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Dates Seed: An Alternative Retanning Agent in Leather Processing

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ABSTRACT
In leather manufacturing, retanning is a process that is directed to improve the roundness, fullness, softness, grain firmness, filling, and suppleness of the final leather. In retanning, mostly resin, syntan, and vegetable tannins are used. Usually, vegetable tannins are selected for retanning because they are natural, non-toxic, biodegradable, and economical. Vegetable tanning agents are rich in polyphenols which are cross-linked via hydrogen bonding with collagen protein. In this study, waste date seeds are used as an alternative source of vegetable retanning agents in leather processing. Date seeds contain polyphenols and flavonoids that are generally discharged as waste. The waste date seeds were collected, washed with distilled water, sun-dried, and oven-dried at 105°C for 24 hours. The dried date seeds were ground by a laboratory crusher. The Soxhlet extractor was used to extract tannin in ethanol as a solvent. The extracted tannin was characterized by Fourier Transform Infrared (FTIR) Spectroscopy. For retanning, tannins were extracted in water from date seeds ground at an optimized temperature (55°C) by a water bath. At the optimum temperature (55°C) tannin extraction was 3.29%. The tannin extracted in water was used in the retanning process for leather manufacturing. The physical properties e.g., tensile strength, percentage of elongation, stitch tear strength, and shrinkage temperature of the produced leather were 296.01 kg/cm^2, 48.8%, 141.5 kg/cm, and 124.4°C, respectively. The experimental leather showed better results compared to the conventional leather. This study indicates a new source of retanning agents, which is economical, feasible, and eco-friendly.

Keywords: Vegetable tanning, Natural tanning agent, Solid waste utilization, Shrinkage temperature, FTIR

1. Introduction

Hides and skins are tanned with various tanning agents such as basic chromium salt, zirconium salt, vegetable tanning agent, aldehyde tanning agent, etc. to make the putrescible hide/skin into stable collagenous materials. Natural organic astringent compounds derived from plants are known as vegetable tannins. Vegetable tanning agents are bio-active compounds found in the bark, wood, leaves, roots, fruits, fruit pods, and plant galls [3-4]. The main components of vegetable tannins are polyphenolic constituents with a medium molecular weight fraction and a molecular weight range of 500-3000 Daltons [5-6]. Tannin can be found in various degrees in practically all plant species. Plant sources with a significant amount of tannin content are employed commercially considering an economical extraction. The extracted tan's color and specific qualities are the additional factors to consider [1].

There are a variety of tanning-bearing plants in every country; however, two important aspects primarily determine their practical application for the manufacture of leather. To start with, they must be available in large quantities and they must also contain enough tannin to make extraction economical [2]. Wattle, babul, myrobalan, konan, avaram, goran, gambier, cutch, quebracho, chestnut, oak, valonia, divi-divi, somac, and other materials are commonly used for vegetable tanning. The color, tanning qualities, and texture of the leather produced by infusions of tanning materials supplied from various sources vary widely. Practically tanners believe that a single vegetable tanning material is inept to impart all of the desirable attributes in the finished leather. Tanners utilize a mixture of various above-mentioned tanning components to achieve the desired attributes of solidity, flexibility, fullness, and color. The rate of tannin penetration is also influenced by proper blending [7].

Dates from the date palm tree are a popular fruit in many countries, particularly as an Iftar item. They are mostly grown in the Middle East and are one of the most widely consumed staple foods in this region. Date seed is one of the waste products produced in large quantities during the date manufacturing process. Date flesh has long been known for its excellent nutritional content and health advantages [8]. Date flesh is also known for being a good source of antioxidants such as phenolic acids and flavonoids [9]. In Bangladesh, due to the increasing demand for consumption, the cultivation of date is increasing with an additional import of approximately 42,931 tons [10]. The date fruit is composed of a fleshy pericarp and seed which constitutes between 13%-15% of date fruit weight [11]. The phenolic contents of seeds of several fruits, such as date palm, mango, avocado, and jackfruit are found higher than their edible flesh [12]. Therefore, these seeds could be considered a valuable source of phenolics mainly in the form of phenolic acid and flavonoids. Phenolics have been shown to possess such benefits as antioxidant [13], anti-carcinogenic [14], and anti-inflammatory activities [15]. Many studies on the vegetable tanning process have been conducted during the last few decades. Vegetable tannins are used in traditional vegetable tanned leather in various combinations. Date seeds can be a good source of vegetable tannin since they contain tanning ingredients that are strong enough. Because it is discarded as waste, it is a free source of tannin content.

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The objective of this work is to extract tannin from date seed for use in the leather tanning process and compare the physical properties with the conventional tanned leather.

2. Materials and Methods

2.1 Date seeds collection

Leftover date seeds were collected both during Ramadan month and from the rotten dates which were purchased at a low price from a local market. The seeds were washed with distilled water, sun-dried, and oven dried at 105°C for 24 hours then they were ground by a laboratory crusher. Fig.1 represents the oven-dried and ground date seeds.

Fig.1 Oven-dried date seeds (a) and ground date seeds (b)

2.2 Vegetable extract preparation and optimization of extraction temperature

The Soxhlet extraction was continued for tannin extraction from date seeds. In this process, the tannin of the date seeds was extracted with water at 45°C, 55°C, 65°C, 75°C, and 85°C in the water bath for 2 hr to optimize the extraction temperature, maintaining the fixed bath volume and weight. The solution was stirred during heating to ease the extraction process uniformly.

Fig.2 Extraction of tannin agent from ground date seeds

Finally, the extract solution was filtered using a cotton filter cloth (Fig.2) and the number of tannins was determined. After the determination of the optimum temperature, the tannins were extracted with the required amount of date seeds powder and bath for retanning.

2.3 Determination of tannin content

After some modifications, the tannin concentration in fruits and vegetables was determined using The International Pharmacopoeia (The International Pharmacopoeia, 2003) and the AOAC technique as shown in Fig.3. In a 1 L conical flask, 25 mL of the infusion was measured by adding 25 mL of indigo solution, and 750 mL distilled water. Titration was performed with a 0.1 N aqueous solution of $KMnO_4$ until the blue solution turns green. Then, a few drops were added at a time until the solution became golden yellow were added. The following is a standard solution of Indigo carmine: 6 g indigo carmine is heated to dissolve in 500 mL distilled deionized water, then 50 mL 95-97% H_2SO_4 is added, and the solution is cooled.

$$\text{Tannin content } (\%) = \frac{(V - V_o) \times 0.004157 \times 250 \times 100}{g \times 25}$$

Where V= volume of 0.1 N aqueous solution of $KMnO_4$ for the titration of the sample in mL; V_o = volume of 0.1 N aqueous solution of $KMnO_4$ for the titration of the blank sample in mL; 0.004157= tannins equivalent of 1mL of 0.1 N aqueous solution of $KMnO_4$; g= mass of the sample taken for analysis in g; 250= volume of the volumetric flask (mL).

Fig.3 Determination of tannin content

2.4 Collection of wet blue leather

Chrome-tanned wet blue leather was collected from the department. The sammying and shaving operations were conducted in the SAF Leather Industries Ltd., Jashore, Bangladesh. The shaved weight was 303 g.

2.5 Wet back, neutralization and retanning

Table 1 depicts the recipe followed for the wet back, neutralization, and retanning process. Some chemicals were introduced to wet-back leather for further manufacturing.

Table 1 Recipe for wet back, neutralization, and retanning

Operation	Reagents	%	Remarks
Wet back	Water	150	Run 25 min
	Wetting agent	0.25	Drained
Neutralization	Water at 45°C	150	Run 30 min
	Sellasol NG	1.5	pH 5.0
	Sodium formate	0.5	Drained & washed
Retanning	Water at 45°C	60	
	Relugan RE	1.5	Run 25 min
	Intan TP 340	3.0	
	Relugan D	4.0	
	Tanigan OS	3.0	Run 60min
	Extracted tannin	14.0	

In the neutralization process, the free and protein-bound acids were efficiently removed either by repeated washing with water or chemical treatment. The pH was raised to the required level and sufficient tanning power to lower the isoelectric point enough to ensure the pelt was adjusted to be anionic. After neutralization, the retanning agents as well as extracted tannin from date seeds were added to improve the leather properties-fullness, roundness, softness, and hand feel.

2.6 Dyeing and fat liquoring

Just after retanning, the dyeing and fat liquoring processing was conducted according to Table 2 for the pelt. Synthetic dyestuffs are prepared from aromatic compounds [2]. Dyestuffs also are obtained from natural sources.

Table 2 Recipe for dyeing and fat liquoring

Operation	Reagents	%	Remarks
Dyeing	Water at 45°C	50	Run 60 min
	Dye-black	2.5	
Fat liquoring	Water 60°C	100	
	Lipsol BSFR	3.5	
	Perfectol HQ	2.0	Run 60 min
	Neopristol SWK	2.5	
	Sulphirol C	0.5	
Fixing	Formic acid	2.0	Run 30 min
Setting out, vacuum drying, natural drying by hanging			

The dyed pelt fibers and fibrils of leather were coated with a layer of oil. The tensile strength, stitch-tear resistance, abrasive resistance, etc. were improved by fat liquoring operation [2].

2.7 Moisture content determination

The Dean and Stark methods were used to determine the moisture content of the tanning chemical [16]. The sample was weighed in a crucible before drying for 3 hours at 105°C in an oven. They were then weighed again after cooling in desiccators. The heating was kept up until the weight remained stable. The procedure was repeated three times in a row. At a 1:10 ratio, the pH of the powder was determined using a calibrated pH meter (UPH-314, UNILAB, USA).

2.8 Shrinkage temperature determination

Fig.4 Tanned leather specimen for determination of shrinkage temperature

Using a shrinkage tester, the temperature of shrinkage was calculated according to the ISO 3380 standard [17]. The sample was clamped after being cut into the desired dimension with a conventional die. The test sample was then immersed in the water, which was gradually raised in temperature. The shrinkage temperature was defined as the temperature at which the sample visibly shrank. During the tanning process, the shrinkage temperature was measured before and after retanning. Fig.4 indicates the tanned leather sample for shrinkage temperature.

2.9 Physical strength determination

Tensile strength and percentage of elongation: The test specimens were first cut according to ISO 2418: 2002/IUP 2 [18] and then conditioned using the ISO 2419: 2002/IUP 3 [19] standard temperature of 23°C and 50% relative humidity. The physical parameters of the material, such as tensile strength and percentage elongation at break, were then determined using the EN ISO 3376: 2002 [20] standard technique as shown in Fig.5. The stitch tear strength was determined using ASTM D 4705-18 procedures.

Fig.5 Tensile strength testing of leather sample

Colorfastness to circular rubbing test was determined according to SATRA TM8 (Fig.6). A specimen of the material was rubbed by a rotating dry or wet circular wool felt pad under a constant force. The test was stopped after a predetermined number of revolutions and the damage to or transfer of color was assessed using a geometric grey scale.

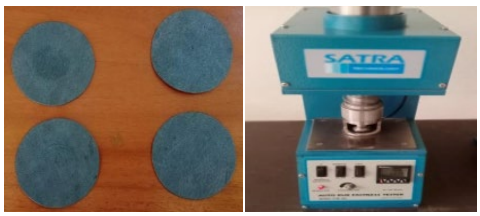

Fig.6 Color rub fastness test

The Break Pipiness test was determined according to SATRA TM36 (Fig.7). The specimen was bent around a semi-circular mandrel so that its grain or outer surface is against the mandrel.

Fig. 7 Break pipiness test

The specimen is viewed through a rectangular hole in the mandrel and any bucking of its surface is graded by the subjective comparison with a standard break/pipiness scale.

3. Result and Discussion

3.1 Physical characteristics

The extracted power had a moisture content of 5.8% and a pH of 5.1, respectively. The pH of the powder showed that it is acidic, allowing for fungal development. However, according to Milner and Woodard [21], fungal degradation happens in the presence of oxygen when the moisture content is greater than 20% and the temperature is between 25 and 40°C. Because the extracted powder had a moisture content of only 5.8%, the proposed retanning agent could be stored in powder form for a long period.

3.2 Fourier-transform infrared spectroscopy (FTIR)

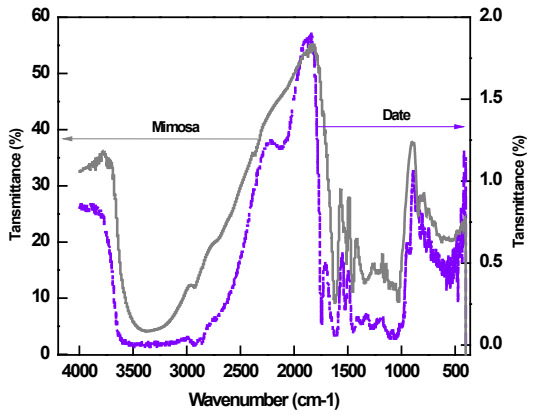

Fig.8 FTIR spectra of extracted tannin from date seeds and conventional mimosa tannin

Fig.8 depicts several peaks at various wavelengths (cm^{-1}) that indicate the presence of various functional groups. The existence of the C=C functional group was shown by the peak at 730-880 wavelength. Between 1540 and 1800 cm^{-1}, there was a lot of interaction between the C=O and N-O functional groups. A strong C≡C group was discovered at 2195 cm^{-1} wavelength. Furthermore, the intermolecular O-H was found at 3200-3500 cm^{-1}, while free O-H is present at 3700-3800 cm^{-1}. From the above two figures, we could say that the FTIR spectra and functional groups present in date seeds extract and mimosa powder was very similar. This study confirmed the existence of the O-H and C=O groups in the sample which aid in collagen bonding during the retanning process.

3.3 Optimum temperature for extraction of tannins

The change in temperature for the extraction of tannins is listed in Table 3. From the table, it can be seen that the tannin percentage increases up to 55°C, and then it decreases with the increase in temperature. The optimum temperature was found at 55°C. At this temperature, the maximum tannin was found and that was 3.29%

Table 3 Percentage of tannins at different temperatures

Extraction Temperature (°C)	% of tannins
45	2.52
55	3.29
65	2.04
75	2.18
85	1.62

3.4 Hydrothermal stability

In Table 4, it has been shown that at the raw stage shrinkage temperature of the skin was 63.25°C. After chrome tanning shrinkage temperature was 116.60°C because the basic chromium (III) sulfate reacted with fibers and formed a carboxylate complex, which was difficult to break down.

Table 4 Comparison of shrinkage temperature

Stages	Experimental value (°C)	Conventional value (°C)	Standard value(°C)
Raw skin	63.25	63.25	65 [1]
Chrome tanned leather	116.60	116.60	105 [22]
Vegetable re-tanned leather	124.40	127.02	117 [23]

Again, the shaved chrome-tanned leather was re-tanned with date seeds extract as a vegetable tanning agent where the unreacted partially charged peptide and phenolic hydroxyls linked together via hydrogen bonding and raised shrinkage temperature to 124.40°C.

3.5 Physical properties of leather

Date seeds tanned leather (Fig.9) provide excellent physical properties.

Fig.9 Date seeds re-tanned leather

The most important physical properties are tensile strength and percentage of elongation of leather where tensile strength and percentage of elongation for the powder and aqueous solution treated tanned leather was determined in parallel and perpendicular directions. Both samples showed greater strength of physical property than the standard.

Table 5 Physical properties of date seed retanned leather

Sample	Experimental value	Conventional value	Standard value
Tensile strength (kg/cm^2)	296.01	255.57	200 [24]
Elongation at break (%)	48.83	45.563	40-65 [24]
Stitch tear strength (kg/cm)	141.46	107.914	100 [2]

In Table 5, it has been shown that the tensile strength, percentage of elongation and stitch tear strength of date seed extract re-tanned leather were 296.01kg/cm^2, 48.83%, and 141.46 kg/cm respectively. Whereas for conventional re-tanned leather, the tensile strength, percentage of elongation, and stitch tear strength were 255.57 kg/cm^2, 45.653%, and 107.914 kg/cm respectively. Both experimental and conventional re-tanned leather met the standard value.

From Table 6, we can see that both sample and conventional leather have shown good wet and dry rub fastness properties. In the case of the dry rub fastness sample and conventional changed their shade in 2048 rotations and got the felt and leather value 4/5 for both. But in the wet rub fastness test sample leather started to change its shade at 512 rotations and for the conventional leather, shade change started at 1024 rotations. But both types of leather didn't exceed the value 4/5 after completing the test and were within the standard. So, we could say the date seed extract did not affect the dyeing operation.

Table 6 Assessment of dry and wet rub fastness

Sample	R_n	Conventional		Sample		Acceptable value
		L_R	Felt	L_R	Felt	
Dry	128	5	5	5	5	3-5 [23]
	256	5	5	5	5	
	512	5	5	5	5	
	1024	5	5	5	5	
	2048	4/5	4/5	4/5	4/5	
Wet	128	5	5	5	5	3-5 [23]
	256	5	5	5	5	
	512	5	4/5	5	4/5	
	1024	4/5	4/5	4/5	4/5	

R_n= Number of rotations, L_R= Leather

Table 7 indicates that both experimental and conventional have shown similar results in the case of the break pipiness test and that was 2. This value indicated that both sample and conventional leather contained fine breaks on their surface.

Table 7 Assessment of break pipiness

Sample	Experimental value	Acceptable value
Experimental	2	1-3/4 [23]
Conventional	2	1-3/4 [23]

4. Conclusion

In this study, waste date seed was used as an alternative vegetable retanning agent. It was observed that the proposed investigation increased the hydrothermal stability and physical characteristics of leather. The utilization of waste date seed might be able to interest the tanners as an alternative retanning agent as well as it can minimize waste. In addition, the shift towards vegetable tanning could also reduce the use of chromium, which indeed will be very beneficial for the environment.

5. References

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