters**

Employing IUP methods for sampling and analysis, the strength parameters were determined for both control and experimental leathers.<sup>9-12</sup>

#### **Antimicrobial and Antifungal Susceptibility Test**

The antimicrobial and antifungal resistances of the experimental leathers were evaluated by incubating the leathers in a Muller Hilton agar medium for 1 day for bacterial growth and 5 days for fungal growth. Positive and negative control was carried out simultaneously to check the efficiency of ethanol extracted wattle extract. After the required incubation period, the plates were evaluated for the growth of the microorganisms.

## **RESULTS AND DISCUSSION**

This paper revolves around a futuristic situation for the leather industry, where in sustainable leather production would depend on complete elimination of water in processing, through adoption of easily recyclable medium as mode of transport of the chemicals. As most of the leather auxiliaries

available today in the market have been tuned to perform best under aqueous conditions, there is also a need to look at the feasibility of preparing these auxiliaries under conditions which could give more yield and also avoid the step of water solubilization such as sulfitation, sulfonation etc. which is commonly practiced. This paper therefore reports a process through which wattle is extracted in ethanolic medium and the tanning is also performed in the ethanolic medium. Though no cost considerations have been adopted at the present moment, the potential advantages of this method are highlighted in this paper.

#### **Tannin to Non-tannin ratio**

The potential advantages of the ethanolic extraction process vis-à-vis water were the shorter duration of time and lower temperature (~9h, 70°C) than that of water (~26 h, ~100°C). Table II highlights the differences in the tannin and non-tannin content based on the extraction method. T/NT ratio, a measure of the astringency and hence the ability to tan was higher with the ethanolic extract, owing to more efficient extraction of the tannins. Absorptivity of tannins was found to be the same for leathers processed under ethanolic as well as water medium (89.5 ± 0.5%).

#### **Functional Groups**

From the FTIR spectra in Figure 2 a strong OH stretching at 3383 cm<sup>-1</sup> was observed for both the extracts. Characteristic peaks associated with wattle such as the -C = C- bond stretching (1622 cm<sup>-1</sup>), - C - C- (1456 cm<sup>-1</sup>) and - CH (2920 cm<sup>-1</sup>) were similar for the both extracts and comparable to a commercial wattle extract dissolved in water.

#### **Size and stability**

The dynamic light scattering technique provides information on the hydrodynamic diameter, number or intensity average diameter, polydispersity index and depending on the instrument the zeta potential. A difference between the hydrodynamic diameter and the number average diameter is a measure of the wide particle size distribution in the sample, which can further be confirmed from the high polydispersity index (PI) values. PI greater than 0.3 is a measure of the polydispersity in size of the given sample. Zeta potential (ZP), when measured, provides an indication of the charge and degree of repulsion between the particles – a measure of its stability in the given medium. ZP values closer to zero indicates an unstable system wherein particles would settle out of the medium. The ZP values generally range from -200 to +200 mV. Table III provides information on the particle size, ZP and PI for the wattle extract in water and ethanol and compares it with commercial extract in water. The hydrodynamic size was similar for all the three products – indicating a more or less similar penetration through the pores. A variation between hydrodynamic diameter and the number average diameter is an indication of the wide particle size distribution, which was further confirmed from the PI value

that was higher for ethanolic extract (0.53 as against 0.35/0.28 for water extract/commercial product). The zeta potential value was also 4 fold higher for ethanolic extract. Tannins will form self aggregates at unique thresholds associated with dispersing medium.<sup>13</sup> Tanning molecule, due to its highly polarisable nature develops van der Waals forces between the particles that are very strong in nature. This leads to particle – particle interaction and aggregation. The probability of repulsion between particle to particle is associated with two forces, viz., solvation and electrical double layer arising from the surface ionization of the particles. The high zeta potential value for the ethanolic

extract of wattle indicates a highly stable system. It was observed visually that the water extract as well as commercial extract in water agglomerated within a few days, while the ethanolic extract was stable over a longer period of time.

#### Stability against thermal and mechanical forces

Collagen when treated with ethanol brings about a displacement of the associated water and thus changes to the hydration network and free rotation along the collagen backbone. This could alter the collagen – water bonds and bring about newer levels of cross-linking between ethanolic OH and collagen. Such changes

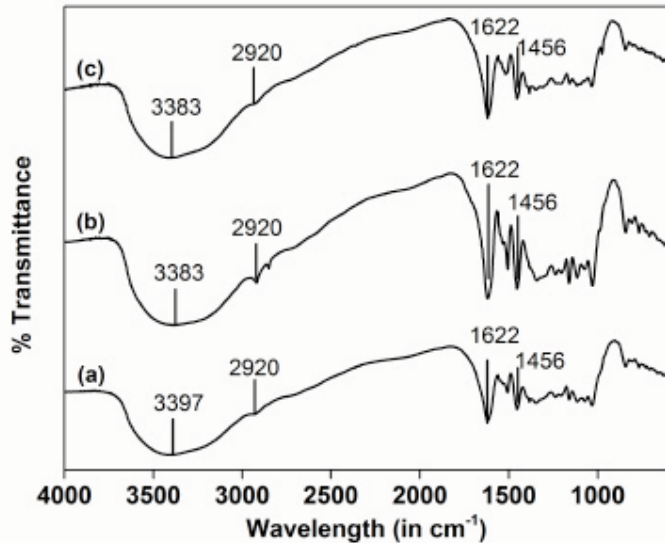


Figure 2. FTIR spectra of a) commercial wattle b) wattle extracted in ethanol and c) wattle extracted in water.

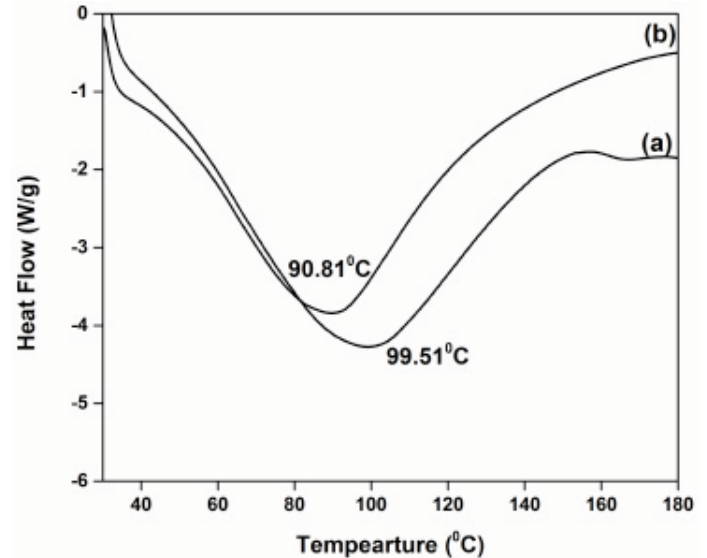


Figure 3. DSC thermograms for rat tail tendon treated with a) Ethanol and b) Water extracted wattle in corresponding medium.

**TABLE II**  
**Characteristic features of extracted wattle.**

Solvent	Time taken for the extraction (hrs)	Extraction efficiency (%)	Total soluble (%)	% of Tannins	% of Non-Tannins	T/NT%	Absorptivity of tannin in to leather (%)
Water	26	64	83	67	16	4.1	90
Ethanol	9	44	87	74	13	5.7	89

**TABLE III**  
**Particle size distribution and Zeta potential of extracted wattle vis-à-vis commercial product.**

Sample	Avg Size (nm)	Zeta potential (mv)	Size (nm)	PDI
Commercial	458	-14.5	422.8	0.350
Water	330	-19.5	446	0.281
Ethanol	377	-76.9	742.9	0.532

could also lead to changes in the hydrothermal stability of collagen. To nullify the influence of factors such as pore size associated with hides/skins, these measurements were carried out on rat-tail tendon. DSC curves presented in Figure 3 indicates a 9 degree rise in the hydrothermal stability of collagen when treated with ethanolic extract in ethanolic medium as against water extract in water medium, an observation that can be related to the displacement of water – collagen H-bond networks with ethanolic –OH – collagen bonds.

Commensurate with the results in the tendon level, the thermal and mechanical stability of the leathers tanned using ethanolic extracted and water extract in the respective medium was more or less similar (Table IV). The  $T_s$  of the leathers were in the range of 81-87°C.

### Morphology of surface and cross-section

It is quite possible that the replacement of water – collagen H-bond networks could lead to fiber-fiber coalescence. Scanning electron microscopic images of skins (Figure. 4) treated with ethanolic wattle extract in ethanolic medium had good surface

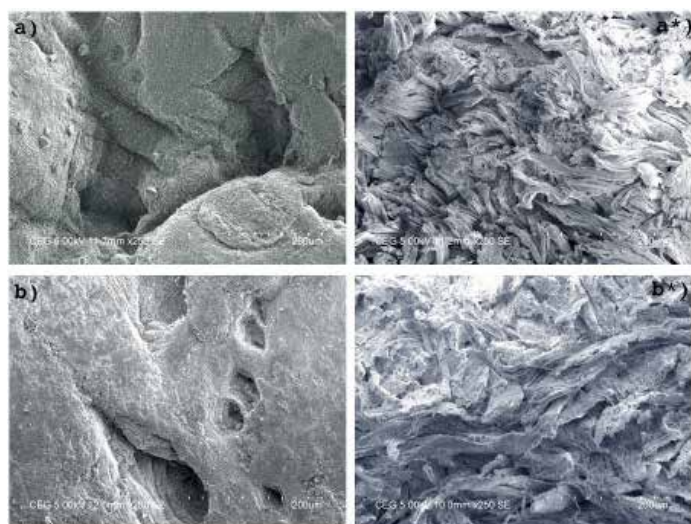


Figure 4. Scanning electron microscopic images a) grain surface of water extracted wattle tanned leather, a\*) cross section of water extracted wattle tanned leather b) grain surface of ethanol extracted wattle tanned leather, b\*) cross section of ethanol extracted wattle tanned leather.

and cross-sectional features such compactness of fibers, absence of coalescence, good grain smoothness etc and were comparable with control. That ethanolic extract and tanning in ethanolic medium did not bring about coalescence could be attributed to the presence of bound water associated with collagen, which remained unaffected during the ethanolic treatment. It could thus be concluded that ethanolic treatment affected only the free water associated with collagen, which also emphasizes the need for choosing solvents that are compatible with water.

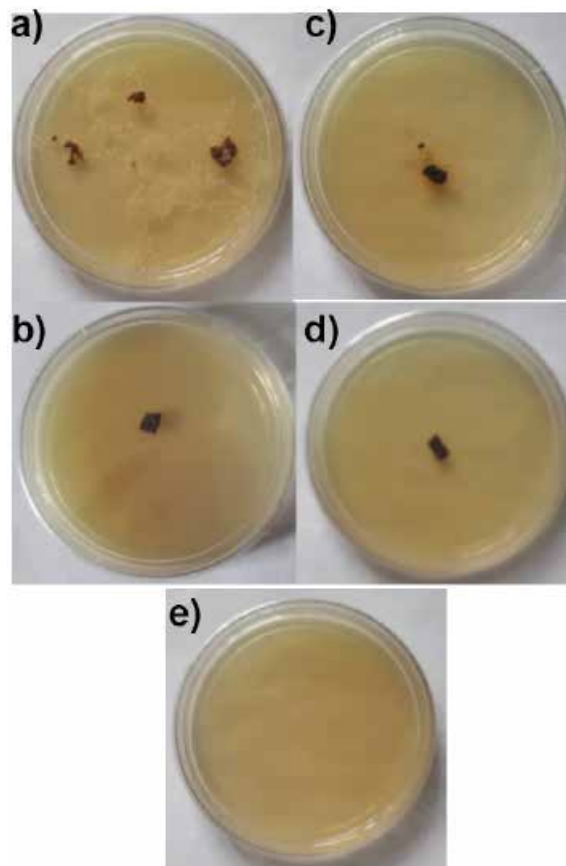


Figure 5. Antimicrobial and antifungal evaluation of the leathers tanned with ethanolic and water extracted wattle: a) water extracted wattle – bacteria, b) ethanol extracted wattle – bacteria, c) water extracted wattle – fungi, d) ethanol extracted wattle – fungi, e) control.

TABLE IV

**Comparative assessment of the physical properties of leathers prepared from water extracted wattle (control) and ethanol extracted wattle (experimental) in respective medium.**

Name of the sample	Tensile strength (N/mm <sup>2</sup> )	Elongation at break (%)	Tear strength (N/mm)	Load at grain crack (kg)	Distention at grain crack (mm)	Shrinkage temperature (°C)
Control	17.7 ± 2.5	47.7 ± 3.2	38.1 ± 1.5	45.0 ± 2.0	9.1 ± 1.2	83.0 ± 2.0
Experimental	16.4 ± 1.2	49.2 ± 1.7	29.4 ± 1.8	39.0 ± 1.6	8.3 ± 3.2	85.0 ± 1.8

**Notable advantages of tanning with ethanolic extract**

Anti-fungal and anti-bacterial activity of tannins extracted into solvents has been reported previously.<sup>14,15</sup> In order to confirm the same on leather, antimicrobial and antibacterial susceptibility tests were carried out on the leathers (Figure 5). The antagonistic properties of ethanol extracted wattle may account for the higher extraction efficiency of biologically active components like tannins, alkaloids, terpenoids, flavonoids, and some essential oils that are responsible for anti bacterial and fungal activity and their enhanced properties when ethanol is an extracting medium. Further, the percentage of non-tannins in the ethanolic extract, being lower, makes it unfavorable for the growth of the bacteria and fungi.

**CONCLUSIONS**

The present work highlights a futuristic possibility for the leather industry to employ solvent extracted wattle without the need for water solubilizing methods such as sulfitation for tanning in a solvent medium. Compared to commercial wattle extracts in water medium and water extracted tannins in water medium, the present work has the following advantages

- a. On the extract – a better particle size distribution and higher stability in the ethanolic medium, devoid of aggregation.
- b. On the RTT and leather – higher thermal stability, absence of fiber coalescence and good anti-fungal and anti-bacterial properties.

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