Textile & Leather Review

ISSN 2623-6281 | www.tlr-journal.com | 10.31881/TLR

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How to cite: Mia MAS, Malitha SB, Nur-E-Alam M, Akter M, Rahman Ria M, Alam MZ. Ultrasound-Assisted Extraction, Characterization and Assessment of Vegetable Tannins from Guava (*Psidium guajava*) Leaves for Leather Tanning. Textile & Leather Review. 2024; 7:872-892. https://doi.org/10.31881/TLR.2024.030

How to link: https://doi.org/10.31881/TLR.2024.030

Published: 28 May 2024

Ultrasound-Assisted Extraction, Characterization and Assessment of Vegetable Tannins from Guava (*Psidium guajava*) Leaves for Leather Tanning

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Article

https://doi.org/10.31881/TLR.2024.030

Received 16 February 2024; Accepted 6 May 2024; Published 28 May 2024

ABSTRACT

For commercial leather processing, chrome tanning is the most used approach but it significantly contributes to environmental pollution. Vegetable tannins, which are large polyphenolic compounds, form strong interactions with proteins and carbohydrates, thereby enhancing the adaptability and value of vegetable-tanned leather as well as reducing environmental impact. In this study, vegetable tannins were extracted from the leaves of Guava plants (Psidium guajava) using ethanol as the solvent, facilitated by ultrasound. Extracted tannins were quantified using the Folin–Ciocâlteu reagent with ultraviolet-visible spectroscopic method. Ultrasound enhanced the extraction process producing a high yield in less time due to its mechanical, thermal, and cavitation impacts. The extracted tannins were characterized by a variety of spectroscopic techniques, including Proton (1H) Nuclear magnetic resonance, Fourier-transform infrared, and ultraviolet-visible spectroscopy. The effect of various process variables, such as temperature, solid-liquid ratio, ultrasonic power, extraction period, and powder fineness, were also investigated to optimize the extraction process. Finally, the extracted tannins were employed in leather tanning processes to assess their potential as tanning agents. The extracted tannins ensured uniform diffusion of tannins, improved thermal stability and reduced the number of tannins in effluent by 68% making it an environmentally friendly leather tanning process.

KEYWORDS

ultrasound, extraction, vegetable tannins, guava, Psidium guajava, leather, tanning

INTRODUCTION

Leather is a versatile and long-lasting stuff manufactured from tanning the hides and skins of animals, primarily sourced from cows, buffalos, and goats. It is crafted into a multitude of products, including footwear, vehicle upholstery, clothing, handbags, book covers, fashion accessories, and furniture [1,2]. The leather sector is a big industry in Bangladesh, and the government of Bangladesh has designated it as a priority industry. In the fiscal year 2017–18, footwear, leather items, and leather earned $1.29

billion for Bangladesh through exports. An increase of 4.2% has been made to the export target for 2018–19. The growth rate needs to be gradually increased to reach the 2020 target of $5 billion. Data from the Export Promotion Bureau shows that for the second year in the fiscal year 2018–19, leather and leather goods exports exceeded $1 billion [3,4]. Now, this industry stands out as one of the most polluting sectors. The method of preparing leather is to blame for the adverse effects on the environment. Tanning is linked to the foul stench produced by waste materials and the presence of ammonia, sulfide, and additional volatile substances [5]. Raw trimmings, keratin, animal hairs, body wastes, and polishing dust wastes are examples of solid waste generated in the leather industry [6]. In chrome tanning hides and skins are typically treated with chromium (III) oxide to form wet blue, a stable substance that is resistant to deterioration [7]. The most environmentally polluting stage of tanning occurs in developing countries like Bangladesh, which subsequently exports the products to developed countries that enforce more stringent environmental regulations [8]. High concentrations of organic and inorganic substances are produced by the tannery effluent, which increases the need for dissolved oxygen [9]. Scientists were worried about causing stability on raw skins and hides during the global leather era [2]. There weren't many alternatives for the manufacturers, such as aluminium tanning and tanning with smoke, oil, or vegetables, before the development of chrome tanning [10]. Chromium disposal, where treatment produces sludge polluted with chromium, is one of the main issues facing the leather industry [11]. The harmful effects of hexavalent chromium, which can enter the body through the food chain, the derma, and other body parts, have been studied by many researchers. These effects can include respiratory disorders, skin diseases, bone loss, kidney failure, renal problems, liver damage, cancer, and even birth abnormalities [12]. Tanners are advised to employ more environmentally amicable tanning techniques, such as vegetable tanning, in light of these drawbacks with chrome tanning. The global industry wants to process leather in a less polluted manner due to changes in manufacturing practices and increased environmental awareness [13].

Vegetable tannins are large molecular-weight polyphenolic chemicals that form strong complexes with proteins and carbohydrates [14,15]. Generally, vegetable-tanned leather is highly valued because of its adaptability and the process is eco-friendly [16]. Basic chromium sulphate used in tanning might occasionally be left behind by traditional chrome tanning techniques [17]. Higher quantities of chromium compounds are carcinogenic and highly hazardous to public health [18]. Tanning products designed for the new millennium use cleaner tanning technology to reduce chromium pollution. Vegetable tanning is the alternative in this aspect [19].

Tannins derived from vegetable/ plant sources are used to tan leather that has been vegetable-tanned, such as peel, nuts, leaves, etc. The most commonly used tanning materials are wattle, acacia, avaram, konnam, myrobalan, babul, quebracho, cutch, etc. [1]. The fruit tree *Psidium guajava* L. is a member of the Myrtaceae family. It is well-known and is typically found in tropical and subtropical areas. Many tree parts, including the fruit, blossoms, shoots, bark, and leaves, have been widely utilized in traditional medicine to treat a variety of illnesses [20].

In this study, vegetable tannins were extracted from the leaves of Guava trees (Psidium guajava), using ethanol as the solvent with the help of ultrasound technique, which contains around 10% tannins. Tannins were measured in UV-visible spectroscopy using the Folin-Ciocalteu reagent. Because of its cavitation, mechanical, and thermal impacts, ultrasound improved the extraction process of tannin. Several spectroscopic techniques, including UV-Vis, IR, and ^{1}H NMR, were used to analyze the extracted tannins. To improve the extraction process, the effects of several process variables, including temperature, solid-liquid ratio, ultrasonic power, length of extraction, and granularity of the powder, were also examined. The extracted tannins were used to test their potential as tanning agents by tanning leather. FESEM, TGA, and DSC data were used to evaluate the tanning efficiency of the extracted tannins. An environmental study was also conducted to study the effect of ultrasound on reducing the quantity of unbound tannins in the spent liquor.

EXPERIMENTAL

Materials and Method

Chemicals and Plant Material

Research-grade Ethanol was purchased from Merck, Germany. Double-deionized water was used. Standards and other reagents were purchased from Sigma-Aldrich (USA). Middle-age intense green leaves of *Psidium guajava* L. were harvested in Gaibandha, Bangladesh. Before the analyses, the samples were air-dried at 25 °C until constant weight was achieved, ground, and sieved (particle size 0.6–0.8 mm).

Extraction of Phenolic Compounds from Psidium guajava L. Leaves

Ultrasound was used to extract tanning materials from granular air-dried guava leaves (Figure 1(a)). The proportion of solid to solvent was 1:80 (w/v). The average number of cycles was set at 0.5 cycles/s, while the frequency was maintained at 24 kHz. Using a digital multimeter mod, temperature readings were taken every fifteen seconds during the procedure. To determine the optimal process parameters, the experiment's initial phase involved changing the extraction duration (20, 40, and 60 min), ethanol/water proportion (50, 70, and 90% (v/v), and ultrasonic power (500 W) on guava leaves. Each batch of samples was extracted, concentrated under the absence of air, and then redissolved in 2 mL of 50% methanol/water (v/v). The mixture was then filtered through a 0.20 µm RC needle filter and stored at 20 °C until additional analysis was performed.

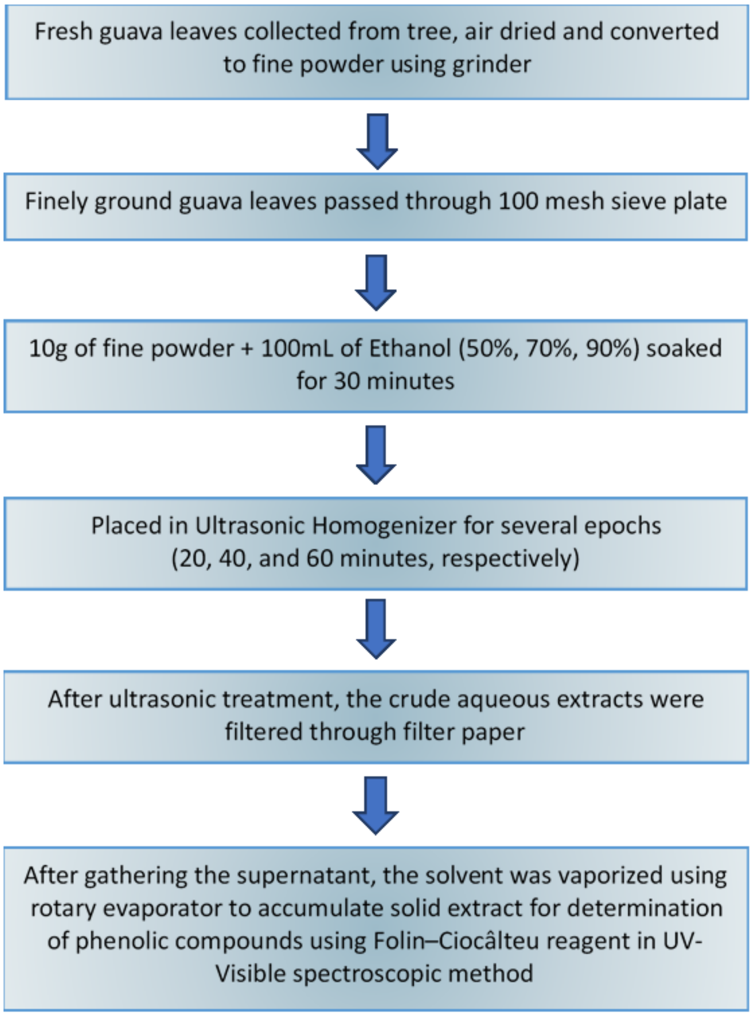


Figure 1(a). Flow Diagram of Extraction of Tannins from Guava Leaves

Folin-C test for determining total phenolic content

To create a blue-coloured complex, phenols were initially extracted in water and then combined with the Folin-C reagent, a complex mixture of hetero-poly phosphotungstate molybdate in the presence of sodium carbonate. The quantity of reactive phenolic chemicals in the sample correlates with the observation of blue hue intensity. The phenolic content was ascertained by analyzing the sample solution's absorbance at 765 nm and comparing the results with the calibration curve using gallic acid as a standard.

Calibration standard solution formulation: Formulation for gallic acid was made using 1.1 (±0.1) g which was then transferred into a 1000 mL volumetric vessel. When the solids were completely dissolved, roughly 750 mL of water was added, and they were sonicated in an ultrasonic bath with roughly 3 cm of water for up to 10 minutes. Then, it was mixed thoroughly after being diluted with water to volume. The solution was stored at 2 - 8 °C, and this stock standard solution (around 1000 mg/L gallic acid) can be used for up to one month.

https://doi.org/10.31881/TLR.2024.030

List of materials used in vegetable tanning

The method of turning raw hides or skins into leather is called tanning. Different types of rawhides are treated with various chemicals according to the final use of the product. Raw cowhide is used here to find out the different rates of tanning with ultrasound and the Conventional process. The chemicals and natural products from Guava plants (*Psidium guajava*) used in vegetable tanning process are given below:

For Vegetable Tanning:

- 2% Hypo (Sodium thiosulfate)
- 3% RWP (CALCOFLUOR WHITE RWP)
- 3% Os (Osmium)
- 2% Potassium aluminium sulfate (Potash alum)
- 2% GTW (Tripterygium Wilfordii Hook root extract)
- 20% Guava leaves powder (*Psidium guajava*)
- 4% Chestnut
- 4% Neo Syn (Phenylephrine hydrochloride)
- 2% RF (Rutherfordium)

For Basification:

- 0.25% Busan 30L (2-(Thiocyanomethylthio) benzothiazole)
- 1.5% Sodium formate
- 0.2% Sodium Bicarbonate

Tanning procedure of pickled pelt

The process of tanning involves two distinct sets of unit operations. These are pre-tanning such as soaking, liming, deliming, bating and pickling operations and tanning methods. Most of the key experiments were conducted on an experimental unit of laboratory scale.

Sample preparation

Initially, 12 leather samples were cut into 2 inch × 2 inch taking from the equivalent lateral position of the pelt corresponding to the line of the backbone of the animal and weighed with an electronic balance (Shimadzu ATY224). Finally, full pieces of leather were divided into two parts for carrying out experiments with ultrasound and conventional methods.

Water bath and Ultrasonic unit

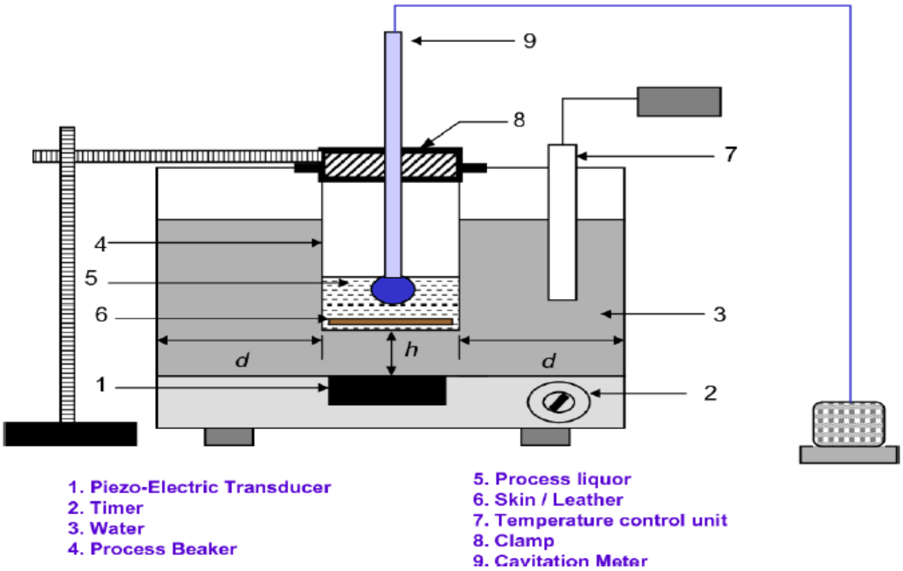


Figure 2(b). Sonication unit used for vegetable tanning of leather

Vegetable tanning experiments were carried out in a beaker with a flat bottom inside an ultrasonic bath bearing water. The maximum capacity of producing frequency of this ultrasound is 35 KHz. It contains different operating frequency levels of 10% to 100%. To investigate the vegetable tanning process with different Ultrasonic wave frequencies, 100%, 75%, 50%, and 25% of 35 KHz frequency levels were used. Operating time could be changed according to the time required for vegetable tanning, especially for heavy leather; it requires 3 - 5 h time for a satisfactory tanning process. In the Ultrasonic bath, water was filled up to the level mark inside the ultrasound, and the bottom of the beakers was immersed in water contained in the sonication bath. Temperature was needed to keep uniform by manually adjusting cold and hot water to obtain better results.

Tanning in Ultrasonic Bath

The main reason behind vegetable tanning in an ultrasonic bath is to speed up the tanning process and reduce energy and time consumption. The process of tanning vegetables was done in an ultrasonic bath using a 500 ml flat glass beaker submerged in water. The maximum capacity for producing the frequency of this ultrasound is 35 KHz. To investigate the vegetable tanning process with different Ultrasonic wave frequencies, 100%, 75%, 50%, and 25% of 35 KHz frequency levels were used.

Conventional tanning in Drum and Hotplate

The drum method is a widely used worldwide method for vegetable tanning. It involves using a metal drum with tanning liquor and a 60-100 RPM speed for 12-18 hours. Raw cowhides are collected from the Hagaribagh market and undergo trimming, soaking, liming, deliming, and pickling for 2 - 3 days. Water is added to the drum, and tanning agents are given according to the recipe. The rotating speed is maintained at 100 RPM for better tanning. The leather is then air-dried overnight and covered with polythene to ensure quality. In this case, vegetable tanning was carried out in a hotplate instead of ultrasound to determine the difference between Tannin uptake associated with ultrasound and in a conventional way. A 500 ml flat glass beaker, which contained tanning liquor and tannin, was put on the upper surface of the hotplate. 12 leather samples (2 inch × 2 inch) were placed in the beaker; a leather sample must be sunk in tannin liquor. Then, temperature and vibration were maintained according to the tanning procedure. After vegetable tanning had been finished, the leather sample was allowed to dry in the air, and liquor was collected to compare the uptake of tannin.

Upon completion of the tanning operation, the tanned leathers were covered by polythene and were piled up for several days to complete the fixation of tanning chemicals and dried in the air. Tanned leathers obtained in both ultrasound and conventional methods were then used for analysis and characterization.

Analytical Techniques

The concentration of tanning liquor was determined using a UV-visible photometer, following the Beer-Lambert Law. FTIR analysis was conducted to ascertain the molecular composition, presence of different functional groups, and structure of the material**.** Information about the sample, including its exterior appearance (texture), chemical composition, and the orientation and crystalline structure of the components that make up the sample, was found through SEM (scanning electron microscope). TGA, or thermogravimetric analysis, was employed to calculate component composition, water content, solvent content, filler material, and thermal stability. Differential Scanning Calorimetry (DSC) was conducted to analyze a similar thermal stability study.

Determination of tannin uptakes by leather sample

Ultrasound cavitation produced significantly higher vegetable tannin uptake in leather samples compared to conventional methods. Tannin uptake was measured based on tannin consumption in a tanning bath, with the percentage of tannin penetrated calculated using equation 1:

$$\text{Uptake} = (C_iV_i - C_fV_f)/W \text{ mg/gm} \tag{1}$$

Where C_i & C_f are the initial and final tannin concentration in the liquor, Vi & Vf are the initial and final tannin volume of the liquor, and W is the weight of the sample.

Initial and final tannin concentrations in the liquor and tannin volume were measured using a dilution factor and distilled water. The maximum absorption of Guava was calculated using a UV-visible spectrophotometer at 275 nm. The tannin solution was taken out at different stages of the tannin liquor and diluted with distilled water for absorbance measurements.

RESULTS AND DISCUSSION

Quantitative Analysis of Guava Leaves Extraction

Table 1. Quantitative Analysis of Extracts from Guava Leaves Showing the Effect of Varying Extraction Time and Solvent Concentration, Extraction Yield, and Total Phenolic Content as Gallic Acid Equivalent

Concentration of Ethanol (%)	Time of Extraction (min)	Power of Ultrasonic Homogenizer (W)	Yield (mg)	Concentration (ppm)	Total Phenolic content (gallic acid equivalents, %w/w)
50	20	500	1284.6	565.8356	4.404761015
50	40	500	1621.9	496.272	3.059818731
50	60	500	640.7	129.6277	2.023219916
70	20	500	1240.8	397.1937	3.201109768
70	40	500	1273.4	214.1654	1.681839171
70	60	500	523.8	72.3201	1.380681558
90	20	500	563.4	33.34	0.591764288
90	40	500	480.8	8.7912	0.182845258
90	60	500	433.7	0.871	0.020083007

FTIR Analysis of Extracts from Guava Leaves

The infrared spectrum of guava extract (Figure 2) shows the following bands: a broad absorption band observed at 3340 cm^{-1} may be due to the presence of O–H stretching of acids, with another very strong absorption band appearing in the region 1049 cm^{-1} due to C–O stretching vibration. The combination of these two bands reveals the presence of alcohol. Two other bands found at 1442 cm^{-1} and 2927 cm^{-1} were associated with C=C and =C-H of aromatic hydrocarbons. The bands present at 1049 cm^{-1}, and 1221 cm^{-1} are possibly related to the C-O ether grouping. The absorption band present at 1724 cm^{-1} is due to the C=O ketones group. The absorption band appearing in the region 1672 cm^{-1} is due to the C=C stretching vibration of the alkenes group[21].

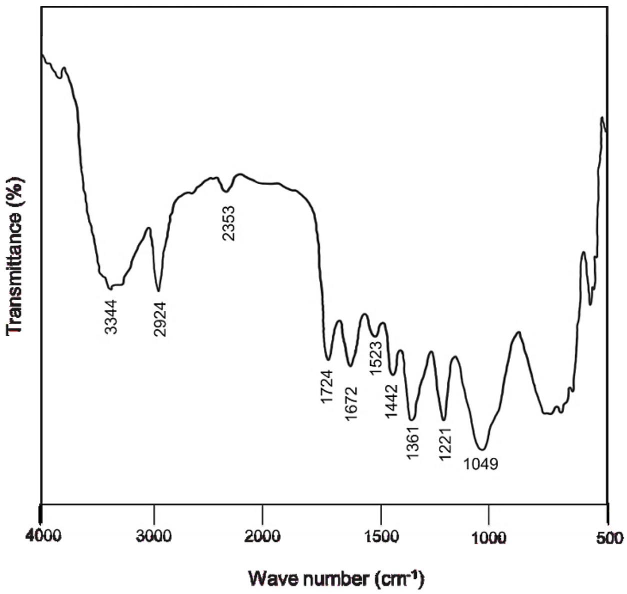


Figure 2. FTIR spectrum of Extracts from Guava Leaves

Characterization by ^{1}H NMR spectroscopy

Figure 3 shows the ^{1}H NMR spectra of the extracted tannin. The peaks at 0.50 to 2.50 ppm are due to the presence of $-CH_3$ and $-CH_2$ protons. There are peaks at 3.5 to 5 ppm due to the hydrogens of the methoxy group. The aromatic protons showed characteristic peaks at 7.0 - 8.0 ppm. The protons associated with aldehyde and ester are observed at higher delta values (greater than 10.0 ppm). Thus, the ^{1}H NMR spectra show a good agreement with the IR spectra of extracted tannins, which are a mixture of different organic compounds [22].

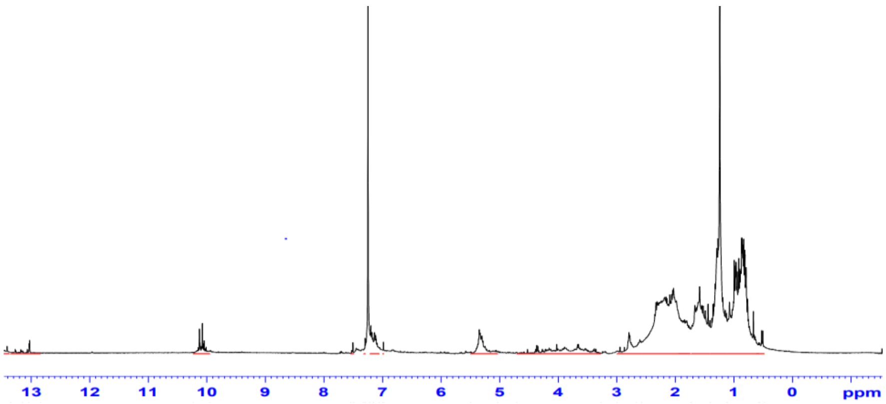


Figure 3. NMR spectra of the extracted tannin

Effect of Ultrasound for Tannin Uptake

Ultrasound may have enhanced the tanning process due to the rapid bubble formation and cavitation onto the leather sample in a liquid medium at a constant temperature. Ultrasonic waves reduced the processing time significantly and promoted uptakes of a large portion of tannin agents in a short period.

As a result, a large amount of energy consumption was saved to operate the conventional machine for the tanning of any leather sample. It could be seen that tannin uptake in the leather sample was lower than 20% of the weight of the leather sample in 3 h during the conventional tanning process, whereas the tanning process conducted by ultrasound at 30 KHz frequency consumed more than 50% of the tanning agent according to the leather weight at 30–40 degree temperature. On the other hand, the leather sample was uptaken by more than 91% tanning agent according to its sample weight of only 5 hours in ultrasound at 35 KHz, which is more than 60% higher compared to the conventional process operating at the same parameters.

The competitive comparison of tanning uptake in cowhides in the Conventional process and with ultrasound was illustrated in Figure 4.

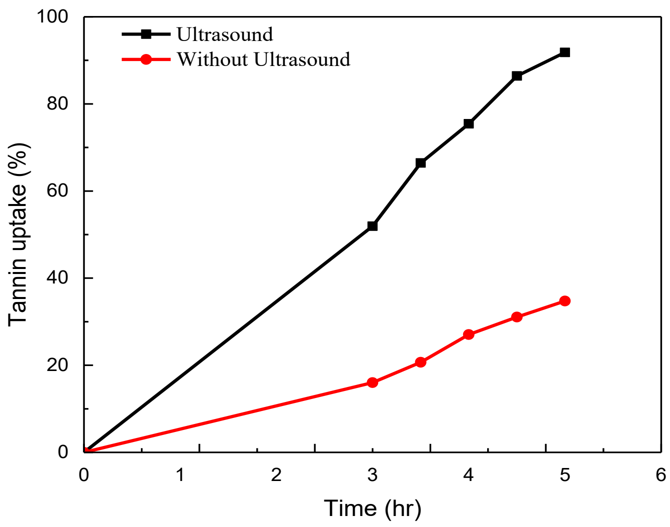


Figure 4. Effect of tannin uptake in tanning with and without ultrasound; Ultrasound operated at 35 KHz frequency at a temperature of 30-40 °C

Moreover, it is observed that the tanning process was much faster in the ultrasonic system compared to the conventional process. In the ultrasound operating process at 26.25 KHz frequency, the tanning agent penetrated almost 80% at 5 hours, as shown in Figure 5. In the conventional process, less than 40% of tannin was penetrated in the tanned leather at the same period.

Therefore, the notation was fruitfully established that ultrasound could have the ability to enhance the tanning operation process much higher than the conventional process.

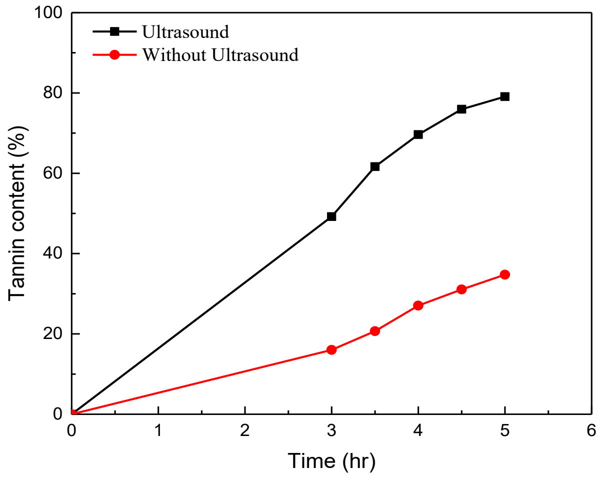


Figure 5. Effect of tannin uptake in tanning with and without ultrasound; Ultrasound operated at 26.25 KHz frequency at a temperature of 30-40 °C

Ultrasonic waves may have played a significant role in the reduction of vegetable tanning time as well as energy consumption. Vegetable tanning is the most time-consuming process compared to other tanning processes, especially for heavy leather, which usually takes 2-3 weeks because it uses only natural materials from plants. To commercially apply this tanning process, a speed-up technique is highly required. Ultrasonic wave technique is one of them that can enhance the tanning uptake in leather samples within a short period and reduce the running time of the operating machine, consequently helping to reduce energy consumption. Figure 6 shows a clear output of the vegetable tanning process using ultrasound compared to the conventional vegetable tanning process without the help of ultrasonic waves.

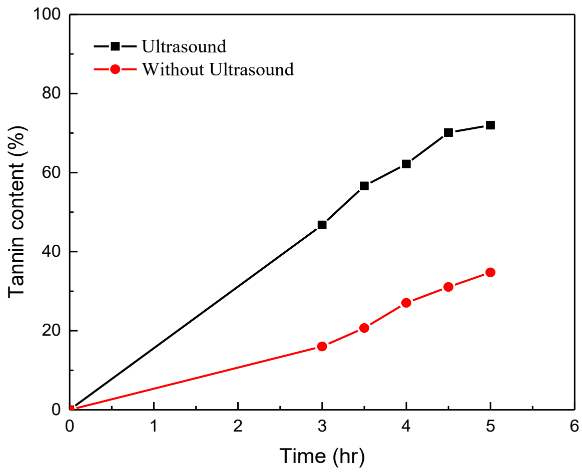


Figure 6. Effect of tannin uptake in tanning with and without ultrasound; Ultrasound operated at 17.5 KHz frequency at 30-40 °C

It can be seen that the tanning agent penetrated in Conventional tanned leather was only 16% and 37% in 3 h and 5 h respectively, whereas ultrasound aided vegetable tanned leather contained more than 50% and about 40% tannin in the same time.

On the other hand, energy consumption is also reduced due to the effect of ultrasound. In the conventional vegetable tanning process, only 37% tannin uptake was found, whereas more than 40% tannin was penetrated with the help of ultrasound in only 3 hours.

Overall, it can be seen that the ultrasound-aided vegetable tanning leather process reduced both process times by a significant portion, as shown in Figure 7. Only 25% of the 35 kHz operating frequency of ultrasound reduced 2.5 hours of process time of vegetable tanning compared to the vegetable tanning process without ultrasound and conventional process.

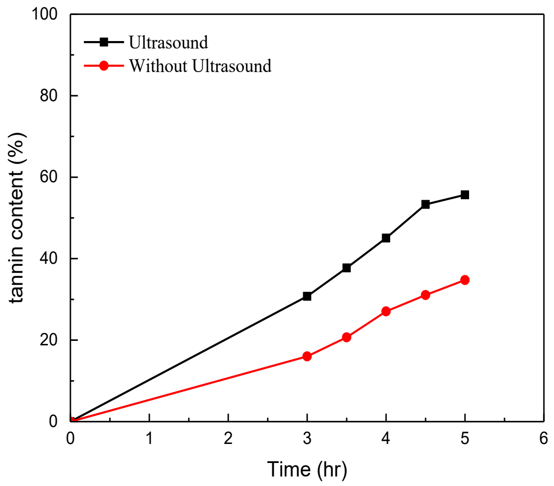
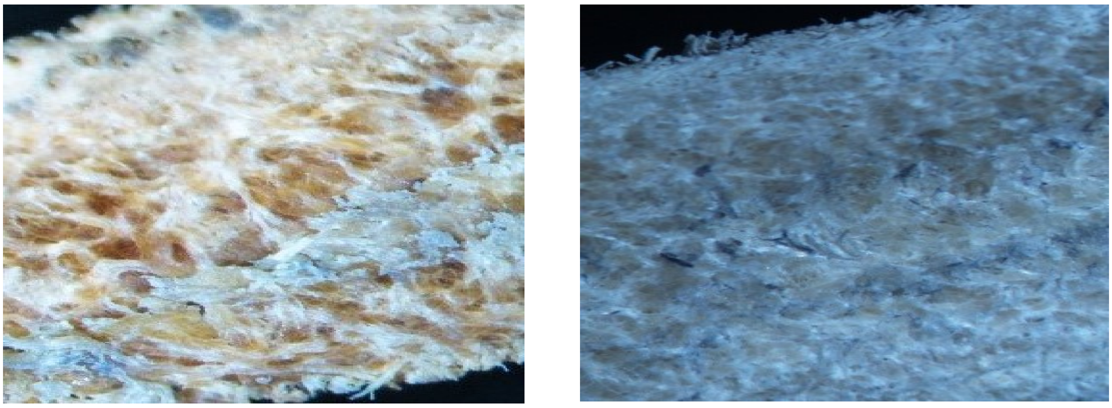


Figure 7. Effect of Ultrasound in the process of Vegetable tanning compared to without ultrasound; Ultrasound operated at 25% of 35 KHz frequency at 30-40 °C

Penetration of tanning agent - Photomicrographic Analysis

Ultrasound can also increase tannin penetration. The degree of tannin penetration in a leather sample was measured using an optical microscope. The results obtained from the optical microscope are shown in the following figure. It was seen that for the sample with the ultrasonic process, tannin penetration into the sample was enhanced. In this process, tannin penetrated even the inner layer of the given leather compared to the conventional process shown in Figure 8 (b). However, the tannin penetration depends on the types of samples and the chemicals used in the tanning process. The tannin penetration with ultrasound was 50% higher than that without ultrasound, and the tannin completely penetrated the cross-section of the leather sample (Figure 8).

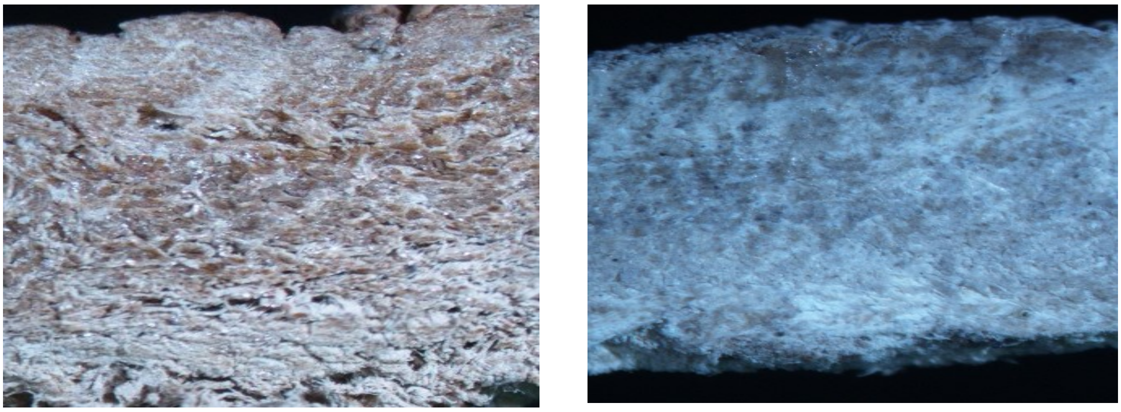


(a) (b)

Figure 8. Optical microscopic view of the cross-section of tanning leather (X12) (a) without ultrasound, (b) with ultrasound

Moreover, ultrasound helps in the uniform diffusion of tannin through the inner part of the leather sample, which is normally difficult in the conventional process. Finally, it can be said that ultrasound enhanced to achieve a better penetration of tannin in leather samples.

Figure 9 shows the degree of tannin penetration in the leather sample in a cross-section view at a 4-hour tanning period using ultrasound and without ultrasound.

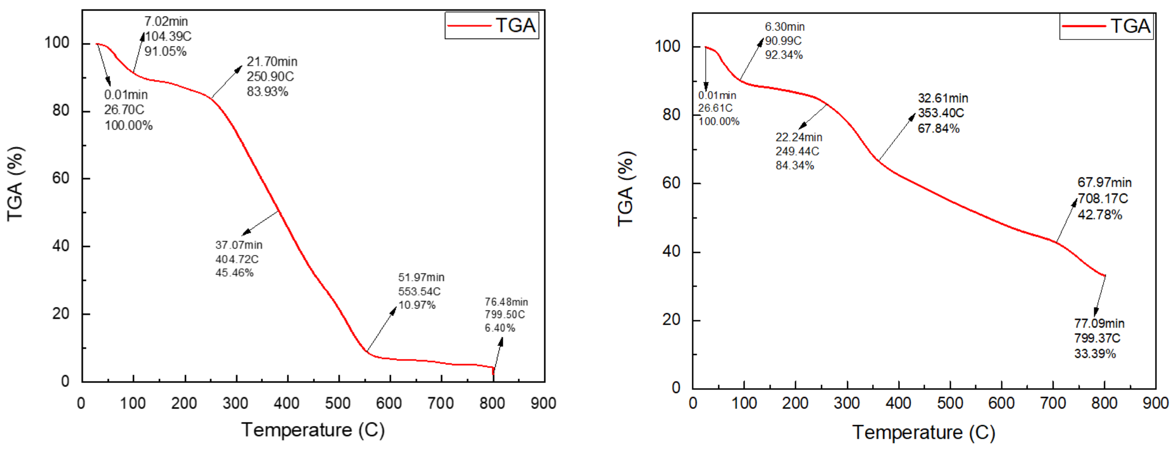


(a) (b)

Figure 9. Photomicrograph of the cross-section of tanning leather(X12) (a) without ultrasound, (b) with ultrasound at 4 hr tanning time

Thermogravimetric Analysis (TGA) of Tanned Leather

This TGA analysis was carried out in an inert atmosphere like an N_2 atmosphere. In the Drum process, at 800 ^oC temperature, only 6.40% mass of leather was observed in 76.48 minutes (Figure 10). However, in vegetable tanning with the help of ultrasound, 33.39% mass of leather was found at 77.09 minutes time period which means Ultrasonic waves improved the thermal stability of the leather sample because of enhancing penetration of tannin through the inner surface of leather.



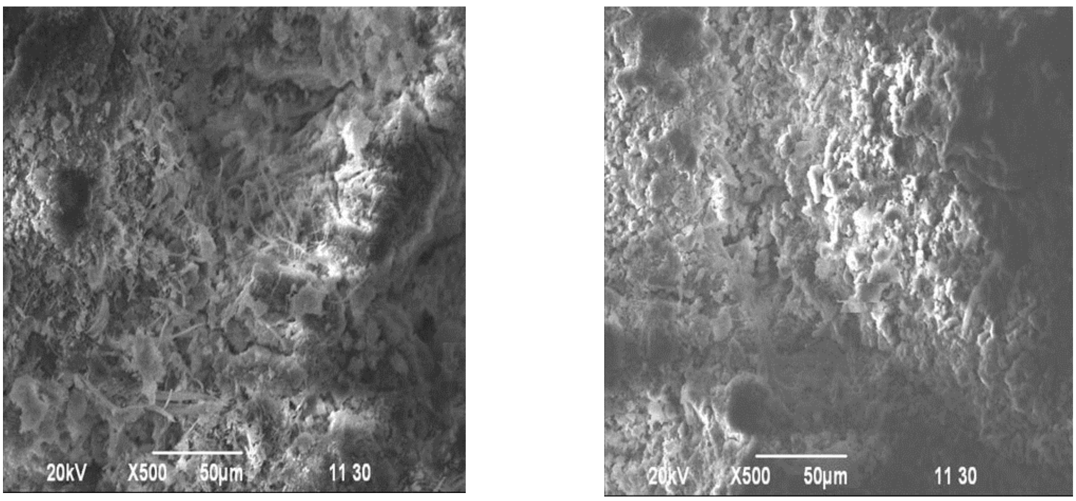
(a) (b)

Figure 10. TGA of Tanned leather without ultrasound at 30-40 °C with 5hr Tanning period (a) and TGA of tanned leather with ultrasound at 30-40 °C with a 5-hour tanning period (b)

It was proven that ultrasound has maximum thermal stability for vegetable tanning operated in both hot plate and drum processes. Ultrasound enhanced the tannin uptakes as a result of a higher degree of the reduction of thermal degradation properties (Figure 10(b)). Therefore, ultrasonic waves helped to improve the thermal degradation value of vegetable-tanned leather due to proper penetration of tannin into a leather sample [23].

SEM analysis of tanned leather

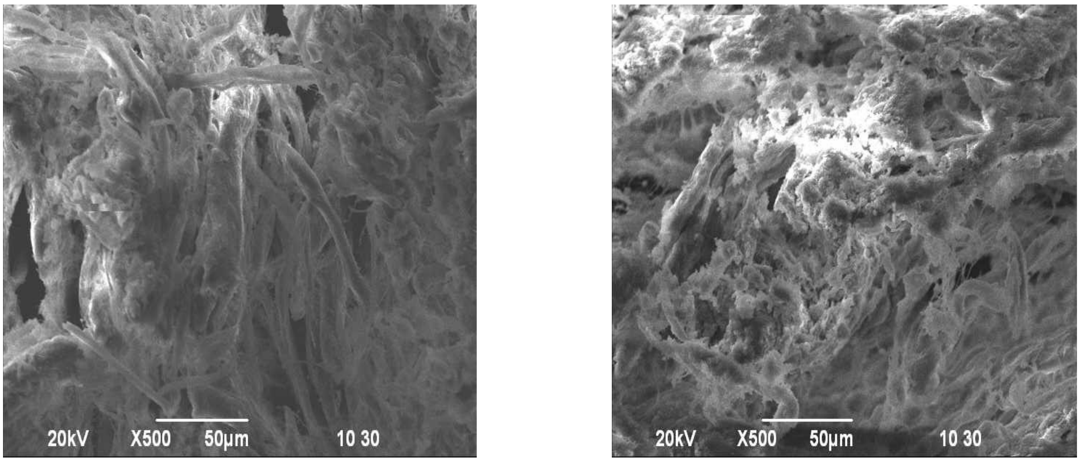
The electrons sharpen with atoms in the sample, creating various signals that contain information about the surface topography and composition of the sample. The quality of the leather sample (a) with the aid of ultrasound has a higher penetration of tannin compared to (b) without ultrasound.



(a) (b)

Figure 11. Quality of fibre structure (Surface view) with Ultrasound (a) and without Ultrasound (a)

Ultrasound aided in achieving almost complete penetration of tannin entirely a cross-section and surface area of leather, compared to tanning leather without ultrasound. Moreover, SEM images indicated that the tanning agent penetrated more uniformly throughout the inner portion of the leather sample, which was difficult for a conventional process (Figure 11). This improved the quality of the fibre structure of the finished product due to ultrasonic wave operation, whereas the fibre structure was ruptured because of the non-uniform motion of the drum, which had a significant impact on leather tanning [24].



(a) (b)

Figure 12. Quality of fibre structure (cross-section); With Ultrasound (a) and Without Ultrasound (b)

In terms of the cross-section view (Figure 12), the tanning agent penetrated the inner portion of the leather without rupture of leather fibre in (a), which was treated by ultrasound compared to (b).

Effect of Tannin Concentration on Tannin Uptake

In the ultrasound-assisted vegetable tanning process, a competitive study was conducted using 16%, 20%, and 24% guava leaf extract as the main tanning agent. This study indicated (Figure 13) that using 20% guava leaf extract was optimum for the vegetable tanning process having the effect of ultrasonic waves. Using 16% guava leaf extract had a lower penetration result (around 70% tannin uptake) and using 20% guava leaf extract showed much better tannin uptake capability (Around 92% tannin uptake). Again, 24% guava leaf extract gave a slightly higher penetration of tanning agent compared to the using 20%. Therefore, using 20% guava leaf extract has the best result in the amount of tannin penetration for tanning in the vegetable tanning process.

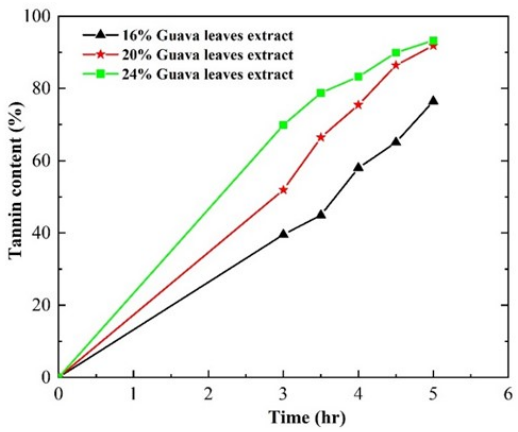
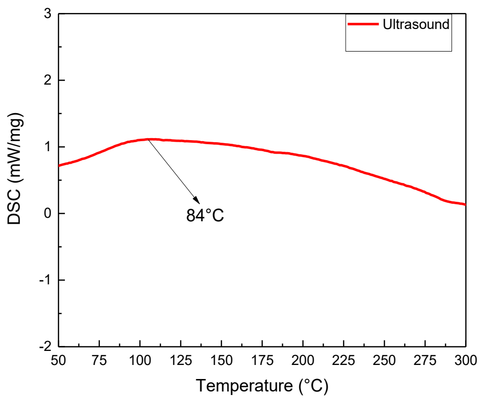
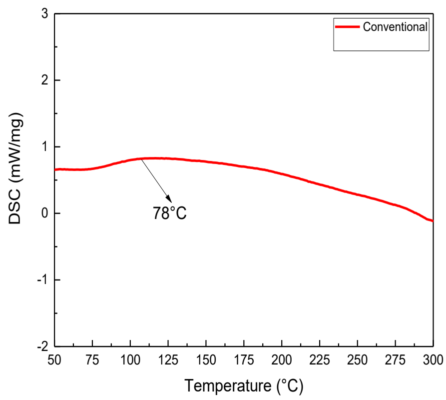


Figure 13. Effect of tannin uptake in various percentages of tanning agent with ultrasound

DSC analysis of tanned leather sample



(a)



(b)

Figure 14. DSC analysis of leather (a) Ultrasound vegetable tanned sample, (b) conventional tanned sample

The shrinkage temperature (Ts) of tanned leather is an effective indicator that can be used to assess the progress of tanning. From the results, it can be seen that the shrinkage temperature of the ultrasound-aided leather is 3-6 °C higher than those not subjected to ultrasonic waves. From the DSC study, the quality of leather tanned with ultrasound is not affected by the use of ultrasound. This is because the portion of tannin in the leather sample was increased after ultrasound treatment. In both Figure 14 (a) and (b), it is shown that the leather sample tanned with ultrasound had a lower DSC value than conventional vegetable-tanned leather and the value varied from 1 to 2 mW/mg each other. That means, ultrasound gives higher thermal stability and does not damage the inner fibre structure of the finished product [25].

Environmental benefits

Ultrasound technology offers several advantages for clean and green leather production. By optimizing the use of chemicals, such as tanning agents, ultrasound can reduce the overall pollution load associated with leather production. It's fascinating how technology can be harnessed to make industrial processes more sustainable. The experiment was carried out with a variation of time with different operating conditions to observe the uptake of tanning agents in vegetable tanning. It was proved that ultrasound reduced tanning agents and chemical consumption (Table 2) by a significant portion compared to conventional processes without ultrasonic waves.

Table 2. Amount of tanning agent (guava leaves extract) required in different operating conditions with and without ultrasound

Tanning time (hr)	% of frequency in 35KHz	Amount of tannin in the spent tanned liquor (ppm)		Reduction	% of Tannin Reduction
		With Ultrasound	Without Ultrasound		
5	100	595	1865	1270	68
4.5	100	621	1589	968	61
5	75	794	1913	1119	58
4	75	829	1731	902	52

Therefore, the Vegetable tanning process with the help of ultrasound operated at 5hr with 35 KHz was given the optimum reduction of tannin, which was 68% value reduction.

CONCLUSION

In this study, vegetable tannins were extracted, characterized and quantified from Guava leaves using the assistance of ultrasound. The effect of varying extraction time, ultrasonic power and solvent concentration was studied. Ultrasound made it possible to extract tanning materials in a short time and environment-friendly manner without applying heat. FTIR and ^{1}H NMR results confirmed the presence of different oxygen-containing organic groups. The application of the extracted tannins on samples has also been studied extensively. Ultrasound improved tannin content, tannin diffusion onto leather and thermal properties of tanned leather. The strong attachment of vegetable tannins reduced the number of unbound tannins in spent-tanned liquor reducing the environmental impact. From this study, Guava leaf extract has come out as a potential tanning agent alternative to conventional chemicals. Hopefully, this research will help reduce the use of chromium salts in leather tanning, which results in the abatement of environmental pollution.

Author Contributions

Alam NE and Mia MAS conceived the idea of the research. Mia MAS and Alam MZ coordinated all the laboratory work. Mia MAS, Malitha SB and Akter M conducted all the laboratory work and helped to prepare the manuscript. Mia MAS, Rahman M and Alam NE contributed to the manuscript preparation and conducted all the necessary corrections and revisions to it.

Conflicts of Interest

All authors declare no conflict or competing interests.

Funding

This research was funded by the DU 100 years project, University of Dhaka.

Hazards

All the chemicals, procedures or equipment that have been used in this research do not have any unusual hazards inherent in their use.

Availability of data

Data will be made available on request.

Acknowledgements

Bangladesh Council of Scientific and Industrial Research (BCSIR), Atomic Energy Centre, Dhaka, and Centre for Advanced Research in Sciences (CARS), University of Dhaka supported this research work.

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