

ULTRASOUND ASSISTED DIFFUSION IN VEGETABLE TANNING FOR LEATHER PROCESSING

by

V. SIVAKUMAR*, K. GOPI, M.V. HARIKRISHNAN, M. SENTHILKUMAR, G. SWAMINATHAN

Chemical Engineering Division, Central Leather Research Institute, Council of Scientific and Industrial Research (CSIR)

ADYAR, CHENNAI – 600020, INDIA

P.G. RAO

North East Institute of Science and Technology (CSIR)

JORHAT, ASSAM - 785006, INDIA

ABSTRACT

Vegetable tanning is one of the more versatile tanning methodologies involving natural materials. The problem associated with this tanning method is that it takes longer time for diffusion of vegetable tanning agents (VTA) through the pelt matrix. Therefore, there is a pressing need to transform this traditional eco-friendly tanning process into a tanner friendly efficient methodology by way of augmentation techniques such as the use of ultrasound. In the present paper, influence of ultrasound on vegetable tanning process has been studied. The influence of important process parameters such as process time, ultrasonic power, pre-tanning on VTA uptake has been investigated. The effect of ultrasonic power on shrinkage temperature of tanned leather has also been studied. The results indicate that there is a significant enhancement in vegetable tanning process due to the use of ultrasound. There is about 30-40% increase in %uptake of VTA due to the use of ultrasound for 120 – 210 watts. In order to find out the possible mechanism for the enhancement with ultrasound, effect of pre-sonication of substrate (pelt matrix) as well as substance (VTA) has been studied. There is an appreciable reduction in the particle-size of VTA due to sonication prior to tanning process aiding penetration. Diffusion coefficient (D) of VTA during the tanning process has been calculated from the experimental data which indicates nearly two fold increase in the D value ($2.64 \times 10^{-5} \text{ cm}^2/\text{sec}$) due to ultrasound under the given process conditions. Therefore, ultrasound application in vegetable tanning process could improve the diffusion rate leading to significant savings in process time and enhancement in quality of the tanned leather. This methodology can be easily adopted in existing paddle or tanning pit systems for large scale production. Hence, this novel technique is a viable option for tanners in near future.

ABSTRACTO

El curtido vegetal es una de las tecnologías de curtición más versátiles que impliquen empleo de materiales naturales. El problema asociado con este método de curtición es que tarda más tiempo para la difusión de agentes curtientes vegetales (VTA) a través de la matriz de la piel. Por lo tanto, hay una necesidad apremiante de transformar este tradicional proceso ecológico de curtido en una metodología eficiente adoptable por el curtidor, por medio de técnicas de intensificación como el uso de ultrasonido. En el presente trabajo, la influencia del ultrasonido en procesos de curtido vegetal se ha estudiado. La importante influencia de los parámetros del proceso, como el tiempo de proceso, energía ultrasónica, la asimilación de los curtientes vegetales por el precurtido, ha sido investigada. El efecto de la potencia de ultrasonido en la temperatura de encogimiento del cuero curtido también ha sido estudiado. Los resultados indican que hay una mejora sustancial en procesos de curtido vegetal debido al uso de ultrasonido. Hay alrededor de 30-40% de incremento en el porcentaje de absorción de los curtientes vegetales debido al uso de ultrasonido en 120-210 vatios. Con el fin de averiguar el posible mecanismo para la mejora con ultrasonido, el efecto de pre-sonoridad de sustrato (matriz de la piel), así como la sustancia (VTA) ha sido estudiado. Existe una apreciable reducción en el tamaño de partículas de VTA debido al ultrasonido previo a la penetración en los procesos de curtido. El coeficiente de difusión (D) del VTA que durante el proceso de curtido se ha calculado a partir de los datos experimentales indican que se incrementa el valor de D casi dos veces ($2.64 \times 10^{-5} \text{ cm}^2/\text{seg.}$) debido al ultrasonido bajo las condiciones de proceso establecidas. Por lo tanto, la aplicación de ultrasonido en proceso de curtido vegetal podría mejorar la tasa de difusión que conduzcan a un ahorro significativo en tiempo de proceso y la

*Corresponding author - Email: vsiva1clri@gmail.com

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mejora de la calidad del cuero curtido. Esta metodología puede ser fácilmente adoptada en aspás o piletas de curtido existentes para producción a gran escala. Por lo tanto, esta nueva técnica es una opción viable para los curtidores en un futuro próximo.

INTRODUCTION

Vegetable tanning is one of the oldest methods of eco-friendly tanning process carried out using plant materials containing active ingredients called as tannins. The vegetable tannins are water-soluble polyphenolic compounds having molecular weight in the range of 500 – 3000 Daltons^{1,2}. Based on their chemical structure, the vegetable tannins are classified as hydrolysable type (e.g. Myrobalan, Sumac etc.) and condensed type (e.g. Wattle, Quebracho etc.), which are condensed proanthocyanidins based on flavonoids and poly hydroxy flavan, used as the main tanning agent. One of the main problems associated with vegetable tanning is that it takes more time for penetration of the tanning agents through the pelt. The sequence of transport and various factors affecting diffusion in tanning process has been explained earlier³.

Because of stringent environmental norms concerning the discharge of process industries such as leather industry, eco-friendly approaches in processing are gaining importance. The application of ultrasound in process industries such as chemical, textiles and leather has high potential. The application of ultrasound in leather processing has been reviewed in detail earlier^{4,5}. Studies on influence of ultrasound on beam house and tanning operations⁶⁻⁹, dyeing¹⁰⁻¹⁴, and fatliquoring^{15,16} have been reported. Our earlier studies demonstrated ultrasound helps to improve the efficiency of the soaking process⁶, properties of the dyed leathers¹⁰, diffusion rate of dye¹¹, and reduce the unspent dye in the spent liquor for a given process time, thereby reducing pollution load¹² and positive influence of power ultrasound on dye penetration in leather dyeing made through photo micrographic analysis¹³. Enhancement of fatliquoring process and better emulsification of vegetable fatliquor due to ultrasound has also been reported^{15,17}. Our recent publication clearly explains the diffusion phenomena through skin or leather matrix in leather processing and influence of ultrasound on the same, taking into account of porosity and tortuosity of the matrix¹⁸.

Use of power ultrasound

Ultrasound may be broadly classified according to frequency range as power ultrasound (20 kHz to 100 kHz) and diagnostic ultrasound (1 to 10 MHz)¹⁹. When a liquid is agitated by ultrasound, micro bubbles can appear, grow and oscillate extremely fast and even collapse violently if the acoustic pressure is high enough. These collapses occurring near a solid surface will generate micro jets and shock waves²⁰. Moreover, in the liquid phase surrounding the particles, high micro mixing will increase the heat and mass

transfer and even the diffusion of species inside the pores of the solid²¹.

Ernst and Gutmann²² in 1950 conducted experiments on calf pelts in vegetable tanning using ultrasound with oscillator output from 17.5 to 25 (W). Experiments were carried out with wattle and mimosa liquors for periods from 1 - 3 hours. A study of irradiated sections showed that the tanning agent had penetrated deeply as compared to non-irradiated blanks. They also explained that the depolymerizing action of ultrasound on the highly polymerized and coiled-up structure of tannins facilitates penetration of the tanning agent into the pelt.

In 1954, Fridman et al. completed vegetable tanning in the presence of ultrasound in 18-hours compared with 114-hours in the absence of ultrasound²³. Karpmann²⁴ in 1962 irradiated ultrasound (400W and 300kHz) in liquid vegetable tan liquor and observed an increase in tannin content from 49.6% to 51.4% after 90-minutes irradiation and decrease in viscosity. Our recent study indicates significant 3-5 fold improvement in the extraction of vegetable tannins from myrobalan nuts and the extract thus prepared has better application in tanning²⁵.

Although, some earlier studies on ultrasound aided vegetable tanning have been reported, systematic investigations with respect to enhancement of vegetable tanning using ultrasound has not been reported so far with suitable mechanism. Therefore, the present study has been focused with the following objectives,

- Study the effect of ultrasound on vegetable tanning as compared to stirring effect as a control process.
- Study the influence of process parameters such as ultrasonic power, time, as well as effect of pre-tanning agent
- Study the influence of pre-sonication of the substrate (pelt) as well as substance (vegetable tanning agent) in the subsequent tanning process
- Study the effect of ultrasound on the particle-size distribution of tanning agent.

Need for ultrasound in vegetable tanning: Diffusion Rate Enhancement

The skin/hide matrix is composed of a three-dimensional weave of collagen fiber bundles. The diameter of the collagen fiber-bundles varies from 0.01-0.05 cm. Leather processing involves diffusion of various chemicals through the pores of the hide/skin, where the pore size ranges from 5×10^{-8} to 1.5×10^{-2} cm^{3,26-27}. The diffusion in conventional processing is achieved by drumming/paddle action. Considering the example of vegetable tanning process, the rate of diffusion of vegetable tanning agents through the pelt matrix depends on various parameters¹⁸ and given by the Equation 1,

$$R_{Diff} = f(C_{vb}, pH, B_{vf}, T, P_a, M) \quad (1)$$

Where, C_{yb} - Concentration of tanning agent in the vegetable tanning bath; pH - pH of the pelt, B_{vf} - Degree of binding and adsorption of tanning agents on pelt fiber; T - temperature of the tanning bath; P_a - Particle /aggregate size of the tanning agent, M - mechanical agitation.

Some of the parameters in Equation 1 such as pH and B_{vf} are fixed for a given pelt matrix in the conventional tanning process. The parameter T has constraint due to shrinkage temperature restriction of the pelt. P_a may be altered carefully during the process facilitating the diffusion process through some methods such as ultrasound. The parameter M may not be increased due to possible damage to the pelt. Hence, additional driving force in the form of ultrasound is employed with expectations to increase the diffusion rate of tanning agents through the pelt, reduce the process time and improve the quality of tanned leather.

EXPERIMENTAL

Ultrasonic equipment set-up

Ultrasonic tanning experiments were carried out using ultrasonic probe (VCX 400, Sonics and Materials, USA, 20 kHz & 0-400 W) in a jacketed glass vessel with provisions to set required output power and time as described earlier¹¹. The temperature of the process can be controlled by circulating water through the jacketed process vessel. The control experiments for the ultrasound tanning were carried out in magnetic stirrer equipment with a provision to adjust the speed of stirring.

Materials and Methods

(All chemicals are based on $1.2 \times$ pickled pelt weight basis)

Tanning experiments were carried out using pickled buffalo pelt with pH ~ 5.0 . Sample pieces typically of size 6×6 cm (for ultrasound & control process) have been cut from the butt portion of the pelt parallel to the backbone following the IUP/1 prescribed method of sampling and analysis²⁸. The weights of the two samples were recorded individually. Then the pelts were treated with 20% (w/w) of wattle tannin extract GS Powder (Tanext chemicals, Mettupalayam, Tamil Nadu, India). 400% distilled water was used for the experiments. 20% wattle powder was added in two installments at 1 hour interval of time. The process temperature was maintained throughout the tanning operation at 35°C. The tanning process was carried out for 5 hours time. Ultrasonic process was compared with control experiment using magnetic stirring (MS control). Sample spent tan liquor was collected for analysis and a small rectangular portion was cut from the pelt for shrinkage temperature analysis. Then the treated sample leathers were tested for shrinkage temperature (T_s) after 5 hours of tanning.

Process Parameters Studied

Effect of Ultrasonic Output Power

Experiments were conducted with variation in ultrasonic output power such as 60, 80, 120, 130 and 210 W. The kinetics of tanning agent uptake has been monitored for every hour. At the end of 5 hours spent tan liquor and leather samples were taken for analysis.

Effect of pre-tanning agent

The influence of pre-tanning agent has been studied using Basyntan P (BASF Chemicals Ltd.). 3% Basyntan P and 400% water has been used in the process. The pre-tanning solution along with pelt was sonicated at 80 W for 30 minutes. Then half of the amount of the wattle powder is added. The sonicator was again run for an hour. After which the remaining wattle powder was added. At the end of 5 hours spent tan liquor sample was taken for analysis.

Effect of ultrasound on tanning substance (Wattle: GS powder)

100 ml of 5% (w/v) tannin solution was initially sonicated with 80 W for 1 hour. The pelt was then immersed in the sonicated tannin solution (with wattle 20% w/w of pelt) and tanning was carried out for 5 hours in the magnetic stirrer set-up. Another tanning experiment was carried out in magnetic stirrer equipment with un-sonicated tanning solution as a control process. The effect of particle size of the tannins used for tanning has also been studied.

Effect of ultrasound on substrate (pelt matrix)

The effect of pre-sonication of pelt on subsequent tanning process was studied. The pelt was immersed in 400% (based on pelt weight) brine solution 10% (w/v). After 1 hour sonication (80 W) of the pelt, tanning was carried with 20% wattle powder for 5 hours in the magnetic stirrer set-up. The control for this experiment was carried out in magnetic stirrer equipment with an un-sonicated normal pelt. At the end of 5 hours spent tan liquor sample was taken for analysis.

Diffusion coefficient

If a semi-infinite porous solid such as pelt matrix is brought into contact with a liquid containing diffusible substance such as vegetable tanning material with initial concentration of y_0 , then the total amount of VTA (F) diffused across a unit area of leather at time ' t ' is given by^{29,30} the Equation 2,

$$F = 2y_0 \sqrt{\frac{Dt}{\pi}} \quad (2)$$

From the slope of the graph with Equation 2, apparent diffusion coefficient of vegetable tanning agents though the pelt matrix has been calculated adopting the procedure applied for leather dyeing process as published earlier^{10,11}. Enhancement factor in diffusion coefficient (D) due to the use of ultrasound (us) as compared to magnetic stirring process (ms) was calculated as given in Equation 3,

$$\epsilon_{us} = \frac{D_{us}}{D_{ms}} \quad (3)$$

Analytical methods

Total tanning agent (solids) uptake

Spent tan liquor samples collected at regular time intervals during the course of the vegetable tanning process from both ultrasound and control experiments were taken separately in clean, dried and weighed glass Petri dishes with suitable marking. The samples were dried in a hot-air oven till all the water evaporated and only the extract was left. The dishes were then cooled in a desiccator and then weighed. The drying, cooling and weighing procedures were repeated to get the constant weight and the weight of the extract in the spent liquor was determined. The % uptake of vegetable tanning agent (VTA) in the pelt for a given time t has been calculated using the Equation 4,

$$\% \text{ Uptake of VTA in the pelt at time 't'} = \frac{\text{VTA offered in g} - \text{VTA in spent liquor in g}}{\text{VTA offered in g}} \times 100 \quad (4)$$

$$\begin{array}{l} \text{Increase in \% uptake} \\ \text{of tanning agent due} \\ \text{to ultrasound} \end{array} = \begin{array}{l} \% \text{ Uptake of tanning agent} \\ \text{for US process} - \% \text{ uptake} \\ \text{in MS control process} \end{array} \quad (5)$$

Shrinkage temperature (T_s) analysis of tanned leather

Shrinkage temperature, which is a measure of degree of tanning, was analyzed for tanned pelt. The measurements were performed using shrinkage tester as per IULTCS official testing method³¹ IUP 16.

Particle size analysis of vegetable tanning agent

The particle size of wattle tanning agent one of the important parameter which influence diffusion has been determined using Light scattering measurements using Malvern Instruments—Zetasizer 3000 HSA. 1% (w/v) solution of wattle GS powder was sonicated in the ultrasonic tank (33 kHz, 150 W) as well as in ultrasonic probe (10 kHz, 80 W) for 1 hour. Control sample was prepared and kept under similar conditions without sonication. Then the particle size of vegetable tanning agent was analyzed after suitable dilution of the sample.

Analysis of cross section of tanned leather - penetration of VTA

Visual analysis of cross section of tanned leather was made to check the penetration of VTA in the tanning process (20% GS powder) with ultrasound, 80 W and compared with magnetic stirring process.

RESULTS AND DISCUSSIONS

Effect of ultrasonic power

Influence of ultrasound (60 -210 W) on the uptake of vegetable tanning agent as compared to the MS control process during the course of the tanning process is shown in Figure 1. The results indicate that increase in the %uptake of tanning agent with increase in ultrasonic power from 60 –

210 W. There is a significant improvement (30-40%) in the uptake due to ultrasound (120 -210 W). % uptake of VTA with various ultrasonic powers as compared to magnetic stirring process is shown in Table I. There is an increase in T_s of tanned leather with ultrasonic output power due to increase in VTA uptake and reach 85°C for 210 W for 5 hours tanning process.

Effect of pre-tanning agents

Effect of 3% pre-tanning agent Basyntan P on tanning with 20% Wattle GS powder was studied and the results are shown in Table II. It can be seen that at the end of 5 hours, the % uptake of tanning agents in the tanning carried out with pre-tanning agents using ultrasound, 80 W shows nearly 6% increase as compared to magnetic stirring process. It is interesting to note that the use of pre-tanning agent gives nearly 24% and 22% increases in the uptake as for ultrasonic and magnetic stirring process respectively.

Effect of pre-sonication of substance (wattle GS powder)

Effect of pre-sonication (80 W) of wattle GS powder solution on uptake of tanning agent with 20% GS powder on tanning for 5 hours is shown in Table III. The results indicate that there is an increase in uptake of tanning agents due to pre-sonication. The results also indicate that there is no adverse effect of ultrasound on the tanning agent structure under the given process conditions. There is a significant reduction of mean particle size of synthetic wattle GS powder, from 339.2 nm (100%) to 280.7 nm (97%) with ultrasonic tank (150 W, 33 kHz); to 192.9 nm (60%) with ultrasonic probe 80 W as shown in Figure 2. Influence of ultrasound on particle-size distribution of tanning agent prior to tanning process aid in penetration through the pelt matrix.

Effect of pre-sonication of substrate (pelt)

Effect of pre-sonication of substrate (pelt) for 1 hour with ultrasound, 80 W on subsequent tanning with 20% wattle GS powder for 5 hours with respect to % uptake of tanning agent is shown in Figure 3. The results show that pre-sonicated pelt gives 4.8% increase in the %uptake of tanning agent for 5 hours. The results also indicate pre-sonication of pelt has not resulted in any adverse damage to the pelt matrix and provides only some positive influence on tanning agent uptake. Therefore, the pre-sonication experiments on substrate further signify that ultrasound effect is realized in a better manner while diffusion in tanning process takes place while pelt is under the ultrasonic field, which may result in reversible pore-size changes aiding penetration of vegetable tanning agents though the pelt matrix.

Diffusion coefficient

As mentioned in the Equation 2, graph was drawn between $\sqrt{t}$ ($s^{0.5}$) in x -axis and the amount of tanning agent uptake in per unit area of leather (g/cm^2) at time ' t ' in y -axis. Experimental data for vegetable tanning with ultrasound, 210 W have been used in comparison with magnetic stirring process for drawing the graph and shown in Figure 4. Graph

drawn gives straight line passing through the origin with equation $y = kx$ was obtained,

Where slope of the Equation 2, $k = 2y_0 \sqrt{\frac{D}{\pi}}$ (6)

Since the initial concentration of vegetable tan liquor employed in the tanning process $y_0 = 0.05$ g/cc, the Equation 2 becomes, Amount of tanning agent uptake per unit area of the pelt (gcm^{-2})

$$= 2 \times 0.05 \times \sqrt{\frac{D}{\pi}} \quad (7)$$

Where slope of the Equation 7, $k = 2 \times 0.05 \times \sqrt{\frac{D}{\pi}}$

Therefore, with the slope of the graph drawn (Figure 4) diffusion coefficient was calculated and shown in Table IV. The diffusion coefficient so calculated represents the apparent diffusion coefficient of vegetable tanning agent through the skin/hide/pelt matrix. The enhancement factor calculated ε_{us} shows 2.3-fold increase in the diffusion coefficient due to ultrasound as compared to magnetic stirring process.

Analysis of cross section of tanned leather

Cross sections of tanned leathers were visually analyzed for the penetration of VTA after 5 hours tanning with 20% GS powder. The cross section of leather tanned with ultrasound, 80 W show complete penetration throughout the cross section (Figure 5a, as inferred from brown coloration due to VTA) as compared to partial penetration for middle layer for magnetic stirring process (Figure 5b) under the given process conditions.

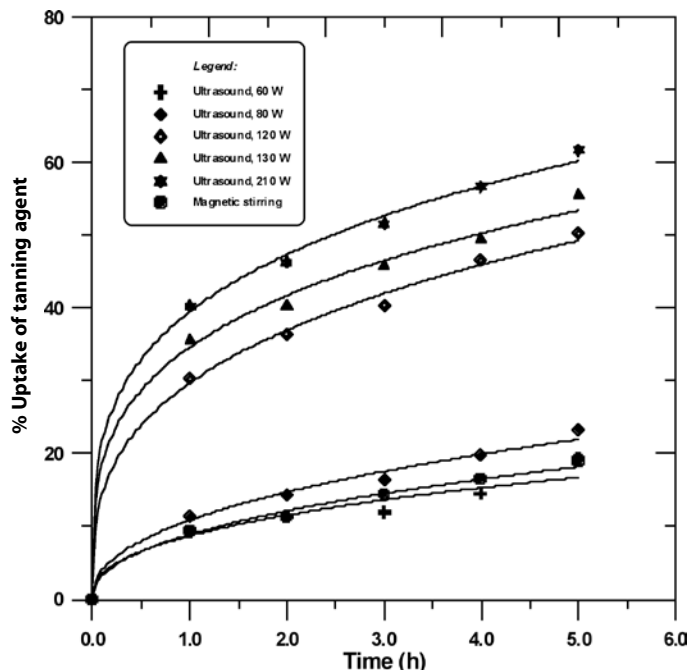


Figure 1: Influence of ultrasound with various powers on the uptake of vegetable tanning agent as compared to the magnetic stirring process using 20% wattle GS powder for 5 hours.

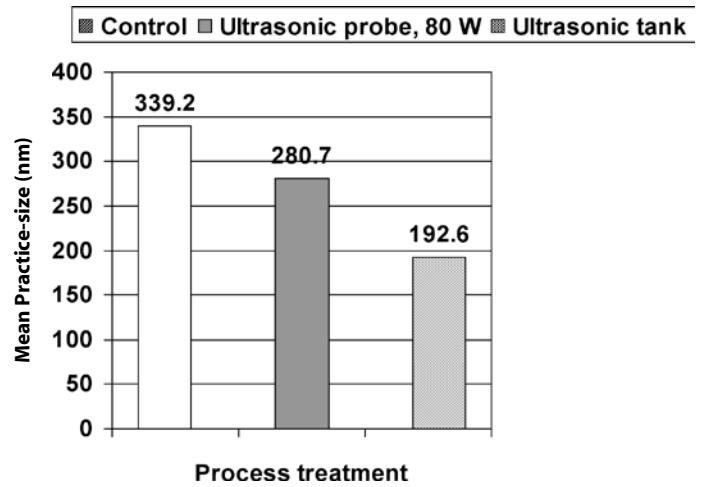


Figure 2: Effect of sonication for 1 hour on particle-size distribution of wattle GS powder 1% (w/v) solution using different ultrasonic equipments.

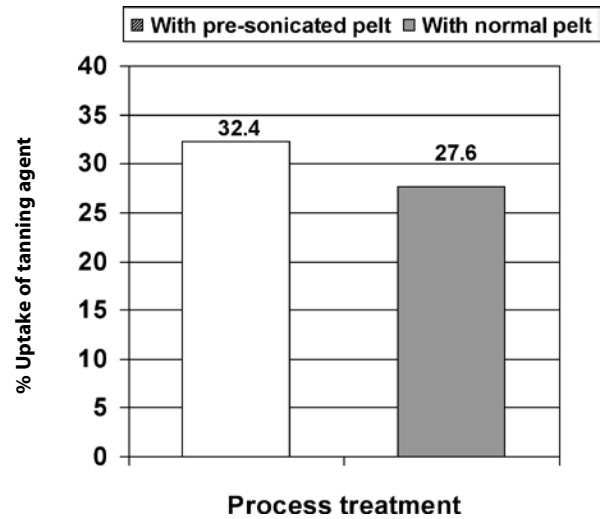


Figure 3: Effect of pre-sonication of substrate (pelt) for 1 hour with ultrasound, 80 W on subsequent tanning with 20% wattle GS powder for 5 hours.

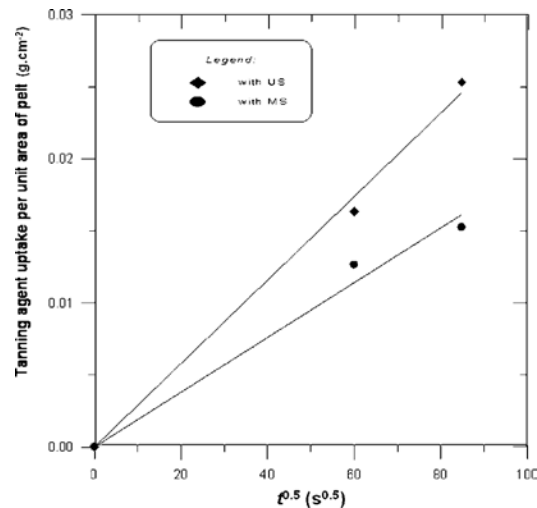


Figure 4: Graph drawn between vegetable tanning agent uptake per unit area of the pelt (gcm^{-2}) vs square root of time ($s^{0.5}$) with ultrasound, 210 W (US) and magnetic stirring process (MS).

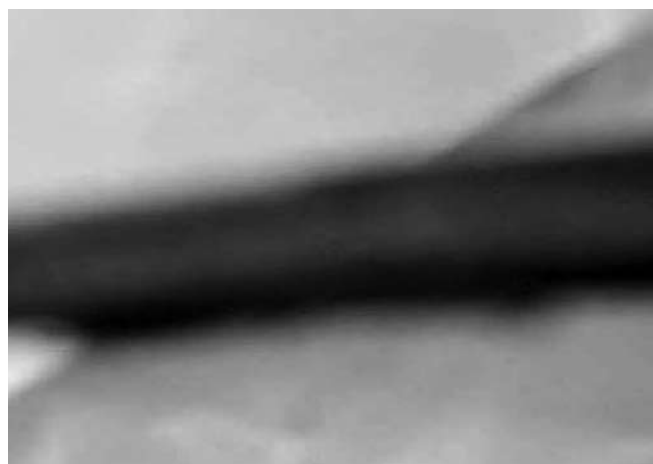


Figure 5a: Photograph of the cross section of leather after 5 hours tanning with 20% GS powder with magnetic stirring.

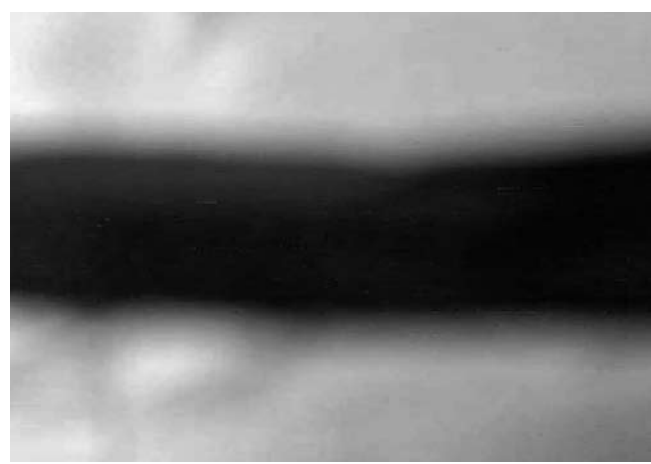


Figure 5b: Photograph of the cross section of leather after 5 hours tanning with 20% GS powder with ultrasound, 80 W.

TABLE I

% uptake of tanning agent and shrinkage temperature of tanned leather with various ultrasonic powers as compared to control process with 20% Wattle GS powder for 5 hours

Process	% uptake	Shrinkage temperature T_s (°C)
Ultrasound, 60 W	19.3	-
80 W	23.2	-
120 W	50.3	82
130 W	55.5	84
210 W	61.7	85
Magnetic stirring control	18.9	-

TABLE II

Effect of 3% pre-tanning on tanning agent uptake with ultrasound, 80 W as compared to control process with 20% Wattle GS powder solution for 5 hours

Parameter	With pre-tanning agent		Without pre-tanning agent	
	Ultrasound	Magnetic stirring	Ultrasound	Magnetic stirring
%Tanning agent uptake	47.6	41.4	23.2	18.9

TABLE III

Effect of pre-sonication (80 W) of wattle GS powder solution on tanning agent uptake with Wattle GS powder solution 20% (*w/v on pelt wt.*) for 5 hours

Parameter	Process	
	Pre-sonication	Magnetic stirring (control)
%Tanning agent uptake	20.35	19.65

TABLE IV
Improvement in apparent diffusion coefficient of vegetable tanning agent
through the pelt matrix as compared to MS control process

Process	Diffusion coefficient (cm ² sec ⁻¹)	Enhancement factor ϵ_{us}
Ultrasound, 210 W	2.64×10^{-5}	2.34
Magnetic stirring	1.13×10^{-5}	

CONCLUSIONS

The results indicate that there is a significant 30-40% increase in %uptake of vegetable tanning agent as well as in the T_s of the tanned leather due to the use of ultrasound, 120 – 210 W for 5 hours process time. There is a significant improvement in the uptake of tanning agents due to pre-tanning operation carried out for both ultrasonic as well as MS control process. Positive influence of ultrasound (4.4% increase in % uptake) has been found on pre-sonication of substrate. Particle-size distribution analysis of wattle GS powder show significant reduction in mean particle-size of the tanning agent with sonication aiding penetration. There is an appreciable 2.3-fold improvement in apparent diffusion coefficient (D) of tanning agents due to the use of ultrasound under the given process conditions. Vegetable tanning processes, involve diffusion of substances with particle-size ranging from 100-500 nm binding to collagen fibers. These may block the pores within the skin/hide/pelt matrix and further hinder the subsequently diffusing substances. The influence of ultrasound on the particle-size distribution of vegetable tanning material on one hand and reversible matrix pore-size changes on the other may have an important role on the diffusion rate through the pelt matrix.

Hence, the use of power ultrasound has significant improvement in the diffusion rate of vegetable tanning process, even under static and room- temperature conditions. Therefore, ultrasound aided processing technique could be adopted even in the existing vegetable tanning pits or paddles. Therefore, use of ultrasound in vegetable tanning process is a viable eco-friendly advantageous option for tanners in near future.

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