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A Simple Approach to Potential Application of Vegetable Tanning Techniques by the Indigenous Bovine Fat and *Notholithocarpus densiflorus* Extract

Md. Abdulla-Al-Mamun[1,*], *Bashudev Sarkar*[1]
[1] Institute of Leather Engineering and Technology, Dhaka University, 44-50 Hazaribagh, Dhaka-1209, BANGLADESH

ABSTRACT
Indigenous bovine fat has been introduced into the vegetable tanning process to produce water-resistant vegetable-tanned leather for the first time. The bark and wood have been collected from the Tanoak tree (*Notholithocarpus densiflorus*) abundant in the leather institute, Dhaka University and bovine fat have collected from the local market Hazaribagh, Dhaka, Bangladesh. The vegetable tanning extract and modified indigenous bovine fat have been used in the tanning process together as stuffing techniques for water-resistance leather. Lower acid value, lower iodine value and high saponification value have been found in a satisfactory level of bovine fat and this is the best qualification for use in water resistance leather. The Tanoak extract was systematically analyzed and found mainly two types of tannin catechol in bark and pyrogallol in wood. Resultant bark and wood extract tanning leather have been tested by the Society of Leather Technologists and Chemists (SLC) official analysis method. The tensile strength, stitch tear strength, water resistance, waterproofness, grain crack resistance, flexing endurance, softness etc. be at a satisfactory level. The water resistivity was analyzed by contact angle meter and found the average contact angle of bark-tanned leather was greater than 100° and wood-tanned 88° at solid-liquid interface respectively. These results indicated the low wettability of leather as a water resistance leather. These new kinds of water-resistance vegetable tanning processes will help to replace the chromium tanning, sustainable tanning approach, save the environment and to earn more foreign currency.

Keywords: Vegetable Tanning; Indigenous Animal Fat; Indigenous Tanonk Tree Extract; Tanning techniques.

1. Introduction (Top heading should be in bold)

The leather industry has been one of the traditional industries operating in Bangladesh and is very much significant to the economy of our nation. Chromium (III) salts are currently the commonest method of tanning, almost 90% of the world`s output of leather is tanned in this method [1]. At present time, the leather industry has suffered a serious crisis according to environmental issues and manufacturing compliance. Global competition has been the major driver that forced the leather industry to upgrade its technology to cope with pollution issues. Vegetable tanning is an alternative to manufacturing leather as eco-sustainable, natural, traditional, and safer for those tanning the leather.

Vegetable tannins, which are often produced using bark extracts, leaves, fruit, and roots, all include the fragrant, organic component phenol, which is necessary for tanning leather [2]. 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.

Vegetable tannage is the earliest one to practice 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 [3].

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 once more in the twenty-first century. Vegetable-tanned leathers are preferred by designers due to their adaptability and versatility. For a sense of environment and health, vegetable tanning should be done more frequently. And for replacing chromium with vegetables, it is needed to develop vegetables. 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 whose different parts like leaves, bark, wood, and roots have tanning power. Many of them are known to us like mimosa, quebracho, oak, pine, babul etc. the more we know about vegetable tanning material the more we will be able 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 and find out its feasibility, which is situated in the Institute of Leather Engineering and Technology, Dhaka University campus. The local name of this tree is "Benni Gach".

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 them, causing them to become less water-soluble and more resistant to bacterial attack. The process also causes the hide to become more flexible. The primary barks processed in bark mills and used in modern times are

* Corresponding author. Tel.: +88-01764198278
E-mail addresses: mamun.ilet@du.ac.bd

tanoak, chestnut, oak, redwood, hemlock, quebracho, mangrove, wattle (acacia; see catechol), 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 [4, 5].

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 [5]. We collected the fat from the local market and distilled it through different treatments for the application of the stuffing treatment of leather.

Water resistance is typically applied only for shoes and boots, with the possible inclusion of 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 moister 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. Vegetable tannin materials have also been collected from localized plant sources and extract technology made by us. This 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 the commercial one.

2. Methodology

The bark and wood powder was applied on goat skins as vegetable tanning materials. Initially, bark and wood were collected from *the Notholithocarpus densiflorus* tree abundant in the leather institute, Dhaka University and then dried and ground into a powder. The extracted substance was then combined with ethanol and water. The extract solutions were filtered and dried when the extraction process was complete. The extraction was only used for the characterizations. Then tannin identification tests, including FTIR (Bruker, Germany), were carried out. Resultant-made leather, physical tests were performed on the finished leathers, waterproofness was tested by a water droplet contact angle meter (Kyowa Interface Science) and the leather's quality was compared to that of skins quebracho- and mimosa-tanned.

2.1 **Synthesis of bovine fat liquor**

2000 gm of bovine fat have been collected from the local market in Hazaribagh, Dhaka, Bangladesh. 1000 gm raw sample (bovine fat) and 1000 mL, 25% HCl mixture is heated by water vapour until the fats are completely separated. Using a separating glass funnel, the fat layer was separated. The separated fat was collected by pipetting. Fat is taken into a glass vessel. Then 500mLwater and100ml H_2SO_4 solution is added slowly. It is stirred with Eurometer for 2 hours. 50 gm of anionic surfactant (Sodium Laureth sulfate) is added to the fat-liquor as an emulsifier which increases the penetration of fat content into the leather in the tanning process.

2.2 **Tanning process**

4 Fresh raw skins of goats are weighed and percentages are taken based on this weight.

2.2.1 Soaking:

200% water, 0.3% wetting agent, 0.2% Preservative, 0.5% soda ash -Run for 3 hours.

2.2.2 Un-hairing:

6% Sodium sulfide is added to water to make a paste. The paste is added to the flesh side of the hide. After 6 hours hair is removed by scudding.

2.2.3 Liming:

200% Water, 6% lime, 1.5% Sodium sulfide, 1% lime auxiliary – Stay for 2-3 days with regular hauling.

2.2.4 Chemical washing:

200% water, 0.3% Sodium meta bisulphate-Run for 30 minutes then drain

2.2.5 Deliming:

6% Boric Acid is dissolved in 100 % Hot Water firstly and cooled to 35 °C. Then pelts are placed into the drum. It is run for 2 hours and checked the cross-section by Phenolphthalein (colourless). pH-8.3

2.2.6 Bating:

100% water, 0.5% bating agent-Run for 60 min then drain

2.2.7 Pickling:

80% water, 5% salt, 0.3% improper co- Run for 20 minute, 0.5% formic acid (1:20 dilution) run 30 minute, 1.2% sulfuric acid (1:10 dilution) run 120 minute, 0.4% hypo Run 30 minute, Leave overnight and drain half of the bath.

2.2.8 Chrome capping:

1 % chrome
+1 % NN. The drum is run for 60 minutes.
+3 %RWP. The drum is run for 60 minutes.
+1 % Tx-50. The drum is run for 30 minutes.
+1 % RF. The drum is run for 30 minutes.
Half of the bath is drained.
+6% Soda Ash. The drum is run for 180 minutes.
Now the pelts are piled up for 7-15 days

2.2.9 Vegetable Tanning and stuffing:

100% water and 100% vegetable tannin agent (*Notholithocarpus densiflorus*) were mixed with the previous 30% fatliquor at 60 °C. Piled pelt is put into the drum of tanning with regular hauling. Drumming is continued till the absorption of the stuffing mixture is found satisfactory. The entry of the fatliquor into the leather is rapid and so there is a possibility of completely penetrating the interfibrillar space. This process is run until proper penetration occurs.

3. Results and discussion

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. This latter categorization was created on the basis that, with the right chemical treatments, some tannins may yield pyrogallol and some catechol.

3.1 **Presence of tannin**

3.1.1 Ferric chloride test

3 ml of a 5 percent (w/v) ferric chloride solution was added to 3 ml of the extract. The greenish-to-black colour precipitation indicated the presence of tannins shown in Fig.1 [6].

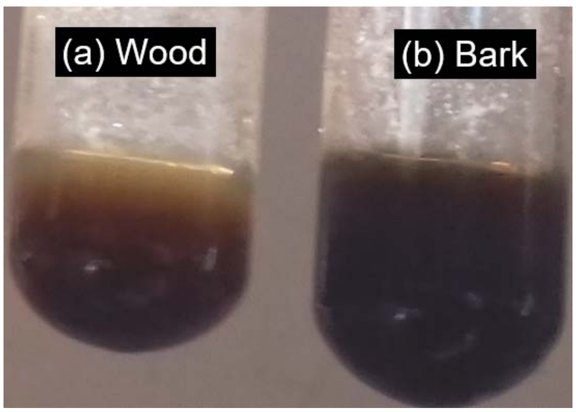

Fig.1 Ferric chloride reagent test (a) wood and (b) bark powder for tannin detection

3.1.2 Presence of catechol and pyrogallol tannins

3 ml $FeSO_4$ solution is added to 3 ml Sodium Potassium Tartrate solution to make the required solution. The bark tannin extract is given to the solution across the tube slowly a black layer is created indicating that bark tannin is catechol. However, the wood extract is given to the solution across the tube slowly no black layer is created and it indicates that wood tannin is pyrogallol. After shaking the two test tubes bark tannin becomes black fully but not the wood tannin shown in below Fig.2.

Fig.2 Ferrous sulphate reagent test. Indicated presence of (a) Catechol in bark and (b) pyrogallol in wood

3.2 **Physico-chemical properties of vegetable-tanned developed leather**

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. 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.

The tanned leather was cut (three pieces for both parallel and perpendicular to the backbone for each test) following sampling location and specific measurements for every test. The leather was conditioned for 48 h at a temperature of 23 ± 2 °C, and relative humidity of 65±2% following the ISO-2419 standard. 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.

Summarized physical and chemical test results showing in below table:

Table 1 Summary of all physical & chemical tests for bark and wood extract tanned leather

Name of Test	Results		
	Bark Extract Tanned Leather	Wood Extract Tanned Leather	Standard For Garments Leather [3, 7]
Tensile strength	149.48 Kg/cm^2	142.12 Kg/cm^2	Minimum 100 Kg/cm^2

Elongation at Break	57 %	66%	Maximum 60%
Stitch Tearing strength	123 Kg/cm	112 Kg/cm	Minimum 60 Kg/cm
Instant lactometer test	206 Kg/cm	183 Kg/cm	100-300 kg/cm
Flexing endurance test (25000 cycles)	Pipe labelling scale rating 3	Pipe labelling scale rating 3	Not below 3 (Max 50000 Cycles)
Waterproofness test	8 min	7 min	Minimum 5 min
Colour rub fastness test	Gray scale rating 5	Gray scale rating 5	Not below rating 3
Fat content	13.04%	12.88%	Maximum 10%

3.3 **Wettability of the vegetable-tanned leather surface**

As shown in the pictures of Fig. 3a and 3b, bark and wood powder vegetable-tanned leather surface water droplets as well. While the surface of vegetable-tanned leather is relatively hydrophilic with a contact angle of less than 90° [5]. The stuffing new-techniques process vegetable tanned leather shows the hydrophobic with a contact angle of a water droplet greater than 100° of bark tanned and wood-tanned is 88° respectively.

Fig.3 Pictures of a water droplet on (a) Bark-powder tanned and (b) wood-powder-tanned leather. The contact angle of a water droplet on the leather-water droplet interface.

The improved hydrophobicity of the stuffing-modified leather might be attributed to the increased amounts of the alkyl or hydroxyl group at the surface.

4. Conclusion

In general, Conventional vegetable-tanned leathers have no waterproofing properties. We developed and investigate new technology for the production of water-resistant vegetable-tanned leather for wearing garments leather. 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 shrinkage temperature and shaving potency. This technology has been reducing toxic and carcinogenic Chromium. Collagen fibre was treated with stuffed fatliquor and 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 colour helps to reduce the usage of dye. Extra softness and smooth feeling help to satisfy the user's mind. 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. We hope, that foreign buyers will be more interested in this leather. This new technology can help to develop it, save our environment, increase foreign income and increase the usage of vegetable-tanned leather.

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