Ultrasound Assisted Enhancement in Wattle Bark (*Acacia Mollissima*) Vegetable Tannin Extraction for Leather Processing

by

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Abstract

This paper analyzes the effect of ultrasound on a batch wattle bark tannin extraction process. Extraction from wattle bark presents a unique case of a two-component system in the form of condensed tannins and non-tannins. Hence, quantitative analysis of tannin content in the extract by spectrophotometery as well as total extracts analysis has been performed. The influence of various process parameters such as ultrasonic power, time, agitation and temperature on extraction has been studied. The results show significant 2-3 and 1.2-1.7 fold improvement respectively for total extract and tannin content due to the use of ultrasound 40-120 W as compared to control at 30°C suggesting mass transfer enhancement in leaching of strongly bound tannins from wattle bark due to ultrasound. The results indicate total extract and tannins obtained in ultrasonic process (80 W), devoid of external heating is better than control at 30°C. Better total extraction and comparable tannin content obtained using ultrasound, 120 W when compared to control at 60°C. Efficacy of tannin extract has been analyzed which indicates significant improvement in rate of tannin uptake for ultrasonic extract as compared to control extract by the bovine pelt. Therefore, the present study clearly indicates use of ultrasound in wattle tannin extraction is a viable enhancement with added advantages even dispensing with external heating.

Resumen

Este trabajo analiza el efecto que el ultrasonido tiene sobre el proceso de extracción de taninos sobre un lote de corteza de mimosa. La extracción de corteza de mimosa representa un caso único de un sistema de dos componentes que conforman taninos condensados y no-taninos. Por lo tal, un análisis espectroscópico cuantitativo del contenido de taninos como el análisis de extractos totales fue efectuado. La influencia de varios parámetros de proceso tal como potencia ultrasónica, tiempo, agitación, y temperatura de la extracción fue estudiada. Los resultados indican sustanciales mejorías por factores de 2-3 y 1,2-1,7 respectivamente de extracto totales y contenido de taninos debido al uso de ultrasonido, 40-120 W, en comparación a un control a 30°C así sugiriendo un incremento en transferencias de masa en la extracción de taninos fuertemente ligados a la corteza de mimosa, debido al empleo de ultrasonido. Los resultados indican que una extracción por procesamiento ultrasónico (80W), sin calentar es superior a un control a 30°C. Superior extracción total y congruente contenido de taninos se obtuvo utilizando ultrasonido a 120W, en comparación a un control a 60°C. La eficacia del tanino así extraído se encontró ser superior en el caso de extracto por ultrasonido por incrementada proporción de absorción en la piel bovina en comparación con el control. Por lo tal, el presente estudio claramente indica que el empleo de ultrasonido en la extracción del tanino de mimosa es una factible mejora con varias ventajas incluyendo la eliminación de calentamiento externo.

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INTRODUCTION

Vegetable tanning is one of the oldest methods of eco-friendly tanning. About 90% of the vegetable tannin extract produced in the world is utilized in leather industry.[1] The vegetable tannins are water-soluble polyphenolic compounds having molecular weight in the range of 500 – 3000 Daltons[1]. Based on their chemical structure, vegetable tannins are classified as, hydrolysable type (e.g. Myrobalan, Sumac etc.) and condensed type (e.g. Wattle, Quebracho etc.), used as the main tanning agent.[2]

Conventional tannin extraction is done by solid-liquid extraction process by leaching from the tannin bearing material using solvent (usually water). Spray drying can then be done to get the product in powder form. In case, the product is desired in the form of solid, vacuum drying is preferred.

Vegetable materials generally contain active solute, but most of the time with high added value, which justifies the development of high performance separation processes. The conventional method of extraction offers low extraction efficiency due to low mass transfer rates. This is because of the effect of the resistances to the diffusion of a component from the solid particle to the liquid bulk. The resistances that come into play in the solid liquid extraction process include.[3]

1) Resistance of the liquid film surrounding the solid particle and
2) Intra-particle diffusion resistance

Stirring has for long been a widely used option for enhancing the mass transfer rate. While effective stirring can only reduce the resistance of the liquid film surrounding the solid particle, it does not have any effect on the intra-particle diffusion resistance. Moreover, stirring cannot increase detachment of the effective component from solid materials. There are basically two components in wattle bark viz., tannins and non-tannins. Tannins are generally strongly bound to plant cell membranes and pose larger mass transfer resistance in leaching as compared to non – tannins. Therefore, wattle bark presents a special case, which contains substances in the form of tannins and other in the form of non-tannins for leaching process making the extraction process challenging one. Although tannins are mainly responsible for tanning process, non – tannins are also required in stabilizing the skin / hide protein matrix. Consequently there is a need for new efficient methods of increasing leaching rates, for instance, ultrasound assisted extraction. In the present paper, we therefore quantitatively analyze the tannin content from the leaching process with ultrasound and for the control process, while analyzing the total extract obtained for each process.

Use of ultrasound in solid–liquid tannin extraction process

Ultrasound is a sound wave with a frequency above the human audible range (16 Hz to 16 kHz). Ultrasound having frequency range of 20 kHz to 100 kHz is known as 'power ultrasound' and commonly employed for enhancing physical processes and chemical reactions.[4] The basic mechanism utilized in the extraction process is ultrasonic cavitation in liquid media. The effect of ultrasound on solid-liquid tannin extraction process has been reported[5-6]. The ultrasonic enhancement of extraction is attributed to the disruption of cell walls, particle size reduction and enhanced mass transfer through cavitation bubble collapse. The primary benefits of ultrasonic sonication may include an enhanced hydration process and plant material fragmentation. Experiments on the effect of ultrasound on the leaching process of *geniposide*[3] from *Gardenia* fruit resulted in an increase by 16.5% as compared to extraction in the absence of ultrasound and in another experiment the extraction of *saponin* from *Ginseng*[7] increased by about 30% on sonication. Unlike stirring, ultrasound is believed to affect both the resistances to mass transfer namely the resistance due to thin film and intra particle diffusion resistance.[3,8]

Efficacy of tannin extract obtained is generally analyzed by tanning process, which involves reaction between tannins and amino acids of collagen present in skin /hide. Recently, the use of power ultrasound in leather processing had been studied and analyzed in detail for its potential benefits[9-10]. The application of power ultrasound in leather dyeing[11-13] and fatliquoring[14] has also been studied. Influence of ultrasound on diffusion through skin/hide matrix has been reported recently[15]. Use of ultrasound in myrobalam extraction process has also been investigated[16]. Increase in the extraction of tanning material under the action of ultrasonic vibration at a frequency of 800 kHz has been reported.[6] The extraction was completed in 45 min using ultrasound as compared to 8 h taken by stirring at 1400 rpm. Increase in tannin content and decrease in viscosity of vegetable tanning liquor was found.[5] A combined extraction – filtering system was designed, modeled and tannins extracted from *Salix phylicifolia.*[17] Development in the ultrasound technology and its potential benefits has triggered interest on the application of power ultrasound on a wider range of chemistry and processing.[18]

The main advantage of using ultrasound as a physical method of activation instead of chemical methods is that it will not contribute to additional pollution load in the form of chemical entities and also provide possibilities for energy efficient process.

In this paper, the use of power ultrasound in the extraction of vegetable tanning material (wattle bark) has been studied with the following objectives, a) Improve the efficiency of the solid-liquid wattle extraction process. b) Carry out the extraction in milder process conditions such as choice of lower temperature using ultrasound. c) Study the effect of important process parameters such as ultrasonic output power, time, temperature in extraction and scale up trials. d) Analyzing the tannin content as well as total extract of the ultrasonic process in comparison with control process. e) Studying the kinetics of ultrasonically extracted tannin solution in the tanning diffusion process in comparison with control process.

Overview of the tannin extracts manufacture

CLRI, India has developed a microprocessor based multistage counter current leaching technique to improve the extraction efficiency. Generally, extraction is carried out in such a way that materials undergo three changes of float (water in this case) to obtain as maximum extract as possible. Temperature of the float is maintained at around 70°C. Since tannins, in general, are sensitive to temperature, extraction could not be carried out at higher temperatures and the liquors are not over exposed to the atmosphere, to avoid possible oxidation. Care should be taken in the material of construction of process equipment to prevent the contamination of iron with the liquor[1] as it reacts with tannin solution to form a complex.

EXPERIMENTAL

Experimental set-up

Ultrasonic extraction 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[12]. Control experiments were carried out in a water bath with provisions to control temperature.

Materials and Methods

Wattle barks (*Acacia Mollissima*) of Indian origin obtained from *Tanext chemicals*, India were cut into to smaller sizes of average ~2 cm. Extraction was carried out using water as solvent with the ratio of wattle bark to water as 1:30. Experiments were carried out typically with 2 g wattle bark in 60 ml distilled water was transferred in two different 250 ml clean beakers. Experiments using ultrasound have been compared with those in absence of ultrasound at stationary condition as control process. Influence of ultrasonic power 40 – 120 W without any external heating or cooling has been studied and compared with control process at temperature (30 – 60°C).

Tanning trials

Efficacy of tannin extracts obtained was studied by tanning trials. Two process beakers were taken each containing 10 g of wattle in 100 ml of water. One was subjected to sonication at 120 W. The other beaker is the control at room temperature. The tannin content of the extract solutions of the two beakers was analyzed using spectrophotometer after 8 h. The effectiveness of wattle extract obtained using ultrasound in leather tanning process has been studied by conducting tanning trails. For this purpose, pickled buffalo pelt with pH-4.5- 5.0 has been taken for the tanning trials. Two sample pieces (E & C) with 5×5-cm sizes have been cut from the butt portion of the pelt parallel to the backbone. The weights of the two samples were recorded individually. Then the pelts were treated with 20% (*w/w*) of tannin extract (*on pelt weight basis*) using tannin extract solutions taken as *w/v* basis. The sample pelt 'E' was treated with ultrasonically extracted wattle tannin solution (UE_S) and 'C' with control tannin solution prepared from magnetic stirring (C_S). The pelt along with tannin solution were taken in a 250 ml conical flask and agitated in a Magnetic stirrer. Then the treated sample pelts were tested for shrinkage temperature (T_s) after 5 h of tanning. Samples were withdrawn at the end of every 1 h and the analyzed using spectrophotometer. The amount of tannin (in terms of *catechin*) equivalents and the percentage exhaustion at different times was measured using the following formula.

$$\%\ \text{Exhaustion} = \frac{\text{Initial tannin content} - \text{Tannin content at time 't' h}}{\text{Initial tannin content}} \times 100$$

Analytical methods

Gravimetric analysis

Every 30 minutes, samples were taken from both ultrasound and control extracts in clean, dried and weighed glass dishes. The extracts 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 weighed. The drying, cooling and weighing procedure was repeated to get the constant weight and the weight of the extract was determined. The weight of the extract obtained per gram of the nuts used was calculated.

Quantitative analysis of tannin content

The Folin-Ciocalteau method of analysis of condensable type of tannin is used to estimate the tannin content of the extract[19]. The Folin-Ciocalteau reagent is a mixture of Tungstophosphoric and molybdophosphoric acids. Tannins aromatic hydroxyl groups like catechol, resorcinol and pyrogallol that react with the Folins reagent to form a blue colored complex that can be analyzed spectrophotometrically at a suitable wavelength.

Preparation of reagents required (all chemicals are AR grade) Reagents: $CuSO_4$, Sodium potassium tartrate, NaOH, Na_2CO_3, Folin - Ciocalteau reagent (*SD fine chemicals India Ltd.)* and Catechin with CAS Registry No. 100786-01-4. Solution A: 1% $CuSO_4$ and 2% Sodium potassium tartrate (*AR Grade*) mixed in the ratio of 1:2. Solution B: 1 g of NaOH in 150 ml of water + 5 g of Na_2CO_3 in 250 ml.

Solution C: 1ml of solution A + 50 ml of solution B. 0.5 ml of the extract sample was taken. It was neutralized to a pH of 7 using a 0.1N NaOH. Then 1 ml of this neutralized solution was taken. To that added 0.5ml water, 5 ml of solution C and 0.5 ml of Folin - Ciocalteau reagent (1:1 with water) and the rest was made up to 10 ml with water. The made up solution was allowed to stand for 30 min to ensure good color development. The solution was then analyzed using UV spectrophotometer for the absorbance at 760.5 nm.

Preparation of Standard Graph

Catechin was used for the preparation of the standard graph, since it acts as a building block in the formation of wattle tannin material. Known concentrations of *catechin* were prepared and the solutions were analyzed as per the method of spectrophotometric analysis mentioned above. The OD readings were plotted against the known concentration of *catechin* in each sample and calibration curve was drawn. Unknown tannin concentration (X) in wattle extract solution with OD value (Y) was determined as *Catechin* equivalents from the calibration graph with slope m as $Y = m \times X$ form. Tannin content was calculated after taking into account of the dilution factor.

Yield, Maximum extractable material and Efficiency

Yield of the extraction process has been calculated based on the amount of wattle bark employed in the process and calculated as given in Equation 1 and 2,

$$\text{\% Yield (for total extracts)} = \frac{\text{Total Extracts obtained, g.}}{\text{Amount of wattle used, g.}} \times 100 \quad (1)$$

$$\text{\% Yield (for tannins)} = \frac{\text{Total tannins obtained, g.}}{\text{Amount of wattle used, g.}} \times 100 \quad (2)$$

Maximum extractable material as total solubles[20] present in the wattle bark has been found to be 0.6 g/g of wattle. The total tannin content present in the wattle bark was estimated to be 0.35 g/g of wattle. Hence the efficiency of the process for the tow cases has been calculated using the Equation 3 and 4,

$$\text{\% Efficiency for total extract } (\eta) = \frac{\text{Total Extract obtained, g.}}{\text{Total solubles, g.}} \times 100 \quad (4)$$

$$\text{\% Efficiency for tannin content } (\eta') = \frac{\text{Tannins extracted, g.}}{\text{Total tannins available, g.}} \times 100 \quad (5)$$

Enhancement factors with ultrasound

The influence of ultrasound on extraction can be defined with different enhancement factors as α and β (Equation 6 and 7),

$$\alpha = \frac{Y_{us\_power}}{Y_c} \quad (6)$$

Where, Y_{us_power} – Yield of ultrasonic process for set power Y_c – Yield of control process at 30°C

In order to distinguish the effects of ultrasound on tannin extraction from that of total extracts obtained two factors viz., α and α' are designed.

α - Enhancement factor for total extraction
α' - Enhancement factor for tannin content in the extract

$$\beta = \frac{Y_{us\_temp}}{Y_c} \quad (7)$$

Where, Y_{us_temp} – Yield of ultrasonic process for set power Y_c – Yield of control process at set temperature (*t*)

Similarly, β – Enhancement factor for total extraction β' – Enhancement factor for tannin content in the extract

Shrinkage temperature (T_s) measurement

Shrinkage temperature, which is the measure of degree of tanning, has been analyzed for pickled as well as wattle extract (UE_S & C_s) treated pelts. The measurements were carried out using shrinkage tester as per SLTC official testing method.[20]

Effect of different process parameters

Effect of ultrasonic output power

The experimental set up consists of an ultrasonic probe immersed in a process beaker, which contains 2 g of wattle in 60 ml water. The sample was sonicated at different wattages of 40, 60, 80,100 and 120 W. At intervals every 1 h for 8 h, samples were withdrawn and subjected to spectrophotometric analysis and gravimetric analysis by methods mentioned above. The tannin content and weight of dried extract per gram of wattle at different time intervals was calculated.

Effect of temperature

The effect of temperature on the leaching of tannins from wattle bark has been studied. The experimental set up consists of a water bath with a thermostatic control unit to maintain the temperature. The process beaker, which contains 2 g of wattle immersed in 60 ml of the solution, is placed in the water bath. The temperature of the water bath was maintained at different values of 30, 40, 50 and 60°C. Ultrasonic output power has been maintained at 80 W. Samples were withdrawn at end of every 1 h, for 8 h and subjected to gravimetric and spectrophotometric analysis as mentioned above. The values of tannin content and the weight of dried extract per gram of wattle were calculated corresponding times, for each of the temperatures.

Effect of mechanical agitation

The effect of stirring on the leaching of tannins from wattle bark has been studied. 2 g of wattle and 60 ml of water are added to a process beaker. The process beaker is placed in a magnetic field where agitation is effected by the use of a magnetic pellet. Ultrasonic output power has been maintained at 80 W. Samples are withdrawn at intervals of every 1 h for 8 h and the Spectrophotometric and gravimetric analysis was performed. The values of tannin content and weight of extract per gram of wattle are measured and noted down.

RESULTS AND DISCUSSIONS

Quantitative analysis of wattle tannin

Calibration graph for wattle tannin as *atechin* equivalents with absorbance value at 760.5 nm has been drawn and equation was found to be equation Y = 0.04965 × X. Tannin content was calculated after taking into account of the dilution factor. Tannin content of the unknown extract solution has been determined by adopting the procedure as described in the earlier section.

Effect of ultrasonic output power

The total amount of extract obtained (which include tannins and non-tannins) after sonication for 8 h showed a significant increase from 0.32 g/g wattle at 40 W to 0.49 g/g for 120 W, as shown in Figure 1. A steep increase in the amount of total extract can be observed at ultrasonic output powers till 60 W after which the increase is gradual. Enhancement factors α and α' for given ultrasonic power as compared to control process is given in Table I. This trend suggests ultrasound effect is realized in a better manner for overall extraction process including the tannin materials present in the wattle bark. Ultrasound also helps in overcoming mass transfer resistance in leaching of tannin from wattle bark.The extraction of tannins improved with increase in power of sonication from 176.4 (mg/g wattle) at 40 W to 257.6 (mg/g wattle) at 120 W as shown in Figure 2. There is significant increase in % efficiency of total extraction from 53% to 81% with increase in power of ultrasound from 40 W to 120 W as compared to of 28% for control (30°) for 8 h extraction as shown in Figure 3. Similarly, the % efficiency of tannins extracted increased from 50% to 74% as compared to 44% for the control.

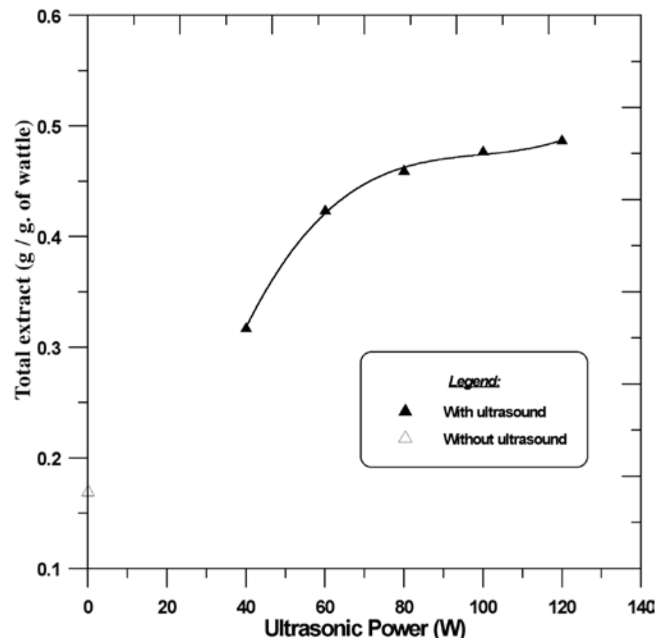

Figure 1. – Effect of Ultrasonic output power on total extraction compared to control at 30°C.

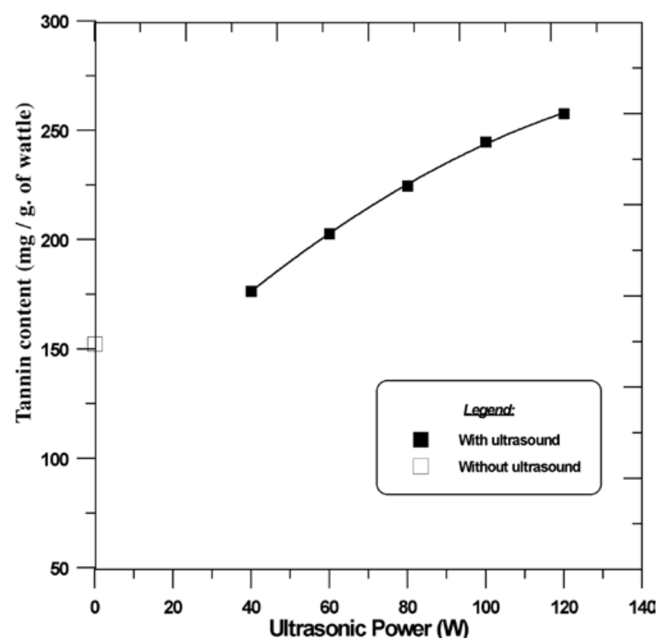

Figure 2. – Effect of Ultrasonic output power on tannins extracted compared to control at 30°C.

Effect of ultrasound on extraction kinetics

The amount of extract increases as time progresses to a certain value and then reaches a steady value after equilibrium is attained as show in Figure 4a. The time taken to attain equilibrium is approximately the same for all powers of sonication. However the equilibrium extraction shows an increasing trend with increase in power. It is interesting to note that, during the initial stages sonication at 60 W yields a greater amount of extract than sonication at 80 W. Similar to the trend for total extract, the tannin content increases with increasing ultrasonic power as show in Figure 4b.

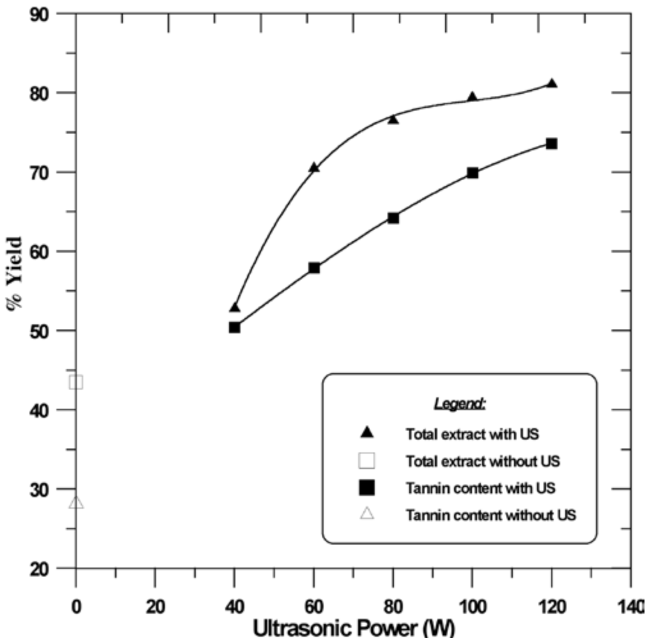

Figure 3. – Effect of ultrasound on % yield of extract compared to control at 30°C.

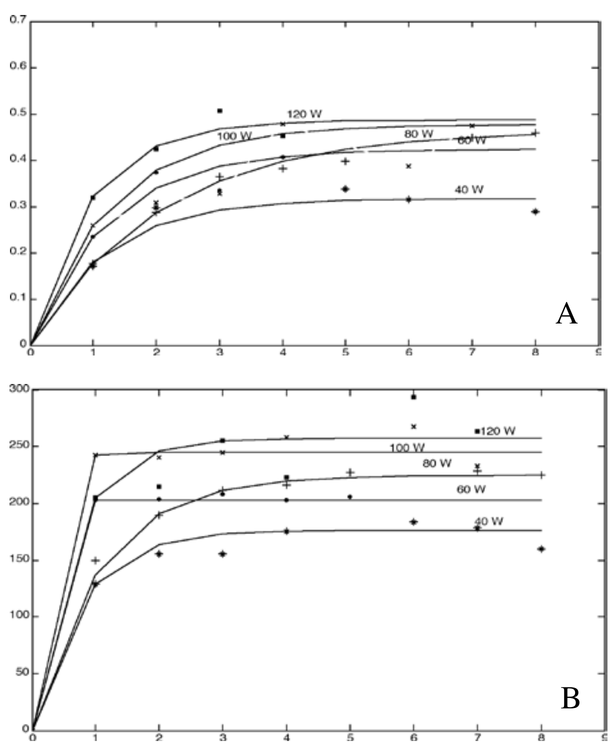

Figure 4. – Effect of ultrasound power on kinetics of extraction a) Total extraction b) tannins extracted.

Effect of temperature on control process

In case of control process, increase in temperature gives increase in total extracts obtained from 0.17 (g/g wattle) at 30°C to 0.43 (g/g wattle) at 60°C as shown in Figure 5. The amount of extracts obtained on increasing the temperature shows a 2 fold increase at 40°C to 2.5 fold increase at 60°C, on comparing with extract obtained at 30°C. A significant increase in the amount extracted at 40°C can be noted when compared to 30°C. At higher temperatures there is a steady increase in the amount of total extraction. It was observed that higher rate of extraction during the initial stages after which the amount of extract reaches an equilibrium value.

Tannin content also increases as the temperature increases. Unlike the trend for total extract, the tannin content does not show a drastic increase when temperature is raised from 30°C to 40°C, which implies that extraction of non-tans increases as temperature increases from 30°C to 40°C. A steady increase in tannin content at higher temperatures is observed. Increase in tannin content increases (152.3 to 275 mg/g. of wattle) with temperature (30 – 60°C) indicating that solubility of tannins increases with temperature. Enhancement factors β and β' with ultrasound, 120 W as compared to control process at set temperature are given in Table II. These results are similar to the case of α and α' suggesting ultrasound helps in over coming mass transfer resistance of tannin leaching process.

Effect of magnetic stirring

Magnetic stirring has resulted in a significant increase as seen in Figure 5, in the total amount of extract obtained in the control process. The increase is 2.06 times as compared to that at 30°C. However, higher temperatures of 40°C, 50°C and 60°C yield a better extraction than magnetic stirring. The betterment of yield on stirring may be explained by the lowering of resistance of the liquid film surrounding the solid particle.

Effect of ultrasound on extraction efficiency

Effect of ultrasound on % efficiency ($\eta_{us\text{-}power}$) of extraction for different ultrasonic power is shown in Table I. Effect of ultrasound on percentage yield (η_{temp}) of extraction for different set of temperature is shown in Table II. The results show better extraction efficiency for ultrasonic process (40 – 120 W) at ambient condition as compared to control process for temperature (30 – 60°C) in the case of total extracts obtained. Extraction efficiency for ultrasonic process at 120 W is better than control at temperature (30 – 50°C) and comparable with 60°C.

Efficacy of tannin extract – Tanning trials

The comparison of percentage exhaustion of tannin of the extract obtained by sonication at 120 W and the control extract is shown in Figure 6. The percentage exhaustion of the extract obtained by sonication is 35% greater than that of the control extract, indicating that the extract obtained by sonication has a better rate of diffusion through the pelt matrix. The reason is due to significant particle-size reduction in wattle extract obtained by ultrasonic method[2]. The percentage exhaustion increases till about 1 h after which it remains nearly constant, indicating that a saturation limit has been reached.

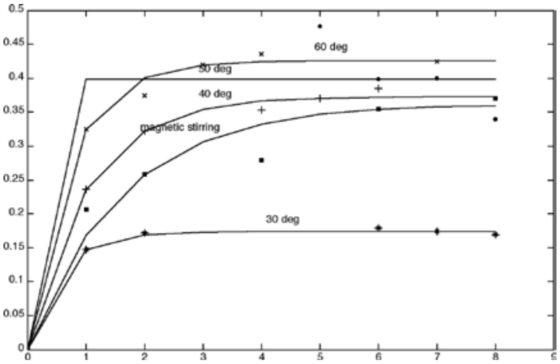

Figure 5. – Effect of magnetic stirring on total extraction for control process.

Shrinkage temperature (T_s)

T_s analyses indicate 84°C for 20% (*w/v*) UE_s treated pelt as compared to that of 80°C for commercial wattle powder. Better thermal stability for UE_s treated pelts can be attributed to the possible particle size reduction of tanning agents and better diffusion through the pelt matrix.

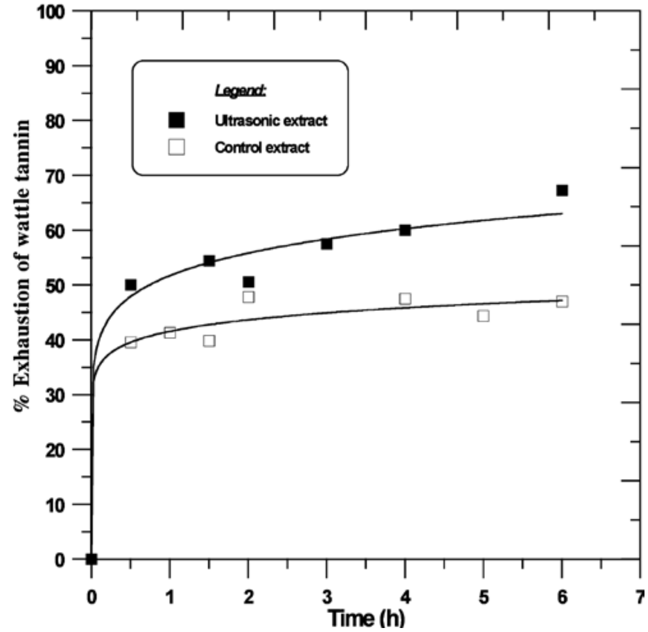

Figure 6. – Comparison of % Exhaustion of tannins for ultrasonic and control extract.

TABLE I

Enhancement Factors (α) and % Extraction Efficiency (η) for Various Ultrasonic Output Powers with respect to Control Process at 30°C for 8 h

Power (W)	40	60	80	100	120
α	1.9	2.5	2.7	2.8	2.9
α'	1.2	1.3	1.5	1.6	1.7
$\eta_{us\text{-}power}$ (%)	53	71	77	79	81
$\eta'_{us\text{-}power}$ (%)	50	58	64	70	74

TABLE II

Enhancement Factors (β) and % Extraction Efficiency (η) for Ultrasonic Output Power (120 W) at Ambient Condition with Respect to Control at Various Temperatures for 8 h Process

Improvement factor	Temperature of control extraction (°C)			
	30	40	50	60
β	2.7	1.2	1.2	1.1
β'	1.7	1.3	1.1	0.9
η_{temp}	28	62	67	71
η'_{temp}	44	59	70	79

CONCLUSIONS

The present study leads to following conclusions,

- Two distinct substances present in wattle bark in the form tannins and non – tannins in the leaching process, effectively monitored by quantitative and total extract analyses for the processes with ultrasound as well as control process.

- The overall results indicate significant 2-3 and 1.2-1.7 fold improvement respectively for total extract and tannin content due to the use of ultrasound 40 -120 W as compared to control at 30°C.

- The enhancement factors α, α' and β, β' (for 120 W) suggests ultrasound helps in overall enhancement in wattle extraction process for leaching tannin as well as well as non - tannins both of which are essential for any tanning process to achieve better stabilization of the pelts.

- Tanning experiments conducted on pieces of buffalo pelt using extract obtained by sonication at 120 W and control at room temperature revealed that % exhaustion of tannin in the former case was around 35% greater than the latter, indicating a better quality and superior rate of diffusion through the pelt matrix.

- The results show that significant improvement in mass transfer enhancement in wattle bark tannin extraction is possible due to the use of ultrasound even on dispensing with external heating as compared to control process at 60°C.

- Therefore, the present study clearly indicates use of ultrasound, as an effective tool in wattle tannin extraction is a viable option with added advantages. This technique is useful and applicable for extracting bioactive components from plant materials.

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