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Sono-leather technology with ultrasound: A boon for unit operations in leather processing – review of our research work at Central Leather Research Institute (CLRI), India

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ABSTRACT

Ultrasound is a sound wave with a frequency above the human audible range of 16 Hz to 16 kHz. In recent years, numerous unit operations involving physical as well as chemical processes are reported to have been enhanced by ultrasonic irradiation. There have been benefits such as improvement in process efficiency, process time reduction, performing the processes under milder conditions and avoiding the use of some toxic chemicals to achieve cleaner processing. These could be a better way of augmentation for the processes as an advanced technique. The important point here is that ultrasonic irradiation is physical method activation rather than using chemical entities. Detailed studies have been made in the unit operations related to leather such as diffusion rate enhancement through porous leather matrix, cleaning, degreasing, tanning, dyeing, fatliquoring, oil–water emulsification process and solid–liquid tannin extraction from vegetable tanning materials as well as in precipitation reaction in wastewater treatment. The fundamental mechanism involved in these processes is ultrasonic cavitation in liquid media. In addition to this there also exist some process specific mechanisms for the enhancement of the processes. For instance, possible real-time reversible pore-size changes during ultrasound propagation through skin/leather matrix could be a reason for diffusion rate enhancement in leather processing as reported for the first time. Exhaustive scientific research work has been carried out in this area by our group working in Chemical Engineering Division of CLRI and most of these benefits have been proven with publications in valued peer-reviewed international journals. The overall results indicate that about 2–5-fold increase in the process efficiency due to ultrasound under the given process conditions for various unit operations with additional benefits. Scale-up studies are underway for converting these concepts in to a real viable larger scale operation. In the present paper, summary of our research findings from employing this technique in various unit operations such as cleaning, diffusion, emulsification, particle-size reduction, solid–liquid leaching (tannin and natural dye extraction) as well as precipitation has been presented.

1. Introduction

Ultrasound with a frequency from 20 to 100 kHz is generally called as power ultrasound used for enhancing physical as well as chemical processes and those with frequency range 1–10 MHz are called as diagnostic ultrasound. Considering skin or hide or leather (S/H/L) which is immersed in a chemical solution of initial concentration C_0. Schematic representation of diffusion is shown in Fig. 1. Initially bulk diffusion of chemical takes place from bulk solution to the S/H/L thin boundary layer, from thin boundary layer to S/H/L surface layer. Then diffusion has to take place through pores of S/H/L matrix. Conventional process vessels such as drum or paddles can only bring the chemicals from bulk solution to the S/H/L surface layer. Then further pore diffusion is dependent mainly on the concentration gradient across the layers and degree of binding on the fibre surface [1]. In case of binding of substances on the fibre surface (Fig. 2), may block the subsequently diffusing substances ending up in hindered diffusion in conventional leather processing. Complete penetration throughout the cross-section of S/H/L is essentially required for good quality of the final leather. Therefore, skin or Leather as a matrix of three-dimensional collagen or tanned collagen fibre bundles weave has diffusional restrictions for chemicals diffusing into the cross-section and may pose

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Fig. 1. Diffusion phenomena in leather processing.

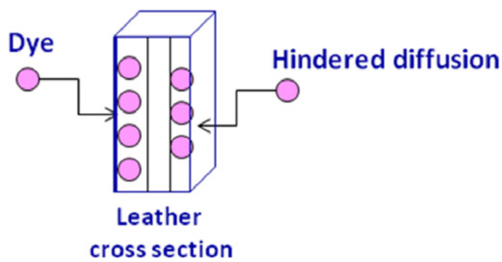

Fig. 2. Blocking of path leading to hindered diffusion through skin or leather matrix.

resistance to the larger sized molecules. Hence, some advanced techniques such as use of ultrasound for facilitating the pore diffusion process by providing additional driving force are being pursued [1]. In the present paper, review of our research findings from employing ultrasound technique covering about ten unit operations related to leather processing has been presented as salient outcome.

1.1. Ultrasonic cavitation

Generally, the sonochemical activity arises mainly from acoustic cavitation in liquid media explained as nucleation, creation, growth and collapse of micro bubbles in a micro second time scale [2–4]. The acoustic cavitation occurring near a solid surface lead to micro-jet formation and facilitate the liquid to move with a velocity of upto 10^4 cm s^{-1} resulting in increased diffusion of solute inside the pores of the specimen. Modelling of batch sonochemical reactor considering the acoustic cavitation parameters for a liquid phase reaction was made earlier [5]. In the leather state, localized temperature raise and swelling effects due to ultrasound may improve the diffusion [6]. Low ultrasonic intensities of the order 1–3 W cm^{-2}, experienced in the case of the ultrasonic tank produce stable cavitation bubbles in liquid medium [6]. The stable cavitation bubbles oscillate often non-linearly around some equilibrium size. There is an acoustic streaming effect associated with the stable cavitation responsible for the enhanced molecular motion and stirring effect of ultrasound. In case of leather dyeing, the effects produced due to stable cavitation may be realized at the interface of leather and dye solution [6].

2. Experimental setup

Experiments with ultrasound have been carried out using two types of ultrasonic equipments (i) ultrasonic tank (4 L) 33 kHz, 150 W (Roop-Telsonic ultrasonics Ltd., India). The available ultrasonic output power in the process vessel as measured by the calorimetric method is 76 W [6]. (ii) ultrasonic probe, 20 kHz (VCX 400, Sonics & Materials, USA) for variation in ultrasonic output power [9,10]. Control experiments in a static condition were carried out in a water bath (Buchi, Switzerland) having temperature controller. Drumming experiments were carried out using a sample drum (Ronald, India) having 22-cm diameter × 8.5-cm width and having temperature and rotation speed control.

3. Influence of ultrasound in various unit operations of leather processing

The influence of ultrasound on various unit operations in leather processing has been studied, reviewed and analyzed by our group citing the similar previous studies carried out in the area [7]. Review of the earlier studies carried out was also available elsewhere [8]. In the present paper, important results of influence of ultrasound in various unit operations with specific mechanism and ultrasonic condition are presented as Table 1.

3.1. Ultrasound aided diffusion in leather processing

If α is the fraction of the volume occupied by the channels or pores and τ is the tortuosity (the ratio of the length of channel to the direct path), the flux, J, the amount of dye crossing unit area of leather in the one dimension 'x' may be written as Eq. (1),

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

Substituting the value for α and τ from the literature the Eq. (1) be,

$$J = \frac{0.5}{3} D_i \frac{\partial C_i}{\partial x} \quad (2)$$

A diffusion model for leather processing has been proposed taking into account of pore characteristics in leather [1]. Apparent diffusion coefficient (D), a measure of diffusion rate of chemicals through the pores of skin/leather matrix has been calculated from the experimental data and found to be improved due to ultrasound [6,9]. As described in Section 1, ultrasound also helps in the case of hindered diffusion involving larger sized substances as well as clogging of pores. Pre-sonication studies on substrate as well as substances have been carried out and found that ultrasonic effect is better realized when both of them are present during the operation [10]. This gives evidence for possible real-time reversible pore-size changes in the skin/leather matrix, during the ultrasound propagation which could be one of the reasons suggested for the enhancements obtained with ultrasound in leather processing. Distribution of chemicals across the thickness for a given area as well as in entire area of the skin/leather which is another important parameter for any unit operation and for the quality of final leather has been studied and found to be improved due to the use of ultrasound.

3.2. Leather dyeing process

Dyeing experiments were carried out under ultrasonic field and compared with process without ultrasound as well as conventional drumming conditions. The results indicate that there is a substantial increase in the rate of diffusion of dye through leather matrix under ultrasonic field as evident from D values for various types of dyes. Typically, D value of 1.2×10^{-5} cm^2 s^{-1} for metal complex dye has been obtained with ultrasound as compared to 9.01×10^{-7} cm^2 s^{-1} for control process under similar conditions, yielding 20-fold improvement in D value due to the use of ultrasound. The order of rate of uptake of chemicals has been found to be ultrasound (static) > conventional drumming > without ultrasound (static) [10]. The possible mechanisms for enhancements obtained with ultrasound has been studied through (i) variation in diffusivity of same generic substances such as dyes (acid, direct, metal complex) [6] and (ii) variation in diffusional resistance of substrate (Leather, powdered leather) [1]. Interestingly, it has been found that (i) ultrasound effect is more realized for substances having low diffusivity due to their larger sizes and (ii) for leather as substrate as compared to powdered leather which is having lesser