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Novel Vegetable Tanning Techniques by *Notholithocarpus densiflorus* Extract and Fatliquoring with Indigenous Bovine Fat

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Article

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ABSTRACT

*The major technical challenge of vegetable tanning is to improve the higher wear-comfort, leather strength and water resistance efficiency in daily necessities of leather products, aiming as an alternative to chrome tanning. The demonstration has been made by indigenous bovine fat and Tanoak tree (*Notholithocarpus densiflorus*) bark-wood extract for usage in the tanning process as a new kind of stuffing tanning technique for the first time. The tannin content maximum efficiency was found at 34.25% for the bark and 28.5% for the wood sample. The presence of tanning content was characterized by using UV-visible absorption spectroscopy, FTIR spectroscopy and HPLC techniques. The characterization data revealed mainly catechol presence in the bark and pyrogallol presence in the wood. The stuffing techniques tanned leather showed a shrinkage temperature of 95 ± 2 °C. Other physical properties such as tensile strength, tear strength, grain cracking load, and flexing endurance were comparable to conventional chrome-tanned leather. The cross-sectional morphology and thermal degradation of the tanned leathers were characterized by FE-SEM and TGA techniques which revealed a fat-coated compact structure of the leather fibres and decomposition at mainly 100 °C to 300 °C respectively. The average contact angle of a water droplet on bark-tanned leather was greater than 100° and wood-tanned 88° at the solid-liquid interface respectively, which indicated the low wettability of leather as a water resistance leather. These new kinds of stuffing techniques of vegetable tanning processes will help to replace the chromium tanning, sustainable tanning approach and save the environment.*

KEYWORDS

vegetable tanning, bovine fat, stuffing techniques, chrome-alternative tanning, sustainable tanning

INTRODUCTION

Chromium (III) salts are currently the commonest method of tanning, almost 90% of the world's output of leather is tanned by this method [1]. However, chrome-tanned leather is comparatively costly and in some cases, has a risk of forming Cr (VI) species from unbound chromium causing carcinogenic diseases [2]. In the case of vegetable-tanned leather, there is no harmful incident like chrome. The leather industry has suffered a serious crisis according to environmental issues and manufacturing

compliance. Global competition forced the leather industry to upgrade its technology to cope with pollution issues. The metal-free tanning agents are employed for the production of leather. Vegetable tanning is an alternative to manufacturing leather as eco-sustainable, natural, traditional, and safer for those tanning the leather [3].

Vegetable tannage is the earliest one to be practised in tanning. The oldest exploitation of plant polyphenols in technology is their ability to stabilize collagen in the skin against putrefaction. The plant polyphenols that can be leached out of vegetable matter or plant parts have the power to react with the collagen, rendering it resistant to biochemical degradation, but more importantly, remaining soft after the wetting-drying cycle [4].

Vegetable-tanned leather has a less adverse effect on the environment, but generally, it becomes harder and more hydrophilic. When being soft and hydrophobic, customers prefer to buy it and use it more. Having no chrome content but flexible leather, buyers will give attention to investing, manufacturing and buying leather. Local working sector and foreign currency will increase. After tanning, vegetable-tanned leather is soft, has better wear-comfort, leather strength and water resistivity to meet the standard of daily necessities such as footwear, belts, clothing, bags, sofas, car seats, etc. to compete for chrome-tanned leather.

However, vegetable tannins, which are often produced using bark extracts, leaves, fruit, and roots, all include the fragrant, organic component phenol necessary for tanning leather. Vegetable tanning is a labour-intensive method that takes longer than chrome tanning, which can be completed in a single day but is probably much more beneficial to the environment [5].

Based on consumer demand for the outstanding characteristics of vegetable leather, such as surface aesthetics, a patina that improves through time, and the lifespan in use, vegetable tanning has started to flourish in the 21st century. Vegetable-tanned leathers are preferred by designers due to their adaptability and versatility. Vegetable tanning should be done more frequently for a sense of environment and health. And for replacing chromium with vegetables, it is needed to develop vegetable tanning. Vegetable tanning can be improved by choosing a proper vegetable tanning agent and improving the process techniques.

In nature, there are various kinds of plants, those different parts like leaves, bark, wood, and roots have tanning power. Many of them are known as mimosa, quebracho, oak, pine, babul etc. [6-8]. The more there is knowledge on vegetable tanning material the more it will be possible to improve vegetable-tanned leather. For these reasons, attempts should be taken to find out whether new vegetable tanning material and testing new tanning methods are feasible or not. Attempts have been taken to tan hides or skin with *Notholithocarpus densiflorus* tree's bark and wood as a new tanning material to find out its feasibility. The local name of this tree is "Benni Gach". *Notholithocarpus densiflorus*, commonly known as the tanoak or tanbark-oak, is an evergreen tree in the family of

Fagaceae, native to the western United States, in California as far south as the Transverse Ranges, north to southwest Oregon, and east in the Sierra Nevada [9].

Vegetable tanning uses tannins (a class of polyphenol astringent chemicals), which occur naturally in the bark, wood and leaves of many plants. Tannins bind to the collagen proteins in the skin and coat causing them to become less water-soluble and more resistant to bacterial attack [10]. The primary barks processed in bark mills and used in modern times are tanoak, chestnut, oak, redwood, hemlock, quebracho, mangrove, wattle and myrobalan from Terminalia species such as Terminalia chebula. Skins are stretched on frames and immersed for several weeks in vats of increasing concentrations of tannin. Vegetable-tanned skins are not very flexible and are used for luggage, furniture, footwear, belts, and other clothing accessories [11-12].

Animal fat is saturated fat. In-room temperature it is solid. Its melting point is 40 °C and its boiling point is 214 °C. It is not toxic to the skin when it is used to produce cosmetics. Generally, we get animal fat from pigs, sheep, cows and other animals [13]. The meat by-product fat was collected from the local market and distilled through different treatments for the application of the stuffing treatment of leather.

Water resistance is typically applied only for shoes and boots, possibly including clothing leather. Such a process is usually applied to chrome tanning leather since other methods of tanning make the leather too hydrophilic to allow high levels of water resistance to be conferred. It is common to refer to the treatment for leather with hydrophobic reagents as waterproofing. This implies that water is completely excluded from the cross-section of the leather so that no transmission of moisture occurs. In this study, attempts have been made to the potential application of local bovine fat to make waterproof vegetable-tan leather by new innovative techniques. The local technology ensures a significant cut in the import cost of vegetable tannin and fatliquor. The effectiveness of prepared fatliquor and vegetable-tanned leather has been standard tested for comparison with conventional chrome tanning. Moreover, to our knowledge, we report here for the first time the vegetable tanning techniques using localized animal fat and vegetable extract.

EXPERIMENTAL

Materials Collection

The green bark and wood samples were collected from *Notholithocarpus densiflorus* trees abundantly at the Institute of Leather Engineering and Technology (ILET), Dhaka University, Dhaka, Bangladesh. Approximately, 8-10 kg of fresh bark and wood sample were collected from *N. densiflorus* trees of branches 10 to 15 m tall, and the bark and wood were identified and validated by a taxonomist of the Biomedical and Toxicological Research Institute, Bangladesh Council of Scientific and Industrial

Research (BCSIR), Bangladesh. 2000 gm of bovine fat and 10 pieces of wet-salted goat skin have been purchased from the local market in Hazaribagh, Dhaka, Bangladesh.

Chemicals and reagents

All chemicals of analytical grade were used in the experiment. Methanol (99.5%) (Merck, Germany), FeCl_3 (99.1%) (Research Lab, India), FeSO_4 (99.0%) (Research Lab, India), HCl (BDH chemicals, India), H_2SO_4 (Merck, Germany), Sodium Potassium tartrate (98.4%) (Research Lab, India), Na_2SO_3 (Merck, Germany), KOH (Merck, Germany), CaCl_2 (98%) (Research Lab, India), all HPLC standard chemicals Pyrocatechol (Catechol, O-dihydroxy benzene, Research Lab, India), Gallic acid (97.9%, (Merck, Germany), Rutin trihydrate (94%, Research Lab, India), and Cinnamic acid (99%, Research Lab, India), were collected and used without further purification. The basic chromium sulphate (Stahl, India) and other tanning chemicals have been collected from the local market in Dhaka, Bangladesh.

Experimental Methods

Tannin extraction

The tannin extraction process was reported elsewhere [21,33] and the process was modified by us. In detail, collected wood and bark were cut into small pieces using a chopper and then a hammer was applied to make those soft pieces and dried them in the sunlight. Hammered soft wood and bark pieces were ground to size 0.25 mm using the crushing machine in ILET, Dhaka University mechanical workshop. The ground powder was preserved in an airtight container and stored in an anhydrous dark condition, towards to next use. The ground powder was dissolved in 80% of methanol solution and shaken for 12 hours at room temperature. Then the sample was filtered with a 0.45 μm pore size filter membrane and residual materials were rinsed out with additional solvents (300 mL) for 8 h and filtered accordingly. Extracts were shifted to a round-bottom flask and evaporated under vacuum by rotary evaporator, and were dried in a vacuum oven at 50 °C to gather solid material. The yield percentage of extracts was calculated by the following equation;

$$\text{Extraction efficiency of tannin} = \frac{\text{Weight of the obtained extract (g)}}{\text{Weight of the moister free sample (g)}} \times 100\% \quad (1)$$

The identification process of tannin

3 ml of a 5% (w/v) FeCl_2 solution was added to 1 g of the sample extract. The greenish-to-black colour precipitation indicated the presence of tannins shown in Figure 1 (a) [14,22]. 3 ml of FeSO_4 solution is added to 3 ml of sodium potassium tartrate solution to make the required solution. The bark and wood

tannin extract is given to the solution across the tube. After shaking the two test tubes bark tannin becomes fully violet-blackish but not the wood tannin shown in Figure 1 (b) [15,22].

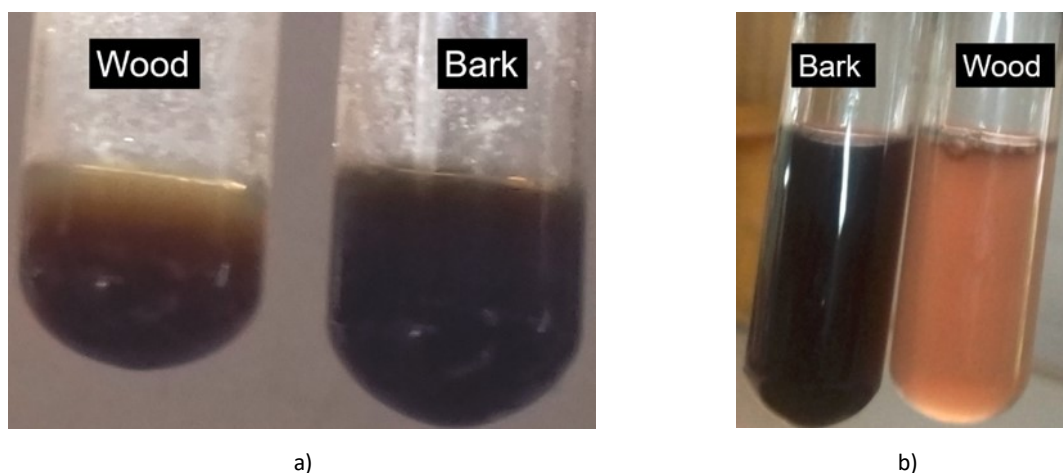


Figure 1. Presence of tannin. a) Ferric chloride reagent test wood and bark powder for tannin detection, b) Ferrous sulphate reagent test. Indicated the presence of catechol in bark and pyrogallol in wood

Synthesis of sulphonated bovine fat

In separation for fatty matter and non-fatty matter, 25% of HCl was added to 1000 gm of the raw sample (bovine fat) and then heated in a reflux vessel, until the fats were completely separated as the following method [13]. Using a separating glass funnel, the separated fat was collected by pipetting. Fat was then placed into an acid-resistant vessel. The 100 ml of H_2SO_4 with 500 ml of water was added slowly and the mixer was vigorously stirred with a euro meter. Then 50 gm of anionic surfactant (Sodium laureth sulfate) is added to the fat-liquor as an emulsifier. The fat was additionally rotated for 6 hours and then semi-liquid fat is collected. The resultant fat liquor was preserved for future usage. The synthesized fat, acid value, iodine value, and saponification value were determined by the following standard methods of SLC-304, SLC-305 and SLC-303 respectively [16].

Application techniques for extracted tannin in leather processing

Soaking to pickling was carried out by following the conventional leather manufacturing process. The required amount of *Notholithocarpus densiflorus* was mixed with the modified bovine fatliquor at 50 °C temperature and applied to the re-tanning process as following the recipe depicted in Table 1. Shaved piled pelt was put into the drum with a stuffing solution, and then tanning and drumming were done with regular tumbling techniques. Drumming was continued till the absorption of the stuffing mixture have been found satisfactory. The entry of the fatliquor into the leather is rapid so there is a possibility of completely penetrating the interfibrillar space. This process was run until proper penetration occurred.

Table 1. Recipe of tanning and re-tanning process of goat skin

Process	Dosage (%)*	Chemicals	Time (min)	Remarks
Tanning	80	Water (25 °C)	120	pH 3.8-4.0
	1	Cr-Tanning agent		
	1	Sodium-bicarbonate (1 :10)	20x3 and 120	
	0.2	Fungicide	35	
Ageing, shaving, conventional steps, and processes were done				
Re-tanning (Stuffing tech.)	80	Water at (50 °C)	60x3	Kept 1 day with 5min/hours of tumbling
	10x3	<i>Notholithocarpus densiflorus</i>		
	8x3	Modified sulphated fat		
		(Mixed and applied on leather)		
	6	Syntan	60	
	0.5	Formic acid	15x2	
After re-tanning other conventional processes were done for making crust leather				

*Dosage percentage based on pelt weight for tanning and shaved weight for re-tanning

Characterization of *Notholithocarpus densiflorus* tannin and tanned leather

Absorption spectra of tannin extract

Absorption spectra of the tannin extract were recorded by using a UV-visible spectrophotometer (Varian, 50 Conc, USA) using a 1 cm path-length quartz cuvette. UV-visible spectrophotometer measurement, 0.1 g of extract sample was dispersed in 50 ml methanol and then 1 ml of dispersed solution was diluted to 100 ml methanol before performing the UV-visible spectra.

HPLC analysis of tannin extract

HPLC was performed on SIL 20 series Prominence HPLC (Shimadzu, Japan) equipped with an autosampler (Model SIL-20 AC), dual pumps (Model 20 AD), column oven (Model CTO-20A), vacuum degasser (Model DGU-20A), UV-visible detector (Model SPD-20A), and LC solution software was used. Analytical reversed-phase C-18, Luna 5 μ , 250 x 4.6 mm, Phenomenex, Inc., Japan was used. Chromatographic conditions: Mobile phase: Acetic acid (10%) (A pump), Acetonitrile (B pump) UV detection: 280 nm, Run time: 40 mins, Flow rate: 1.0 mL/min, Column temperature: Room temperature, Injection volume: 20 μ L, Elution: Gradient. The 4g of extract samples were weighed with a weight box and taken into a falcon tube. Then 10 mL of methanol was added and mixed by vortexing. Then it was centrifuged (Hettich MIKRO 220R, Germany) at 4000 rpm for 20 minutes. The supernatant was collected and filtered by a 0.45 μ m nylon filter. Then, inject the sample into HPLC. To prepare a standard solution Pyrocatechol, Gallic acid, Rutin trihydrate, and Cinnamic acid were weighed and volumed with 100 ml of methanol in a volumetric flask containing a concentration of 100 ppm. Then

the solution was mixed by vortexing for 5 minutes and was filtrated by a 0.45 μm nylon filter. Serial dilution was done to get a concentration of 5 ppm to 90 ppm with methanol. The supernatant was filtrated by a 0.45 μm nylon filter and then standard samples were injected into HPLC and attained a linear calibration curve.

FT-IR analysis of tannin extract and tanned leather

The Fourier-transform infrared (FT-IR, Bruker, Alpha II) spectra were used to identify the functional groups of the extract and tanned leather with the frequency range of 4000–500 cm^{-1} . Both background and sample scans were measured sequentially at a scanning rate of 1 Hz, and 4 cm^{-1} resolution. Before starting the analysis, background measurement was executed with KBr without a sample. Then automatic baseline correction and normalization were carried out by the FTIR built-in software.

SEM analysis of tanned leather

Before SEM measurements, the tanned leather and cross-section of tanned leather samples were attached on a carbon tape-attached metal plate. Then the metal plate containing the sample was coated with platinum by using The JEOL auto fine coater (JEC-3000FC) and placed in the FE-SEM (JSM-7610F, JEOL, Japan) for the analysis with desired magnifications.

TGA analysis of tannin extract and tanned leather

Thermogravimetric analysis (TG) was performed, using a Thermogravimetric analyser (PerkinElmer, TGA 8000) apparatus recording TG. TG was carried out in the temperature range from 50 $^{\circ}\text{C}$ up to 700 $^{\circ}\text{C}$ under a nitrogen atmosphere at a heating rate of 10 $^{\circ}\text{C}/\text{min}$. 3–5 mg of samples were weighed in ceramic pans and analysed accordingly.

Water resistivity analysis of tanned leather

Water droplet was measured by a contact angle meter (DMe-211, Kyowa Interface Science Co. Ltd., Japan) to test the water resistivity. A micrograph of water droplets was taken by a stereo microscope (A23.3645-B8LT, Opto-Edu (Beijing) Co., Ltd.).

Hydrothermal analysis of tanned leather

Hydrothermal stability by the shrinkage temperature (T_s) apparatus (Satra, Ser. No.:032388) of bark and wood-tanned leather was carried out following the standard method IUP-16 [17].

Physical testing analysis of tanned leather

The physical, chemical and mechanical properties of tanned leather were determined by tensile strength, percentage of elongation, tear strength, instant lastometer, flexing endurance, waterproofness, and fat content [18-20] followed by standard methods of SLC [16]. All the tests were performed three times for both parallel and perpendicular to the backbone and reported the mean with standard deviation in this study. Before the testing, the leather was conditioned for 48 h at a temperature of 23 ± 2 °C, and relative humidity of $65 \pm 2\%$ following the ISO-2419 standard.

RESULTS AND DISCUSSION

The methanol was used for the tannin extraction process as a solvent. Literature review showed that the tannins were extracted by different procedures and techniques, among them methanol extraction process is the best [5,12,21]. The extraction yield was found 34.25% for bark and 28.5% for wood. The extraction method in methanol solvents is ideal at a pH of around 4, which was reported previously [21,33]

There have been numerous attempts to organize tannins into various categories based on their various characteristics, but the most significant one was to divide them into two types: the pyrogallol type and the catechol type. An extract composition of traits is often needed and *N. densiflorus* is no exception. The FeCl_2 reagent test was done to assure the presence of tannin and showed respective changes in the test solution followed by precipitate formation as shown in Figure 1(a), confirming tannin presence in both bark and wood extract. The FeSO_4 chemical tests for the presence of catechol and pyrogallol tannins in *N. densiflorus* extracted were done followed by the appearance changes of precipitate as shown in Figure 1(b). Bark extract shows the violet-blackish indicated the main catechol type tannin. Interestingly, a wood extract shows a reddish appearance indicating the main pyrogallol in presence of *N. densiflorus*, which is in similarity to other researcher findings [21-22].

The UV-visible absorption spectra of the *N. densiflorus* extract were clearly shown the ultraviolet region peaks (Figure 2). The UV absorption spectra of the bark extract have shown a peak maximum at 275 nm, (Figure 2), indicating the presence of catechol and tannic acid [21-22]. But, the wood extract showed maximum peaks at 265 nm, (Figure 2) indicating the presence of gallic and tannic acids [21-22]. These suggest that the extract has the presence of tannic acid, catechol in bark and gallic acid in wood extract, which facilitated the potential application to tanning.

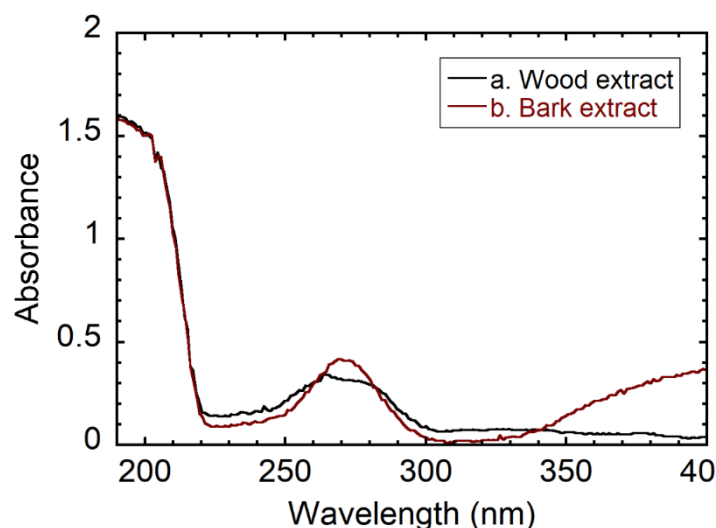
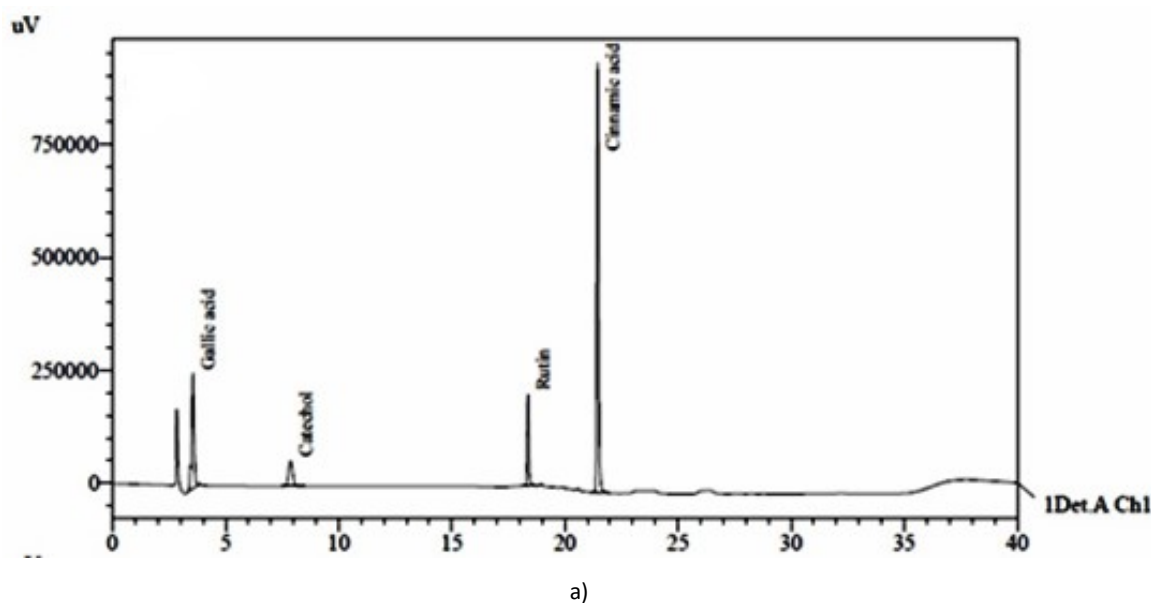
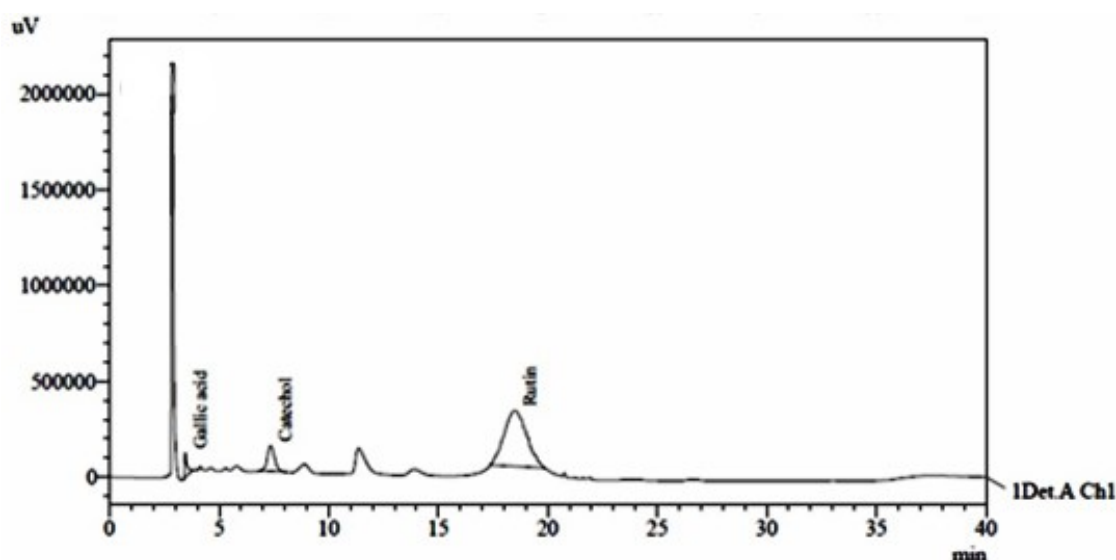


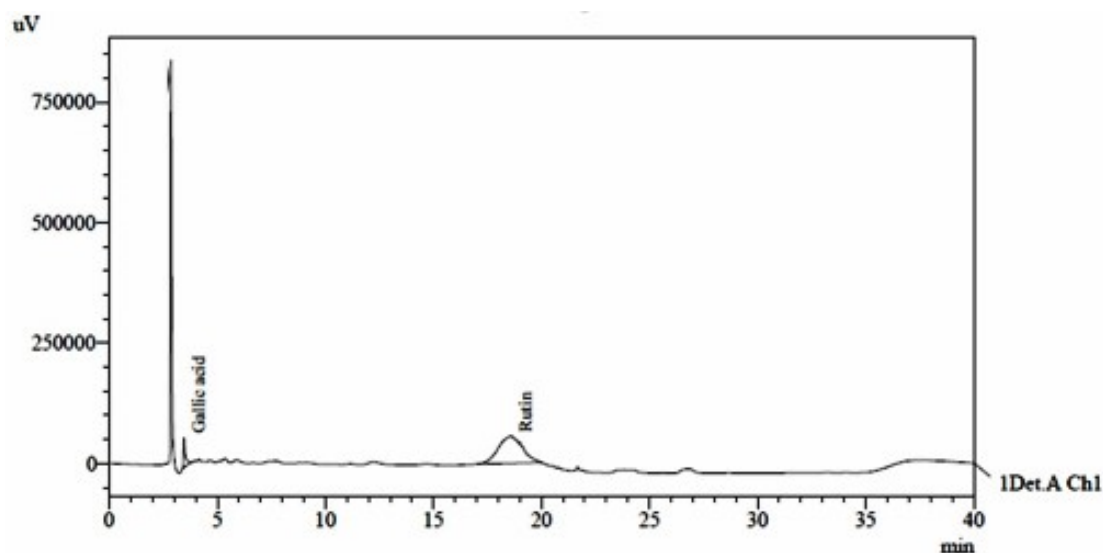
Figure 2. UV-vis absorption spectra of *N. densiflorus* bark and wood extract prepared in methanol solvent

Further confirmation of individual polyphenolic compounds of *N. densiflorus* extracted tannin was identified and quantified by HPLC. The chromatographic separations of the polyphenolic standard are shown in Figure 3 (a). Each polyphenolic compound was quantified from the corresponding calibration curve of bark and wood-extracted tannin. In HPLC analysis, pyrocatechol, gallic acid, rutin trihydrate, and cinnamic acid standard sample solution was run as references, where pyrocatechol, rutin trihydrate polyphenolic compounds were identified in bark extract and gallic acid, rutin was identified in the wood extract of *N. densiflorus* tannin shown in Figure 3 (b-c). Extracted contained a high concentration of catechol (306 mg/4 g dry extract) and a moderate concentration of rutin (90 mg/4 g dry extract) in the bark. A high concentration of gallic acid (190 mg/4 g dry extract) and a moderate concentration of rutin trihydrate (90 mg/4 g dry extract) have been identified in wood extract.





b)



c)

Figure 3. (a) HPLC reference chromatogram of a standard mixture of polyphenolic compounds, (b) bark tannin, (c) wood tannin, of *Notholithocarpus densiflorus* tannin.

The high concentration of catechol identified in the bark of *N. densiflorus* tannin signifies the presence of condensed type tannin known as Flavan-3-ols and the high concentration of gallic acid identified in wood signifies the hydrolysable tannin [23]. The condensed and hydrolysable tannin determination test was carried out three times for attaining better accuracy. The average percentage of condensed tannin was found at 39.80 ± 1.52 for the *N. densiflorus* tannin of bark whereas wood hydrolysable tannin was found at 28.78 ± 1.92 respectively. Therefore, the extracted bark and wood tannin from *N. densiflorus* could be claimed as a potential condensed and hydrolysable type tanning material.

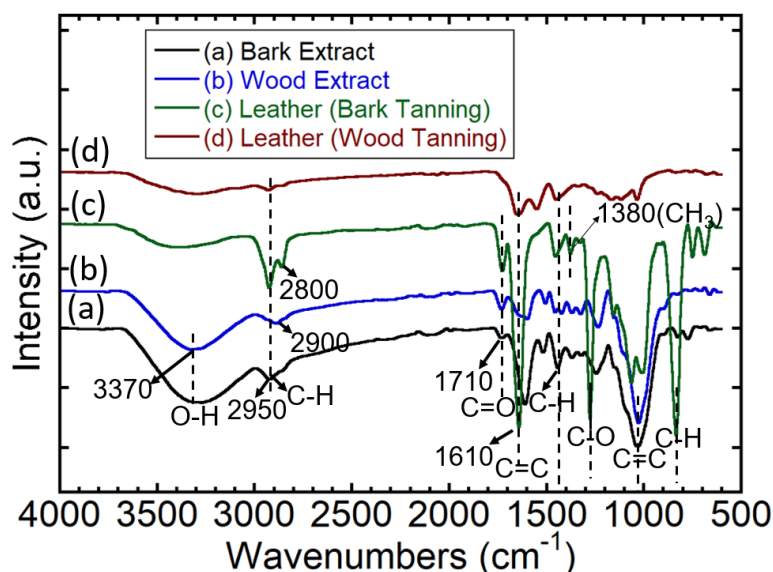


Figure 4. FTIR spectra of *Notholithocarpus densiflorus* (a) Bark extract (b) Wood extract (c) Bark-tanned leather and (d) Wood-tanned leather

The FTIR spectra of *Notholithocarpus densiflorus* tannin and tanned leather are shown in Figure 4. The spectra were recorded in the spectral region of 4000–500 cm^{-1} and their frequency assignment was discussed. The intense broadband 3370 cm^{-1} peaks are specific probably due to the OH stretching vibration of polyphenols such as flavonoids, pyrogallol and tannins which strongly appeared in bark and wood extract [21,24–26]. The band in the region of 2950 cm^{-1} for bark extract typically indicate the condensation tannin and around 2900 cm^{-1} indicates the hydrolysable tannin respectively for C-H stretching vibration [24,26–27]. A sharp peak around 2800 cm^{-1} is exhibited in bark-extract tanned leather, typically indicating stretching of aliphatic CH groups. A weak signal 1710 cm^{-1} indicated the presence of flavonols in the mixture to a C=O...H bond interaction in a polymeric matrix condensed tannin [26]. A strong peak of 1610 cm^{-1} is consistent with the presence of a substituted benzene system [26]. A peak was observed around 1452 and 1446 cm^{-1} which corresponds to the vibration of C-H elongation of aromatic rings [24]. The 1290 cm^{-1} band is considered a recognition pattern for flavonoid-based tannins as a bark tanned, occurring as a shoulder in flavanol-based compounds and being absent in hydrolysable wood-tanned leather [24]. A 1005 cm^{-1} band is C=C aromatic and can be considered for the stretching deformation of hydroquinone, glucose, and pyrogallol [28–29]. The 810 cm^{-1} band is C-H suggesting the aromatic out-plane symmetric C-H bend of phenol, hydroquinone, and catechin [28–29].

The modified bovine fats acid value, iodine value, and saponification value were determined by the following standard methods of SLC-304, SLC-305 and SLC-303 respectively [16]. The acid value was found 3.65 mg out of 2 gm of the sample, indicating a low amount of free fatty acid. The iodine value and saponification value were found 26 and 192 respectively indicating the high melting point and soft

lubricating value of bovine fat. Animal fats have to contain single bonds that are easily solidified at room temperature. A lower iodine value is indicated by the sulphonated modified fat's lower degree of unsaturation and the emulsifier active methylene group next to the double bonds of oils [30] gives the stability of fat. FTIR data (Fig. 4(c)) of the bark-tanned leather showed a peak at 1380 cm^{-1} which was attributed to the CH_3 group and hydrophobicity of the leather. There are many polar functional groups in collagen fibres such as $-\text{OH}$, $-\text{COOH}$, $-\text{NH}_2$ and $-\text{CONH}-$. Waterproof leather can be produced by the impregnation with the incorporation of water-insoluble substances, such as solid fats, waxes or particular polymers [31-32]. The functional groups make the fatliquoring emulsion with low surface tension, but there are no active groups that have a poor combination with collagen fibres. These afford the leather a static waterproof property and special feeling definitely but simultaneously reduce the air penetrability [31]. New stuffing tanning techniques fatliquoring and vegetable give the dual effect of tanning and waterproofing on leather.

Hydrothermal stability was done based on the shrinkage temperature (T_s) of the leather sample. The shrinkage temperature of the bark-tanned was found $95 \pm 2\text{ }^\circ\text{C}$ and wood tanned $89.59\text{ }^\circ\text{C}$ of three several determination values, which indicated that the maximum functional group of polypeptide chain might be satisfied by the vegetable tannin and fatliquor. Similar findings were recently reported by Das et al. [33] who found a maximum shrinkage temperature is $86.36\text{ }^\circ\text{C}$. The synergistic bovine fat and vegetable tannin might affect and enhances the thermal properties of skin collagen. A before fatliquor had a lower shrinkage temperature ($\sim 80\text{ }^\circ\text{C}$) compared to that of skin treated with *N. densiflorus* extract followed by sulphonated bovine fat, which was close to $95\text{ }^\circ\text{C}$ and an increment of about $15\text{ }^\circ\text{C}$. The polyphenolic constituents of vegetable tannin participate in non-specific interactions with collagen via hydrogen bonding, and the SO_3 group of bovine fat incorporates the collagen matrix electrostatically, this dual effect might increase the thermal stability and hydrophobicity of leather [1]. The physical, chemical and mechanical properties testing of *Notholithocarpus densiflorus* tanned leather are illustrated in Table 2. Experimental tanned leather showed a very high tensile strength of 149.48 kg/cm^2 for bark tanned and 142.12 kg/cm^2 for wood-tanned leather, which is well above the UNIDO standard garments leather (100 kg/cm^2) [34-35]. Further, experimental leather showed a very high percentage of elongation 57% of bark-tanned leather whereas wood-tanned leather shows 66%. The bark-tanned leather is a well-accepted value (max. 60%) recommended by UNIDO but wood-tanned leather is a little higher than the maximum, which might be due to the higher void space in leather and needing more tanning. Therefore, stitch tearing strength, instant lastometer, flexing endurance and waterproofness, and colour rub fastness test was found greater than the standard shown in table 2. The content of fat little higher than standard. All physical, chemical and mechanical properties revealed that bark-tanned leather is more suitable than wood-tanned leather and leather could be comparable to conventional chrome-tanned leather.

Table 2. Summary of physical, chemical and mechanical properties of leather tanned by bark and wood extracted tannin (mean $\pm$ SD)

Name of Test	Results		
	Bark Extract Tanned Leather	Wood Extract Tanned Leather	Standard For Garments Leather [34, 35]
Tensile strength (Kg/cm ²)	149.48 $\pm$ 3.52	142.12 $\pm$ 3.42	Minimum 100
Elongation at Break (%)	57 $\pm$ 2.35	66 $\pm$ 2.12	Maximum 60
Stitch Tearing strength (Kg/cm)	123 $\pm$ 2.21	112 $\pm$ 2.31	Minimum 60
Instant lastometer test (Kg/cm)	206 $\pm$ 1.12	183 $\pm$ 1.52	100-300
Flexing endurance test (25000 cycles)	Pipe labelling scale rating 3	Pipe labelling scale rating 3	Not below 3 (Max 50000 Cycles)
Colour rub fastness test	Greyscale rating 5	Greyscale rating 5	Not below rating 3
Waterproofness test	8 min	7 min	Minimum 5 min
Fat content (%)	13.04 $\pm$ 3.61	12.88 $\pm$ 3.40	Maximum 10

The morphology of *Notholithocarpus densiflorus* tanned leather fibre structure, fibre bundles splitting, filling properties and fibre coating were investigated by FE-SEM. Figure 5 (a) and Figure 5(b) show the surface and cross-sectional micrograph of bark tanned and Figure 5 (c) and Figure 5(d) show the wood-tanned leather respectively. Figures 5(a) and (c) showed a compact fibre structure, which is well coated with fatliquor and is characteristic of fibre opening. Figures 5 (b) and (c) confirm vegetable tannins are densely packed in a compact fibre matrix and are characteristic of vegetable-tanned leather [33]. It is clear from the FE-SEM of the tanned leather that the bovine fat-assisted process has coated the fibre matrix and is well-filling vegetable tannins. The tanned leathers have large voids space between fibre bundles and individual fibres can move over each other as evidenced by the softness properties.

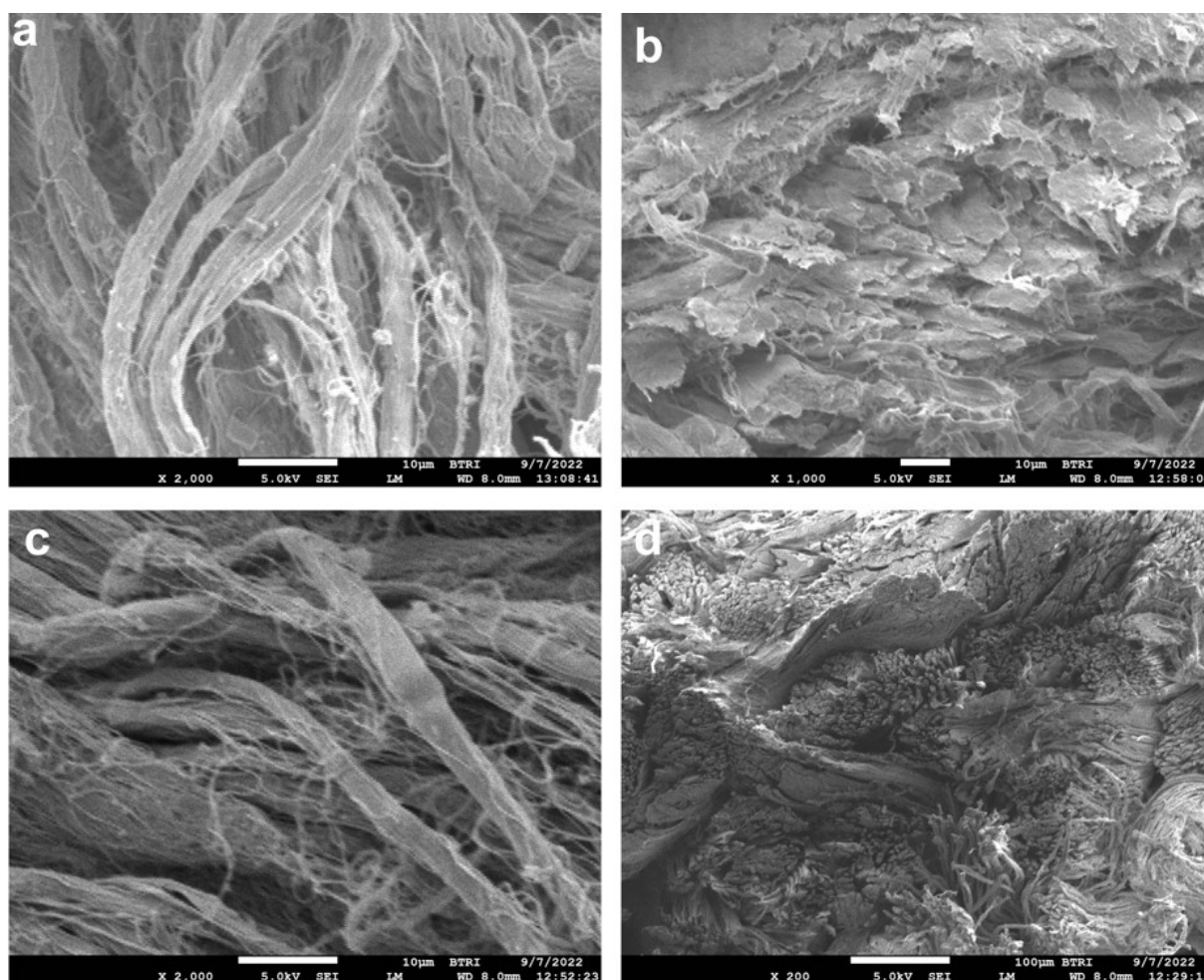


Figure 5. FESEM images of the (a) bark-tanned inner (b) bark-tanned cross-section (c) wood-tanned inner (d) wood-tanned cross-sectional morphology of *Notholithocarpus densiflorus* extract-tanned leather

The thermal mass losses evaluation of *Notholithocarpus densiflorus* bark powder, wood powder, bark extract tanned leather and wood extract tanned leather overall TG curves are presented in Figure 6. Three regions appeared in the temperature range from room temperature to 700 °C, corresponding to water-removal, main decomposition (active pyrolysis) and passive pyrolysis, respectively. The first region of mass losses observed from room temperature to 100 °C could be attributed to the evaporation of absorbed and bound water of the tanned sample. Whereas, the extract has no losses due to the dry powder, indicating no moisture in the sample. The main weight loss from 100 °C to 300 °C is assigned to the decomposition of proteinic material and shows the same attribute in both bark and wood-tanned leather [36]. A similar attribute was observed in another vegetable tannin mimosa, tara and chrome-tanned leather reported by other researchers [37]. The extract powder's main decomposition temperature is 240 °C to 280 °C may be due to poor thermal conductivity whereas tanned leather has a higher decomposition temperature may be due to crosslinking with the amino groups via hydrogen bonds of phenolic and aromatic structures of extract. A long tail was observed at

a high-temperature range (500–700 °C) and manifested an extremely low mass loss rate, which can be ascribed to the continuous pyrolysis of very stable residues [36].

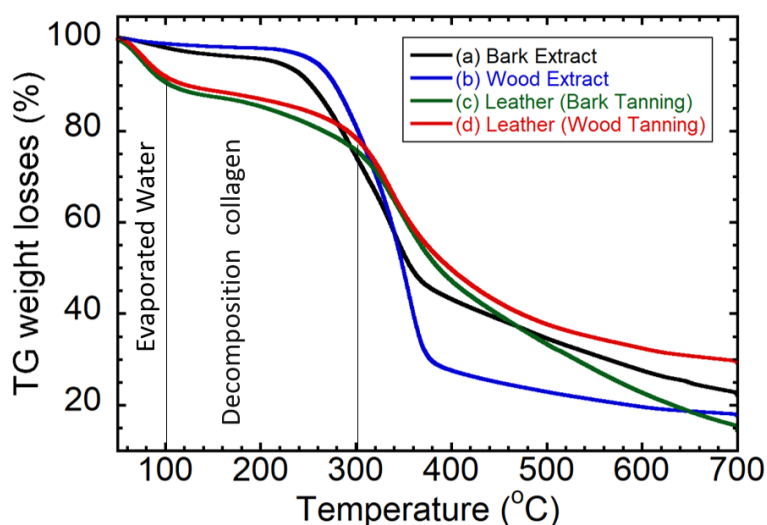


Figure 6. Thermal gravimetric analysis (TGA) of (a) Bark extract (b) Wood extract (c) Bark extract tanned and (d) Wood extract tanned leather of *Notholithocarpus densiflorus*

As shown in the pictures of Figures 7a) and 7b), bark and wood powder vegetable-tanned leather surface water droplet's contact angle was tested as well. The stuffing new-techniques process vegetable tanned leather shows the hydrophobic with a contact angle of a water droplet greater than $100^{\circ} \pm 3^{\circ}$ of bark tanned and wood tanned is $92^{\circ} \pm 2^{\circ}$ respectively of three difference point. The relative micrograph is exposed to water droplets on the tanned leather Figures 7 (a1) and (b1), indicated that tanned leather is relatively hydrophobic. The interfacial wettability of materials' surfaces depends on the contact angle and contact angle introduced to quantify the wettability. This reveals the self-cleaning capacity of vegetable-tanned leather, liquid droplet on a solid surface, the water droplets can easily roll off the surface, taking away contamination particles, such as dust or dirt [38]. However, the leather surface is rough Figure 7 (a1) and (b1)) and the water-droplet easily moved away from the surface. The improved hydrophobicity of the stuffing-modified leather might be attributed to the increased amounts of the alkyl or hydroxyl group at the surface shown in the FTIR figure.

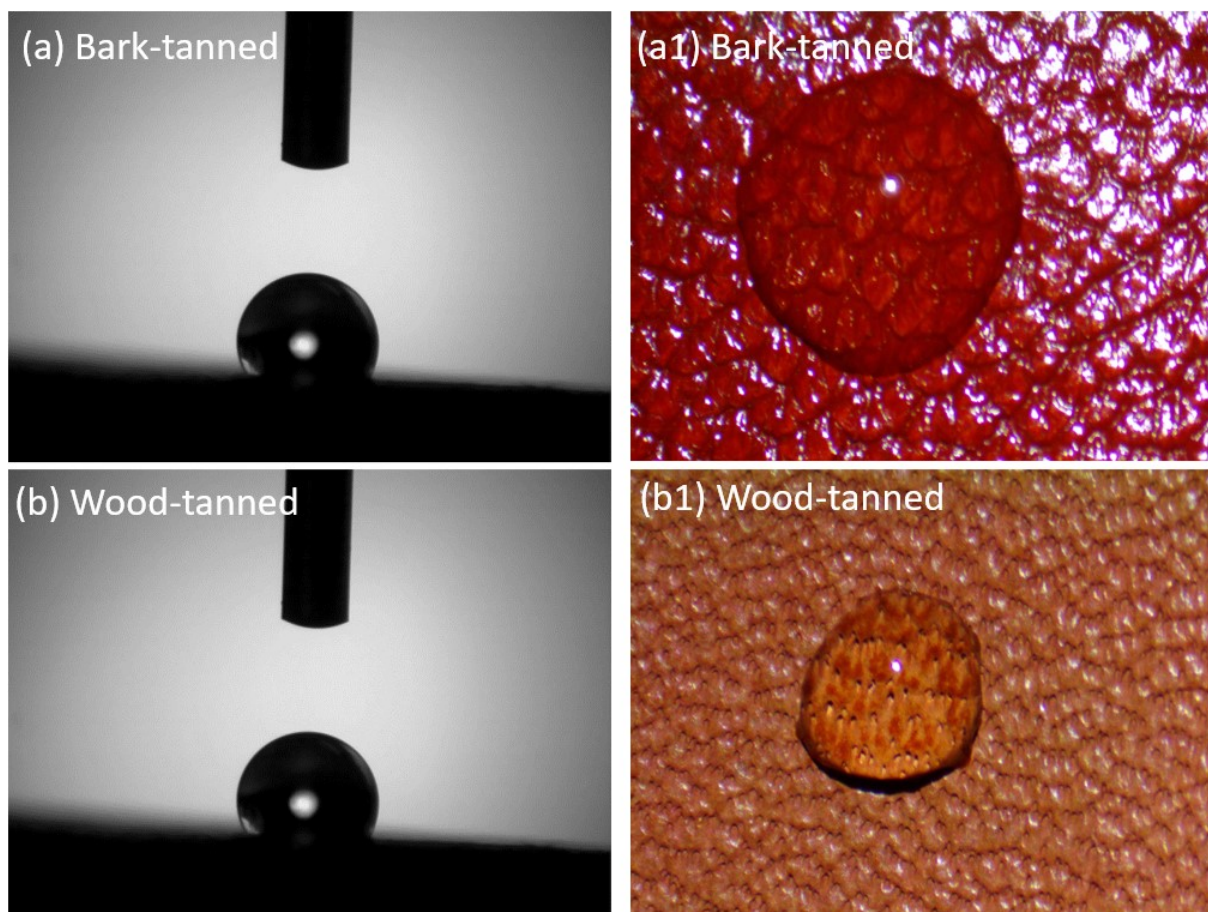


Figure 7. The contact angle of a water droplet on the (a) Bark tanned leather and (b) Wood-tanned leather as a function of the water resistance. Water droplet test on the leather surface (a1) Bark-tanned (b1) wood-tanned leather for waterproofness by stereo microscope

The family of plant polyphenols is characterized by the presence of phenolic hydroxyls, capable of reacting with collagen, at the basic groups on sidechains and the partially charged peptide [12,39]. It has also been reported that the tanning mechanism of vegetable tannins or natural polyphenols is due to the formation of numerous hydrogen bonds with collagen basic groups, for example, lysine, arginine and the peptide backbone [37].

CONCLUSION

In general, conventional vegetable-tanned leathers have no waterproofing properties. We developed and investigated new technology for producing water-resistant vegetable-tanned leather for apparel. In this research, a conventional vegetable tanning process has been developed by using indigenous Tanoak extract and bovine fat. Here only 1% chromium powder has been used for chrome capping to increase the shaving potency. This technology has been reducing the chrome and improving the tanning systems for chrome-free and metal-free leathers for sustainable leather making. Collagen fibre was treated with stuffed fatliquor and it becomes waterproof. This application offers new and

interesting perspectives for the leather industry to protect the environment and reduce pollution. Tanoak extract having handsome and glossy colours helps reduce dye usage. Extra softness and smooth feeling help to satisfy users. Colour rub fastness ensures the authentic colour for long time usage. Tensile strength, stitch tear strength and grain crack strength which satisfy the standard values ensure the best quality leather. High-fat content means more waterproof properties. This new technology can help develop the potential application in the leather industry, save the environment and increase the usage of vegetable-tanned leather.

Author Contributions

Conceptualization – Abdulla-Al-Mamun M, Sarker B; methodology – Abdulla-Al-Mamun M, Sarker B; formal analysis – Abdulla-Al-Mamun M, Sarker B; investigation - Sarker B; resources – Abdulla-Al-Mamun M, Sarker B; writing-original draft preparation – Abdulla-Al-Mamun M, Hossain N, Sarker B; writing-review and editing – Abdulla-Al-Mamun M; visualization – Sarker B, Islam D, and Rahman A; carried out FESEM Image and Tanok tree validity - Islam D; Carried out HPLC - Rahman A; supervision – Abdulla-Al-Mamun M. All authors have read and agreed to the published of the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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REFERENCES

- [1] China CR, Maguta MM, Nyandoro SS, Hilonga A, Kanth SV, Njau KN. Alternative tanning technologies and their suitability in curbing environmental pollution from the leather industry: a comprehensive review. *Chemosphere*. 2020; 254:126804.
<https://doi.org/10.1016/j.chemosphere.2020.126804>

- [2] Scopel BS, Baldasso C, Dettmer A, Santana RMC. Hydrolysis of chromium tanned leather waste: Turning waste into valuable materials – A review. *Journal of the American Leather Chemists Association*. 2018; 113(4):122-129.
- [3] Elgailani IEH, Ishak CY. Determination of tannins of three common Acacia species of Sudan. *Advances in Chemistry*. 2014; 2014:192708. <https://doi.org/10.1155/2014/192708>
- [4] Kanth SV, Madhulatha W, Madhan B, Venba R, Chandrababu NK. Stabilization of natural fiber collagen using vegetable tannins: an effective enzyme assisted process. *Journal of Natural Fibers*. 2008; 5(4):404-428. <https://doi.org/10.1080/15440470801983793>
- [5] Kanagaraj J, Panda RC, Kumar MV. Trends and advancements in sustainable leather processing: Future directions and challenges-A review. *Journal of Environmental Chemical Engineering*. 2020; 8(5):104379. <https://doi.org/10.1016/j.jece.2020.104379>
- [6] Kilicariskan C, Ozgunay H. Ultrasound extraction of valonea tannin and its effects on extraction yield. *Journal of the American Leather Chemists Association*. 2012; 107(11):394-403.
- [7] Pisitsak P, Hutakamol J, Jeenapak S, Wanmanee P, Nuammaiphum J, Thongcharoen R. Natural dyeing of cotton with *Xylocarpus granatum* bark extract: Dyeing, fastness, and ultraviolet protection properties. *Fibers and Polymers*. 2016; 17(4):560-568. <https://doi.org/10.1007/s12221-016-5702-x>
- [8] Galvez JMG, Riedl B, Conner AH. Analytical studies on Tara tannins. *Holzforschung*. 1997; 51:235-243.
- [9] Manos PS, Cannon CH, Oh SH. Phylogenetic relationships and taxonomic status of the paleoendemic Fagaceae of western North America: recognition of a new genus, *Notholithocarpus*. *Madroño*. 2008; 55(3):181-190. <https://doi.org/10.3120/0024-9637-55.3.181>
- [10] Sarkar KT. *Theory and Practice of Leather Manufacture*. 1995.
- [11] China CR, Nyandoro SS, Munissi JJE, Maguta MM, Meyer M, Schroeffer M. Tanning capacity of *Tessmannia burtii* extracts: the potential eco-friendly tanning agents for the leather industry. *Journal of Leather Science and Engineering*. 2021; 3(1):1-9. <https://doi.org/10.1186/s42825-021-00055-2>
- [12] Covington AD. *Tanning chemistry: the science of leather*. Cambridge: The Royal Society of Chemistry; 2020. 442 p.
- [13] Nyamunda BC, Moyo M, Chigondo F. Synthesis of fatliquor from waste bovine fat for use in small scale leather industry. *Indian Journal of Chemical Technology*. 2013; 20(2):116-120.
- [14] Abdelfatah AM, Fawzy M, El-Khouly ME, Eltaweil AS. Efficient adsorptive removal of tetracycline from aqueous solution using phytosynthesized nano-zero valent iron. *Journal of Saudi Chemical Society*. 2021; 25(12):101365. <https://doi.org/10.1016/j.jscs.2021.101365>

- [15] Hagerman AE. Tannin - protein interactions. In: Ho CT, Lee CY, Huang MT. Phenolic Compounds in Food and Their Effects on Health I. American Chemical Society; 1992. p. 236-247.
- [16] Society of Leather Technologists and Chemists. Official Methods of Analysis. 1996.
- [17] International Union of Leather Technologists and Chemist Societies. IUP-16. Measurements of shrinkage temperature up to 100°C. 2001.
- [18] International Union of Leather Technologists and Chemist Societies. IUP-06. Measurement of tensile strength and percentage of elongation. 2001.
- [19] International Union of Leather Technologists and Chemist Societies. IUP-08. Measurement of tearing strength. 2001.
- [20] ISO-3378/IUP-12. Leather-physical and mechanical tests. Determination of resistance to grain cracking and grain crack index. Journal of the Society of Leather Technologists and Chemists. 2002.
- [21] Ishak CY, Elgailani IEH. Methods for extraction and characterization of tannins from some Acacia species of Sudan. Pakistan Journal of Analytical & Environmental Chemistry. 2016; 17(1). <https://doi.org/10.21743/pjaec/2016.06.007>
- [22] Falcão L, Araújo MEM. Tannins characterisation in new and historic vegetable tanned leathers fibres by spot tests. Journal of cultural heritage. 2011; 12(2):149-156. <https://doi.org/10.1016/j.culher.2010.10.005>
- [23] Meyers KJ, Swiecki TJ, Mitchell AE. Understanding the native Californian diet: Identification of condensed and hydrolyzable tannins in tanoak acorns (*Lithocarpus densiflorus*). Journal of Agricultural and Food Chemistry. 2006; 54(20):7686-7691. <https://doi.org/10.1021/jf061264t>
- [24] Ricci A, Olejar KJ, Parpinello GP, Kilmartin PA, Versari A. Application of Fourier transform infrared (FTIR) spectroscopy in the characterization of tannins. Applied Spectroscopy Reviews. 2015; 50(5):407-442. <https://doi.org/10.1080/05704928.2014.1000461>
- [25] Sillero L, Prado R, Welton T, Labidi J. Extraction of flavonoid compounds from bark using sustainable deep eutectic solvents. Sustainable Chemistry and Pharmacy. 2021; 24:100544. <https://doi.org/10.1016/j.scp.2021.100544>
- [26] dos Santos Silva PM, Fiaschitello TR, de Queiroz RS, Freeman HS, da Costa SA, Leo P, Montemor AF, da Costa SM. Natural dye from *Croton urucurana* Baill. bark: Extraction, physicochemical characterization, textile dyeing and color fastness properties. Dyes and Pigments. 2020; 173:107953. <https://doi.org/10.1016/j.dyepig.2019.107953>
- [27] Liu X, Sun ZL, Jia AR, Shi YP, Li RH, Yang PM. Extraction, preliminary characterization and evaluation of in vitro antitumor and antioxidant activities of polysaccharides from *Mentha piperita*. International journal of molecular sciences. 2014; 15(9):16302-16319. <https://doi.org/10.3390/ijms150916302>
- [28] Tondi G, Petutschnigg A. Middle infrared (ATR FT-MIR) characterization of industrial tannin

- extracts. *Industrial Crops and Products*. 2015; 65:422-428.
<https://doi.org/10.1016/j.indcrop.2014.11.005>
- [29] Liu L, Ge C, Zhang Y, Ma W, Su X, Chen L, Li S, Wang L, Mu X, Xu Y. Tannic acid-modified silver nanoparticles for enhancing anti-biofilm activities and modulating biofilm formation. *Biomaterials Science*. 2020; 8(17):4852-4860. <https://doi.org/10.1039/D0BM00648C>
- [30] Yu Y, Huang M, Lv J, Zeng Y, Sun Q, Shi B. Evaluation and improvement of the oxidative stability of leather fatliquors. *Journal of Leather Science and Engineering*. 2021; 3(1):1-10.
<https://doi.org/10.1186/s42825-021-00070-3>
- [31] Zhang Y, Wang L. Recent research progress on leather fatliquoring agents. *Polymer-Plastics Technology and Engineering*. 2009; 48(3):285-291. <https://doi.org/10.1080/03602550802675611>
- [32] Jankauskaitė V, Jiyembetova I, Gulbinienė A, Širvaitytė J, Beleška K, Urbelis V. Comparable evaluation of leather waterproofing behaviour upon hide quality. I. Influence of retanning and fatliquoring agents on leather structure and properties. *Materials science*. 2012; 18(2):150-157.
<http://dx.doi.org/10.5755/j01.ms.18.2.1918>
- [33] Das RK, Mizan A, Zohra FT, Ahmed S, Ahmed KS, Hossain H. Extraction of a novel tanning agent from indigenous plant bark and its application in leather processing. *Journal of Leather Science and Engineering*. 2022; 4(1):1-5. <https://doi.org/10.1186/s42825-022-00092-5>
- [34] John G. Possible Defects in Leather Production: Definitions, Causes, Consequences, Remedies and Types of Leather. Lampertheim; 1996.
- [35] United Nations Industrial Development Organization. Acceptable quality standards in the leather and footwear industry. Vienna, Austria. United Nations Industrial Development Organization (UNIDO). 1996.
- [36] Liu J, Luo L, Hu Y, Wang F, Zheng X, Tang K. Kinetics and mechanism of thermal degradation of vegetable-tanned leather fiber. *Journal of Leather Science and Engineering*. 2019; 1(9).
<https://doi.org/10.1186/s42825-019-0010-z>
- [37] Yorgancioglu A, Onem E, Yilmaz O, Karavana HA. Interactions Between Collagen and Alternative Leather Tanning Systems to Chromium Salts by Comparative Thermal Analysis Methods: Thermal stabilisation of collagen by tanning process. *Johnson Matthey Technology Review*. 2022; 66(2):215-226. <https://doi.org/10.1595/205651322X16225583463559>
- [38] Ganesh VA, Raut HK, Nair AS, Ramakrishna S. A review on self-cleaning coatings. *Journal of Materials Chemistry*. 2011; 21(41):16304-16322. <https://doi.org/10.1039/C1JM12523K>
- [39] Onem E, Yorgancioglu A, Karavana HA, Yilmaz O. Comparison of different tanning agents on the stabilization of collagen via differential scanning calorimetry. *Journal of Thermal Analysis and Calorimetry*. 2017; 129(1):615-622. <https://doi.org/10.1007/s10973-017-6175-x>