Ultrasound-assisted Process Intensification in Leather Making: Diffusion Rate Enhancement in Retanning Process

by

Venkatasubramanian Sivakumar,* P.T. Anusha, Radhika Narayan and M. Shravya
Chemical Engineering Division, CSIR - Central Leather Research Institute
Adyar, Chennai - 600 020, India.

Abstract

Retanning is one of the essential steps in leather processing. It follows the primary tanning process, utilizing synthetic tanning agents (syntans) in order to impart certain functional properties to the final leather. This research study aimed at investigating the effect of ultrasound (US) on the uptake of syntans in the retanning process as compared to magnetic stirring (MS) process control. Different types of syntans based on phenolic, melamine resin and acrylic compound were investigated. The influence of process parameters such as US power, process time, float, syntan offer, US pulse mode were studied. The effects of pre-sonication of substrate (leather) as well as substance (syntan solution though particle size analysis) were also investigated. There was the possibility of about 10% to 60% increase in exhaustion due to the use of US over MS for different syntans under various process conditions. The Apparent Diffusion coefficient (*D*) of syntan through the leather matrix was calculated from the experimental uptake data, which indicates significant improvement (~1.5 times) in the *D* value due to US over MS under the given process conditions. Therefore, the present study clearly indicates positive influence of ultrasound on diffusion of these special types of organic compounds (syntans) through more complex porous matrix such as leather, leading to significant improvements in diffusion rate of syntans, considerable savings in process time and subsequent enhancement in the quality of retanned leathers.

Resumen

El recurtido es un paso esencial en el proceso del cuero. El proceso prosigue el curttido propiamente dicho, utilizando agentes curtientes sintéticos (sintanes) para impartir ciertas propiedades funcionales finales al cuero. Esta investigación tiene por objetivo determinar el efecto de ultra-sonido (US) en el agotamiento de sintanes durante el recurtido en comparación a un mesclador magnético (MS) como equipo controlador. Diferentes tipos de sintanes basados en fenólicos, resina melamínica y un compuesto acrílico fueron investigados. La influencia de los parámetros del proceso tales como la potencia del US, tiempo del proceso, tamaño del baño, oferta del sintán, modalidad del pulso de US fueron estudiados. Los efectos de pre-sonidación del substrato (cuero) y del sintán (análisis de tamaño de partículas en solución) también fueron investigados. Se encontró la posibilidad de un 10% a 60% de aumento en el agotamiento por el uso de US sobre el MS para los diferentes sintanes utilizados bajo las varias condiciones del proceso. El aparente coeficiente de difusión (D) del sintán através de la matriz tal como el cuero, se calculó de los datos del agotamiento de los productos, lo que indicó un significativo mejoramiento (~1,5 veces) en el valor de D debido a US comparado con MS bajo las condiciones dadas del proceso. Como tal el presente estudio indica influencia positiva de ultrasonido sobre la tasas de difusión de estos compuestos (sintanes) através de matrices más complejamente porosas tales cómo cuero, orientándonos hacia incrementos en la tasa de difusión de estos compuestos químicos orgánicos, conduciendo a ahorros en tiempo de proceso y subsecuente mejoría en la calidad del cuero recurtido.

*Corresponding author e-mail: vsiva1clri@gmail.com
Manuscript received January 30, 2013, accepted for publication April 15, 2013

INTRODUCTION

The process of subjecting tanned leather involving similar or more usually, different chemical substances known as syntans is called retanning in leather processing. The retanning process is performed to improve the quality of leathers obtained through the main tanning step. Retanning of leather provides physical properties of leather such as fullness, levelness, grain characteristics etc., as desired depending upon the end product. The process involves diffusion, absorption and interfibre deposition of syntans in leather matrix. With the use of same wet-blue (chrome tanned) or vegetable tanned leather, different types of leathers could be obtained with different retanning agents.

The syntans are generally organic molecules used for leather processing.[1] They have less tanning effect but good dispersing properties. Resin type syntans are polymers such as condensation products based on phenolic or melamine resins, which are generally used for selective filling of looser areas of leather. Acrylic syntans are next class of syntans based on acrylic polymers, which are used for getting levelness and improving grain characteristics in leather. The application of eco-benign products and processes are also gaining importance due to environmental related issues. Efficient processing methodologies such as ultrasound, which would achieve significant enhancements in % uptake of chemicals thereby minimizing process wastes in one hand and bring about economic benefits on other for processes such as retanning are necessary. In this regard, use of each kind of these syntans viz., phenolic resin, melamine resin and acrylic has been investigated as given in Table I. The schematic representation of chemical base for these syntans is shown in Figure 1. Investigation on influence of ultrasound on diffusion and uptake of these types of organic compounds for retanning in leather matrix has been studied in the paper.

TABLE I
Three types of syntans and their chemical base employed in the present study.

S. No	Type	Name of the syntan	Chemical Base
1.	Phenolic	Basyntan DI	Phenol formaldehyde condensate
2.	Resin	Basyntan FB6	Melamine formaldehyde syntan
3.	Acrylic	Relugan RE	Acrylic copolymer

Ultrasound in Leather Application

Ultrasound shall be broadly classified according to frequency range as power ultrasound (20- 100 kHz) and diagnostic ultrasound (1 - 10 MHz).[2] Acoustic cavitation in liquid media is mainly responsible for ultrasound induced effects. When a liquid is irradiated by ultrasound, micro bubbles can appear, grow and oscillate extremely fast and even collapse violently if the acoustic pressure is high enough leading to a phenomenon called cavitation. These cavitation collapses occurring near a solid surface would also generate micro jets and shock waves[3] leading to mass transfer enhancements.

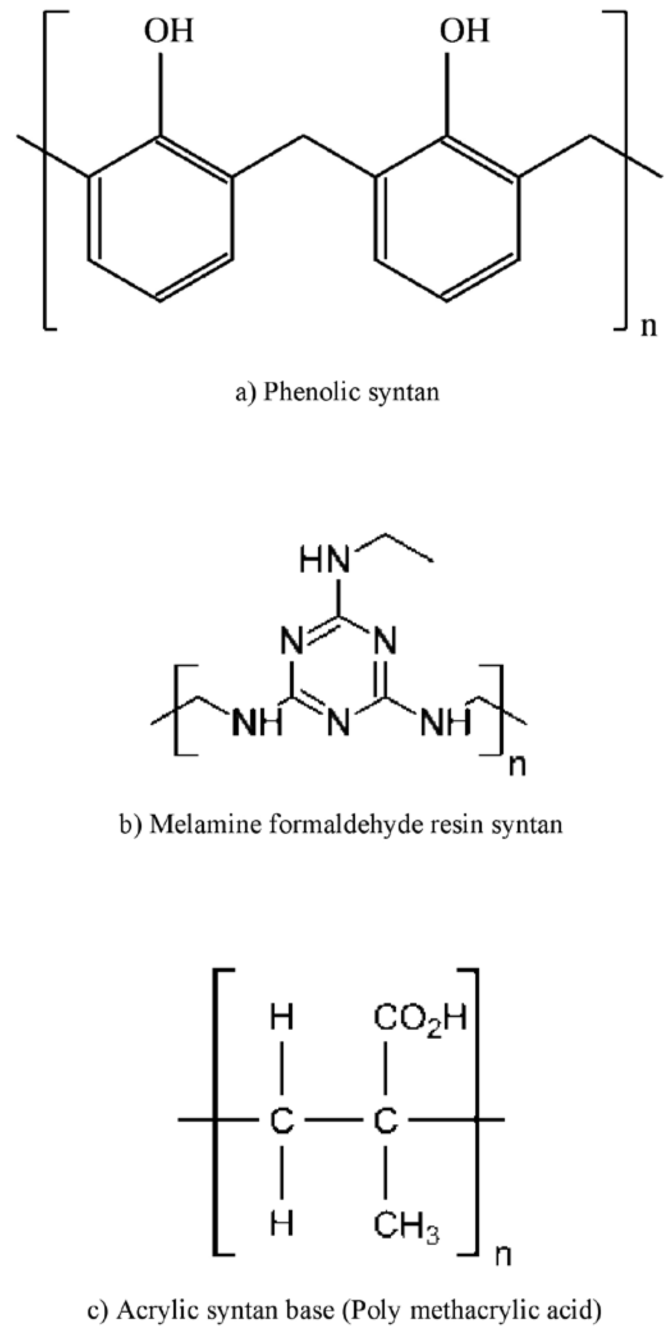


Figure 1. The schematic structure of chemical base for syntans a) Phenolic b) Melamine resin c) Acrylic.

The application of ultrasound in leather processing has been reviewed earlier.[4-6] Studies on influence of ultrasound on beam house and tanning operations,[7-13] dyeing,[14-18] and fatliquoring[19,20] have been reported. Our recent publications clearly explain the diffusion phenomena through skin or leather matrix in leather processing and influence of ultrasound on the same[21] and potential benefits in enzymatic assisted processes.[22] The beneficial effects ultrasound in solid-liquid extraction process such as tannins,[23-26] natural dye extraction process[27, 28] and oils/fats emulsification process[29, 30] for leather application have been investigated. Investigation on process parameters influencing the scale-up of ultrasonic process in leather processing has been made earlier.[31] Use of ultrasound is expected to accelerate the diffusion process in retanning, thereby obtaining beneficial effects such as process time reduction, better distribution of syntans and improvement in overall process efficiency. The study is focused on the effect of ultrasound on the rate of diffusion of syntan onto the matrix of chrome-tanned leather and related process parameters.

EXPERIMENTAL

Experimental Set-up

Ultrasound (US) assisted experiments were carried out using ultrasonic probe (*VCX 400, Sonics and Materials, USA*, 20 kHz & 0-400 W) with provisions to set required output power and time[13]. The control experiments were carried out using magnetic stirring process (MS) with magnetic paddle at ~85 rpm.

Process Details (All The % Based on Shaved Wet-blue Weight)

Goat we-blue leather after shaving to 1 mm was taken and used for the experiments. A central line was drawn across the backbone and the sides were marked as left and right. Small circles of 7-cm diameter were cut on both sides of the leather. The ones cut from the left side of the line were marked as 'E' and those on the right as 'C'. They were serially numbered such that the corresponding E and C leather pieces were geometrically symmetric to one another from the centre line. The leather pieces were put into small zip-lock packets with some water for temporary storage. A pair consisting of corresponding E and C leather pieces (wet-condition) were taken and gentle surface dabbing with tissue paper has been done for better weighing accuracy. They were individually weighed and the weights were noted down. The leather pieces were then neutralized with water (200% of wt. of leather) and sodium formate (1%) as 10% *w/v* solution were taken in a conical flask and agitated in MS for 30 min. Sodium bicarbonate solution (1%) as 10% *w/v* solution was prepared and one third of this was added to the system. The remaining portion of the solution was added at the intervals of 10 min. This process was continued till the pH- 6.5 - 6.7 at cross section.

The neutralized leather pieces E and C were taken separately in different beakers. Then water (1000% or 1500%) and syntan (DI, FB-6 or RE) solution (10% or 15% as *%w/w*). Fresh stock syntan solution was prepared for each experiment by taking suitable quantity of syntan in 100 ml water. The suitable volume of stock solution containing required amount of syntan (as *%w/w*) was taken for the experiments and added to the beaker containing leather piece. The beaker containing E leather piece was kept under the ultrasonic probe. The power (80, 100 or 120 W) and required time were set and the process was started. At the same time, the beaker containing the C piece was kept for magnetic stirring. Experiments were carried out without external heating or cooling in both the cases. Duplication of the experiments was done in some of the cases for calculating Standard deviation in the uptake of syntan. As a special case, the effect of pre-sonication of leather, processing of two leather pieces, ultrasound pulse mode operation and retanning with combination of three syntans (DI, FB-6 and RE) have been investigated.

Analytical Procedure

In order to analyze the syntan content in spent process liquor, 1 ml of the sample after suitable time intervals '*t*' was drawn using a micropipette from both E and C onto separate previously weighed petri dishes. The petri dishes with the samples were kept in a hot air oven set to 60-70°C temperature for about 3 h. After all the moisture was fully evaporated, the petri dishes were cooled in a dessicator. The weights of the petri dishes with the residue were found and noted down. The volume of the spent liquor left behind in each beaker at time '*t*' was also noted as V_t. Let W_1 = Weight of the empty petri dish;

W_2 = Weight of the petri dish + Sample at time t

Weight of Syntan left in whole spent liquor (W_t) at time $t = (W_2 - W_1) \times V_t$

The % uptake of syntan in the leather for a given time t has been calculated using the Equation 1,

$$\begin{array}{c}\text{\% Exhaustion}\\ \text{of syntan in the}\\ \text{leather at time `}t\text{'}\end{array} = \frac{\text{Syntan (Offered, g} - \text{Spent liquor } W_t\text{, g)} \times 100}{\text{Syntan offered, g}} \quad (1)$$

The values of % exhaustion for E and C at each time interval were calculated for ultrasound assisted as compared to magnetic stirring process. These results were drawn graphically by plotting the given data as Time Vs % Exhaustion of syntan. The improvement in the retanning process due to ultrasound has been analyzed.

Calculation of Process Intensification Parameters
Enhancement in Uptake of Retanning Agents

$$\text{Increase in \% uptake of retanning agent due to ultrasound } (\xi_{us}) = \text{\% Exhaustion of retanning agent for (US process – MS control process)} \quad (2)$$

$$\text{\% Increase in \%uptake of retanning agent due to ultrasound } (\eta_{us}) = \frac{\xi_{us}}{\text{\% uptake in MS control process}} \times 100 \quad (3)$$

Diffusion Co-efficient of Syntans Through Leather Matrix

If a semi-infinite porous solid such as leather matrix is brought into contact with a liquid containing diffusible substance such as synthetic tanning material with initial concentration of y_0, then the total amount of syntan (F) diffused across a unit area of leather at time 't' is given by[14] the Equation 2,

$$F = 2y_0 \sqrt{\frac{Dt}{\pi}} \quad (4)$$

From the slope of the graph with Equation 4, apparent diffusion coefficient of syntan though the leather matrix has been calculated adopting the procedure as published earlier.[11,14] 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 5,

$$\in_{us} = \frac{D_{us}}{D_{ms}} \quad (5)$$

Area of leather piece (Φ7 cm) = $\pi \times r^2 = \pi \times 3.5 \times 3.5 = 38.48$ cm^2

Syntan up take in leather (mg) = % Exhaustion × Amount of syntan given, (mg)

Syntan up take/unit area of leather (mg/cm^2) = Syntan up take/ Area of the leather

A graph was drawn between square root of time ($t^{0.5}$) and syntan take up per unit area of leather (mg/cm^2). Two straight lines (one for E and another for C) were obtained whose slopes (k) were used to calculate the diffusion coefficient.

Where, slope, $k = 2 \times y_0 \times \sqrt{(D/\pi)}$, from which apparent diffusion coefficient could be calculated.

Effect of Process Parameters
Effect of Ultrasound and Type of Syntan on Uptake of Syntan

Effect of ultrasound power 80, 100 and 120 W has been studied using three types of syntans Phenolic (DI), Melamine (FB6) and Acrylic (RE) as compared to magnetic stirring. Effect of float level 1000 and 1500% was also studied for the two methods using three types of syntans.

Effect of Ultrasound on Apparent Diffusion Coefficient of Syntans

Effect of ultrasound on apparent diffusion coefficient of three types of syntans as compared to magnetic stirring process has been studied. The process for ultrasound (80 W) for phenolic syntan, DI (float -1000%), ultrasound (100 W) for Resin syntan, FB-6 (float -1000%) and ultrasound (80 W) for Acrylic syntan, RE (float -1500%) compared to magnetic stirring process has been analyzed. Whereas, 10% syntan offer has been used in all the cases.

Effect of Ultrasound on Substrate: Pre-sonication of Leather

Pre-sonication of leather was conducted, wherein the leather piece E was first sonicated (80 W) for 1 h with water (1000%) alone and then retanning was carried out using agitation in a mechanical shaker using 10% respective syntans and 1000% float. The effect of pre-sonication (100 W) of leather on the % exhaustion of Resin syntan FB-6 (float -1000%) as well as pre-sonication (80 W) of leather on the % exhaustion of Acrylic syntan Relugan RE (float -1500%) compared to magnetic stirring process have been studied.

Effect of Ultrasound on Substance: Particle-size Analysis of Syntans

Particle-size of syntans an important property for diffusion through the leather matrix and the effect of ultrasound on the same has been studied using particle-size analyzer (Microtrac S3500, Microtrac Inc., USA). 10% (*w*/*v*) solution of each syntans were prepared and subjected to sonication (100 W) for 30 min and then taken for particle-size analysis with suitable dilution.

Effect of Ultrasound Pulse Mode

With a view of reducing electrical energy consumption, the effect of ultrasound (100 W, Pulse mode 1 s ON and 1 s OFF) on the % exhaustion of Acrylic syntan Relugan RE (float -1000%) compared to magnetic stirring process has been studied.

Effect of Combination of Syntans

As in the case of leather processing practice, the use of combination of syntans (as DI – 3%, RE- 4%, FB6 – 4%) and the effect of ultrasound (80 W) on the % exhaustion with float -1000%) as compared to magnetic stirring process has been investigated.

Effect of Retanning with Two Pieces

In order to have the initiative for process scale-up, the effect of ultrasound (80 W) with two leather pieces instead of one, on the % exhaustion of Resin syntan FB-6 (float -750%) compared to magnetic stirring process has also been attempted.

RESULTS AND DISCUSSIONS

Effect of Ultrasound and Type of Syntan on Uptake of Syntan

a. Phenolic syntan

There is a significant 35% improvement in enhancement in η_{us} value due to the use of ultrasound (80 W) on the % exhaustion of phenolic syntan, using 10% Basyntan DI and float -1000% compared to magnetic stirring process at the end of 5 h process time as shown in Figure 2a. Whereas, there found to be 27% improvement in enhancement in η_{us} value due to the use of ultrasound (100 W) for the similar process at the end of 4 h process time as shown in Figure 2b. The Figure 2c indicates that there is a significant 66% improvement in enhancement in η_{us} value due to the use of ultrasound (100 W) on the % exhaustion of phenolic syntan, using 10% Basyntan DI and float -1500% compared to magnetic stirring process at the end of 5 h process time.

b. Melamine Resin Syntan

The Figure 3a indicates that there is a significant 15% improvement in enhancement in η_{us} value due to the use of ultrasound (80 W) on the % exhaustion of Resin syntan, using 10% Basyntan FB6 and float -1000% compared to magnetic stirring process at the end of 2 h process time. Whereas, there is a 30 & 13% improvement in enhancement in η_{us} value due to the use of ultrasound 100 & 120 W respectively on the % exhaustion of Resin syntan, using 15% Basyntan FB6 and float -1500% compared to magnetic stirring process at the end of 4 h process time as shown in Figure 3b.

c. Acrylic Syntan

The Figure 4a indicates that there is a significant 114% improvement in enhancement in η_{us} value due to the use of ultrasound (80 W) on the % exhaustion of Acrylic syntan, using 10% Relugan RE and float -1000% compared to magnetic stirring process at the end of 4 h process time. Whereas, there is a significant 9%, 19 & 11% improvement in enhancement in η_{us} value due to the use of ultrasound 80, 100 & 120 W respectively on the % exhaustion of Acrylic syntan Relugan RE, using 10% Relugan RE and float -1500% compared to magnetic stirring process at the end of 4 h process time as shown in Figure 4b.

Effect of Ultrasound on Apparent Diffusion Coefficient of Syntans

Apparent Diffusion coefficient was calculated from the slope of the straight line graph drawn between square root of time ($t^{0.5}$) in x-axis and syntan up take per unit area ($mgcm^{-2}$) of leather in y-axis. The Figure 5a shows the graph drawn for the process for ultrasound (80 W) on the % exhaustion of phenolic syntan, DI (float -1000%) compared to magnetic stirring process. The Figure 5b shows the graph drawn for process ultrasound (100 W) on the % exhaustion of Resin syntan,

A

B

C

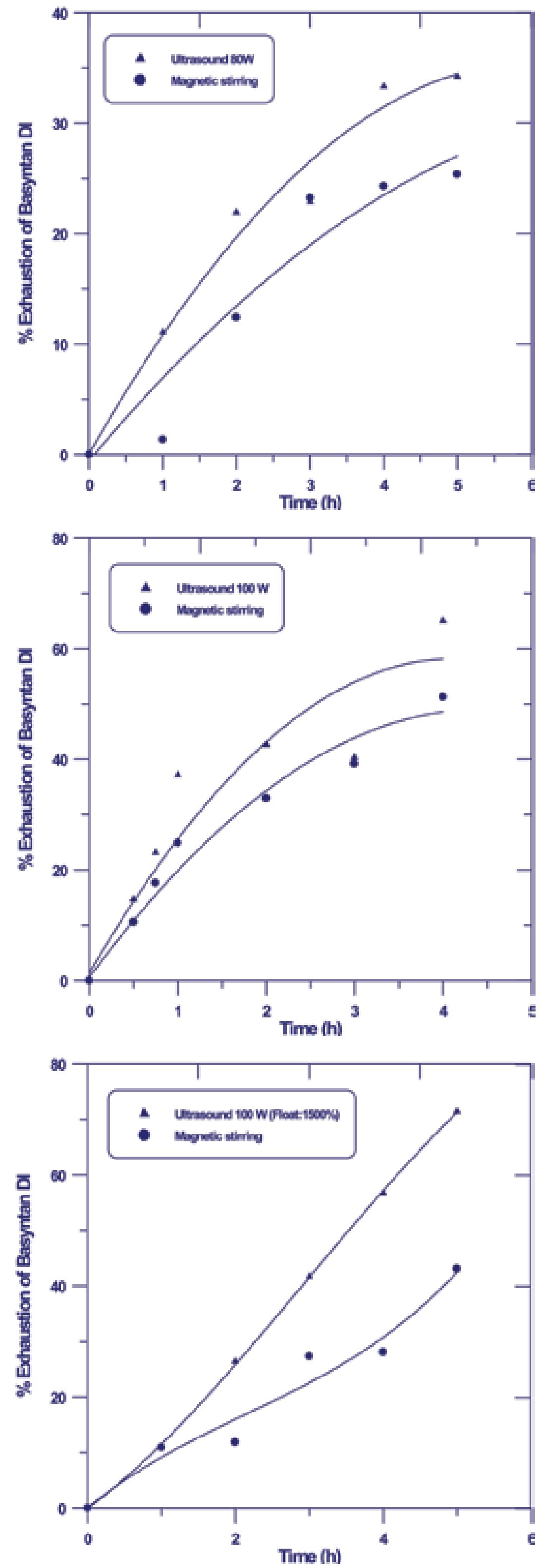


Figure 2a. The effect of ultrasound (80W) on the % exhaustion of phenolic syntan, DI, 10% (float -1000%) compared to magnetic stirring process.

Figure 2b. The effect of ultrasound (100W) on the % exhaustion of phenolic syntan, DI, 10% (float -1000%) compared to magnetic stirring process.

Figure 2c. The effect of ultrasound (100W) on the % exhaustion of phenolic syntan DI, 10% (float -1500%) compared to magnetic stirring process.

FB-6 (float -1000%) compared to magnetic stirring process. The Figure 5c shows the graph drawn for the process ultrasound (80 W) on the % exhaustion of Acrylic syntan, Relugan RE (float -1500%) compared to magnetic stirring process. There is about ~1.5 enhancement in apparent diffusion coefficient due to the use of ultrasound in retanning process for different types of syntans as shown in Table II.

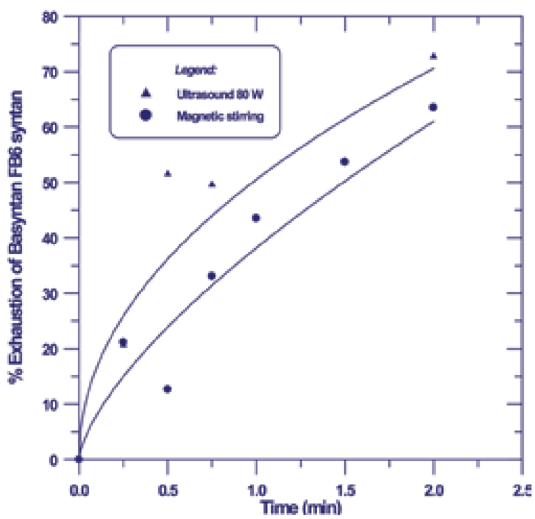
Effect of Ultrasound on Substrate: Pre-Sonication of Leather

The Figure 6a indicates that there is a 18% improvement in enhancement in η_{us} value due to pre-sonication of leather alone using ultrasound (100 W) on the % exhaustion of Resin syntan, using 10% Basyntan FB6 and float -1000% compared to magnetic stirring process at the end of 4 h process time. The Figure 6b indicates that there is a significant 32% improvement in enhancement in η_{us} value due to pre-sonication of leather alone using ultrasound (80 W) on the % exhaustion of Acrylic syntan, using 10% Relugan RE and float -1500% compared to magnetic stirring process at the end of 4 h process time.

Effect of Ultrasound on Substance: Particle-Size Analysis of Syntans

The effect pre-sonication of syntans analyzed through particle-size analysis indicate that there is a decrease in particle-size of different type of syntans due to sonication (100 W, 30 min) as shown in Table III. There is a significant effect for phenolic syntans which recorded decrease from 49.7 µ to 42.0 µ which could aid the diffusion through the matrix.

A



B

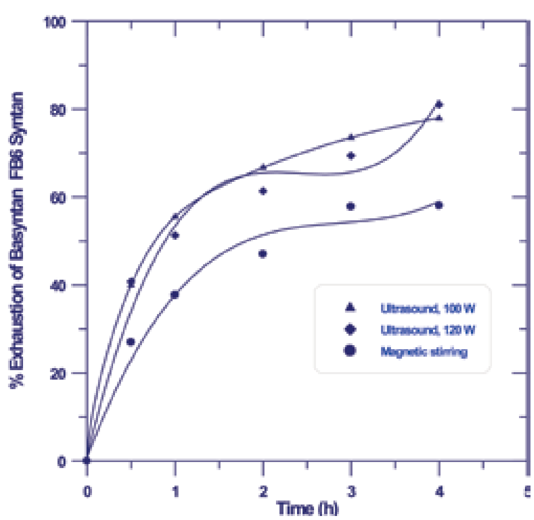
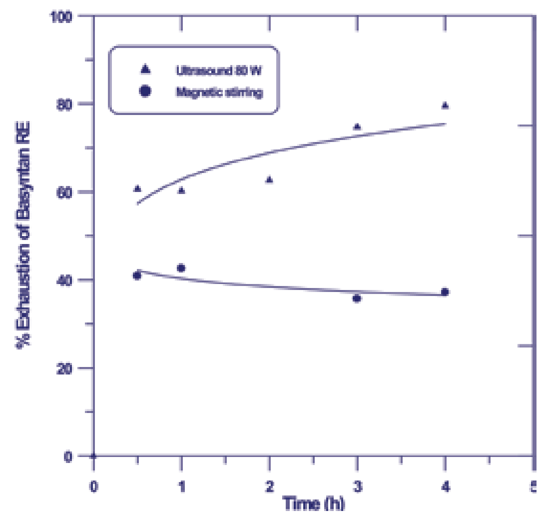


Figure 3a. The effect of ultrasound (80W) on the % exhaustion of Resin syntan FB-6, 10% (float -1000%) compared to magnetic stirring process.

Figure 3b. The effect of ultrasound (100 & 120 W) on the % exhaustion of Resin syntan FB-6 (float -1500%, syntan-15%) compared to magnetic stirring process.

A



B

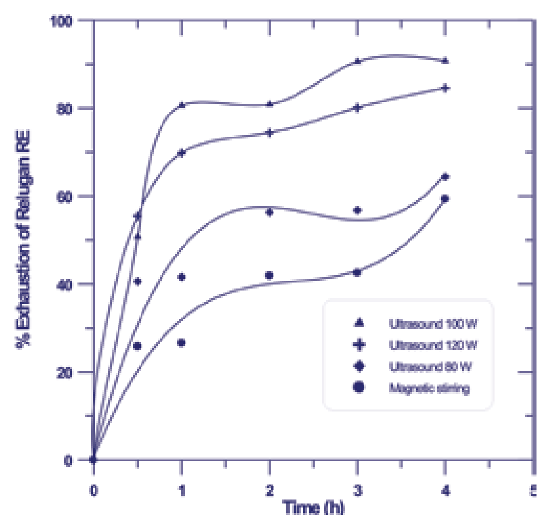
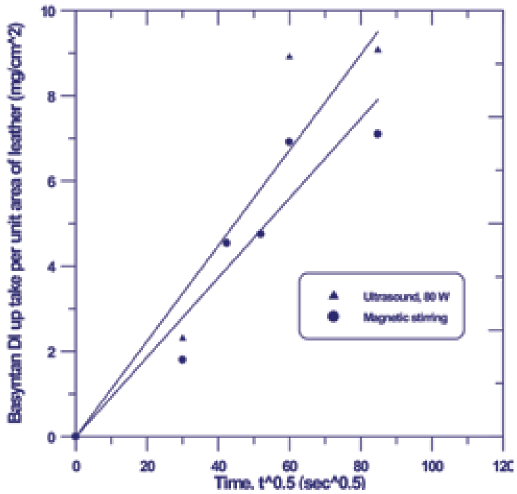


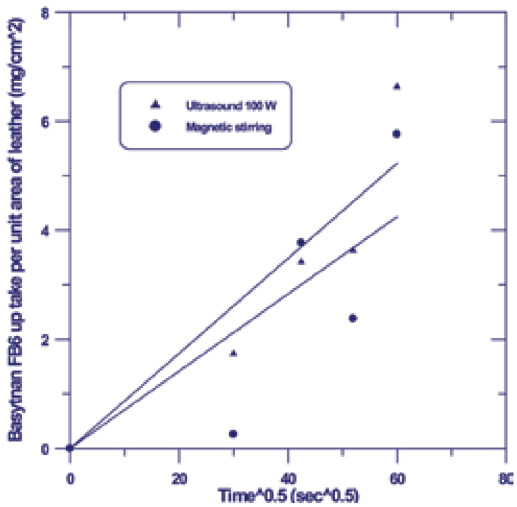
Figure 4a. The effect of ultrasound (80W) on the % exhaustion of Acrylic Syntan Relugan RE, 10% (float -1000%) compared to magnetic stirring process.

Figure 4b. The effect of ultrasound power (80, 100, 120 W) on the % exhaustion of Acrylic Syntan Relugan RE, 10% (float -1500%) compared to magnetic stirring process.

A



B



C

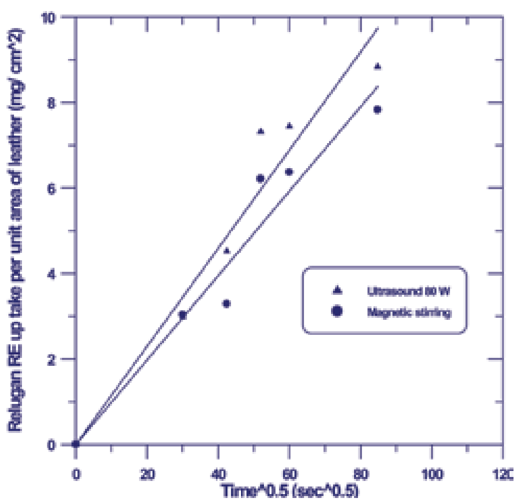
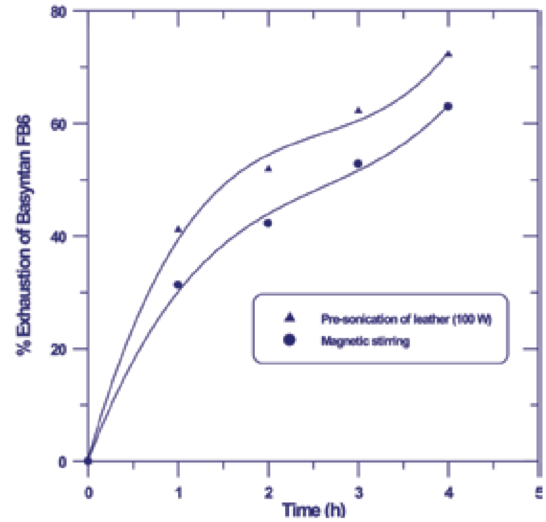


Figure 5a. Graph drawn between square root of time ($t^{0.5}$) in x-axis and syntan up take per unit area ($mgcm^{-2}$) of leather in y-axis for the calculation of Apparent Diffusion coefficient process for the process ultrasound (80 W) on the % exhaustion of phenolic syntan, DI, 10% (float -1000%) compared to magnetic stirring process.

Figure 5b. Ultrasound (100 W) on the % exhaustion of Resin syntan, FB-6, 10% (float -1000%) compared to magnetic stirring process.

Figure 5c. Ultrasound (80 W) on the % exhaustion of Acrylic syntan, Relugan RE, 10% (float -1500%) compared to magnetic stirring process.

A



B

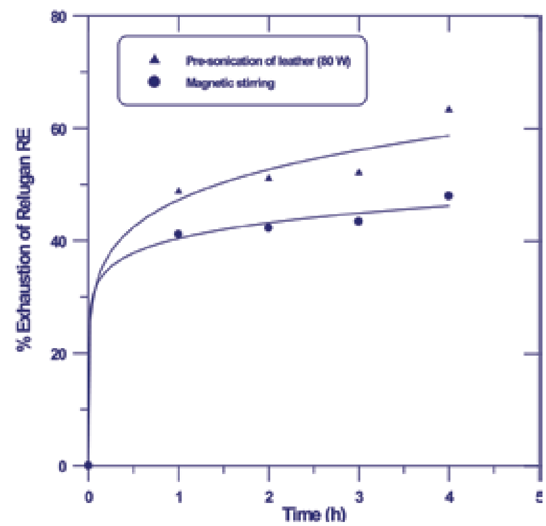


Figure 6a. The effect of pre-sonication (100 W) of leather on the % exhaustion of Resin syntan FB-6, 10% (float -1000%) compared to magnetic stirring process.

Figure 6b. The effect of pre-sonication (80 W) of leather on the % exhaustion of Acrylic syntan RE, 10% (float -1500%) compared to magnetic stirring process.

Effect of Ultrasound Pulse Mode

The Figure 7 indicates that there is a significant 32% improvement in enhancement in η_{us} value due to pulse mode (1 s – 1 s) operation of ultrasound (100 W) on the % exhaustion of Acrylic syntan, using 10% Relugan RE and float -1000% compared to magnetic stirring process at the end of 4 h process time.

Effect of Combination of Syntans

The Figure 8 indicates that there is a significant 22% improvement in enhancement in η_{us} value due to the use of ultrasound (80 W) on the % exhaustion of combination of 3 syntans and float -1000% compared to magnetic stirring process at the end of 3 h process time.

TABLE II
Enhancement in apparent diffusion coefficient due to the use of ultrasound in retanning process for different types of syntans.

S. No	Experiment	Apparent Diffusion coefficient (*D*), (x 10^{-5} cm^2/sec)		Enhancement factor (ϵ_{us}) due to ultrasound
		Ultrasound	Magnetic stirring	
1	Phenolic syntan (DI), 10% offered, 1000% float (Ultrasound, 80 W) & Control	9.9	6.8	1.4
2	Resin syntan (FB-6), 10% offered, 1000% float (Ultrasound, 100 W) & Control	6.0	3.9	1.5
3	Acrylic syntan (RE), 10% offered, 1500% float (Ultrasound, 80 W) & Control	10.3	7.7	1.4

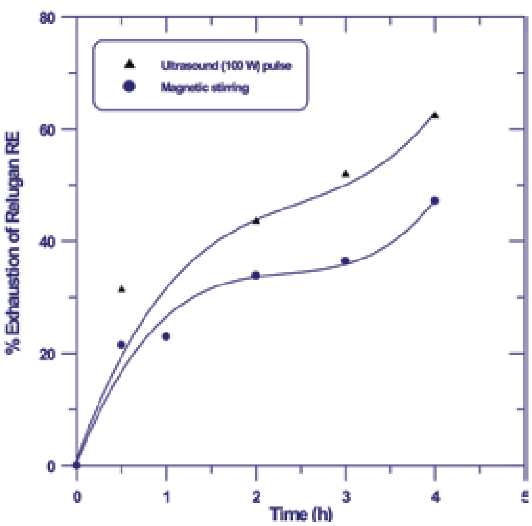


Figure 7. The effect of ultrasound (100 W, Pulse mode 1 s – 1 s) on the % exhaustion of Acrylic syntan Relugan RE, 10% (float -1000%) compared to magnetic stirring process.

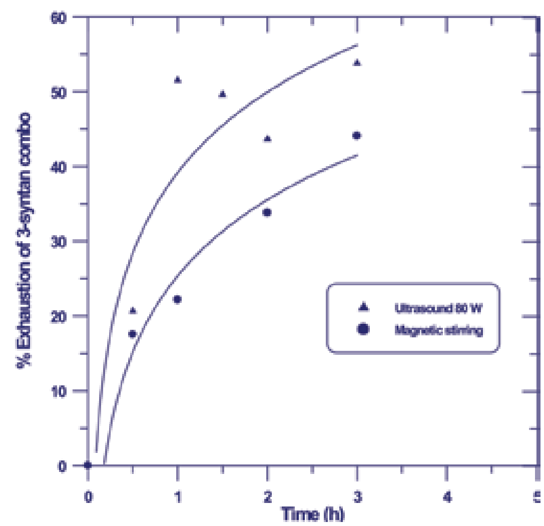


Figure 8. The effect of ultrasound (80 W) on the % exhaustion of a combination of 3 syntans (float -1000%) compared to magnetic stirring process.

Effect of Retanning with Two Leather Pieces

The Figure 9 indicates that there is a significant 60% improvement in enhancement in η_{us} value due to the use of ultrasound (80 W) on the % exhaustion processing two pieces of leather with Resin syntan, using 10% Basyntan FB6 and float - 750% compared to magnetic stirring process at the end of 4 h process time.

Statistical Analysis

Since the uptake of chemicals vary with different areas of same leather, there is bound to have Standard Deviation (S.D) from one area to another with respect to the uptake of syntan. Therefore, S.D has been calculated for the % Exhaustion of syntan after repetition (duplicates) and found to be in the range of 5-10% for different experiments (as % Exhaustion of syntan). This value for S.D in case of leather is not unexpected. The statistical analysis of experimental data through curve fitting and for obtaining various Figures with values of Coefficient of Determination (R^2) value has been performed as shown in Table IV. R^2 approaching the value of unity indicates better curve fitting and validity of experimental data obtained from different experimental results.

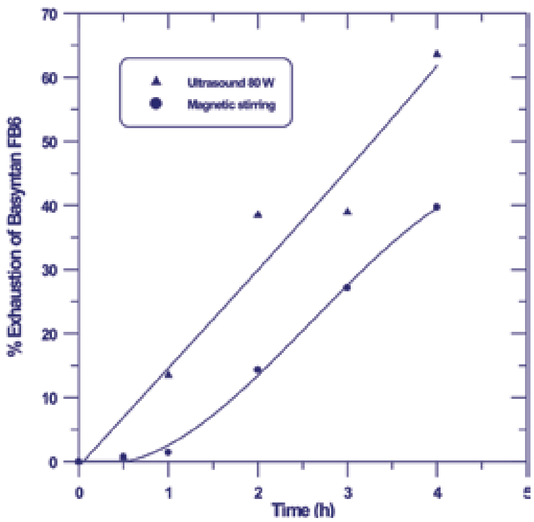


Figure 9. The effect of ultrasound (80 W) of two leather pieces on the % exhaustion of Resin syntan FB-6, 10% (float -750%) compared to magnetic stirring process.

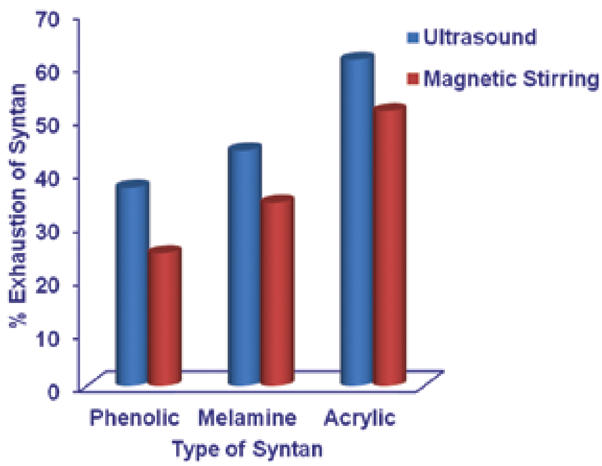


Figure 10. Comparison of % exhaustion for different syntans at 1 h using US, 100 W and 1000% float with MS process.

TABLE III
Effect of ultrasound on particle-size distribution of syntans.

S. No	Synatan	Mean Particle-size of Syntans (μ)	
		Control	Ultrasound (100 W)
1	Phenolic (Basyntan DI)	49.7	42.0
2	Melamine Resin (Basyntan FB-6)	1.6	1.5
3	Acrylic (Relugan RE)	52.5	50.4

Conclusions

Comparison of % exhaustion for different syntans at 1 h using US 100 W, 10% syntan and 1000% float as compared to MS is shown in Figure 10, which indicates that 50, 29 and 19% improvement in % exhaustion due to the use of US, 100 W for phenolic, melamine resin and acrylic syntans respectively as compared to MS. The Overall results analyzed through enhancement factors indicate that use of ultrasound in leather retanning process gives better results as compared to magnetic stirring. The results show that effect of different process parameters such as time, type of syntans, US power, float ratio and amount of syntan has considerable effect on uptake of syntans. There is a significant improvement (~1.5 times) in the apparent diffusion coefficient (*D*) value due to US over MS under the given process conditions for different types of syntans. Positive trend also felt due to pre-sonication of leather or syntan alone (through particle-size reduction). Experiments on combination of syntans, two leather pieces and US pulse mode operation suggest realistic and scale-up feasibility. Therefore, the present study clearly indicates positive influence of ultrasound on diffusion of different types of syntan through more complex porous matrix such as leather, leading to significant improvements in diffusion rate of syntans, considerable savings in process time and subsequent enhancement in the quality of retanned leathers.

Acknowledgements

One of the authors (VS) thank Prof. Dr. AB Mandal, Director, CSIR-CLRI for encouragement. Dr. PG. Rao, Former Director and Emeritus Scientist, NEIST, Jorhat, Dr. T. Ramasami, Secretary, DST, India and Dr. KV. Raghavan, RC Chairman, CLRI for their motivation. Prof. R. Kumar and Prof. KS. Gandhi, IISc, Bangalore; Dr. C Muralidharan, Chief Scientist, CLRI for useful discussions. Authors are grateful to CSIR, New Delhi India for the financial support.

References

1. Dutta, S.S.; An Introduction to the Principles of Leather Manufacture, ILTA, Calcutta, 1985
2. Mason, T.J.; Sonochemistry, Oxford University Press, New York, 1999.
3. Contamine, F., Faid, F., Wilhelm, A.M., Berlan, J and Delmas, H.; Chemical reactions under ultrasound. *Chem. Eng. Sci*. **49,** 5865–5873, 1994
4. Sivakumar, V., Swaminathan, G., Rao, P.G., Ramasami, T.; Sono-Leather Technology with Ultrasound: A boon for unit operations in leather processing - Review of our research work at Central Leather Research Institute (CLRI). *Ultrason. Sonochem*. **16,** 116-119, 2009.

TABLE IV
Statistical analysis of curve fitting data obtained for different experimental results with values of coefficient of determination (R^2) value.

Fig. No	Equation used	Coefficient of Determination (R^2) for the curve fitting data used	
		With ultrasound	Mechanical stirring
Fig. 2a	$y = a + bx + cx^2$ (Polynomial degree, P = 2)	0.989	0.955
Fig. 2b	$y = a + bx + cx^2$ (Polynomial degree, P = 2)	0.931	0.983
Fig. 2c	$y = a + bx + cx^2 + dx^3$ (Polynomial degree, P = 3)	0.999	0.978
Fig. 3a	Power, log(Y)=B*log(X)+A	0.742	0.675
Fig. 3b	$y = a + bx + cx^2 + dx^3$ (Polynomial degree, P = 3)	0.979 (80 W)	0.986
Fig. 4a	Power, log(Y)=B*log(X)+A	0.743	0.703
Fig. 4b	y = a + bx + cx2 + dx3 (Polynomial degree, P = 3)	0.989 (120 W)	0.989
Fig. 6a	Power, log(Y)=B*log(X)+A	0.665	0.747
Fig. 6b	y = a + bx + cx2 + dx3 (Polynomial degree, P = 3)	0.996	0.998
Fig. 7	y = a + bx + cx2 + dx3 (Polynomial degree, P = 3)	0.955	0.987
Fig. 8	Log, Y=B*log(X)+A	0.623	0.941
Fig. 8	y = a + bx + cx2 + dx3 (Polynomial degree, P = 3)	0.966	0.998

5. Ding, J.F., Xie, J.P., Attenburrow, G.E.; Power ultrasound in leather technology. In: *Advances in Sonochemistry*, Ed. T.J. Mason, Vol. 5, JAI press, London, 1999.
6. Sivakumar, V., Rao, P.G.; Application of power ultrasound in leather processing: An Eco-friendly approach. *J. Clean Prod*. **9,** 25-33, 2001.
7. Sivakumar, V., Swaminathan, G.. Rao, P.G.; Use of ultrasound in soaking for improved efficiency. *J. Soc. Leather. Technol. Chem. Soc*. **88,** 249-251, 2004.
8. Alpa, Spa., Italy, Reducing the Load: Ultrasound in liming and unhairing. *World Leather* **8,** 89-91, 1995.
9. Sivakumar, V., Rao, P.G.; Use of power ultrasound in beam house and tanning operations. In: *Proceedings of XXV IULTCS Congress,* CLRI, Chennai, India, PIO-1, 216–219, 1999.
10. Mantysalo, E., Marjoniemi, M., Kilpelainen, M.; Chrome tannage using high-intensity ultrasonic field. *Ultrason. Sonochem*. **4,** 141-144, 1997.
11. Sivakumar,V.,Gopi,K.,Harikrishnan,M.V.,Senthilkumar, M., Swaminathan, G., Rao, P.G.; Ultrasound assisted diffusion in vegetable tanning in leather processing. *JALCA*. **103,** 330-337, 2008.
12. Morera, J., Bartoli, E., Combalia, F., Castell, H., Sorolla, S.; Study of the application of ultrasound in vegetable tannage. *JALCA*. **105,** 369-375, 2010.
13. Morera, J.M., Bartolí, E., Serrano, M., Combalía, F., Borràs, E., Ollé, L., Bacardit, A.; Effect of ultrasound on several chromium tanning parameters. *JALCA*. **105,** 150-159, 2010.
14. Sivakumar, V., Rao, P.G.; Studies on the use of power ultrasound in leather dyeing.*Ultrason. Sonochem*. **10,** 85-94, 2003.
15. Sivakumar, V., Rao, P.G.; Diffusion rate enhancement in leather dyeing with power ultrasound. *JALCA* **98,** 230-237, 2003.

16. Sivakumar, V., Rao, P.G.; Power ultrasound assisted cleaner leather dyeing technique: Influence of process parameters. *Environ. Sci. Technol.* **38,** 1616-1621, 2004.
17. Sivakumar, V., Swaminathan, G., Rao, P.G.; Studies on the influence of power ultrasound on dye penetration in leather dyeing using photomicrographic analysis. *J. Microsc (oxf).* **220,** 31-35, 2005.
18. Xie, J.P., Ding, J.F., Attenburrow, G.E., Mason, T.J.; Influence of power ultrasound on leather processing. Part.I: Dyeing. *JALCA* **94,** 146-157, 1999.
19. Sivakumar, V., Swaminathan, G., Rao, P.G.; Studies on the application of power ultrasound in fatliquoring process. *JALCA* **100,**187-195, 2005.
20. Xie, J.P., Ding, J.F., Attenburrow, G.E. and Mason, T.J.; Influence of power ultrasound on leather processing. Part. II: Fatliquoring. *JALCA*. **95,** 85-91, 2000.
21. Sivakumar, V., Swaminathan, G., Rao, P.G., Ramasami, T.; Influence of ultrasound on diffusion through skin/leather matrix, Chem. Eng. Process.: Process Intensification. **47,** 2076-2083, 2008.
22. Sivakumar, V., Deepak Kumar , Randhir Kumar and Raushan Kumar, Leather bio-process intensification: ultrasound assisted novel enzymatic hair-loosening system for leather processing. *Indian J. Biotechnol*.**11,** 326-329, 2012.
23. Sivakumar, V., Ravi Verma, V., Swaminathan, G., Rao, P.G.; Studies on the use of power ultrasound in solid – liquid myrobalan extraction process. *J. Clean. Prod.* **15,** 1815-1820, 2007.
24. Sivakumar, V., Jayapriya, J., Shriram, V., Srinandini, P., Swaminathan,G.; Ultrasound Assisted Enhancement in Wattle bark (*Acacia Mollissima*) Vegetable tannin extraction for leather processing. *JALCA* **104,** 375-383, 2009.
25. Kilicarislan, C., Ozgunay, H.; Ultrasound extraction of valonea tannin. *JALCA* **108,** 63-71, 2013.
26. Kilicarislan C., Ozgunay, H.; Ultrasound extraction of valonea tannin and its effects on extraction yield. *JALCA* **107,** 394-403, 2012.
27. Sivakumar, V., Lakshmi Anna, J., Vijayeeswaree, J., Swaminathan, G.; Ultrasound assisted enhancement in natural dye extraction from Beetroot for industrial applications and natural dyeing of leather. *Ultrason. Sonochem.* 16, 782-789, 2009.
28. Sivakumar, V., Vijayeeswaree, J., Lakshmi Anna, J.; Effective natural dye extraction from different plant materials using ultrasound, *Ind. Crop. Prod.* **33**, 116 – 122, 2011.
29. Sivakumar, V., Poorna Prakash, R., Rao, P.G., Ramabrahmam, B.V., Swaminathan, G.; Power ultrasound in fatliquor preparation based on vegetable oil for leather application. *J. Clean. Prod.* **16,** 549-553, 2008.
30. Sivakumar, V., Gayathri, K., Pranavi, P.S., Chandrasekaran, F.; Ultrasound assisted cleaner alternate emulsification method for oils and fats: Tallow emulsion - Fatliquor preparation for leather application. *J. Clean. Prod.* **37**,1-7, 2012.
31. Sivakumar, V., Swaminathan, G., Rao, P.G., Ramasami, T.; Ultrasound aided leather dyeing: A preliminary investigation on process parameters influencing ultrasonic technology for large-scale production. *Int. J. Adv. Manuf. Technol.* 45, 41-54, 2009.