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Ultrasound assisted chrome tanning: Towards a clean leather production technology

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ABSTRACT

Nowadays, there is a growing demand for a cleaner, but still effective alternative for production processes like in the leather industry. Ultrasound (US) assisted processing of leather might be promising in this sense. In the present paper, the use of US in the conventional chrome tanning process has been studied at different pH, temperature, tanning time, chrome dose and US exposure time by exposing the skin before tanning and during tanning operation. Both prior exposure of the skin to US and US during tanning improves the chrome uptake and reduces the shrinkage significantly. Prior exposure of the skin to US increase the chrome uptake by 13.8% or reduces the chrome dose from 8% to 5% (% based on skin weight) and shorten the process time by half while US during tanning increases the chrome uptake by 28.5% or reduces the chrome dose from 8% to 4% (half) and the tanning time to one third compared to the control without US. Concomitantly, the resulting leather quality (measured as skin shrinkage) improved from 5.2% to 3.2% shrinkage in the skin exposed to US prior tanning and to 1.3% in the skin exposed to US during the tanning experiment. This study confirms that US chrome tanning is an effective and eco-friendly tanning process which can produce a better quality leather product in a shorter process time with a lower chromium dose.

1. Introduction

Tanning is the process of converting the putrescible skin and hides from different animals into a durable and manageable material called leather. Leather making is a very long process and consists of many different chemical and mechanical process steps [1]. The most important step of the whole leather making process is the tanning step, which is performed commonly either by vegetable or mineral tanning. More than 85–90% of the leather making is performed by chrome tanning, which is the most common type of mineral tanning currently applied [2,3]. Chrome tanning is preferred by most tanners because chrome tanned leathers are characterized by top handling quality, high hydrothermal stability and excellent user properties in addition to the shorter time required to produce finished leather [4].

Conventional chrome tanning is a two-step process. In the first phase, the tanning agent (chromium sulfate) will diffuse through the pores of the skin to reach the reaction site, i.e., the carboxyl groups of the collagen. Then, the chromium will react with the carboxyl group of the collagen to form inter- and intra-molecular crosslinks which increase the resistance against physical, chemical and biological agents [5,6].

Due to diffusion limitations of the chrome tanning agents (as well as the other chemicals used in the rest of the tanning unit operations), in conventional tanning, only 60–70% of the total chromium applied in the tanning process is consumed in the skin matrix while the other 30–40% remains in the spent liquor [1,7]. The low diffusibility of the chrome tanning agents results in different problems in the leather industry. The first problem relates to the quality of the leather produced. One of the methods to measure the quality of leather is the hydrothermal stability, which is dictated by the amount of chrome that has reacted with the carboxyl groups of the collagen and has, thereby, been fixed in the leather matrix. The more chromium can be fixed, the higher the hydrothermal stability [5]. Hydrothermal stability of leather products is commonly measured by shrinkage and boiling tests. The target is to produce leather that has the lowest percentage of shrinking possible (target is to reach 0% shrinkage) when the skin is boiled at 100 °C for 1–5 min or having a higher shrinkage temperature (possibly higher than 100 °C) during the shrinkage test when the skin is tested to determine the temperature at which the skin starts to shrink [8]. If more than the currently maximum chromium uptake of 70% could be achieved, the hydrothermal stability would increase [9,5]. The second problem is a high manu-

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facturing cost due to the loss of chrome tanning agent into the liquor instead of diffusing into the skin and the subsequent intensive technologies involved in the treatment and recovery process [10]. The last but not the least problem is the one caused by the discharge of chrome containing wastes into the environment which creates health problems for human, animal and other life forms [11].

To achieve a higher diffusion rate, in conventional tanning, a higher concentration of chemicals in the liquid is applied, which, however, only results in marginally better uptake efficiencies while causing even higher cost and environmental problems [12,13]. In addition to the dose of the tanning agent, many factors like temperature, pH and tanning time affect the rate of diffusion [14]. It is clear that an eco-friendly and effective alternative has to be explored so as to alleviate these problems. Applying ultrasound during the production process presents a potential answer.

A sound wave with a frequency above the human audible range (16 Hz–16 kHz) is called ultrasound (US). Power US is a sound with a frequency of 20–100 kHz, which is commonly used for enhancing physical processes such as cleaning, emulsification, crystallization, extraction in addition to accelerating chemical reactions [15,13].

The sonochemical activity arises mainly from acoustic cavitation in liquid media [16,17]. The effects of cavitation can either be chemical or physical. Strong acoustic streaming, high shear stress near the bubbles, micro-jets near solid surfaces because of turbulences and collapse of cavitation bubbles, increase in local temperature and pressure and generation of free radicals from the use of power ultrasound are some of the effects which have been used for different applications [18–20]. Detailed studies of power ultrasound have been conducted on the application of the effects of cavitation in environmental sciences, biotechnology, polymer chemistry, electrochemistry, nanotechnology, chemical synthesis, green chemistry, food processing, and other manufacturing processes [19,21–23]

In solid–liquid systems, the implosion of cavitation bubbles accelerates the liquid to move with a velocity of up to 10^4 cm/s and generates micro-jets directed towards the solid surface [24–26]. These micro-jets cause an increase of the pore diameters at the surface of the solids and create micro-mixing in the liquid near the surface. This results in an increased diffusion of solutes inside the pores of the solid surface and thus facilitates mass transfer. In materials like leather, the localized temperature increase and the swelling effect due to US may also improve the diffusion [13,20].

US technology has already been well exploited in the dyeing step of leather processing and was found to be very efficient in increasing the dyeing quality of the finished leather, reducing the environmental risk and costs for dyeing. In an experiment carried out for dyeing wet-blue bovine hides and sheep skins using an ultrasonic bath with a frequency of 38 kHz and intensity of 1.36 W/cm^2 at different temperatures, the process time was shortened by up to 70% and the dye uptake was increased by up to 50% [27]. A dyeing experiment using cow crust leather was also carried out using US (33 kHz and 150 W) at a varying dye amount, temperature, dye type and time. The dye uptake (dye administered minus dye in the spent liquor divided by the dye administered) increased by 30–45% and 15–35% when compared to the control process in stationary and conventional drumming, respectively. The study also indicated that it is possible to achieve 97.5%, 85%, 91.6% dye uptake in 3 h dyeing time using US compared to only 56.3%, 38.9%, 28.9% without US in a stationary condition for acid black, metal-complex black and direct black dyes, respectively [26]. Sivakumar et al. [12] also studied the effect of US on chrome tanning by using a pickled cow pelt at pH 2.8 and 32 °C with an 8% basic chromium sulfate dosage. As a result, they found a 2–3-fold increase of the chrome uptake by using 80-100 W ultrasound at the indicated parameters [12].

In addition, improvement has been achieved by using US in the pre-tanning operations such as soaking, liming and degreasing during which hair and grease are removed from the hides. US (33 kHz and 150 W) helps to improve the fat removal in the degreasing process (duration of 2 h) of sheep skin with kerosene as a solvent from 2.2% in the control (conventional tanning) to 54.6% with the aid of US [28–30].

It is clear that technologies which can increase the diffusion and uptake of chrome into the leather, thereby decreasing the tanning cost, producing quality leather with high hydrothermal stability, and alleviating environmental problems have to be explored. There have been studies before on the effect of ultrasound in leather manufacturing, but these had different processing steps in scope, such as dyeing, unhairing, etc. To the best of our knowledge, there are no detailed investigations performed on the effect of ultrasound exposure prior and during chrome tanning. Moreover, the knowledge gap on the effect of ultrasound on the quality of the leather produced by ultrasound assisted-chrome tanning needs to be filled. In addition, the optimum operational parameters for US assisted chrome tanning have to be determined. Therefore, the aim of this study is to investigate whether US application before or during the chrome tanning process improves the chrome uptake by the skins, thereby improving the leather quality and alleviating environmental burdens that are currently prevailing. Furthermore, if it is demonstrated that US assisted chrome tanning is beneficial, the optimum operational parameters are determined.

2. Material and methods

2.1. Experimental setup

From a wet salted sheep skin a pickle was prepared (by *lowering of the pH* value to the acidic region in the presence of salts to help with the *penetration* of tanning agents) following the conventional procedure at Modjo tannery, Ethiopia during which hair and grease are removed from the skins. Then, the skin was cut into 5 × 5 cm samples taken from the same lateral positions of the skin following the line of the backbone of the animal to achieve samples with a relatively similar thickness and grain surface [12,29,30].

The skin was exposed to US, either before chrome tanning or during chrome tanning. An US power generator UP200S from Hielscher Ultrasonics GmbH (Germany) with working frequency of 24 kHz was used, coupled to an S14 (14 mm diameter) sonotrode (an acoustic power density of 105 W/cm^2) at full pulse. For all US experiments, these frequency and power density settings were kept constant. Fig. 1 summarizes the experimental flow diagram. In the first series of experiments the pickled skin pieces were exposed to US *prior* to chrome tanning for 10 up to 60 min. Then, the exposed skins were chrome tanned with between 4% and 8% by weight basis chromium sulfate for 2 up to 6 h [12,29]. An industrial grade basic chromium sulfate (25.48% Cr_2O_3, 33% basicity) from Soda Sanayii A.Ş (Turkey) was used for all the tanning experiments.

The chrome tanning process was conducted in a 2000 mL glass beaker filled with water, of which the weight was equal to 170 times the weight of the skin and it was kept in a water bath to maintain the temperature at the specified value (within a range of 2 °C).

The beaker was stirred with a magnetic stirrer adjusted to 30 rpm. At the start of the tanning procedure half of the basic chromium sulfate was added, whereas the remaining half was added after one hour. An analytical grade sodium formate (3% by weight of the skin) was used as a masking agent shortly after the tanning