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Extraction of a novel tanning agent from indigenous plant bark and its application in leather processing

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Abstract

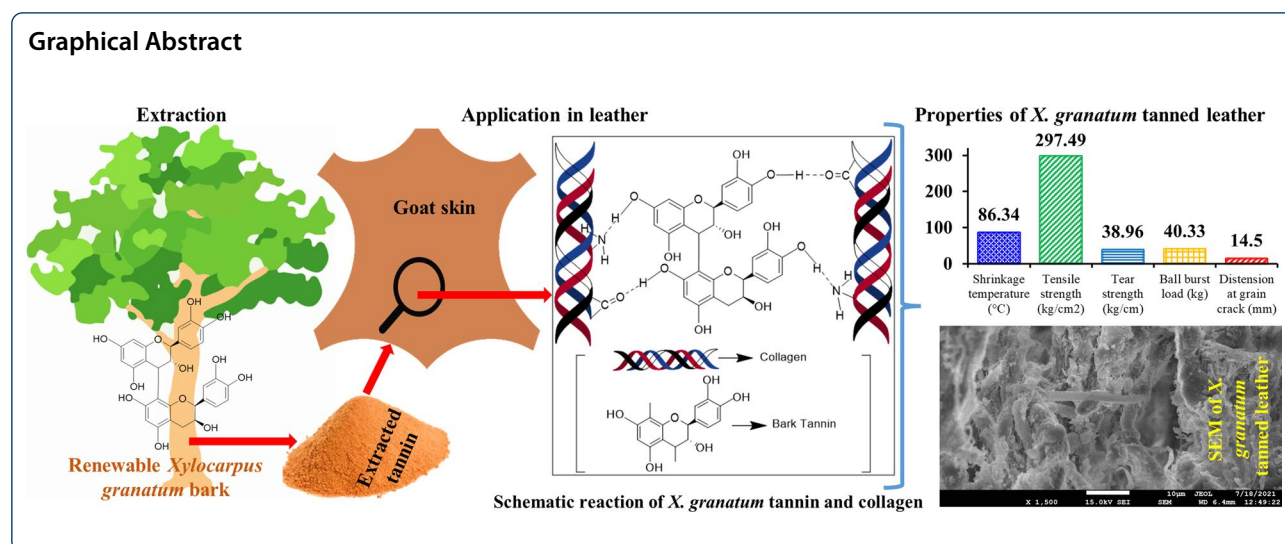
The use of vegetable tanning materials in leather processing has drawn attention as an alternative to basic chromium sulphate for its natural abundance and environmental aspects. In this work, an attempt has been made to extract vegetable tannins from *Xylocarpus granatum* bark using different solvents (e.g., water, methanol, ethanol, and chloroform) and compare with conventional vegetable tanning agents such as mimosa and quebracho. The highest extraction efficiency was observed 31.22% by methanol. The presence of tannin content and polyphenolic compounds, e.g. (-)epicatechin (503 mg/100 g dry extract), catechin hydrate (218 mg/100 g dry extract), catechol (29 mg/100 g dry extract) were ensured by UV-Vis, FT-IR spectroscopy and HPLC. Again, condensed tannins, moisture content, and pH of the methanol extracted tannin were found 47.80%, 5.82%, and 3.97 respectively. The leather tanned by *Xylocarpus granatum* tannin showed a shrinkage temperature of 86.34 ± 1.52 °C. Other properties such as tensile strength, tear strength, grain cracking load, and distention at grain cracking were comparable to conventional vegetable-tanned leather. The cross-sectional morphology of the tanned leathers was also characterized by scanning electron microscopy (SEM) which revealed a compact structure of the leather fibers. In light of the findings from the study, *X. granatum* bark tannin could be a well alternative to chromium and a new source of vegetable tannin for the leather industry.

Keywords: Vegetable tanning agent, Strength properties, Shrinkage temperature, Chrome-free leather, Alternative tannin, *Xylocarpus granatum*

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Graphical Abstract



1 Introduction

Animal raw hides and skins consisting of a multi-dimensional intimate structure, are tanned to convert into durable and flexible leather. Different stages such as pre-tanning, tanning, and post-tanning are associated with the processing of raw hides and skins, out of which tanning is the most inevitable and fundamental phase in the leather-making process [1]. A number of tanning methods, materials, and chemicals are used in leather processing. Among the practiced tanning methods, chrome tanning itself accounts for 88–90% of the total leather production throughout the world [2, 3]. Other methods of tanning include vegetable tanning, aldehyde tanning, oil tanning, mineral tanning, e.g., Zirconium, Titanium, Aluminium, Iron, and combination tanning. Among all, chrome tanning produces leather with high shrinkage temperature (> 100 °C), thermal resistance, lightweight, elevated tensile strength, and better fastness properties [4]. However, the debate about using chromium as tanning material arises due to environmental concerns because only 54–57% of chromium is consumed by the pelt during leather processing while the remaining exists as liquid and solid waste [5]. In addition, chromium-containing solid waste is posing a great challenge for its proper management and safe utilization. Nevertheless, several researchers have addressed the negative impact of hexavalent chromium, which could transfer to the human body via the food chain, skin, and other organs causing diseases e.g., respiratory problems, skin diseases, bone damage, renal issues, liver damage, kidney failure, infertility, cancer, and even birth abnormalities [6–11]. This situation demands a sustainable alternative to chrome tanning agents.

Vegetable tanning has been introduced for the production of eco-friendly leather since they are derived from renewable sources and provide considerable benefits such as comfort, and dimensional stability. It plays a vital role in generating less environmental pollution than chrome tanning and is considered the “green tanning” method [1, 12–14]. Vegetable tanning agents contain tannin, non-tannin, and gum. The most promising advantages of vegetable tannins are based on plant sources and produce full, compact, and embossable leather [5]. Vegetable-tanned leather also possesses better water permeability, solidness, stability, high strength, and molding properties [15]. However, sources of vegetable tannin and the difference in functional groups present in the tannin could affect the tanning efficiency and properties of the tanned leather [16, 17]. The presence of tannin differed from plant to plant, and part to part of a plant since plant polyphenolic compounds are produced naturally in plant's leaves, roots, bark, wood, and fruits [18]. Plant polyphenolic compound has the power to react with the collagen that stabilizes hides or skins against putrefaction and biochemical degradation. Further, vegetable tannin can be of three different categories such as complex tannin, condensed tannin, and hydrolyzable tannin [19]. Hydrolyzable tannin can be hydrolyzed in acid, alkali, or enzyme that contains pyrogallol group (1,2,3-trihydroxy benzene) whereas condensed tannin contains catechol group (3,4-dihydroxy benzene), which is not hydrolyzed in acid, base, or enzyme [19–21]. A large number of phenolic hydroxyl groups are present closely together in hydrolyzable tannin whereas several aromatic hydroxyl groups are dispersed over a bigger molecule of condensed tannin. Therefore, hydrolyzable tannin is more astringent than condensed tannin [19]. The presence

of catechin, epicatechin, leucocyanidin, or a mixture of these is considered condensed tannin whereas gallic acid and ellagic acid represent the existence of hydrolyzable tannin [21]. Moreover, the existence of oligomeric and polymeric flavan-3-ols compounds is responsible for condensed tannin [22]. In addition, the conversion of hides and skins into leathers with vegetable tannin could take place through the hydrogen and/ or covalent bond between the collagen functional groups (e.g., $-\text{COOH}$, $-\text{NH}_2$) and tannins [13].

Nowadays, the most commercially used tannins are mimosa, quebracho, sumac, tara, valonea, divi-divi, oak, and chestnut for chrome-free tanning [23–25]. The *Mimosa tenuiflora* (mimosa tannin) is available in South America and Eastern Africa over Asia [26, 27]. Most of the commercial mimosa used in Bangladeshi tannery is imported from Brazil [26], and Eastern Africa [27]. Mimosa extract contains sugars, organic acids, and hydrocolloids besides phenolic substances which are refined by the purification process [28]. Further, mimosa tanned leather can be stained readily in presence of iron and could be shrunk by direct heat [28]. Most vegetable tannins can not improve the hydrothermal stability of collagen as provided by the chrome tanning agent. Out of a number of extracted vegetable tanning agents, only a few got suitable for the application in leather processing commercially due to their tanning efficiency, quality, properties, and extraction efficiency issues. In the past, several researchers have explored and used tannins made from alternative plant sources such as *Acacia seyal* bark [1], *Acacia nilotica* fruit [5], Henna extract [5], *Acacia xanthoploea* bark [18], *Hogeniabyssinica* bark [18], *Acacia senegal* bark [20, 21], Longan bark [22]. These vegetable tanning materials showed potential results, however, their utilization in the tannery is not practiced commercially so far. As a novel source for vegetable tanning material, the bark of *Xylocarpus granatum* has not been explored yet.

There is a diverse range of mangrove plants in Bangladesh, the majority of which are used for traditional medicine and wood production [29]. Therefore, searching for a new source of vegetable tannin from mangrove plants could pave the way for the leather industry's long-term survival. *Xylocarpus granatum* (Family: Meliaceae) is commonly known as “Dhundul” in Bangladesh which is found in low lying, salt-tolerant forest and swampy locality in the mangrove forest Sundarban [29]. It is also found in tropical areas of East Africa, Polynesia, Thailand, Indonesia, Myanmar, Malaysia, India, China, and Australia [24, 30]. The bark of a mature *Xylocarpus granatum* plant could contain tannin and reddish-brown dye [24]. It has also been reported that different mangrove plants could contain 16–48% of tannin in their bark [19]. The work

aims to evaluate the tanning efficiency of extracted tannin from *Xylocarpus granatum* bark as a new source of tanning material and explore its suitability for commercial use. The properties such as tensile strength, tear strength, grain cracking load, shrinkage temperature, and distention at grain crack tests were conducted on the experimental leather and verified with the recommended standard values of shoe upper leather [31].

2 Material and methods

2.1 Materials

2.1.1 Plant materials, skins, and reagents collection

Xylocarpus granatum bark sample was collected from the world's largest mangrove forest Sundarban, beside the Malancha river at Shyamnagar, Satkhira, Khulna, Bangladesh. This forest covers 6017 sq. km in the southern part of Bangladesh [32, 33]. Approximately, 10–15 kg of fresh bark sample was collected from *X. granatum* trees of 10 to 15 m tall, and the bark was identified and validated by a taxonomist of the department of botany, University of Dhaka, Bangladesh. Eight pieces of wet salted goat skins were collected from the Posta skin market, Dhaka for leather making experiment. Chloroform (AR grade, Merck, Germany), Methanol (99.5%) (Merck, Germany), Ethanol (99.2%) (Merck, Germany), FeCl_3 (99.1%) (Research Lab, India), Gelatin (SRLchem, India), FeSO_4 (99.0%) (Research Lab, India), Butanol (AR grade, SRLchem, India), HCl (37%) (BDH chemicals, India), Formaldehyde (37%) (SRLchem, India), Sodium Potassium tartrate (98.4%) (Research Lab, India), CaCl_2 (98%) (Research Lab, India), all HPLC standard chemicals 3,4-Dihydroxybenzoic acid (97%), Gallic acid (97.9%), Catechol (99%), Catechin hydrate (96%), (-)Epicatechin (90%), Caffeic acid (98%), Rosmarinic acid (98%), Vanillic acid (97%), Rutin hydrate (94%), Syringic acid (95%), p-Coumaric acid (98%), Quercetin (95%), trans-Ferulic acid (99%), Myricetin (96%), Kaempferol (97%), and trans-Cinnamic acid (99%) were collected from Sigma-Aldrich, St. Louis, MO, USA. The mimosa (UCL, South Africa) and quebracho (Unitan, Argentina) tannin have been collected from the local market in Dhaka, Bangladesh, and were considered standard conventional vegetable tanning materials for this study.

2.2 Methods

2.2.1 Tannin extraction

The collected bark sample was chopped into small pieces and sun-dried completely. The sun-dried bark was pulverized in a Wiley mill (2 mm screen) and was kept in an air-tight glass pot with a sticker and stored in a dark, cold ($10 \pm 2^\circ\text{C}$), and anhydrous place for further use. A portion (40 g) of the ground sample was pulsed at room temperature ($22 \pm 2^\circ\text{C}$) for 11 h at 230 rpm separately

with distilled water (23 °C), ethanol (400 mL), chloroform (400 mL), and methanol (400 mL) solvent for extraction. Then the sample was filtered with 0.45 µm pore size filter membrane and each of the residual materials was rinsed out with additional solvents (300 mL) for 8 h and filtered accordingly (Fig. 1). Extracts were shifted to a tared, 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 weight differences were calculated to measure the yield percentage of extracts for different solvents.

X. granatum sample was taken into a 10 mL test tube separately [36]. 7.5 mL of de-ionized water and 0.5 mL Folin-Ciocalteu reagent (without dilution) were added to each tube followed by the addition of 1.0 mL of 35% (w/v) sodium carbonate. The solutions were mixed properly using an advanced vortex mixer (ZX3, VELP Scientifica) at 1200 rpm for 10 s and stored for 30 min for color development. The absorbance was measured at 725 nm against the blank with a double beam UV-Visible spectrophotometer (Specord 205, Analytikjena, Germany). Three replicates were taken per solution to get reproduc-

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

2.2.2 Determination of the composition of *X. granatum* tannin

In this study, moisture content and pH were determined by following the methods of SLC-113 [34] and SLC-120 [35] respectively. The total amount of tannin was measured using the modified Folin-Ciocalteu phenol reagent method where 1.0 mg of mimosa, quebracho, and

ible results. The total tannin content was determined and expressed as mg tannic acid equivalents per gram using the equation obtained from a standard tannic acid calibration curve, $y = 0.32x - 0.12$, $R^2 = 0.997$.

The percentage of condensed tannin in the extract was determined by the Stiasny test. 0.1 g of extracted sample was liquefied with 10 mL distilled water and 1.0 mL of 10 M HCl was added followed by the addition of 37% (w/v) of HCHO (2.0 mL). The mixture was heated for

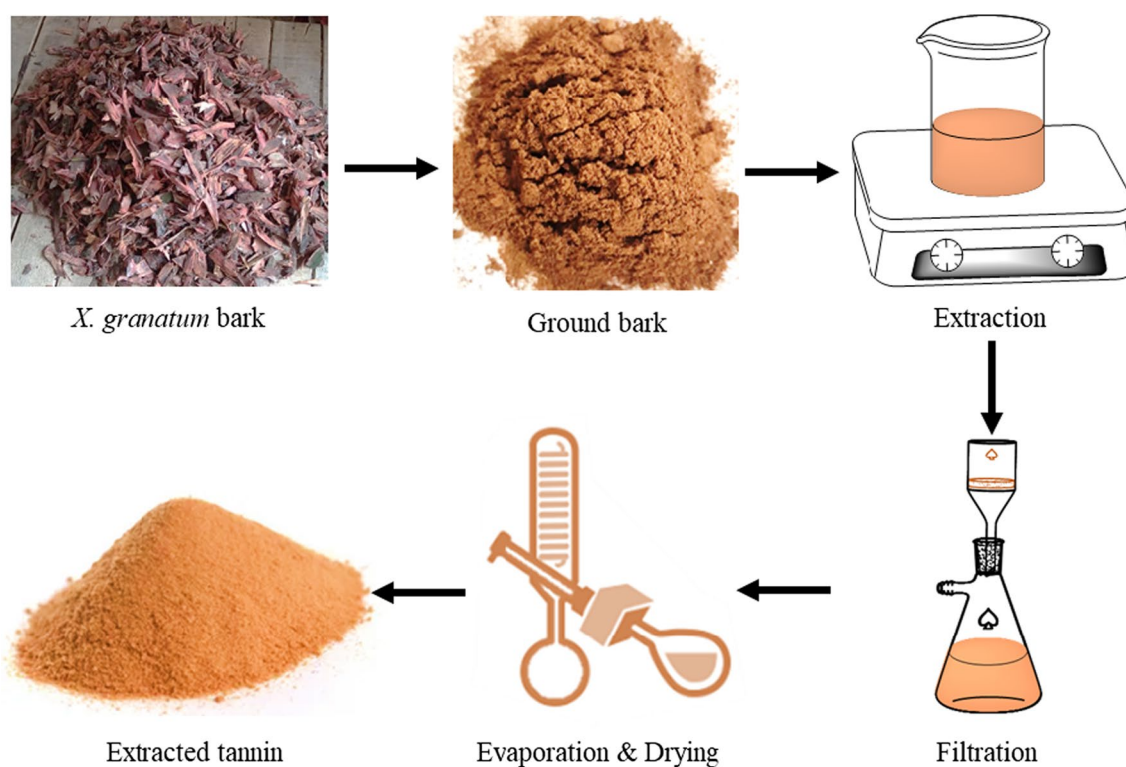


Fig. 1 Schematic extraction diagram of *X. granatum* bark tannin

30 min under reflux. Hot filtration of the reaction mixture was done through 0.45 μm pore size filter paper. Then the precipitate was rinsed with hot water and dried at 60 $^{\circ}\text{C}$ temperature in an air oven. The initial and final weight of filter paper was measured to determine the percentage (%) of condensed tannin [37, 38]. According to the Stiasny test method, flavonoid structures exist in condensed tannins that can react with formaldehyde and aimed to determine percentages of tannin extract which react with HCHO [25]. Condensed tannin was calculated by following the equation:

$$\text{Percentage (\% of Condensed Tannin)} = \frac{\text{Weight after drying} - \text{Initial weight}}{\text{Weight of given sample}} \times 100\%$$

2.2.3 Qualitative identification of *X. granatum* tannin

The presence of tannin in the extracted bark sample was carried out by chemical solutions of FeCl_3 , gelatin, and ferrous sulfate. Firstly, for testing with FeCl_3 solution, 2.0 mg of extracted sample was taken into two different test tubes equally and one was completely diluted with methanol and another with ethanol then five drops of FeCl_3 solution were added to both tests tubes. The appearance of green to black precipitate ensures the presence of tannin [20]. Secondly, for the gelatin solution test, 2.0 mg of extracted sample was taken into two test tubes equally and added 0.1% (w/v) gelatin solution (1.0 mL) with NaCl (1.0 mg) to form a white precipitate for the assurance of the presence of tannin in the sample [20]. Thirdly, in the case of the ferrous sulfate test, 2.0 mg of the extracted sample was taken in two test tubes for adding 0.1% (w/v) FeSO_4 (2 mL) and 0.5% (w/v) sodium potassium tartrate (1.0 mg). The manifestation of violet color indicates the existence of tannin [20].

2.2.4 Characterization of the chemical structure of *X. granatum* tannin

The spectrum of UV analysis was carried out by using UV-1700 PharmaSpec, Shimadzu (Japan) in the 200–800 nm wavelength range using a 1.0 cm quartz cuvette. The baseline was corrected by keeping the solvent cuvette in the reference cell (without sample) and the sample solution cuvette in the sample holder (automatic baseline correction). For sample analysis, 0.1 g of extracted sample was dissolved in 50 mL methanol and again 1 mL of the dissolved solution was diluted to 100 mL methanol before performing the analysis by UV-Vis spectrophotometer.

The Fourier Transform Infrared (FT-IR) spectroscopy (IRPrestige21, Shimadzu, Japan) was used to identify the functional groups of the extract and operated in the range of 4000–400 cm^{-1} with an S/N ratio of 40,000:1. Both background and sample scans were measured

sequentially at a scanning rate of 1 Hz, and 4 cm^{-1} resolution. Before starting sample analysis background measurement was executed with KBr without sample. Then automatic baseline correction and normalization were carried out by the FTIR built-in software.

HPLC–DAD analysis was performed for the detection and quantification of polyphenolic compounds in methanol (100%) extracted *X. granatum*, mimosa tannin (standard), and quebracho tannin (standard) as delineated by Ahmed [36] with some modifications. HPLC instrument (Shimadzu LC-20A, Japan) consisting of the

binary solvent delivery pump (LC-20AT), auto-sampler (SIL-20A HT), column oven (CTO-20A), a detector of photodiode array (SPD-M20A) was used and run by the LC solution software for analysis. The separation of the lab solution was done by applying Luna C_{18} (5 μm) Phenomenex column (4.6 $\times$ 250 mm) at 33 $^{\circ}\text{C}$. In this study, the mobile phase comprising 1.0% acetic acid in acetonitrile (A) and 1.0% acetic acid in water (B) with gradient elution of 0.01–20 min with 5–25% A, 20–30 min with 25–40% A, 30–35 min with 40–60% A, 35–40 min with 60–30% A, 40–45 min with 30–5% A, and 45–50 min with 5% A was utilized. 20 μL sample was injected with 0.5 mL/min flow rate. For validation of the method and analysis, the UV detector was set at 270 nm. A Nylon 6:6 membrane filter (0.45 μm , India) was set to filter the mobile phase before degassing under vacuum. 3,4-Dihydroxybenzoic acid (15 $\mu\text{g/mL}$); Gallic acid (20 $\mu\text{g/mL}$); Catechol, Catechin hydrate (50 $\mu\text{g/mL}$); (-) Epicatechin, Caffeic acid, Rosmarinic acid (30 $\mu\text{g/mL}$ each); Vanillic acid, Rutin hydrate, Syringic acid, *p*-Coumaric acid, Quercetin (10 $\mu\text{g/mL}$ each); *trans*-Ferulic acid, Myricetin, Kaempferol (8 $\mu\text{g/mL}$ each); and *trans*-Cinnamic acid (4 $\mu\text{g/mL}$) standard prepared stock solutions in methanol were used to attain the calibration curve.

2.2.5 Application of extracted tannin in leather processing

Soaking to pickling process of leather manufacturing was carried out by following the conventional process. The vegetable tanning process was done for both conventional and experimental with quebracho and extracted *X. granatum* tannin, respectively following the recipe depicted in “Table 1”. In this study, commercial vegetable tanning agents mimosa, and quebracho were taken as standard tanning material for conventional tanning. After aging, re-tanning and post-tanning processes were done for both conventional and experimental (extracted tannin) by following

Table 1 Tanning, and retanning process of goat skin

Process	Dosage (%)*	Chemicals		Time (min)	Remarks
		Conventional	Experimental		
Tanning	80	Water (25 °C)	Water (25 °C)	120	pH 3.8–4.0
	3	Pre-tanning agent	<i>X. granatum</i> tannin		
	0.8	Sodium Bicarbonate (1:20)	Sodium Bicarbonate (1:20)	20 × 3 & 120	
	0.2	Fungicide	Fungicide	35	
Aging, shaving, conventional steps, and processes were done					
Re-tanning	150	Water (45 °C)	Water (45 °C)	60 × 3	Kept overnight
	6 × 3	Mimosa	<i>X. granatum</i> tannin		
	6	Quebracho	–		
	0.5	Formic acid	Formic acid	15 × 2	
After retanning other conventional processes were done for making crust leather					

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

the recipe shown in “Table 1”. In this study, a total of 21% developed tannin (based on pelt/leather wt.) was used for tanning and post tanning process of experimental leather whereas 27% mimosa and quebracho were used for the same process of conventional leather production. The mimosa used in retanning was 18%, which was replaced by the extracted tannin (18%) in the experimental leather production. The conventional processes and chemicals used for both the experimental and conventional leather processing other than tanning and retanning have not been shown in “Table 1”.

2.3 Determination of the properties of *X. granatum* tanned leather

2.3.1 Hydrothermal stability

Hydrothermal stability of vegetable tanned and re-tanned leather was determined by the shrinkage temperature (Ts) apparatus. The leather samples were cut (50 mm × 12 mm) from the sampling location and the test was carried out following the standard method IUP-16 [39]. Three replicates were tested for this analysis and the mean with standard deviation has been reported in this study.

2.3.2 Physical–mechanical properties

The tanned leather (conventional and experimental) 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 $65 \pm 2\%$ following the ISO-2419 standard [40]. Mechanical and physical properties of experimental and conventional leather were evaluated by

tensile strength, percentage of elongation, tear strength, resistance to grain cracking, and distension at grain crack [41–43]. 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.

2.3.3 Field emission scanning electron microscopic (FESEM) analysis of tanned leather

Samples were cut from the sampling location (butt portion) from the matched pairs of experimental and conventional leathers. All samples had been conditioned at a temperature of 23 ± 2 °C, relative humidity $65 \pm 2\%$, and time 48 h before coating. The JEOL auto fine coater (JEC-3000FC) was used to coat the two specimens with platinum. For analysis, a field emission scanning electron microscope (JSM-7610F, JEOL, Japan) was operated on a 15-kV accelerating voltage and at different magnifications for analyzing micrographs of the cross-section of tanned leather.

3 Result and discussion

3.1 Extraction efficiency of *X. granatum* tannin by different solvents

Water, methanol, ethanol, and chloroform were used as a solvent for extraction purposes. Among them, methanol and ethanol were more efficient than chloroform and water for bark tannin extraction showing the order as methanol (31.22%) > ethanol (30.76%) > water (10.34%) > chloroform (6.22%) (Fig. 2). Therefore, the whole characterization and application of leather in this study have been carried out using methanol extracted vegetable tannin.

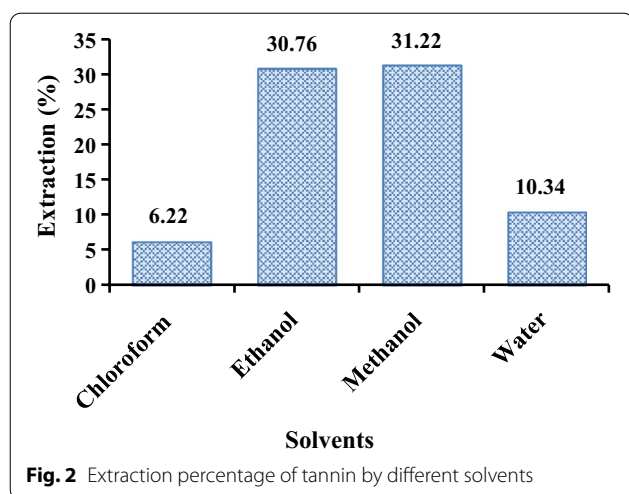


Fig. 2 Extraction percentage of tannin by different solvents

Table 2 pH, moisture content of the extracted sample, and standard tanning materials (Mean $\pm$ SD)

Name of sample	Solvents	pH	Moisture content (%)
<i>Xylocarpus granatum</i> extract	Water	4.27 $\pm$ 0.08	3.04 $\pm$ 0.05
	Methanol	3.97 $\pm$ 0.19	5.82 $\pm$ 0.08
	Ethanol	3.82 $\pm$ 0.23	8.23 $\pm$ 0.10
Mimosa (standard)	Methanol	4.80 $\pm$ 0.09	7.96 $\pm$ 0.12
Quebracho (standard)	Methanol	4.92 $\pm$ 0.22	10.28 $\pm$ 0.16

3.2 Composition of extracted tanning material

The pH and moisture content of the extracted bark sample and standard are exposed in “Table 2”. The pH of the extracted sample was 3.82 (ethanol), 3.97 (methanol), and 4.27 (water) which are closer to standard tannin materials mimosa (4.80) and quebracho (4.92) respectively (Table 2). The difference in the final pH of extracted tannin could be due to the release of the acidic group from the bark sample during the extraction process and the difference in the original pH of the solvent used for extraction. The 3.97 pH of methanol extracted bark sample could be considered ideal for vegetable tanning agent as

reported in the previous studies which demonstrated that the pH around 4.0 is the optimum for vegetable tanning materials [19]. Further, too low pH may cause inadequate penetration of tannin that may cause loose grain, inadequate elasticity, and wrinkled grain leather whereas too high pH in the tanning bath or tanning material might be the cause of lower fixation of tanning material [19, 44]. Thus, the pH of the *X. granatum* extract around 4.0 could enhance the penetration of the developed tannin into the pelt facilitating high solubility, and less sludge formation.

The moisture content of *X. granatum* bark powder was 5.82% (methanol extracted) and 8.23% (ethanol extracted) which revealed that methanol extracted tannin absorbs lower moisture and might facilitate storage. (Table 2). Again, the moisture content of mimosa and quebracho was 7.96% and 10.28% respectively (Table 2).

3.3 Qualitative identification of *X. granatum* tannin

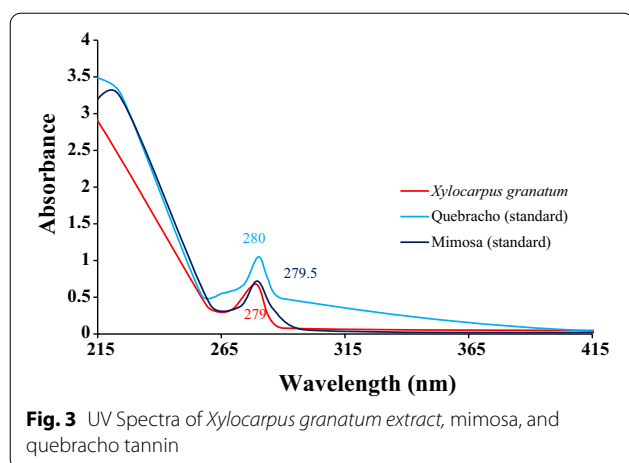
The chemical tests done for the assurance of the presence of tannin showed respective changes in the test solution followed by precipitate formation as depicted in “Table 3”. The chemical tests that include ferric chloride, gelatin, and ferrous sulfate solution test of *X. granatum* extracted sample showed green-black, white, and violet color precipitate respectively. The appearance of these precipitates indicated the presence of tannin for both ethanol and methanol as a solvent which is in congruence with Elgailanis’s findings [21]. These chemical tests for water and chloroform extracted samples were not carried out due to the lower extraction efficiency depicted in Fig. 2 in this study.

3.4 Chemical structure of *X. granatum* tannin

The UV absorption spectra of *Xylocarpus granatum* bark extract, mimosa, and quebracho tannin are shown in Fig. 3. The principal absorption band for extracted tannin was found in the UV region, specifically at 279 nm while mimosa and quebracho were noticed at 279.5 nm and 280 nm respectively. Also, tannic acid and catechin show the principal absorption band at 280 nm [21]. These results represent the presence of tannic acid, catechin,

Table 3 Chemical tests for the presence of tannin in *Xylocarpus granatum* extracted sample

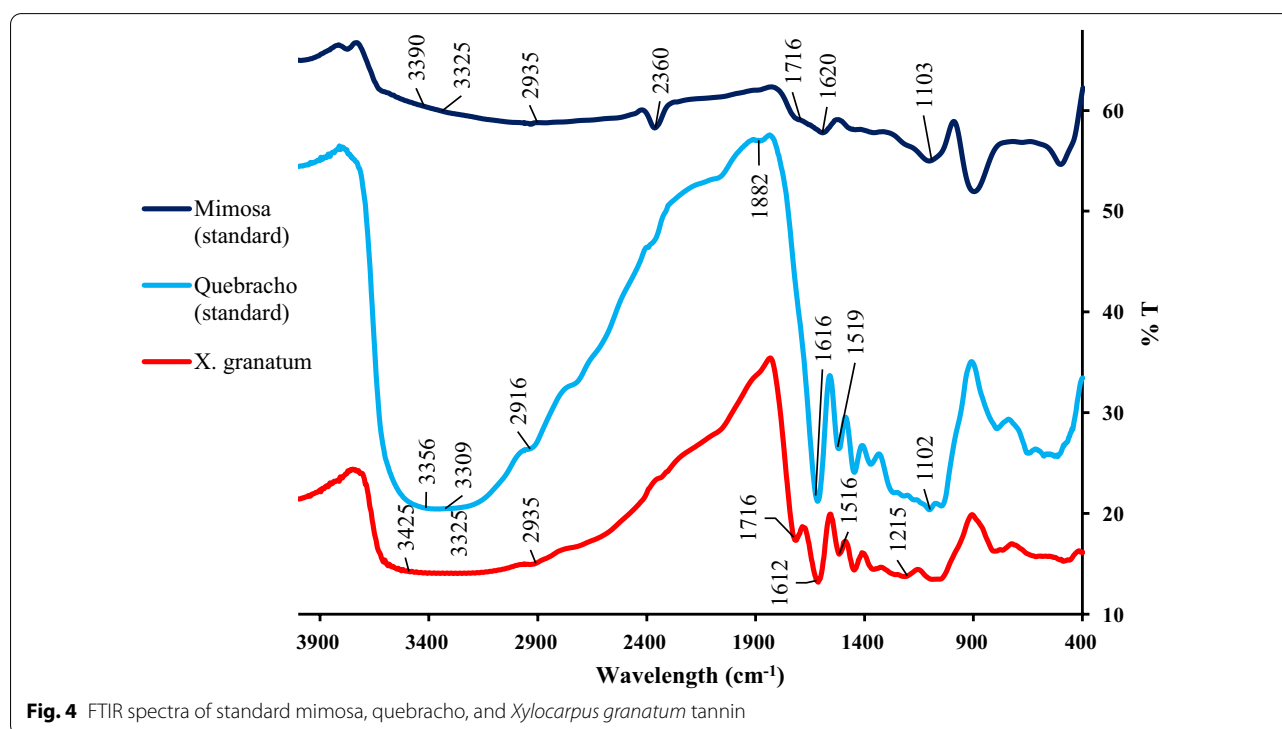
Reagents	Solvent for extraction	Observation	Presence of tannin
Ferric chloride solution	Methanol	Green-black precipitate	Present
	Ethanol	Green-black precipitate	Present
Gelatin solution	Methanol	White precipitate	Present
	Ethanol	White precipitate	Present
Ferrous sulfate solution	Methanol	Violet color precipitate	Present
	Ethanol	Violet color precipitate	Present



and phenolic compounds in the extracted tannin which could facilitate polyfunctional cross-linking with collagen through hydrogen bonding [19].

FTIR results of mimosa, quebracho, and *Xylocarpus granatum* tannin is being plotted in Fig. 4. The extracted sample showed the presence of O–H stretching, C=O stretching, aromatic C–H stretching, C=C ring stretching, C–H bending, C–O stretching, out-of-plane C–H bending compared with the mimosa, and quebracho commercial standard tanning materials. FTIR spectrum of *Xylocarpus granatum* extract showed a relatively

broadband at 3325 cm^{-1} , and 3425 cm^{-1} representing the presence of –OH groups of polyphenols such as tannin and flavonoids which is in congruence with the other studies [45, 46]. Also, well-known vegetable tanning agents mimosa and quebracho showed broadband at 3390 cm^{-1} , 3325 cm^{-1} , and 3356 cm^{-1} , 3309 cm^{-1} respectively is very similar to this study [45, 46]. Besides, a medium band was found at 2935 cm^{-1} for the extracted sample whereas for mimosa and quebracho the band was found at 2935 cm^{-1} , 2360 cm^{-1} , and 2916 cm^{-1} respectively which indicates the presence of aromatic C–H stretching in the extracted sample. Again for *X. granatum*, two strong peaks at 1716 cm^{-1} and 1612 cm^{-1} were noticed while mimosa and quebracho showed peaks at 1716 cm^{-1} , 1620 cm^{-1} , and 1882 cm^{-1} , 1616 cm^{-1} respectively indicating the presence of C=O stretching and C=C ring stretching with substituted benzene ring (Fig. 4). In condensed tannin, a strong peak with high intensity could be found in the range of $1620\text{--}1610\text{ cm}^{-1}$ which shows a high degree of polymerization [46]. Therefore, the extracted sample could be classified and considered as condensed tannin due to the presence of a strong and intense peak at 1612 cm^{-1} (Fig. 4). Galocatechin containing three –OH groups show two peaks around 1535 cm^{-1} and 1520 cm^{-1} while catechin containing two –OH groups show a single peak at around 1520 cm^{-1} [45, 47]. In this study, peak at 1519 cm^{-1} and 1516 cm^{-1} was found for quebracho and *Xylocarpus granatum* tannin



respectively which stipulates the presence of catechin and its near derivatives (e.g., epicatechin). Again, hydrogen atoms of aromatic rings are absorbed due to out-of-plane deformation between 780 and 770 cm^{-1} for procyanidins (condensed tannin, catechin) and near 730 cm^{-1} for prodelphinidin (gallo catechin) [48]. A peak at 775 cm^{-1} was noticed for extracted tannin which indicates the existence of a condensed tannin group. Therefore, the extracted tannin demands the existence of condensed type tanning material-rich compounds due to the presence of several polyphenolic groups in its chain.

Individual polyphenolic compounds of extracted *X. granatum*, mimosa, and quebracho tannin were identified and quantified by HPLC. Figure 5a–d depicts the HPLC chromatogram of standard polyphenol compounds for chromatographic separation, mimosa, quebracho, and *X. granatum* tannin respectively. Each polyphenolic compound was quantified from the corresponding calibration curve of extracted tannin, mimosa, and quebracho tannin. In HPLC analysis, 16 standard sample solution was run where six polyphenolic compounds were identified for both *X. granatum* and mimosa tannin, and four polyphenolic compounds were identified for quebracho tannin (Fig. 5a–d). The structure of the compounds found by HPLC in the *X. granatum* tannin is plotted in Fig. 6. Extracted *X. granatum* tannin contained a high concentration of (-)epicatechin (503 mg/100 g dry extract) and catechin hydrate (218 mg/100 g dry extract), the moderate concentration of caffeic acid (90 mg/100 g dry extract) and lower amount of catechol (30 mg/100 g dry extract), 3,4-dihydroxybenzoic acid (4 mg/100 g dry extract), and rutin hydrate (9 mg/100 g dry extract). Mimosa tannin contained a high concentration of catechin hydrate (199 mg/100 g dry extract), catechol (283 mg/100 g dry extract), vanillic acid (125 mg/100 g dry extract), syringic acid (138 mg/100 g dry extract) and lower amount of myricetin (19 mg/100 g dry extract), (-)epicatechin (28 mg/100 g dry extract). On the other hand, quebracho tannin contained a moderate concentration of rutin hydrate (98 mg/100 g dry extract) and lower concentration of p-coumaric acid (7 mg/100 g dry extract), trans-ferulic acid (5 mg/100 g dry extract), myricetin (5 mg/100 g dry extract). The high concentration of (-)epicatechin and catechin hydrate identified in the *X. granatum* tannin signifies the presence of condensed type tannin known as Flavan-3-ols which is in line with other studies [21].

In addition, the presence of catechol and 3,4-dihydroxybenzoic acid as a polyphenolic compound in the extracted *X. granatum* represents the existence of condensed type tannin [19]. The phenolic hydroxyl groups in *X. granatum* extract can react with collagen, which is

a characteristic of plant polyphenols, and could make it effective tanning material according to researchers [19].

The total tannin content of mimosa, quebracho, and the extracted tannin is depicted in “Table 4”. The total tannin content of mimosa and quebracho was found 114.25 mg (mg of tannic acid equivalent/g of dry extract) and 129.96 mg (mg of tannic acid equivalent/g of dry extract) respectively. 121.24 mg (mg of tannic acid equivalent/g of dry extract) of total tannin content was found for the *Xylocarpus granatum* tannin which denotes that this value is higher than the commercial tanning agent mimosa and lower than quebracho. Polyphenols that contain high tannin content usually have the same chemical patterns with one or more phenolic groups that react for them as hydrogen donors [19]. According to the HPLC analysis of this study, the compounds that contained catechin hydrate, catechol, (-) epicatechin, caffeic acid, and rutin hydrate possess at least two or more phenolic groups in their structure (Fig. 6). Therefore, the total tannin content is well-supportive for *X. granatum* to count it suitable for a tanning material.

The condensed tannin determination test was carried out three times for attaining better accuracy. The average percentage of condensed tannin was found at 47.80 ± 0.92 for the *Xylocarpus granatum* tannin (Table 4). Generally, the bark of the mangrove plant contains about 16–48% of condensed type tannin [19]. The condensed tannin present in quebracho and mimosa bark is 14–26% and 22–48% respectively found in the other research [19]. Therefore, the extracted bark tannin from *Xylocarpus granatum* could be claimed as a potential condensed type tanning material.

3.5 Tanning performances of *X. granatum* tannin

The shrinkage temperature (T_s) of the leather sample represents the hydrothermal stability of the leather and “Fig. 7” describes the T_s values of the pickled pelt, pre-tanned, and re-tanned leather for both the conventional and experimental. The T_s for conventional pre-tanned leather (CPL) and experimental pre-tanned leather (EPL) were found at 73.34 °C and 78.67 °C (Fig. 7) respectively which denotes that the leather pre-tanned by extracted tannin shows more hydrothermal stability than the CPL. The previous statistics reported that the T_s of alternative chromium-free and valonea extract tannage were 65 °C to 72 °C and 75 °C respectively [23]. The shrinkage temperature of the pickled pelt (PP) was 58 °C and increased to 78.67 °C after pre-tanning with extracted tannin which might be due to the cross-linking between collagen and polyphenolic compounds of *X. granatum*. The T_s of conventional vegetable re-tanned leather (CRL) was 81.34 °C and experimental re-tanned leather (ERL) was found at

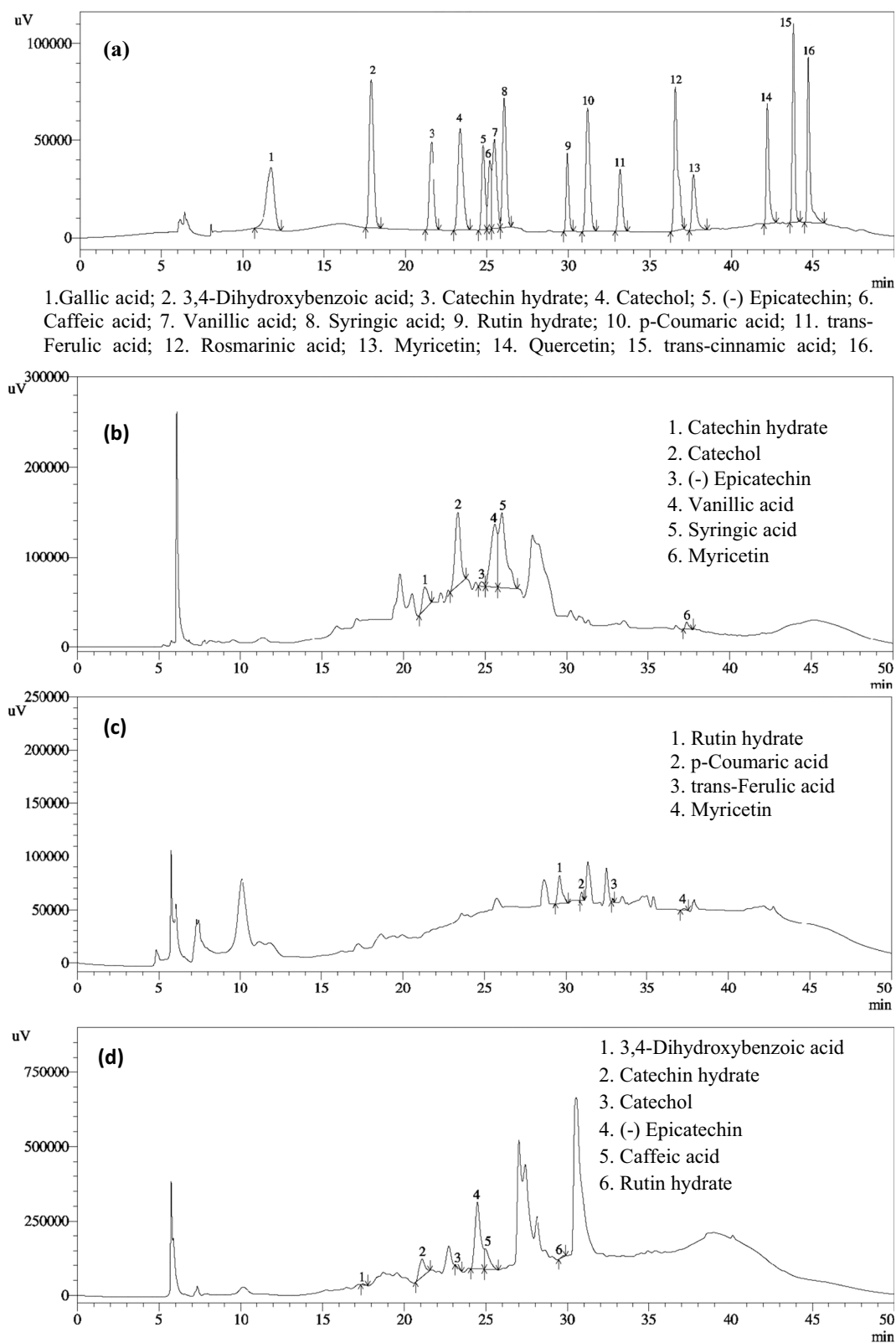
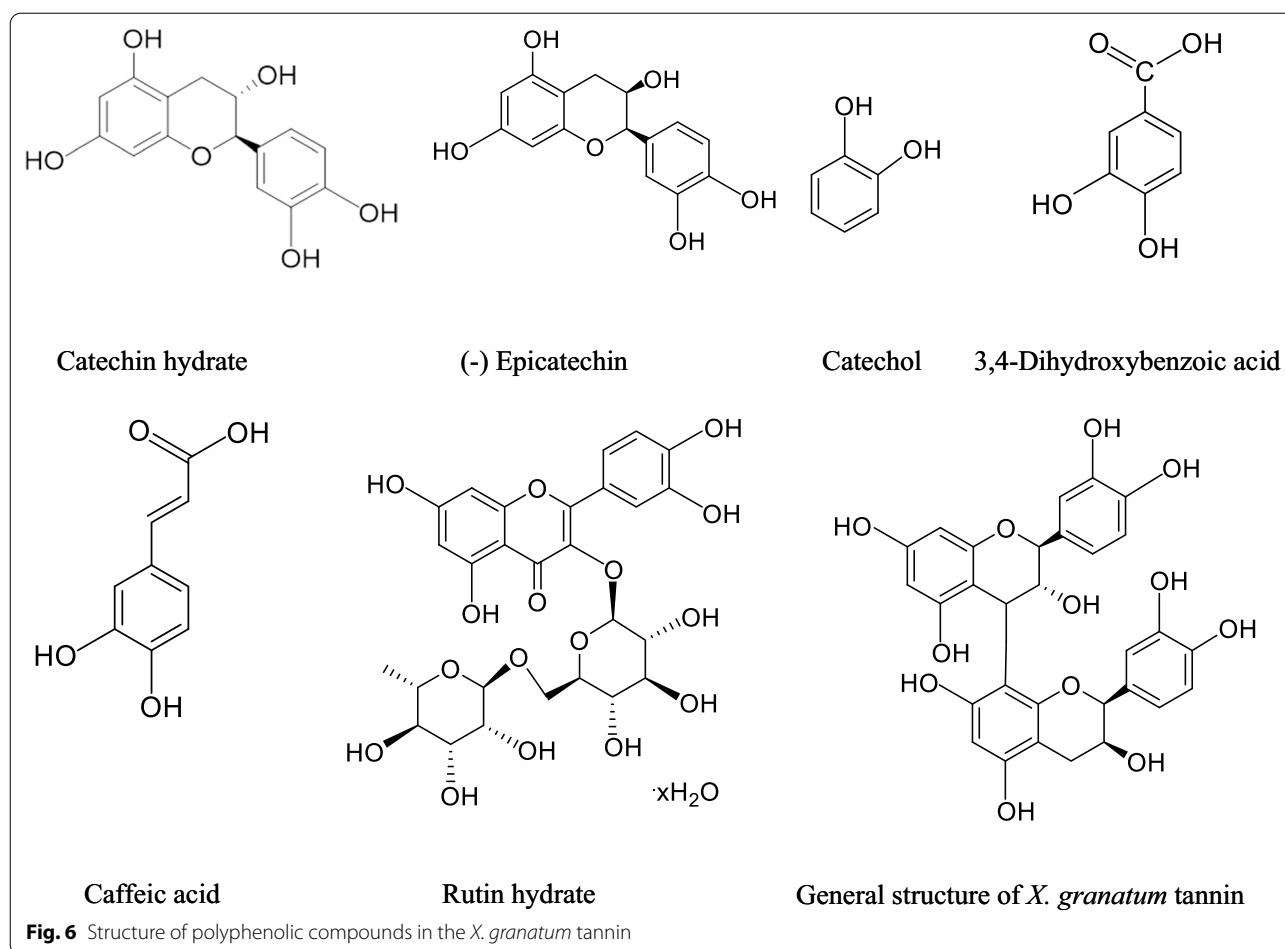


Fig. 5 **a** HPLC chromatogram of a standard mixture of polyphenolic compounds, **b** mimosa tannin, **c** quebracho tannin, and **d** *Xylocarpus granatum* tannin



86.34 °C (Fig. 7) which suggests that the extracted tanning material could substitute conventional mimosa and quebracho tannins in terms of hydrothermal stability. Researchers showed that leathers treated with condensed tannins show T_s above 80 °C, which is an indicator for *X. granatum* tannin of being condensed tanning material as supported by the results of FTIR, HPLC, and condensed tannin percentage in this study [19]. Furthermore, the high content of (-)epicatechin and catechin hydrate in extracted *X. granatum* tannin both of which contain at

least five phenolic hydroxyl groups (Fig. 6) in their structure could crosslink with more collagen leading to higher hydrothermal stability compared to conventional tanned leather.

The physical–mechanical properties tested in this study are illustrated in “Table 5”. Experimental leather showed a very high tensile strength of 298 kg/cm² which is well above the UNIDO standard (230 kg/cm²) and higher than the conventional mimosa tanned leather (259 kg/cm²) (Table 5). Similar studies conducted in Ethiopia and Turkey on indigenous crossbred sheepskin have shown an average tensile strength of 249 kg/cm² and 218 kg/cm² respectively [5, 49]. Further, experimental leather showed a very high percentage of elongation (42.5%) which is a well-accepted value recommended by UNIDO and well above the conventional tanned leather (39%) (Table 5). Therefore, the experimental leather could stretch and may hold more load compared to the conventional vegetable-tanned leather.

Further, there was no significant difference ($p > 0.05$) in tear strength between conventional (37 kg/cm) and experimental tanned leather (39 kg/cm). Other studies

Table 4 Total tannin content and condensed tannin of Mimosa, Quebracho and *Xylocarpus granatum*

Samples	Total Tannin Content (mg of tannic acid equivalent/g of dry extract)	Condensed tannin (%)
Mimosa	114.25 ± 1.74	22–48 [19]
Quebracho	129.96 ± 1.84	14–16 [19]
<i>Xylocarpus granatum</i>	121.24 ± 1.96	47.80 ± 0.92

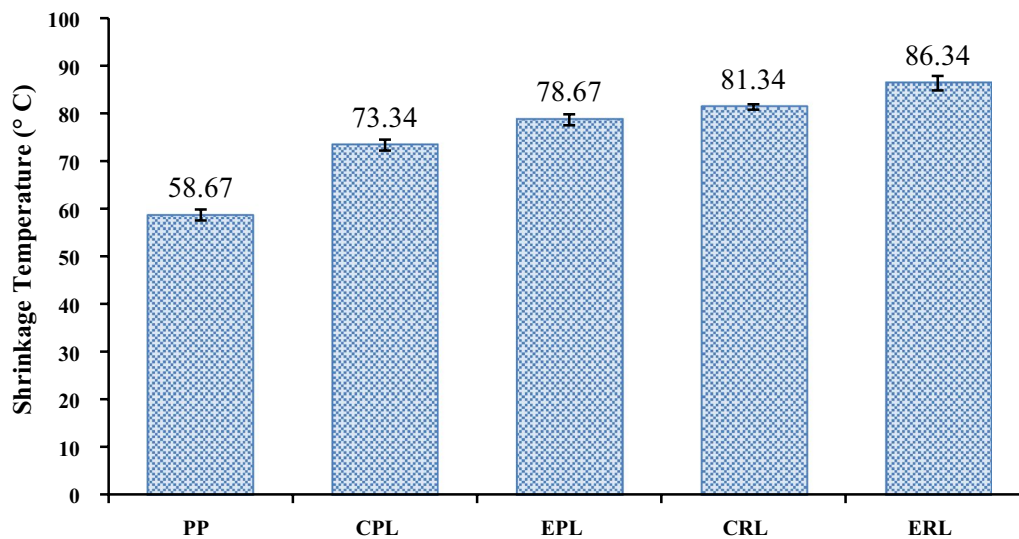


Fig. 7 Shrinkage temperature (T_s) of leather tanned by extracted and conventional tannin

Table 5 Physical–mechanical properties of leather tanned by conventional and extracted tannin (mean $\pm$ SD)

Parameters	Conventional leather	Experimental leather	Standard values [31]
Tensile strength (kg/cm ²)	258.645 $\pm$ 16.43	297.49 $\pm$ 14.17	$\geq$ 230
Elongation (%)	38.675 $\pm$ 3.57	42.545 $\pm$ 2.05	30–45
Tear strength (kg/cm)	37.205 $\pm$ 3.41	38.965 $\pm$ 4.62	$\geq$ 30
Grain crack load (kg)	29 $\pm$ 1.00	29.33 $\pm$ 3.05	$\geq$ 20
Distension at grain Crack (mm)	12.82 $\pm$ 1.08	14.50 $\pm$ 1.89	$\geq$ 7
Strength at ball burst (kg)	42.33 $\pm$ 2.08	40.33 $\pm$ 2.07	–
Distension at ball burst (mm)	15.76 $\pm$ 2.38	16.58 $\pm$ 2.02	–

on combination tanning with 20% *Acacia Nolitica L.* pods tannin have shown a tear strength of 39.79 kg/cm which has a good agreement with this study [50].

Another important physical test for evaluating the overall quality of the leather is the lastometer test which determines the actual cracking and bursting load with distension. In this study, loads of grain cracking and ball bursting were 29 kg and 42.33 kg respectively for conventional leather while the experimental leather showed 29.33 kg and 40.33 kg respectively (Table 5). Also, the distention at grain crack and ball burst for conventional leather were 12.82 mm and 15.76 mm respectively whereas experimental leather showed 14.50 mm and 16.58 mm respectively (Table 5) which are far beyond the minimum recommended value suggested by UNIDO for distention at grain crack (6.5 mm) and distention at ball burst (7.0 mm) respectively for all types of leather. Several researchers found distention at grain crack 6.74 mm/ 9.9 mm, and distention at ball burst 7.72 mm/ 10 mm for

different sheep leather [49]. Moreover, the variation of tensile strength, tear strength and other strength properties vary on the composition of tanning agents, type of tannin, quantity of tannin, the control of beam-house operations, pre-tanning, tanning, post-tanning and /or methods of tanning [18]. In this work, beam house processes were controlled as the same for both conventional and experimental leather, and hence, the higher strength properties of the experimental leather could be due to the high content of condensed tannin. Eventually, although the use of a total of 21% extracted tannin in the experimental leather processing was 6% less than conventional leather processing (total 27%, mimosa 18%, and quebracho 9% on pelt/leather wt.) the quality of the experimental leather was noticed better than the conventional leather. This signifies that the extracted *X. granatum* tannin could be a well alternative to the conventional commercial tanning agent whether in terms of the amount needed and the final quality of the leather.

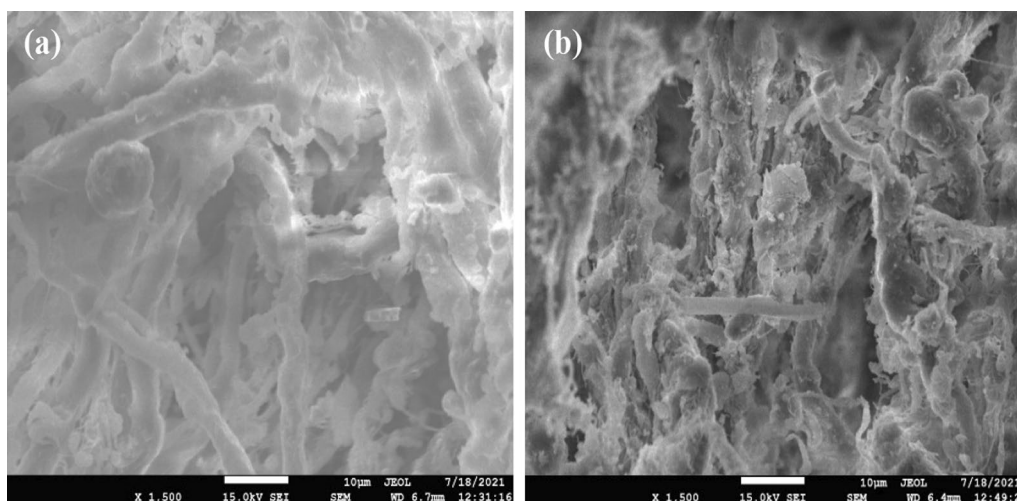


Fig. 8 FESEM images of the cross-section of leather tanned with **a** conventional vegetable tannin and **b** *X. granatum* tannin

The morphology of leather fiber can be assessed through FESEM. Figure 8a–b shows the cross-sectional micrographs of the experimental and conventional leather with a magnification of 1500X. The experimental leather exhibited a more compact fiber structure than conventional leather which is a unique characteristic of vegetable-tanned leather. The leather fiber is densely packed with vegetable tannins, even without a fiber opening which confirms filling up void spaces of the leather after tanning. Similar results of SEM images of vegetable tanned leather were revealed by the other researcher [51]. However, from the FESEM images, it could be demonstrated that the leather was perfectly tanned with both conventional and extracted tanning materials.

The interaction between plant tannin and hide collagen has been investigated broadly for over fifty years to clarify the cross-linking mechanism as well as to search for new vegetable tannin sources [13]. For condensed tannins, hydrogen bonds are formed in between the collagen molecules (peptide oxygen and amino groups) and $-OH$ groups of the tannin polyphenols [52]. In this work, a probable reaction scheme of condensed tannin with collagen is shown in Fig. 9. The phenolic hydroxyl groups of the extracted tannin (Fig. 6) could form hydrogen bonds with the amino acid side chain $-COOH$ and $-NH_2$ group of the collagen molecules (Fig. 9). A similar reaction scheme has been reported for the condensed tannin by the other researchers [19, 52]. In addition, tannin bearing flavonoids, phenolic compounds, and a sufficient number of collagen-binding reactive groups could be regarded as successful tanning agents [13]. Hence, *X. granatum* containing condensed tannins based on polymerized flavonoids especially, catechin monomers could form high

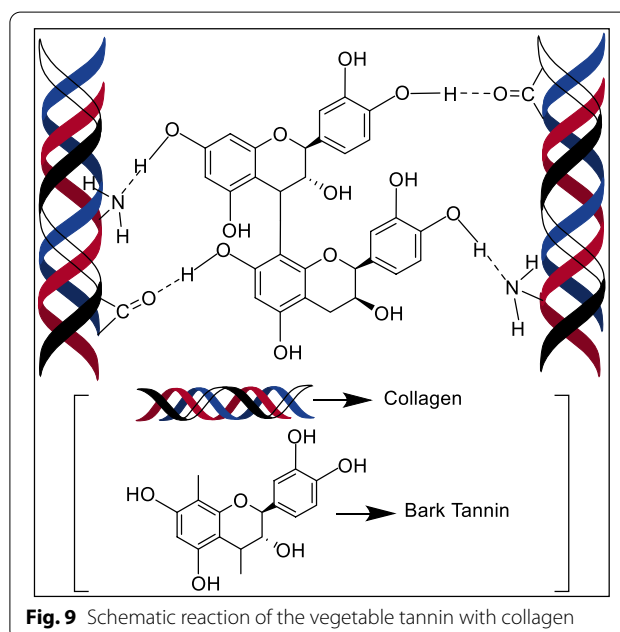


Fig. 9 Schematic reaction of the vegetable tannin with collagen

cross-linkages with collagen leading to higher shrinkage temperature and better physical properties.

4 Conclusions

The extraction, characterization, and comparison results of this study revealed that *Xylocarpus granatum* bark tannin could be a potential new source of vegetable tanning agent. The extraction efficiency, total tannin content, and amount of condensed tannins are in the recommended range compared to

commercial vegetable tannins. Based on the pH (3.97) value, it could be a promising vegetable tannin for introducing a partially pickled tanning process in pre-tanning and suitable for the re-tanning process of leather manufacture. Moreover, the physical–mechanical properties of experimental leather exhibited competitive properties in contrast with the conventional full vegetable-tanned leather and well above the UNIDO recommended values. Further, there are no vegetable tannin sources in Bangladesh currently, and *X. granatum* is locally available thus exploration of this tannin may lower the import dependency of vegetable tannin. In addition, *X. granatum* tree bark has a great property of being replenished within a few months of being peeled off which addresses the renewability of the material. Therefore, the extracted tannin could get preference as a potential vegetable tanning agent in leather processing as an alternative to commercial vegetable tannin.

Abbreviations

X. granatum: *Xylocarpus granatum*; Ts: Shrinkage temperature; SD: Standard deviation; UNIDO: United Nations Industrial Development Organization; FESEM: Field emission scanning electron microscope; HPLC: High-performance liquid chromatography; UV: Ultraviolet; FTIR: Fourier-transform infrared; IUP: International union of physical testing of leather; SATRA: Shoe and Allied Trade Research Association; SLC: Society of leather trades' chemists; CPL: Conventional pre-tanned leather; EPL: Experimental pre-tanned leather; CRL: Conventional vegetable re-tanned leather; ERL: Experimental re-tanned leather; PP: Pickled pelt.

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Author contributions

Raju Kumar Das conceived and designed the experiments, collected research materials, conducted the experiments, processed the data, drafted the manuscript, and evaluated the findings. Al Mizan shared the recipe for leather processing, interpreted the analysis, drafted the manuscript, finalized the conclusion, and revised the manuscript. Fatema-Tuj-Zohra conducted tests, evaluated the results with the standards, edited, and finalized the manuscript. Sobur Ahmed envisaged and contributed to the investigation, supervised the research, edited, and finalized the manuscript. Khondoker Shahin Ahmed and Hemayet Hossain carried out the HPLC experiment and wrote an explanation. All authors read and approved the final manuscript.

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Availability of data and materials

This manuscript contains all of the data generated or analyzed during this research.

Declarations

Competing interests

There are no conflicting interests declared by the authors.

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