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Use of ultrasound in leather processing Industry: Effect of sonication on substrate and substances – New insights

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ABSTRACT

Influence of ultrasound (US) on various unit operations in leather processing has been studied with the aim to improve the process efficiency, quality, reduce process time and achieve near-zero discharge levels in effluent streams as a cleaner option. Effect of US on substrate (skin/leather) matrix as well as substances used in different unit operations have been studied and found to be useful in the processing. Absorption of US energy by leather in process vessel at different distances from US source has been measured and found to be significant. Effect of particle-size of different substances due to sonication indicates positive influence on the diffusion through the matrix. Our experimental results suggest that US effect is better realized for the cases with pronounced diffusion hindrance. Influence of US on bioprocessing of leather has been studied and found beneficial. Attempts have also been made to improve the US aided processing using external aids. Operating US in pulse mode operation could be useful in order to reduce the electrical energy consumption. Use of US has also been studied in the preparation of leather auxiliaries involving mass-transfer resistance. Preliminary cost analysis carried out for ultrasound-assisted leather-dyeing process indicates scale-up possibility. Therefore, US application provide improvement in process efficiency as well as making cleaner production methods feasible. Hence, overall results suggest that use of US in leather industry is imminent and potential viable option in near future.

1. Introduction

Leather processing involves conversion of putrescible raw skin/hide into useful material called leather by the process having common name 'tanning'. Collagen is the fibrous protein responsible in the formation of skin/hide through various hierarchical organizations and form basis material in leather making. The overall tanning process is classified into four main steps as pre-tanning for the removal of non-collagenous materials, tanning for the stabilization of the collagen matrix, post-tanning to impart functional properties and finishing to give aesthetics. Various chemicals employed in these unit operations have to diffuse through the pores of skin/hide [1]. The different pore-size ranges available in skin/hide as well as dimensions of substances utilized in leather processing are available [1]. The diffusion of these substances through skin/hide matrix is governed by Fick's law diffusion involving porosity and tortuosity factor as given by the Eq. (1),

$$J = -\frac{\alpha}{\tau} D_i \frac{\partial C_i}{\partial x} \quad (1)$$

where J, the flux, the amount of substance crossing unit area of leather in one dimension 'x'; α is the fraction of the volume occupied by the channels or pores; τ is the tortuosity (the ratio of the length of channel to the direct path), the flux, J, the amount of chemical crossing unit area of leather in the one dimension 'x'; D_i is the diffusion coefficient within the leather matrix; C_i is the concentration of the substance in the pores present in the imaginary layer 'i'.

In order to have better diffusion rate higher concentration of chemicals are employed in the conventional processing, leading to poor uptake efficiencies and environmental problems (Fig. 1). Therefore there is a need to improve the efficiency of these operations by having additional driving force such as the use of ultrasound. Ultrasound is a sound wave with a frequency above the human audible limit of 16 kHz. Ultrasound with frequency range 20–500 kHz normally employed in enhancing physical and chemical processes is called as 'power ultrasound' [2,3]. Cavitation in li-

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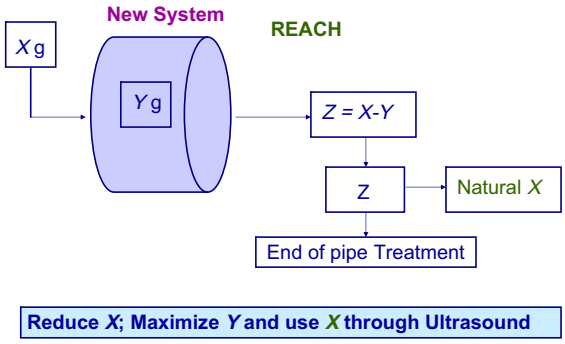

Fig. 1. Ultrasound assisted integrated approach towards near-zero, efficient, cleaner and greener leather making.

quid media is generally responsible for the enhancement apart from the process specific mechanisms [4,5]. In our recent paper, benefits due to the use of ultrasound in various unit operations in leather processing as well as related operations have been well documented [5]. Review paper in this research area has been made earlier [6,7]. We have also recently reported the preliminary investigations on the scale-up of ultrasound aided dyeing process [8] and ultrasound aided wattle tannin extraction [9]. There is a need to study the influence of ultrasound on substances and substrates used in various unit operations for better understanding. Analysis of absorption of ultrasound energy by substrates in leather processing is an important parameter. Since, the present trend is to shift from chemical to biological process in leather making, the influence of ultrasound in enzymatic-aided process has been studied. The effect of frequency (also dual) on the ultrasound-aided leather processing with leather dyeing, another important parameter has also been presented.

1.1. Ultrasound-aided leather processing: Earlier leads

Our earlier studies clearly demonstrated significant improvement in apparent diffusion coefficient of dye diffusing through the leather matrix under ultrasonic field [10] and ultrasound helps in a better manner for more difficult diffusion situation. The effect of substrate and substance in leather-dyeing process has been studied [11], which indicated pre-sonication of substrate (leather) or substance (dye) has no significant effect in enhancement. However, ultrasonic effect is significant when both leather and dye solution are subjected to ultrasonic field. This finding has given a clue for possible reversible pore-size changes during ultrasound-aided leather processing aiding diffusion of substances. We have also reported that stable cavitation is responsible for the enhancement in ultrasound-aided leather dyeing under the given process conditions [10,12]. Whereas, the effect of ultrasound on substrates such as vegetable tannin and fatliquor has yielded positive benefits due to attenuation of particle-size distribution aiding penetration through the matrix [13,14]. Pre-tanning operations studied such as soaking and degreasing resulted in improved efficiency due to better cleaning and emulsification of fat respectively with ultrasound [15,16]. Ultrasound also helps in uniform distribution of chemicals employed in leather making [10,14]. Attempts have also been made to improve the US aided processing using external aids such as air-bubbles or surfactant [12]. Studies on tannin and natural dye extraction showed significant improvements with ultrasound due to lowering of mass-transfer resistance in leaching process; provided cleaner option as well [17,18]. Ultrasound is found to be useful in promoting emulsification of vegetable and other oils which otherwise find difficulty in this process [19]. Another important findings from our studies illustrate pulse mode ultrasound operation is useful in enhancement with the aim to reduce electrical energy consumption [12,17]. Another study on pre-sonication of alkali employed in chrome recovery process from spent liquors is found to be useful in precipitation as $Cr(OH)_3$ [20].

1.2. Use of ultrasound – integrated approach towards near-zero, efficient, cleaner and greener leather making

Use of ultrasound as in-plant control measure in order to provide integrated solution to the diverse problems in leather processing in the growing environmental concern is helpful. Current leather processing systems demand end-of-pipe treatment as binding one for environmental compliance while leaving the inefficient process into practice. Therefore, ultrasound is expected to provide integrated approach towards near-zero, efficient, cleaner and greener leather making possible as shown in Fig. 1. The Fig. 1 depicts processing with *X*g input of chemical wherein *Y*g is taken up in the substrate leaving *Z*g into effluent streams. If *Z* is significant then end of pipe treatment becomes indispensable. One of the objectives of advanced processing systems such as ultrasound is to maximize *Y* and reduce *Z* to possible extent with optimal *X*. This would provide near-zero discharge of chemicals in the spent liquor streams. Another option is to use natural *X* as substance with efficient processing using ultrasound [18]. Thus, this approach would also facilitate to satisfy the recent environmental norm, viz., REACH (Registration, Evaluation, Authorisation and Restriction of Chemical substances) as stipulated by EU directive.

1.3. Objectives of the present study: New insights

In order to have the better understanding of the process, newer insights on the use of ultrasound in leather processing has been studied with the following objectives:

1. To study the effect of ultrasound on the particle-size of chemicals/bio-chemicals employed in leather processing.
2. Absorption of ultrasonic energy by leather in processing vessel.
3. To study the effect of ultrasound frequency and dual frequency in leather-dyeing process.
4. To study the effect of ultrasound on native enzyme based unhairing process.
5. To study the influence of ultrasound in chrome tanning process.

Hence, these aspects have been covered in this paper presented as application of ultrasound in leather processing useful in scale-up to make a viable alternative process.

2. Experimental

2.1. Experimental set-up

Experiments in presence of ultrasound were carried out 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 [12,18]. Control experiments were carried out in a water in absence of ultrasound with provisions to control temperature.

2.2. Materials and methods

Commercial unhairing enzyme *Microdep 'C'* (Textan chemicals Pvt. Ltd. India), Commercial Lime powder (70% purity), Syntan (Synthetic tanning agent) *Basyntan DI* (BASF India chemicals Ltd.). Dyeing experiments were carried out using Bordeaux IV (CI