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Studies on the use of power ultrasound in solid–liquid myrobalan extraction process

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Abstract

Focus on eco-friendly processing techniques makes vegetable tanning a viable option in leather processing and establishes the subsequent need for the more efficient methods of extraction in tannin manufacture. Application of ultrasound has been tried in the extraction of tannins from myrobalan nuts in order to improve the extraction efficiency, to perform the extraction under milder process conditions and to reduce the process time. The influence of process parameters such as ultrasonic output power, time and temperature has been studied. Scale-up trials and the use of ultrasound in pulse mode have also been attempted. The results show that a three- to fivefold improvement is possible with ultrasonic output from 20 to 100 W. Extraction efficiency has been calculated from the maximum extractable materials from myrobalan nuts. Extraction efficiency is found to be 90% for ultrasound, 100 W without external heating as compared to 77% for control process at 70 °C for 4 h. Therefore, ultrasound could be employed even dispensing with provision for temperature controls. The use of ultrasound in pulse mode offered 70% extraction efficiency of continuous mode. Scale-up trials indicate that there exists an optimum ultrasonic output power depending on the amount of nuts used, to achieve better extraction efficiency. The effectiveness of ultrasonically extracted tannin solution has also been tested in the tanning process for its applicability. The degree of tanning efficacy has been assessed by shrinkage temperature measurement. The results indicate that ultrasonically extracted tannin solution is suitable for tanning process. Therefore, application of ultrasound in tannin extract manufacture is a viable option with added advantages.

Keywords: Cleaner tannin extraction; Leather; Tanning; Power ultrasound; Solid–liquid extraction

1. Introduction

Vegetable tanning is one of the oldest methods of tanning. The process was performed using raw plant materials as such up to the middle of the 19th century. Tanning extracts were first introduced in the leather industry during 1860–1870. About 90% of the vegetable tannin extract produced in the world is utilized in leather industry [1]. The term 'tan' is said to have been derived from the Celtic word for Oak and the word tannin was first introduced by Seguin in 1796 to denote the water extractable matter in certain plant tissues capable of converting animal hide/skin in to leather. The vegetable tannins are water-soluble polyphenolic compounds having molecular weight in the range of 500–3000 Da [2,3]. Based on their chemical structure, the vegetable tannins are classified as:

(i) Hydrolyzable type (e.g. Myrobalan, Sumac, etc.); these tannins are esters of phenol carboxylic acid used mainly for preventing the oxidation of condensed tannins and for lightening the dark color in vegetable-tanned leather or making light-colored leathers.
(ii) Condensed type (e.g. Wattle, Quebracho etc.); these tannins are condensed proanthocyanidins based on flavonoids and polyhydroxy flavan, used as the main tanning agent.

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1.1. Power ultrasound

Ultrasound may be broadly classified according to frequency range as power ultrasound (20–100 kHz) and diagnostic ultrasound (1–10 MHz) [4]. The use of power ultrasound is known to have significant effects on the processes such as cleaning, homogenization, emulsification, sieving, filtration, crystallization, extraction, degassing and stripping [5].

When a liquid is irradiated by ultrasound, microbubbles 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 microjets and shock waves [6]. Moreover, in the liquid phase surrounding the particles, high micromixing will increase the heat and mass transfer and even the diffusion of species inside the pores of the solid [5].

1.2. Overview of the tannin extraction process

The manufacture of the vegetable tanning extract is essentially based on the extraction of tannins from the tannin-bearing material using a suitable solvent, usually water, followed by concentration and spray drying (to get powder) or vacuum dried (to get solid). Generally, extraction is performed in wooden vats containing tannin-bearing material connected in series [7]. Liquor from the previous vat is transferred to the next vat by counter current extraction technique so that at the end of the process fairly concentrated liquor is obtained. In some of the methods, extraction is also assisted with agitation. CLRI has developed a microprocessor-based multistage counter-current leaching technique to improve the extraction efficiency [1]. Generally, extraction is performed in such a way that materials undergo three changes of float (water in this case) to obtain as high an extraction percentage as possible. Temperature of the float is maintained at around 70 °C. Since tannins, in general, are sensitive to temperature, extraction should not be performed at higher temperatures and the liquors not overexposed 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].

The use of power ultrasound in leather processing had been studied earlier and analyzed in detail for its potential benefits [8,9]. The application of power ultrasound in leather dyeing [10–12] and fat liquoring [13,14] has also been studied recently. Ultrasound has also been employed in the extraction of tannins from vegetable tanning materials. Increase in the extraction of tanning material under the action of ultrasonic vibration at a frequency of 800 kHz has been reported [15]. The extraction was completed in 45 min using ultrasound as compared to 8 h taken by stirring at 1400 rpm. A liquid willow bark extract of density 1.173 g/ml at 21 °C was treated ultrasonically by 400 W, 300 kHz with 14 kW anodic tension and 22 Mka. Tannin content increased from 49.6% to 51.4% after 90 min and dropped to 50.8% after 180 min. Insolubles decreased from 2.6% to 1.3% after 120 min and increased to 1.6% after 180 min, though the pH value of 4.9 was unchanged. Viscosity of vegetable tanning liquor was found to decrease from 171.6 to 133.4 cp [16,17]. Tanning material was first subjected to ultrasound and extracted at a lower temperature. This method of extraction offered products with a higher rate of diffusion into skin/hide [18].

Although some investigations were performed in the 1950s and 1960s on the extraction of vegetable tannins using ultrasound, they had not been further developed due to the lack of ultrasonic technology at that time and due to the tanning process itself shifting towards mineral-based tanning materials. The growing demand presently for eco-friendly tanning systems calls for a revival of vegetable tanning. The availability of vegetable tanning material being limited, there is a need to improve the extraction efficiency with better techniques. 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 [19].

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 processing.

The use of power ultrasound in the extraction of vegetable tanning material (myrobalan) as a resurgence has been studied in this paper with the following objectives:

- improve the efficiency of the solid–liquid myrobalan extraction process;
- perform the extraction in milder process conditions such as choice of lower temperature using ultrasound;
- study the effect of important process parameters such as ultrasonic output power, time, temperature, pulse mode in extraction and scale up trials; and
- verify the suitability of the ultrasonically extracted tannin solution in the tanning process.

2. Experimental

2.1. Experimental setup

Ultrasonic extraction experiments were performed using ultrasonic probe (VCX 400, Sonics and Materials, USA, 20 kHz and 0–400 W) in a jacketed glass vessel with provisions to set required output power and time (Fig. 1). Control experiments were performed in a water bath with provisions to control temperature.

2.2. Materials and methods

Myrobalan nuts of Indian origin were broken to small sizes. Since the extraction efficiency is generally dependent on the size of the myrobalan nuts used under the given process conditions, particle size analysis was performed. The particle size distribution of the broken myrobalan nuts was measured by sieve analysis as shown in Table 1.

Extraction was performed using water as solvent keeping the ratio of myrobalan nuts to water as 1:6. For the

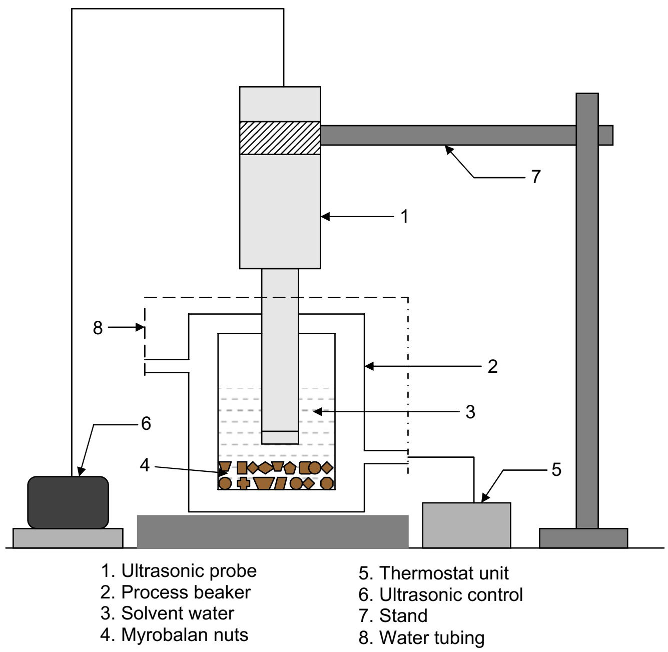

Fig. 1. Schematic representation of the ultrasonic probe experimental setup.

experiments, 20 g myrobalan nuts in 120 ml distilled water were transferred in two different 250 ml clean beakers. Experiments using ultrasound have been performed and compared with those not using ultrasound, in stationary condition (control process).

Influence of ultrasonic power 40–100 W without any external heating or cooling was studied and compared with control process at room temperature (30 °C). Effect of temperature 40–70 °C was also studied for ultrasound, 80 W as well as for control process for comparison.

2.2.1. Tanning trials

The effectiveness of myrobalan extract obtained using ultrasound in leather tanning process was studied by conducting tanning trails. For this purpose, pickled buffalo pelt with pH ~5.0 was taken for the tanning trials. Two sample pieces (E and C) with 6 × 6-cm sizes were 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 tannin solution (UE_S) and 'C' with control tannin solution (C_S). The pelt along with tannin solution were put into a 250 ml conical flask and agitated in a Remi shaking machine with a speed of ~80 strokes/min. Then the treated sample pelts were tested for shrinkage temperature (T_s) after 5 h of tanning.

Table 1
Particle size distribution of the myrobalan nuts used as determined by sieve analysis

Particle size (μm)	% of myrobalan nuts
>2411	68.66
>710	18.06
<500	2.805
>355	2.85
>250	1.91
<250	4.81

2.2.2. Analytical methods

Every 30 min, 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 until 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. The yield was calculated using the equation:

$$\text{Yield} = \frac{\text{Extract obtained (g)}}{\text{Amount of nuts used (g)}} \times 100$$

2.2.2.1. Maximum extractable material (MEM). Experiments were performed to find out the MEM from the myrobalan nuts. Two grams of nuts were soaked in 100 ml of distilled water (I-float) in a clean glass beaker and maintained at 70 °C with magnetic stirring. The beaker was tightly covered with aluminum foil to prevent the evaporation of water from the beaker. Samples were taken every day after 8 h and the weight of dried extract was analyzed by following a gravimetric procedure. Likewise, extraction was performed using fresh II-float and III-float separately to extract maximum soluble material, and analysis was performed. Then total maximum soluble material per gram of the nuts used was calculated and taken as MEM.

The extraction efficiency of a process can be calculated using the equation

$$\text{Extraction efficiency} = \frac{\text{Yield of the process}}{\text{Maximum extractable material (MEM)}} \times 100$$

2.2.2.2. Shrinkage temperature (T_s) measurement. Shrinkage temperature, which is a measure of the degree of tanning, was analyzed for pickled as well as myrobalan extract (UE_S and C_s) treated pelts. The measurements were performed using shrinkage tester as per IULTCS official testing method IUP 16 [20].

3. Results and discussion

3.1. Effect of ultrasonic output power

Experiments were performed with variation in ultrasonic output power, from 20 to 100 W. The extracts obtained per gram of myrobalan nuts used, during the course of the extraction process for ultrasonic output power 20, 40, 60, 80 and 100 W, is shown in Fig. 2. It can be seen that there are improvements in the extracts obtained (three- to fivefold) as

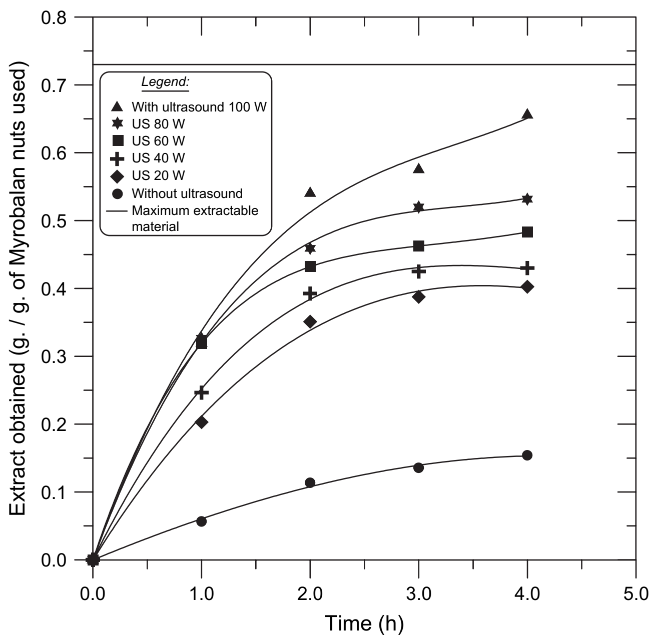

Fig. 2. The effect of ultrasound 20, 40, 60, 80 and 100 W on myrobalan extraction during the course of the extraction process.

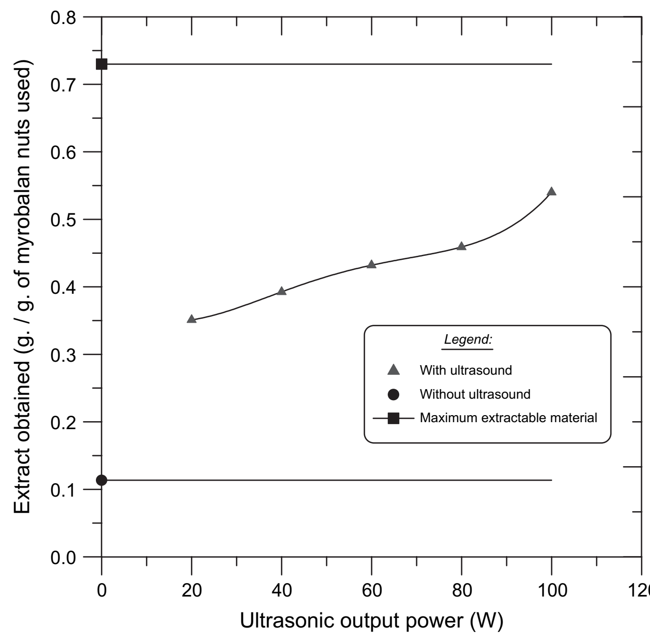

Fig. 3. The effect of ultrasonic output power: 20–100 W, on myrobalan extraction for 2 h extraction time.

ultrasonic output power increases from 20 to 100 W. The effect of output power on the amount of extract obtained for a 2 h process time is shown in Fig. 3. Here, the 2 h process time is considered to be most efficient in view of the fact that the electrical costs increase linearly with time of ultrasound extraction.

The results indicate that there is a significant improvement in the extraction with increase in the ultrasonic output power.

3.2. Effect of temperature

There is an increase in the extract obtained with increase in the temperature range 40–70 °C for the process with and without ultrasound, as shown in Fig. 4. The results indicate that there is a significant improvement in the extraction due to the use of ultrasound for the temperature range 40–70 °C, compared to the process without ultrasound. The effect of temperature for a 2 h extraction time is shown in Fig. 5. The process with ultrasound, 80 W at 40 °C is better than the process without ultrasound at 70 °C, in terms of yield. It can be concluded that ultrasound improves the extraction process even at lower temperatures.

3.3. Maximum extractable material (MEM)

The weight of the dried extract obtained was calculated from MEM experiments. There was no appreciable change in the weight of the dried extract obtained after 72 h for I-float. Therefore, cumulative weight of extract obtained for 72 h plus extract obtained for II-float (24 h) and III-float (24 h) was taken as a MEM from the myrobalan nuts. The results indicate that 0.73 g of dried extract obtained per gram of the nuts was the maximum extractable material (MEM).

3.4. Efficiency of the ultrasonic extraction

Efficiency of the different extraction process was calculated from the TEM value, i.e. 0.73 g of extract per gram of nuts used. The results show that 55–90% extraction efficiency is possible based on MEM for ultrasonic power of 40–100 W for 4 h as compared to that of 21% for the control process. Similarly, 93% extraction efficiency is possible in 4 h at

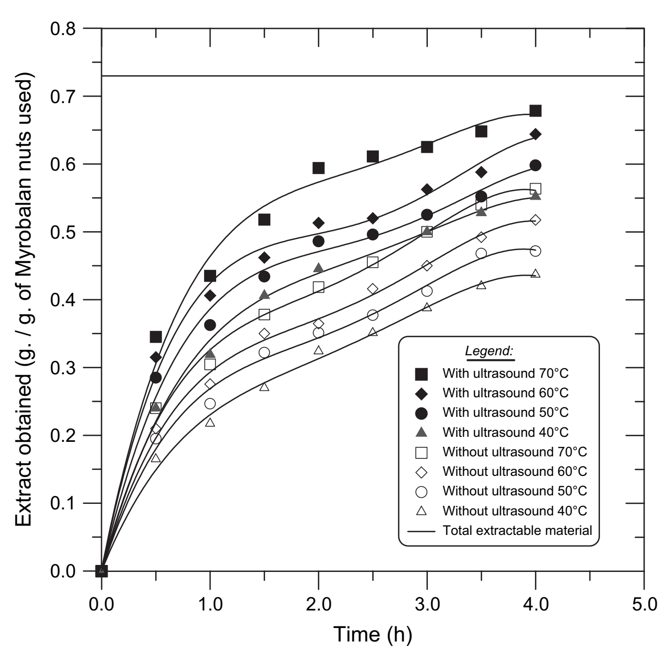

Fig. 4. The effect of temperature 40–70 °C on myrobalan extraction during the course of the extraction process with ultrasound 80 W and without ultrasound.

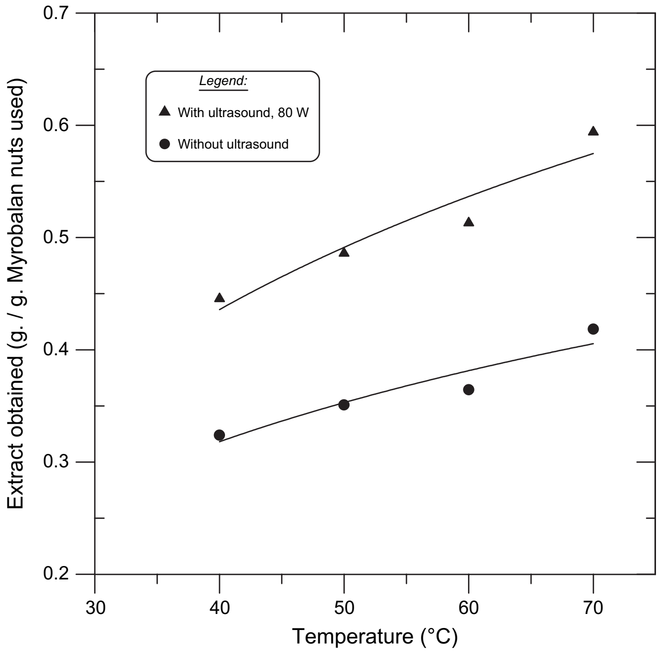

Fig. 5. The effect of temperature 40–70 °C, on myrobalan extraction for 2 h extraction time with ultrasound 80 W.

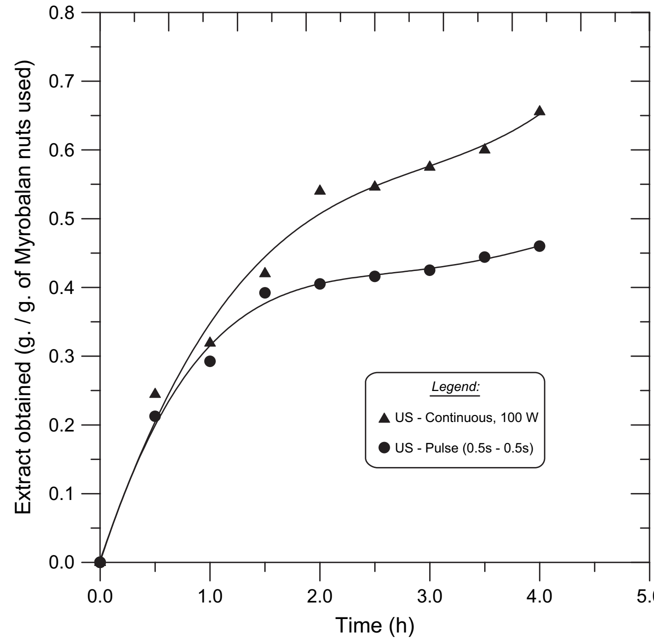

Fig. 6. The effect of ultrasound 100 W in pulse mode: 0.5 s *On* and 0.5 s *Off* on myrobalan extraction compared to continuous mode ultrasound during the course of the extraction process.

70 °C, 80 W as compared to that of 77% for the control process at 70 °C. Since commercial extraction is performed at around 70 °C, ultrasound without external heating gives 90% efficiency for 100 W as compared to 77% for the control process at 70 °C.

3.5. Effect of pulse mode

The effect of ultrasound, 100 W in pulse mode 0.5 s *On* and 0.5 s *Off* compared to ultrasound, 100 W in continuous mode was studied with the aim of reducing the electrical energy consumption, and is shown in Fig. 6. Ultrasonic pulse mode (0.5–0.5 s.) consumes only half of the electrical energy required for the continuous mode operation. The results indicate that 70% of the continuous mode extraction could be achieved using pulse mode for the 4 h process. This is equivalent to a gain of 20% extraction with respect to the electrical energy consumed for pulse mode as compared to continuous mode operation.

3.6. Tanning trials

Tanning experiments were performed for pickled pelts using 20% UE_s as well as C_s described in the Section 2.2.1. T_s of the pelts were measured after 5 h of tanning. The results indicate a T_s of 71 °C for samples treated with UE_s as compared to 66 °C for C_s. The T_s for the untreated pickled pelt extract was 61 °C. The improvement in T_s for pelts treated with UE_s may be due to better diffusion and subsequent tanning action using UE_s. Therefore, myrobalan extract obtained using the ultrasonic method has a better performance in the tanning process.

3.7. Scale-up study

Experiments were performed using 40 g myrobalan nuts, which is double the amount of nuts used in earlier experiments using ultrasound, 100 W. This was compared with extraction using 20 g nuts using same output power of 100 W. The results indicate a significant increase (7.9 g) of extract obtained for the 40 g process compared to the 20 g process for 4 h time period, as shown in Fig. 7. However, while the yield for the

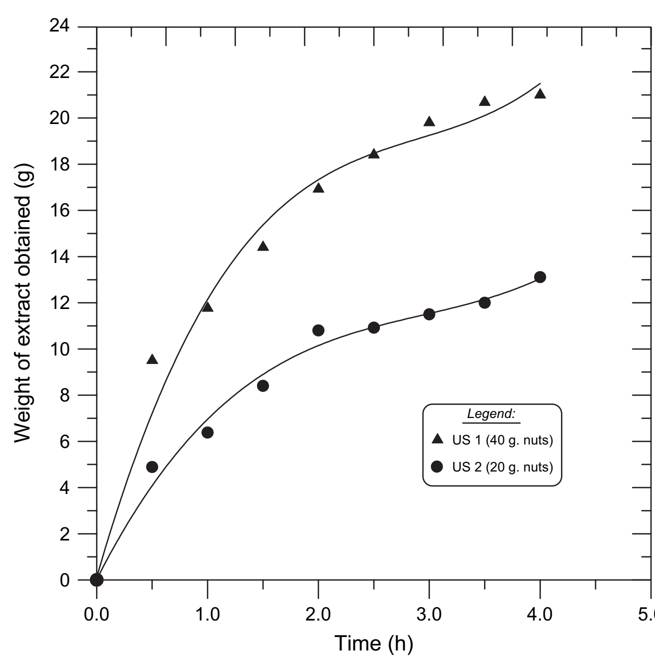

Fig. 7. The effect of amount of nuts used (20 g and 40 g) using ultrasound 100 W on myrobalan extraction during the course of the extraction process.

process using 20 g nuts is 65.5%, the value for 40 g is 52.5% for the same ultrasonic output power of 100 W. Therefore, there may exist an optimum value of ultrasonic output power with respect to the amount of nuts used in obtaining better extraction efficiency.

3.8. Use of ultrasound technology on an Industrial scale

For the extraction process on an industrial scale, it is essential to have suitable design and development of an ultrasound-aided extractor. The material of construction, not being reactive with tannins and having a low absorption coefficient for ultrasound, has to be selected carefully. Ultrasonic transducers as well as substrates have to be positioned suitably in the vessel for the batch extraction process. Also, solvent/liquor can be circulated inside the ultrasonic extractor for a continuous extraction process. Maintaining solid–liquid ratio inside the ultrasound-aided extractor is also essential for getting better efficiency. Our efforts are under way for suitable design and development of an ultrasound-aided solid–liquid vegetable tannin extractor.

4. Conclusions

The potential for use of ultrasound for improving the myrobalan tannin extraction process and the influence of important process parameters were studied at the laboratory level. The results indicate that there is a significant improvement (3–5 times) in the extract (yield) obtained per gram of the nuts used for the ultrasonic output power 20–100 W. The experiments to find out the effect of temperature show the process with ultrasound 80 W at 40 °C is better compared to the process at 70 °C without the use of ultrasound. Extraction efficiency is found to be 90% for ultrasound, 100 W without external heating as compared to 77% for control process at 70 °C for 4 h; whereas there was only a 21% efficiency for the control process at room temperature. Therefore, ultrasound could be used even under milder conditions with beneficial effects. The efficiency of extraction based on pulse mode extraction was observed to be 70% of that obtained on the basis of continuous mode. There is, therefore, a case for saving of energy without compromising significantly on the extraction efficiency. Initial scale-up trials show that optimal conditions can be found between the ultrasonic output power and the weight of nuts in order to achieve high efficiency of extraction. Tanning trials indicate that pelts treated with ultrasonically extracted tannin solution had a higher shrinkage temperature as compared to that of control under the given process conditions. The improvement in T_s for pelts treated with UE_s may be due to better diffusion and subsequent tanning using UE_s. This study clearly indicates the application of ultrasound for improving the extraction efficiency at milder conditions, generally known to be favorable for tannin extraction from plant sources. It is also shown that this technique does not involve any extra energy consumption in the form of heating. Experiments are in progress to: (a) extend the study with larger quantities of vegetable tanning materials and (b) ascertain whether the use of ultrasound technology on an industrial scale is feasible, by suitable design and development of an ultrasound-aided extractor to deal with larger volumes.

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