COMPETENCY OF *Acacia mearnsii* TANNIN EXTRACT FOR VEGETABLE TANNING USING ULTRASOUND TECHNIQUE

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COMPETENCY OF *Acacia mearnsii* TANNIN EXTRACT FOR VEGETABLE TANNING USING ULTRASOUND TECHNIQUE

ABSTRACT. This article describes the potential of *Acacia mearnsii* tannin extract for environmentally friendly vegetable tanning of leather using ultrasound. Vegetable tanning is a versatile but time-consuming process in the leather industry, particularly for heavy leather which needs more than one week for tanning using natural tanning materials. So, it is significant to develop new eco-friendly techniques employing ultrasound to speed up the vegetable tanning process without affecting the quality of the finished leather. In this study, the effect of ultrasound in vegetable tanning has been evaluated to enhance the tanning process. The effects of various parameters for example tannin dose, tanning time, temperature, and variable frequencies were studied. Tannin uptakes and other thermal properties were also investigated.

KEY WORDS: vegetable tanning, *Acacia mearnsii*, ultrasound, thermal stability, optimization

CAPACITATEA DE TĂBĂCIRE VEGETALĂ A EXTRACTULUI DE TANIN DIN *Acacia mearnsii* UTILIZÂND TEHNICA ULTRASUNETELOR

REZUMAT. Acest articol descrie potențialul utilizării extractului de tanin din *Acacia mearnsii* la tăbăcirea vegetală ecologică a pielii folosind ultrasunete. Tăbăcirea vegetală este un proces versatil, dar consumator de timp în industria pielăriei, în special pentru pielea grea, care are nevoie de mai mult de o săptămână pentru tăbăcire folosind materiale de tăbăcire naturale. Prin urmare, este importantă dezvoltarea unor noi tehnici ecologice care utilizează ultrasunete pentru a accelera procesul de tăbăcire vegetală fără a afecta calitatea pielii finite. În acest studiu, s-a evaluat efectul ultrasunetelor asupra procesului de tăbăcire vegetală pentru a îmbunătăți procesul de tăbăcire. S-au studiat efectele diferiților parametri, cum ar fi doza de tanin, timpul de tăbăcire, temperatura și frecvențele variabile. S-au investigat, de asemenea, absorbția de tanin și alte proprietăți termice.

CUVINTE CHEIE: tăbăcire vegetală, *Acacia mearnsii*, ultrasunete, stabilitate termică, optimizare

CAPACITÉ DE TANNAGE VÉGÉTAL DE L'EXTRAIT DE TANIN D'*Acacia mearnsii* PAR TECHNIQUE À ULTRASONS

RÉSUMÉ. Cet article décrit le potentiel de l'extrait de tanin d'*Acacia mearnsii* pour le tannage végétal du cuir par ultrasons respectueux de l'environnement. Le tannage végétal est un processus polyvalent mais long dans l'industrie du cuir, en particulier pour les cuirs épais qui nécessitent plus d'une semaine pour être tannés à l'aide de matériaux de tannage naturels. Il est donc important de développer de nouvelles techniques écologiques utilisant les ultrasons pour accélérer le processus de tannage végétal sans affecter la qualité du cuir fini. Dans cette étude, l'effet des ultrasons sur le tannage végétal a été évalué pour améliorer le processus de tannage. Les effets de divers paramètres, par exemple la dose de tanin, la durée de tannage, la température et les fréquences variables, ont été étudiés. L'absorption des tanins et d'autres propriétés thermiques ont également été étudiées.

MOTS CLÉS : tannage végétal, *Acacia mearnsii*, ultrasons, stabilité thermique, optimisation

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INTRODUCTION

Vegetable substances that can convert animal skin/hide into leather are called tanning agents or tannins. Vegetable tannins are astringent bitter plant polyphenolic compounds that are known to precipitate proteins, amino acids, and alkaloids [1]. The term tannin is used to mean any large polyphenolic compound containing enough hydroxyl groups and other suitable groups capable of forming complexes with several macromolecules [2]. There are mainly two classes of tannins: condensed tannins (catechols) and hydrolysable tannins (pyrogallols). Condensed tannins are oligomers and polymers of flavan-3-ol flavonoid monomers and hydrolysable tannins are esters of sugar, mostly glucose, and gallic acid or gallic acid derivatives [3].

Acacia mearnsii (Wattle) bark extract is well known vegetable tannin and used industrially to produce vegetable-tanned leather. The wattle bark proanthocyanidin oligomers contain 5-deoxy extender units that render the interflavanyl bonds resistant to acid catalyzed hydrolysis [4]. The bonding processes of vegetable tanning agents to collagen occurring during the interaction of tannins with collagen has drawn much attention for a long time. The bonding of tannins to collagen produces leather, which is more elastic than raw hide and shows more resistance to water, temperature, and microorganisms. Such bonds are formed only if the tannin molecules are large enough to join neighboring collagen chains and have enough phenols to form crosslinks in several places [5]. Using ultrasonic waves in vegetable tanning is as a potential viable option for solving this issue and speed up the vegetable tanning by binding collagen with natural tannin materials. Ultrasound is a sound wave with a frequency of 20 kHz-10 MHz that is generally used to enhance physical and chemical processes [6]. The tanning ability and quality of the aqueous solutions of tanning extracts, as a rule, increase after such treatment. This also happens during the treatment of tanning agents from a certain type of raw material, e.g., leaves or barks of *Acacia mearnsii*. This is apparently due to oxidative condensation of catechols [7]. It was found that the tannin molecule cannot penetrate in the tanning process or poorly penetrates the raw hide if it is too large. Therefore, it does not bind collagen or binds it very weakly [8, 9]. Tannins of molecular weight from 500 to 3000, especially 1000, are most responsible for tanning by phenolic compounds [10].

In vegetable tannage of light leather, the intention is to fill up the collagen structure and to confer weight and firmness. In heavy leather, the filling action and weight increase are important [11]. Hydrolysable tannins are used in combination tannages where specifically fewer toxic metals like titanium other than chrome are used to produce superior leathers that are eco-friendly [12]. This practice has been viewed as one of the best available techniques that will lead to increased production of leather products, environmental sustainability, and proper use of available natural resources [13]. This study aims at developing sustainable alternative technology for vegetable tanning process using ultrasound with natural materials.

MATERIAL AND METHODS

Materials

Raw materials used in vegetable tanning were divided into two categories: primary raw materials and auxiliary raw materials. The primary raw materials are cow pickled pelt and *Acacia mearnsii*. To operate the tanning process, different types of chemicals (laboratory reagent grade) were used besides the primary raw materials. The percentage of all chemicals mentioned here are on the basis of weight of pickled pelt.

Tanning Procedure of Pickled Pelt

Vegetable tanning was carried out in an ultrasonic bath with the help of a 600 mL glass beaker emerged in water. To investigate the vegetable tanning process with variable frequencies 10 kHz, 20 kHz, 30 kHz, and 40 kHz were used for a period of 5 hours.

Sample Preparation

The 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). The weight and area of the samples were almost (4.0 g) similar.

Vegetable Tanning

Vegetable tanning was performed using ultrasound and conventional techniques. All samples were divided into two parts for carrying out experiments with ultrasound and conventional methods. In the first group, the pickled pelt samples were taken in a beaker that was placed in a water bath to maintain the temperature exposed to ultrasound. Then, the pelts were vegetable tanned with 16%, 20%, and 24% of *Acacia mearnsii* for 5 hours. At the beginning of tanning half of the *Acacia mearnsii* was added to the pickling liquor (150%) and the other half was added after 30 min and was sonicated. Then sodium formate (1.5% of sample) was added as a masking agent. The tanning bath was then basified using sodium bicarbonate which was divided into three equal portions and was added within an hour. pH of the liquor was monitored (4.8 to 5.0) during adding sodium bicarbonate.

The second part of the sample was tanned by conventional method where a stationary glass vessel and rotary drum were used instead of ultrasound. A hotplate stirrer was used to control the temperature. In vegetable tanning an initial pH of 4.8 to 5.0 and the temperature of 80-98 °C was maintained.

Upon completion of 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 air. Tanned leathers obtained in both ultrasound and conventional methods were then used for analysis and characterization.

Determination of Cr Uptake

The tanning content was determined by UV/visible spectrophotometry. The principle of this method is based on Lambert-Beer law, which shows that absorbance (A) is directly proportional to concentration for dilute solution. A SHIMADZU UV-1700 e spectrophotometer at 540 nm wavelength was used for the analysis. Once the characteristic peak was determined, the subsequent testing and calibration of this sample were conducted on this spectrophotometer. The data obtained from UV spectrophotometers was used to characterize the kinetics of tanning and to calculate the percentage of tannin uptake.

% tannin uptake at time 't' was calculated using the following equation:

$$\%Cr_{uptake} = \frac{Cr_i - Cr_f}{Cr_i} \times 100 \quad (1)$$

where Cr_i is the initial concentration of tannin liquor and Cr_f is the final concentration of tannin liquor.

RESULTS AND DISCUSSION

Vegetable Tanning of Leather

Vegetable tanning is a process that uses tannins derived from plant sources to convert raw animal hides into leather (Figure 1). *Acacia mearnsii*, also known as black wattle, is a tree species native to southeastern Australia. It is valued for its high tannin content in its bark. The use of ultrasound in vegetable tanning is an interesting aspect. Ultrasound can enhance the penetration of tannins into the hide, potentially improving the efficiency of the tanning process. The use of *Acacia mearnsii* tannin extracts and ultrasound in vegetable tanning suggests a specific research focus. This could include optimizing the tanning process for efficiency, exploring the quality of leather produced, or investigating the environmental impact of this method.

Figure 1. Vegetable tanned leather

Effect of Ultrasound on Tannin Uptake of Leather

Tannin uptake was studied during the tanning process for different tanning conditions. In this study, *Acacia mearnsii* tanning agent was used to perform the tanning operations with various frequencies for 5 hours. The tannin uptake of leather samples during vegetable tanning with ultrasound and conventional methods are shown in the Figure 2.

From the figure, it can be seen that the improvement of tannin uptake was more for the samples that had been tanned in presence of ultrasound than that of conventionally tanned samples. Ultrasound improved the penetration of tanning agents through the pores of collagen fibres and hence, enhanced the percentage of tannin uptake by the leather sample.

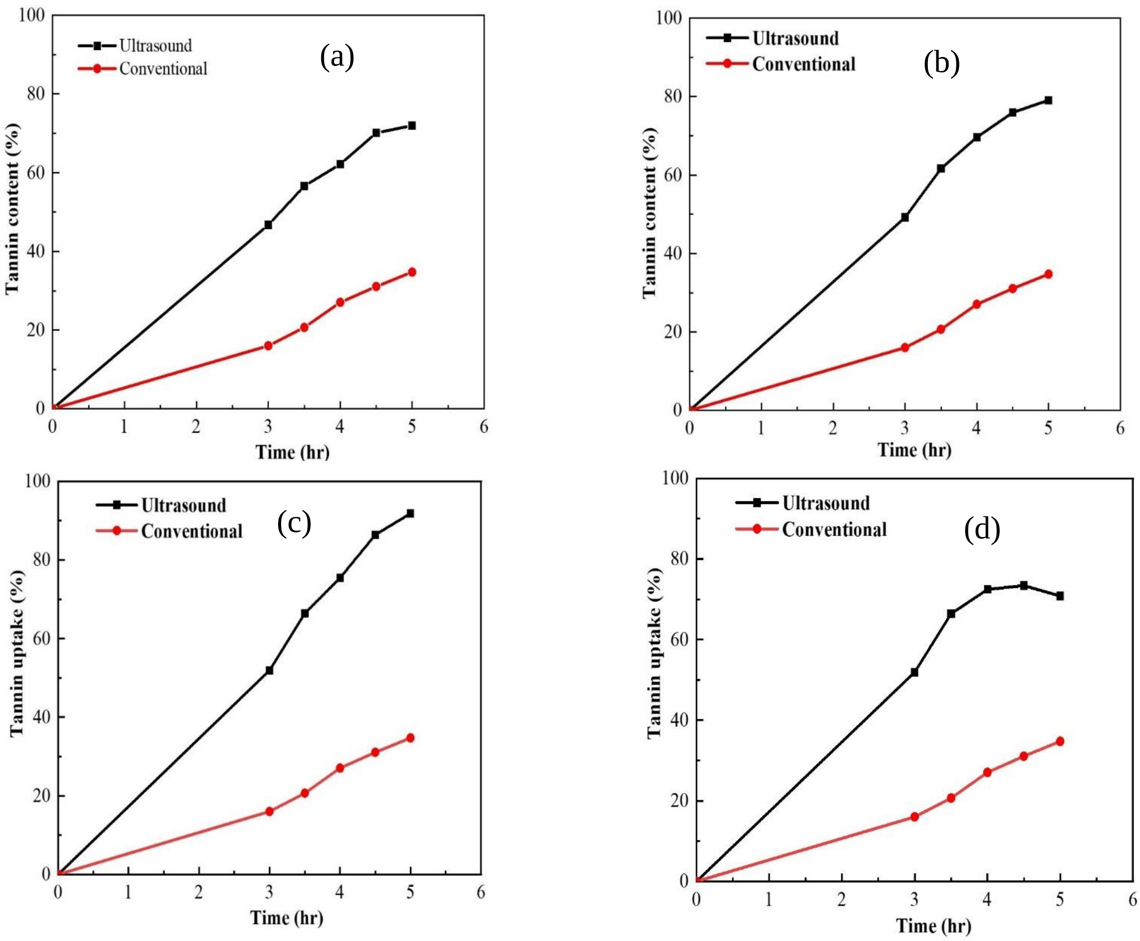

Figure 2. Tannin uptake of leather (%) as a function of time with ultrasound and conventional technique; ultrasound operated at frequency a) 10 kHz, b) 20 kHz, c) 30 kHz and d) 40 kHz

In this study, 71%, 79%, 91%, and 73% tannin uptakes were observed in case of tanning with ultrasound for tanning time of 5 hours using variable frequencies 10 kHz, 20 kHz, 30 kHz, and 40 kHz, respectively while only 34% tannin uptakes were observed in case of tanning with the conventional method for a tanning time of 5 hours. The results showed that the percentage of tannin uptake of the leather samples was increased up to 30 kHz operating frequency and then decreased. Because pickled pelts can absorb a certain maximum amount in a certain time and then it cannot absorb any tannin agent even the processing is carried out for longer time with higher frequency ultrasound. Thus, the use of 30 kHz US for 5 hours is the optimum condition for ultrasound-assisted vegetable tanning of leather.

Effect of Percentages of Tanning Agent on Tannin Uptake with Ultrasound

In the ultrasound-assisted vegetable tanning process, a comparative study was conducted using 16%, 20%, and 24% *Acacia mearnsii* as the main tanning agent. Figure 3 showed that using of 20% *Acacia mearnsii* was the optimum for the vegetable tanning process with ultrasonic waves. 16% *Acacia mearnsii* showed a lower penetration of tanning agents (< 15%) compared to using 20% Acacia. Again, 24% *Acacia mearnsii* gave a slightly higher penetration of tanning agents compared to using 20% of Acacia. Therefore, 20% of *Acacia mearnsii* was considered as the optimum composition of tanning agent in the vegetable tanning process.

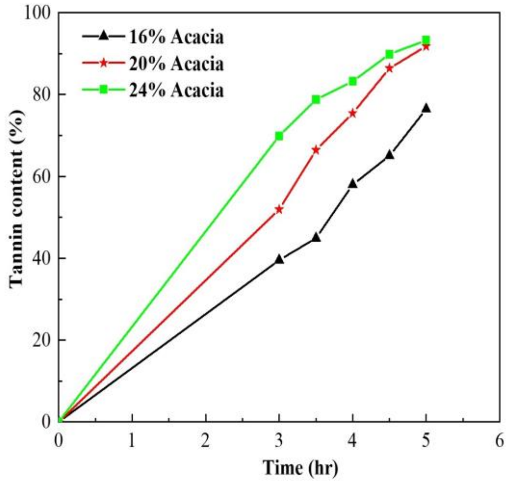

Figure 3. Effect of tannin uptake in various percentages of tanning agent within ultrasound

Thermogravimetric Analysis of Tanned Leather

The thermal degradation of leather tanned with and without ultrasound was compared to investigate the effect of ultrasound on leather tanning. The thermal degradation studies of the vegetable tanned leather samples were performed using thermogravimetric analyzer under N_2 atmosphere.

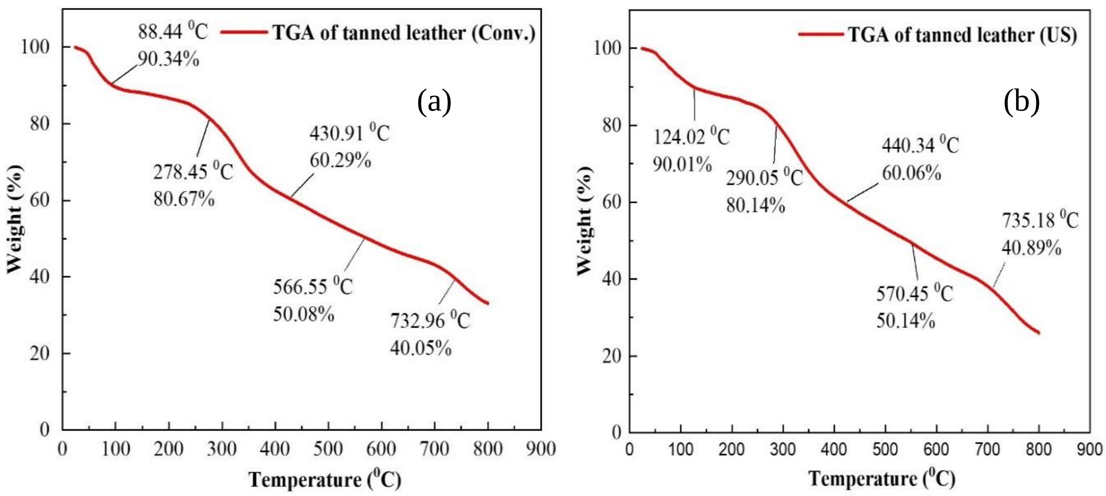

Figure 4. TGA of leather tanned with 10% tanning agent (*Acacia mearnsii*) for the total tanning time of 5 hours (a) with ultrasound, (b) conventional methods

Figures 4 (a) and (b) represent the thermograms of tanned leather with 10% tanning agent (*Acacia mearnsii*) for the total tanning time of 5 hours using ultrasound and conventional methods, respectively. It is seen from the Figures that temperature needed for 10%, 20%, 40%, 50%, and 60% loss of the weight of sample tanned with ultrasound were 124, 290, 440, 570, and 735 °C, respectively. On the other hand, 10%, 20%, 40%, 50%, and 60% loss of weight of the sample tanned with the conventional method under same tanning conditions were found at 88, 278, 430, 566, and 732 °C, respectively. These results reveal that thermal stability of the ultrasound-assisted vegetable tanned leather was greater than that of the conventionally tanned leather. It is assumed that the improvement of the thermal stability of ultrasound-assisted tanned leather occurs due to higher penetration of tanning agents through the pores and formation of tannin-collagen complexes which act as a barrier to the decomposition of leather samples.

DSC Analysis of Tanned Leather

The shrinkage temperature (Ts) of tanned leather is an effective indicator that can be used to evaluate the progress of tanning. Figure 5 showed that the shrinkage temperature of ultrasound-aided leather was higher than that of conventionally tanned leather. It is assumed that number of fixed tannin was increased due to ultrasound treatment. Thus the quality of fibre structure of tanned leather is not affected by the use of ultrasound.

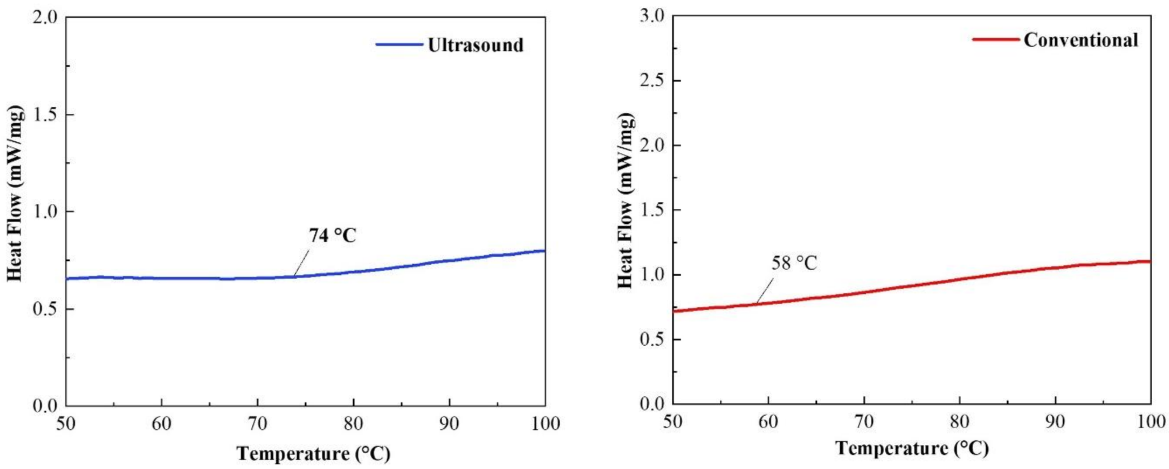

Figure 5. DSC thermograms of leather tanned with ultrasound and conventional methods

SEM Analysis of Tanned Leather

Fibre structure of the vegetable-tanned leather was observed by scanning electron microscope (SEM) and is shown in Figure 6. In micrographs, the darker the shade is, the higher the concentration of tannin agent. It can be seen that the tanned leather samples showed much uniform penetration of tannin agents in presence of ultrasound than that of tanned leather with the conventional method. In the process of ultrasound-assisted vegetable tanning the tanning agent completely penetrated into the full cross-section and grain surface of the leather.

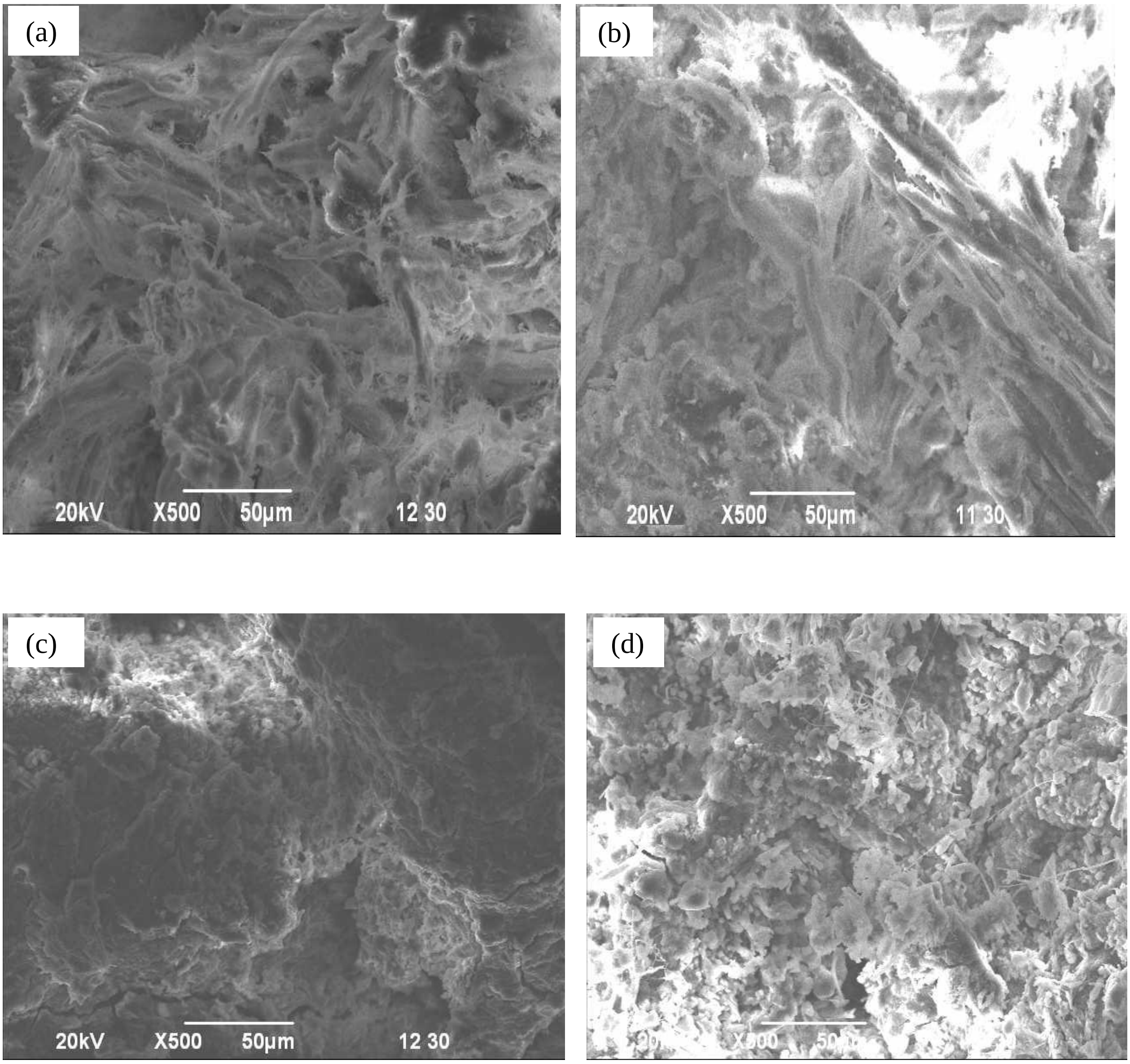

Figure 6. SEM images of cross-section of leather tanned with 10% tanning agent (a) with ultrasound, (b) without ultrasound; and surface view in presence of (c) ultrasound and (d) without ultrasound for 5 hours

The SEM images (Figure 6) also showed that the collagen fibrils are intact in the leather tanned with both ultrasound and conventional techniques. These results prove that the use of ultrasound in the tanning process did not damage the collagen fiber structures during the tanning period of 5 hours.

Diffusion of Tanning Agent

The images of the cross-sectional view of tanned leather obtained from the stereo microscope are shown in Figure 7. The depth of penetration of the tanning agent depends on the type of sample and the tanning agent used.

It is seen that in the case of ultrasound assisted vegetable tanning the degree of tanning agent penetration is higher compared to those samples tanned without ultrasound. It is due to the effect of acoustic cavitation which enhanced the diffusion rate of the tanning agent into collagen fibres. In addition, ultrasound aids in the uniform expansion of tannins by the inner part of the leather sample that is usually difficult in conventional method. Ultrasound helped to achieve a better penetration of tannin in the leather sample.

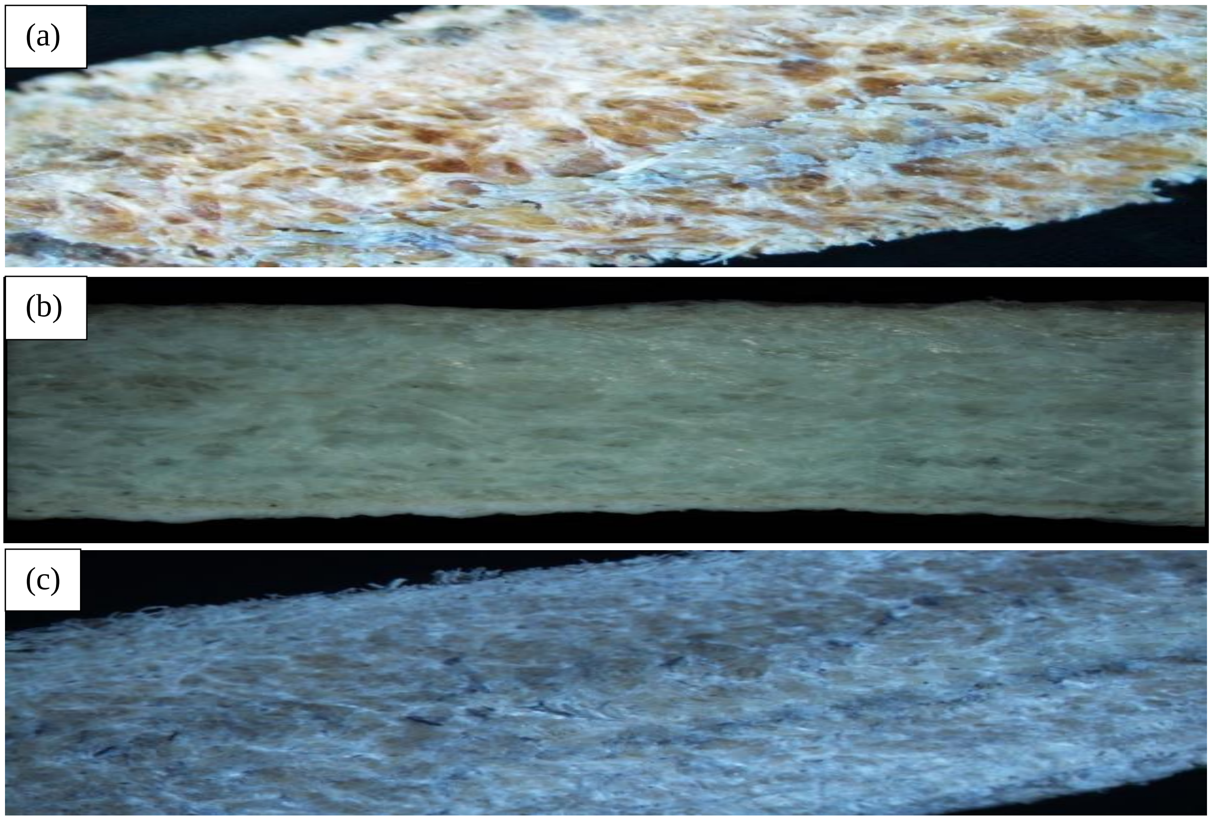

Figure 7. Photomicrograph (×25) of the cross-sectional view of (a) tanned leather in presence of ultrasound, (b) pickled pelt and (c) tanned leather with 10% tanning agent for total time of 5 hours in absence of ultrasound

Environmental Benefits

Ultrasound might be utilized as an efficient device for clean and green leather production. Ultrasonic waves can enhance tannin penetration through the raw hides even in static or ordinary room temperature using a high amount of tanning agent in vegetable tanning. The experiment was carried out with a variation of time under different operating conditions to observe the uptake of tanning agent in vegetable tanning. The results presented in the Table 1 revealed that ultrasound reduced the requirements of tanning agents' consumptions significantly. Therefore, vegetable tanning in presence of ultrasound with 30 kHz for 5 hours showed the optimum reduction (68%) of tanning agent.

Table 1: Amount of tannin in the spent tanned liquor

Tanning Time (hour)	Frequency (kHz)	Amount of tannin in the exhausted tanned liquor (ppm)		Reduction (%)
		Ultrasound	Conventional	
5	30	595	1865	68%
4	30	621	1589	61%
5	20	794	1913	58%
4	20	829	1731	52%

CONCLUSIONS

In the vegetable tanning application of ultrasound reduced the tanning time by 2 to 3 hours and increased the percentage of tannin uptake. Use of 30 kHz for 5 hours is the best condition for ultrasound-assisted vegetable tanning to afford the maximum percentage of tannin uptake. SEM and stereo microscopic images showed that the tanning agent penetrated more uniformly throughout the inner portion of the ultrasound-assisted tanned leather sample which was difficult in the conventional vegetable tanning. Again, thermal characterization of ultrasound-assisted vegetable tanned leather and conventionally vegetable tanned leather reveal that the thermal stability of ultrasound-assisted tanned leather is much better than those of conventionally tanned leather. The thermal stability of ultrasound assisted tanned leather was far better than that of conventionally tanned leather. It is also observed that vegetable tanning with the help of ultrasound of 30 kHz for 5 hours showed the reduction of tannin of 68%.

Authors' Contribution Statement

Professor Dr. Md. Zahangir Alam, Professor Dr. Md. Nurnabi and Dr. Md. Abu Sayid Mia planned and designed the research. Dr. Md. Abu Sayid Mia and Shamima Yeasmin conducted the experiments and wrote the manuscript. Professor Dr. Md. Zahangir Alam and Professor Dr. Md. Nurnabi supervised the whole research and revised the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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