Vegetable Tanning of Sole Fish Skin by Using Tannins Extracted from Plants

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ABSTRACT

Tanning of skins and hides using natural tannins from plant sources is termed as vegetable tanning or green tanning due to its biodegradability and environment friendly features. Fish skin is the new alternative raw material for leather industry. In the present study, bark tannin powder of four plants i.e., Acacia nilotica, Azadirachta indica, Cassia fistula and Pinus roxburghii were used for the tanning of Sole fish skin and the physical properties of leather produced were evaluated and compared with standard. A. nilotica and P. roxburghii tannin powder had best tanning results on fish skin. Highest tensile strength was observed for the A. nilotica tanned leather (21.32 N/mm²) with 33% elongation followed by P. roxburghii tanned leather with a tensile strength of 19.75 N/mm² and elongation of 36%. Tear strength was highest in samples tanned with P. roxburghii tannin powder (74 N/mm) followed by leather tanned with A. indica tannins (70 N/mm). Tara tanned leather had a tensile strength of 15.66 N/mm², elongation of 32% and tear strength of 55 N/mm. Shrinkage temperature of tanned fish leathers were determined and were compared with standard tara tannin powder (89°C) and showed best results; A. nilotica, A. indica, P. roxburghii, C. fistula had shrinkage temperatures 88°C, 83°C, 87°C, 89°C respectively. Results indicated that fish skin can be used as a new source for leather industry and tannins from barks of A. nilotica and P. roxburghii can be used as a good vegetable tanning material.

Keywords: Vegetable tanning, sole fish skin, bark tannin powder, physical properties, leather product, eco-friendly.

1. INTRODUCTION

The main ecological problems arising in tanning industry are the release of chromium by polluted water treatment [1]. Chromium is poisonous, deadly chemical and lethal, when produced in higher concentrations [2]. The vegetable tanning agents are biodegradable and this ability makes...
them green tanning materials which are eco-friendly and so truly secure to use [3].

Various vegetable tanning agents have been used throughout the world to process hides and skins into leathers based on the accessibility and percentage of tannin content. A few of significant plants utilized in tanning and the percentage of tannin are chestnut 10.7%, quebracho 20%, catechu 35%, divi divi 35-45%, sandri bark 11%, gurjan bark 35%, sumac leaves 25%, Avaram senna bark 18%, kahra 16%, ashan bark 12%, Acacia nilotica bark 12%, C. fistula bark 11-14%, g bark 26-36%, Terminalia arjuna 30-40%, Acacia mearnsii tree 30-40%, dhundri bark 28-31% [4]. Raw material for leather manufacture is generally obtained from the farm animals i.e., cow, goat, sheep and buffalo [5]. Processing of fish skins can be solution for insufficiency of raw materials for leather industry and for assessment of wastes of fish farms. Due to their biodegradability, durability, firmness and capability of being permeated by air, fish skins can be transformed and processed into leather products instead of throwing away into garbage. This not only lowers fish waste, but also reduces the use of traditional cow and goat leather [6]. Zengin ACA et al. [7] evaluated the fish skins for leather industry and formulated the manufacturing processes. They also discussed the final features of fish skins and conversion of the skins into custom leather. The anatomical, physical, and chemical characteristics of three types of fish skins i.e., sturgeon, conger, carp were studied. All fish leathers exhibited sufficient physical durability but few leathers were light weight and tough because of their external design and structures. Kucukakkin, E et al. [8] also investigated fish skins (Katsuwonus pelamis) as the new alternative raw material source for leather industry. Solefish (Solea solea) belongs to the family Soleidae (order Pleuronectiformes) [9].

Conventional leather made from cow/goat has fibers that go in one direction but fish skin contains cross fibers that makes it very strong. It is very light and very thin but very durable and firm. It can be utilized in making of handbags, fabrics, belts, shoes, furniture, jewellery etc. The main difference from normal leather is that the temperature tolerance of fish skin is quite low due to its cold blooded nature [10]. In the present study, barks of five plants were used in vegetable tanning of fish skins and physical properties of fish leather were determined and they were also compared with properties of traditional leather.

2. MATERIALS AND METHODS

2.1 Collection of Plant Material

Four plants i.e., A. indica, A. nilotica, C. fistula and P. roxburghii growing in northern areas of punjab, Pakistan were selected based on the criteria viz. easily approachable, cosmopolitan, abundant, available, easy to grow and easy to maintain. Their bark material was collected for extraction of tanning material.

2.2 Processing of Plant Material

The bark materials of all the plants were dried under shade and oven-dried for two days. Dried samples were grounded into a fine powder. A homogenous particle size of bark was obtained by granulometric apparatus and the grounded bark was separated by size number (0.5 mm - 2 mm) in sieve shaker (endecotts limited, london, united kingdom).

2.3 Extraction of Tannins

There is no fixed method for the extraction of tannins from the parts of plant throughout the world, but it can be varied based on whether the tannins used to extract should be solid/powder or liquid. Conventionally, water is used as a solvent in the extraction of tannins. Although, industrial vegetable tannin extracts are mixtures of polyphenolic substances. The manufacture of vegetable tannin extracts depend on the appropriate organic solvents i.e ethanol and followed by concentration and spray drying to get powder extract [11].

Ultrasound-assisted extraction was used for extraction of tannins from powdered plant material. 5.0 g of bark was mixed with 200 ml of methanol as extracting solvent in a 500 ml beaker. The beaker was immersed in ultrasound cleaning bath at 40°C. The amplitude, time of extraction and frequency were set accordingly. Temperature of sample was controlled manually by using water bath. The solution was then filtered through a filter paper. The filtrate was dissolved in 70% methanol/ethanol for different samples, centrifuged and supernatant was collected. 5.0 L aqueous solution of bark extract was prepared after extraction and subjection to rotary evaporation and allowed to settle and filtered. The bark extract was spray dried using co-current spray drier apparatus at 125°C (capacities of spray drier, 500 ml / hr water.
evaporation) and the extract was converted into powder form [12]. The dried powder obtained for each sample was weighed and total yield for each plant sample was calculated using the following formula:

$$\text{Extraction Yield (\%)} = \frac{\text{Weight of the spray-dried extract}}{\text{Weight of the original sample}} \times 100$$

### 2.4 Quantification of Tannins/Phenolics Content

The method for quantification of total phenol was used to determine the efficiency of extraction of phenolics in solvents. This method was coupled with the use of polyvinyl polypyrrolidone (PVPP; binds tannin-phenolics) for measurement of tannins. The results were expressed as tannic acid equivalent based on calibration curve of tannic acid (Fig. 1). The nature of tannic acid varies from one commercial source to the other. Total tannin content in each plant extract was determined by using folin-ciocalteau method [13].

### 2.5 Analysis of Total Phenols

To calculate the tannin and non-tannin content in the plant samples, approximately 50 µl tannin containing extract of each plant sample was transferred with micropipette into labelled test tubes. Then 0.25 ml folin-ciocalteau reagent and 1.25 ml sodium carbonate solution were added into it. All tubes were placed in vortex for five minutes and left at room temperature for 40 minutes. The absorbance of sample was recorded at 725 nm with the help of spectrophotometer (UV-2800 Hitachi).

### 2.6 Removal of Tannins from Extract

PVPP functions to bind tannins. Approximately 100 mg PVPP was taken in test tube. 1.0 ml distilled water and 1.0 ml tannin-containing extract was added to it and vortex. Then placed the tube at 4°C for 15 min, again vortex it and centrifuged (3000 rpm for 10 min) and the supernatant was collected containing tannins. The phenolic content of the supernatant (took at least double the volume used for total phenol) was calculated and the non-tannin content of phenols was measured on dry matter basis (y%).

### 2.7 Fish Tanning Process

Medium sized sole fish (Solea solea) were purchased from tollenton market Lahore (Fig. 2). Fleshing, depigmentation, fiber opening and pickling of the fish skin was carried out before vegetable tanning [14].

#### 2.8 Fleshing

Scales were removed from the body of fish and the skin was separated from the body by pulling with dull knife and cloth. The fresh skin was grey in color. The fleshed skin was rinsed with clean water for 15 minutes. The skin was flipped over and remaining scales left were removed (Fig. 3).

#### 2.9 De-pigmentation and Fiber Opening

The fresh skin was de-pigmented in a drum containing 4% xylanase enzyme (percentage based on fleshed weight), and 30% water for about 5 hrs. The skin was rubbed with brush to remove the pigments, fleshed and the 212 gram weight of skin was noted (Fig. 3).

#### 2.10 Pickling

The de-pigmented skin was pickled in a bath containing 10% salt solution for 10 min, then the bath was kept overnight after addition of 1% sulphuric acid (in water). The pH was adjusted at 2.8 and 50% pickled water was drained (Fig. 3)[15].

#### 2.11 Vegetable Tanning

The repickled skin was tanned in microdrums (Figs 4,5) containing 50% pickle water, 50 gram extracted tannin powder, 1% cationic fat liquor, 1% nonionic fat liquor and the tanning drum was operated for 1 hr. After 1 hr the pH was maintained at 3.8 followed by addition of water for 30 min; followed by addition of 1% sodium formate (in water), and 1% sodium bicarbonate for about 90 min. After 90 min the skin was rinsed and piled through overnight. Next day, the tanned fish skin was hanged for drying (Fig. 6) [16].

#### 2.12 Dyeing of Fish Leather

Five different commercially available colors (green, golden, red, white and brown) were used to dye the fish leather by dyeing process [17]. The resulting fish leather was used to manufacture men wallets (Fig. 7).
**Fig. 1.** Standard calibration curve of tannic acid

\[ y = 3.8057x + 0.0024 \]

\[ R^2 = 0.9997 \]

**Fig. 2.** Sole Fish used as source of leather

**Fig. 3.** Preparing fish skin for tanning, Descaling (A, B); Depigmentation (C); Pickling (D)

**Fig. 4.** Fish skin tanned with *A. indica* (A), *A. nilotica* (B), *C. fistula* (C), *P. roxburghii* (D)
Determination of Physical Characters of Tanned Leather

2.13.1 Measurement of thickness of fish leather

Thickness gauge (SATRA) instrument was used to check the thickness of leather. Thickness gauge (SATRA) instrument was approved standard from IUP/4, IULTCS and by ISO 2589:2002. For measurement of thickness, two pieces of vegetable tanned fish skin samples were taken. Specimens of fish skin were prepared by cutting the skin into 11*3cm by specimen cutter. Took three readings of each and calculated the mean. When sample was fully loaded, the reading was taken [18].

2.13.2 Measurement of tensile strength

The tensile strength was measured by using material testing machine (Lloyd) according to the
approved standard procedure recommended by IUP/6, ISO3376:2011. The sample was taken to check the tensile strength. The samples were clamped within the jaws of machine keeping the jaw at a distance of 50 mm. The machine was operated until the specimen broken and recorded the highest force exerted as the breaking force. The tensile strength is expressed in Newton per square millimeter (N/mm$^2$) and is calculated by dividing the breaking force by the thickness and width of the leather specimen.

2.14 Measurement of Percentage of Elongation

The test was carried out by using the material testing machine (Lloyd) according to the approved standard procedure recommended by IUP/6, ISO3376:2011. The value of elongation was measured by determining the final and initial fish skin sample length divided by the length of initial sample and it was calculated as percentage [19].

2.15 Measurement of Tear Strength

The tearing strength (double edge tear) was measured using material testing machine (Lloyd) according to approved procedure IUP/8 and ISO3377-2:2002. The fish skin sample was placed in parallel position in template machine and the uniform speed of separation of the jaws of machine (100 mm per minute) was used. The reading was noted after calibration (1%). The machine was operated until the test sample was broken apart and the highest load reached during tearing, was noted.

2.16 Shrinkage Temperature Determination

The shrinkage temperature of the tanned skin samples was calculated with the help of STD 114 test (SATRA) machine approved by the IUP/16, ISO3380:2002 and ENISO3380. Strips of leather 50 mm x 2mm (Length x Width) were cut from the plant extracted vegetable tanned leathers samples. Holes were punches at the ends of the leather for holding the specimen in the vertically in the test chamber filled with water. Small weight was attached to the lower end of the sample, to keep it straight. The sample was kept within the STD 114 test (SATRA) machine and the machine was closed. The heating of glass jar containing water was started by applying the external heat source. The shrinkage temperature of leather samples was determined by observing through the glass of machine. The temperature at which the leather started to shrink was taken as the shrinkage temperature [20].

3. RESULTS AND DISCUSSION

3.1 Extraction Yield of Tannins

The extraction yield of tannins in all the selected barks of plants was calculated in percentage. The yield was more than 10% in all the samples with highest value in C. fistula (23.3%) and lowest in A. nilotica (12%) (Table 1). Extraction yield indicates the suitability of the sample to be used as commercial source of tanning agents and also the ability of the plant material to be used in leather tanning.

3.2 Tanning Strength of Plants

Analysis of total phenols in all selected plants was carried out on basis of tannic acid equivalent, based on standard calibration curve. It was expressed on dry matter basis. The amount of total phenols was calculated as tannic acid equivalent (%). Highest tannin contents were observed for A. indica with 10.76% tannins which also had highest tanning strength (21.52) and lowest in A. nilotica (8.7%) which also had lowest tanning strength (4.78). No significant difference was observed in tannin content of the four plants used (p > 0.05) (Table 2).

3.3 Vegetable Tanning of Fish Skin

In the present study, all plants showed good results regarding leather tanning but the P. roxburghii and A. nilotica tannin powders had best tanning results on fish skin. The results were compared with tara tanned leather, which was used as commercial tanning agent. Tanning potential of all the plants was measured in terms of physical characteristics of tanned fish skin as per standard protocols (Table 3). Fish leather has remarkable and striking status in the leather industry and global fashion industry. The fish skin is versatile and environmental friendly alternative exotic leather. Fish leather is the second strongest leather familiar to man. It is the important waste product of aquaculture business. Instead of throwing it away, it can be used to overcome the scarcity issues of raw materials in leather sector.
Table 1. Extraction yield of tannin

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Plant Samples</th>
<th>Extraction Yield of tannins (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A. nilotica</td>
<td>12</td>
</tr>
<tr>
<td>2</td>
<td>A. indica</td>
<td>16</td>
</tr>
<tr>
<td>3</td>
<td>C. fistula</td>
<td>23.3</td>
</tr>
<tr>
<td>4</td>
<td>P. roxburghii</td>
<td>16.6</td>
</tr>
</tbody>
</table>

Table 2. Total phenols and total tannin contents in selected plants

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Plants</th>
<th>Tannins (%)</th>
<th>Non-Tannins (%)</th>
<th>Tanning Strength T/NT</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A. indica</td>
<td>10.76</td>
<td>0.50</td>
<td>21.52</td>
</tr>
<tr>
<td>2</td>
<td>A. nilotica</td>
<td>8.7</td>
<td>1.82</td>
<td>4.78</td>
</tr>
<tr>
<td>3</td>
<td>C. fistula</td>
<td>10.6</td>
<td>1.4</td>
<td>7.57</td>
</tr>
<tr>
<td>4</td>
<td>P. roxburghii</td>
<td>10.06</td>
<td>1.18</td>
<td>8.52</td>
</tr>
</tbody>
</table>

Table 3. Physical properties of vegetable tanned Sole fish leather

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Vegetable tanning agents</th>
<th>Thickness (mm)</th>
<th>Tensile Strength (N/mm²)</th>
<th>Elongation (%)</th>
<th>Tear Strength (N/mm)</th>
<th>Shrinkage Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A. indica</td>
<td>0.8</td>
<td>14.33</td>
<td>30</td>
<td>70</td>
<td>83</td>
</tr>
<tr>
<td>2</td>
<td>A. nilotica</td>
<td>0.9</td>
<td>21.32</td>
<td>33</td>
<td>62</td>
<td>88</td>
</tr>
<tr>
<td>3</td>
<td>C. fistula</td>
<td>0.6</td>
<td>10.23</td>
<td>18</td>
<td>58</td>
<td>89</td>
</tr>
<tr>
<td>4</td>
<td>P. roxburghii</td>
<td>0.8</td>
<td>19.75</td>
<td>36</td>
<td>74</td>
<td>87</td>
</tr>
<tr>
<td>5</td>
<td>Tara</td>
<td>0.6</td>
<td>15.66</td>
<td>32</td>
<td>55</td>
<td>89</td>
</tr>
</tbody>
</table>

3.4 Tensile Strength of Tanned Leathers

Tensile strength, also called fracture stress, is the stress that should be applied to fracture a leather sample of specified thickness and fiber orientation. The elongation percentage is also a measure related to strain and indicates the ability of leather to stretch under stress without breaking. The highest tensile strength in the present study was observed for the leather samples tanned using A. nilotica bark tannins (21.32 N/mm²) with respective elongation of 33% followed by P. roxburghii with a tensile strength of 19.75 N/mm². Highest elongation was observed for the P. roxburghii tanned leather (36%). Tara used as positive control gave a tensile strength of 15.66 N/mm² and elongation of 32% in the tara tanned fish samples (Table 1). Average thickness of all the leather samples varied between 0.6 – 0.9 mm that was above the minimum recommended value (0.5 mm).

Tensile strength of leather is an important indicator of quality of leather. This test can be used for all leather types that are smooth and firm and give accurate thickness measurements. Leather samples that are not properly lubricated and are partially degraded usually have low values of tensile strength [21]. Similarly, elongation percentage value of leather indicates its ability to stretch/lengthen when stress is applied to it. Elongation refers to the maximum limit to which the leather can be stretched without breaking [22]. Elongation values are very important physical characteristics of leather samples to be used for garments because leathers with a high elongation value quickly become deformed so may lose usability while leathers with low elongation values tear very easily [23].

3.5 Tear Strength of Tanned Leather

Tear strength of tanned leather refers to the force (measured in Newton) needed to make a cut in the leather sample in a specified direction. Tear strength of fish leather was highest in samples tanned with bark tannins of P. roxburghii (74 N/mm) followed by leather tanned with bark tannins of A. indica (70 N/mm). The Tara tanned leather that was used as a positive control had tear strength of 55 N/mm. A good quality leather must have high flexibility to prevent cracks and tears in the leather products for example shoes that require high tear resistance. Fish skin tanned with P. roxburghii and A. indica had significantly high tear strength as compared to tara tanned fish skin (p < 0.05). Thus these two
plants can be used for leather tanning of fish skin to get good quality leather from fish skin.

Leather is the raw material in many different industries such as shoe, garment, furniture etc. Each specific use of leather demands specific characteristics. However, from a structural point of view each leather sample is unique in its physical properties depending on the type of animal. Selection of a good leather product depends upon its quality in terms of its handling character, and its physical and mechanical properties that contribute to its ability to withstand wear [23]. Leather produced by vegetable tanning of fish skin was found to have good characteristics in terms of tensile strength, tear strength and elongation. The leather produced was utilized to produce men wallet that gave excellent results. Thus fish leather can be used equally effectively in leather based industries.

4. CONCLUSION

From the results it was concluded that the fish skin can be processed and transferred into quality raw material after tanning. All plants showed good results regarding leather tanning but the P. roxburghii and A. nilotica tannin powders had best tanning results on fish skin. It is highly recommended to consider P. roxburghii and A. nilotica as an eco-friendly leather tanning agent. Tanning of fish skin is also a great opportunity for the fisher men to export the fish skin to the tanneries for the increase of income.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES


