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Towards cleaner degreasing method in industries: ultrasound-assisted aqueous degreasing process in leather making

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ABSTRACT

Studies on ultrasound-assisted processes are gaining importance due to its effectiveness and facilitating green method in processing. Degreasing of skin/hide prior to tanning process is an important unit operation. Presence of large amounts of natural fat at the interior of skin/hide matrix makes degreasing process a challenging one. Conventionally, organic solvent and/or detergent based degreasing process are employed leading to environmental problems. In the present paper, the use of power ultrasound in aqueous degreasing process has been studied and compared with different degreasing systems. Glutaraldehyde pre-tanning has also been employed for carrying out the degreasing process at ultrasonic bath temperature. The results indicate that there is a significant increase in the degreasing efficiency due to the application of ultrasound. About 2-fold increase in fat removal has been observed due to the use of ultrasound as compared to control under the given process conditions. Comparing the degreasing efficiencies of the solvent with aqueous based ultrasonic processes, about 80% of the solvent degreasing efficiency could be obtained for aqueous degreasing process. This novel ultrasonic process helps in making aqueous degreasing process a viable option, which is eco-friendly even dispensing with temperature control measures.

1. Introduction

Degreasing and cleaning of metal parts, delicate instruments, textile/leather garment materials, etc. are essential operations which involve large quantities of hazardous materials such as organic solvents, acids, etc. There is a need for developing suitable eco-friendly degreasing system for these types of industries. Degreasing is also one of the important unit operations in leather making which involve removal of natural fat present in the skin/hide. If degreasing is not carried out properly, it may lead to fatty spue development, stains due to chrome soap formation and non-uniformity in dyeing and finishing. Difficulty in degreasing process is that bulk of natural fat is available at the junction of corium minor (grain) and major at the interior of the skin as depicted in Fig. 1. The natural fat content in the skin/hide depends on factors such as type of animal, place of live stock and climatic conditions. The natural fat content of different animals usually varies between 3 and 50%. The residual fat content after degreasing process may range from 1 to 2% (based on skin weight) for better quality of the final leather. It has been found that while sheep skins in general contain the highest amount of natural fat, those from New Zealand, Australia, UK, merino variety, etc., may contain up to 50% natural fat [1]. In addition to this, there is a non-uniform distribution of fat depending on the area of the skin/hide as reported earlier [2].

The natural fat in the animal skin is generally contained in fat cells, the walls of which consist of a protoplasmic envelope invested in reticular tissue [3]. Therefore, degreasing has to be accomplished by release of fat from the cellular confinement. Degreasing process also involves diffusion problem in skin/hide matrix structure having three-dimensional weave of collagen fibre bundles. The diffusion problem includes: (i) transport of degreasing chemicals into the fat site at the interior of skin/hide; (ii) emulsification of fat at the interior of the skin/hide and (iii) removal of the emulsified fat from the matrix. Thus, uniform and near complete removal of natural fat present in the skin/hide is not an easy task to perform. Hence, large amounts of environmentally sensitive organic solvents (such as white spirit or trichloroethylene) and emulsifiers are used in conventional degreasing process. There is a need to overcome these challenges in the degreasing process through process innovations such as the use of ultrasound to develop more efficient and cleaner technique.

Sound waves with frequency above the human audible range of 16 kHz are called as ultrasound. Ultrasound may be broadly classified according to frequency range as power ultrasound (20–100 kHz) and diagnostic ultrasound (1–10 MHz) [4].

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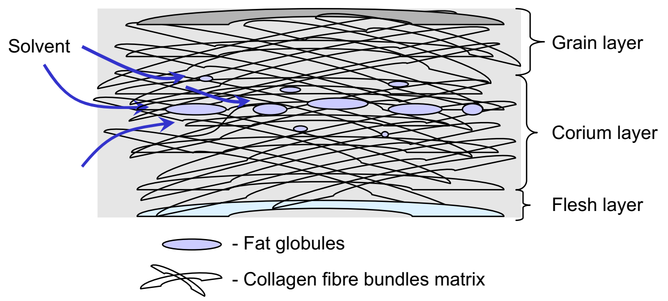

Fig. 1. Schematic representation of presence of fat in skin/hide and flow of solvent in degreasing process.

Ultrasound is known to enhance the emulsification and dispersion of oils/fat [5,6]. Conventional degreasing requires more emulsifier solvent ratio and process time for emulsification and additional solvent for washing out the emulsified fat. It takes about 2–3 h with 1–6 h washing time with brine to remove the emulsified fat [7]. Some physico-chemical principles of water-based degreasing process have also been described recently [8]. Surfactants such as nonylphenol ethoxylates, conventionally used in degreasing process have been banned by European Union from the year 2005. Therefore, it is very essential to develop a degreasing methodology without involving such toxic substances. The present study aims at emulsifying the fat present in the skin/hide and subsequent removal of the same with the aid of ultrasound by aqueous eco-friendly method.

Dry cleaning of finished leather in a tank with solvent was studied earlier with 22 and 44 kHz ultrasonic waves for 8 min to remove the oily dirt adhered with the leather [9]. Dry cleaning was good and there was no change in the property of leather. Ultrasound has been employed successfully for emulsification of oils/fat and in the preparation of fatliquor emulsion with reduction in emulsion particle-size [10,11]. Industrial application of ultrasound including cleaning and degreasing has been reviewed earlier [12]. The application of power ultrasound in leather processing has been studied elsewhere [13]. The uses of ultrasound in soaking [14,15], liming [16], dyeing [17–21], tanning [22,23] and fatliquoring [6,11,24] have been reported. In the present work, the influence of ultrasound in fat removal with different solvent systems has been studied. Generally, most of the ultrasonic processes are carried out in a pseudo-isothermal condition which requires additional heating or cooling of the ultrasonic bath especially for temperature sensitive materials. Hence, pre-tanning with glutaraldehyde has been employed for carrying out the ultrasonic degreasing process at ultrasonic bath temperature. The objective of the present work is to develop eco-friendly effective degreasing system for skin/hide using ultrasound at low intensity at specified frequency range without necessitating temperature controls.

1.1. *Relevant sonochemistry*

The sonochemical activity arises mainly from acoustic cavitation in liquid media, which are nucleation, growth and explosive collapse of microbubbles on a microsecond time-scale. The cavitational collapses occurring near a solid surface will generate microjets and shock waves [25]. 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 [26]. The intense agitation and dispersion effect, which is brought out by the effects of cavitation, results in an increase in the number of collisions between the fat particles and the water and hence better emulsification of fat in water.

2. Experimental section

2.1. *Ultrasonic experimental set-up*

Ultrasonic cleaner experimental set-up (Roop Telsonic Ultrasonics Ltd., India) generating ultrasound at 33 kHz frequency has been employed [17,19]. The power actually dissipated to the system was calculated to be 76 W, whereas the maximum available ultrasonic output power quoted by the manufacturer is 150 W [17]. There is a provision to control the temperature of the process liquor by circulating cold/hot water from thermostatic control. Efficacy of ultrasound in degreasing has been compared with control process under static condition.

2.2. *Materials and methods*

Pickled sheep skin from Arabian origin was used for the degreasing experiment. The initial fat content was analyzed at different areas of the skin. The pelt was cut into two halves through backbone for comparison of the process with and without ultrasound following the IUP/1 prescribed method of sampling and analysis [27]. Influence of different solvents such as, water (aqueous), trichloroethylene (TCE) and kerosene in degreasing has been studied. Experiments have been carried out in presence of ultrasound at 35 °C using 500% (*% based on pelt weight*) TCE along with 1% degreasing agent (*Degreasol WBI, Clariant, Ltd.*) and compared with degreasing process performed without ultrasound as a control process.

In order to find out the influence of ultrasound including the temperature effects, ultrasonic experiments were carried out without external cooling or heating, at ultrasonic bath temperature (T_{us}). The ultrasonic bath temperature, T_{us} rises from room temperature 30–50 °C in 2 h process time.

2.3. *Glutaraldehyde (GT) pre-tanning*

In order to make the pelt withstand temperature rise in the ultrasonic bath, glutaraldehyde pre-tanning was performed on the pickled pelt to improve the hydrothermal stability of the pelt. The cross-linking reaction between hydroxyl group of amino acids in collagen and glutaraldehyde is shown in Fig. 2.

A portion of the skin was cut separately and pre-tanned with 8% glutaraldehyde (25% soln.) for 2 h using 80% water and 8% salt. The final pH of the skin was adjusted to ~4.0 using 0.5% sodium formate and 1% sodium bi-carbonate. The shrinkage temperature of the skin was determined using '*Differential scanning calorimeter*' (*DSC*).

Ultrasound aided solvent degreasing using 500% TCE and 1% degreasing agent as well as aqueous degreasing with 500% water and 1% sodium lauryl sulfate were carried out on pre-tanned pelt at T_{us} for 2 h. Degreasing using 500% kerosene was also carried at ultrasonic bath temperature for 2 h.

Then, fat content in the pelt samples after degreasing has been analyzed and extent of fat removal was calculated.

2.4. *Analysis of fat content in the pelt*

The fat content in the pelt was determined by Soxhlet extraction method using dichloromethane as a solvent following IULTCS prescribed method [28]. The wet pelt sample was cut into small pieces and taken in an evaporating basin and dried at 30–35 °C for 16–18 h. Then the actual weight of the pelt was recorded (W). Then the dried pelt was transferred to the extraction thimble made out of Whatmann No. 1 filter paper. The extraction flask was cleaned and dried in the oven at 102 °C and cooled in a desiccator and its weight along with boiling bits (porcelain) was noted (W_1).

The Soxhlet extraction was carried out with apparatus of 60 ml capacity using dichloromethane as solvent for 5 h and

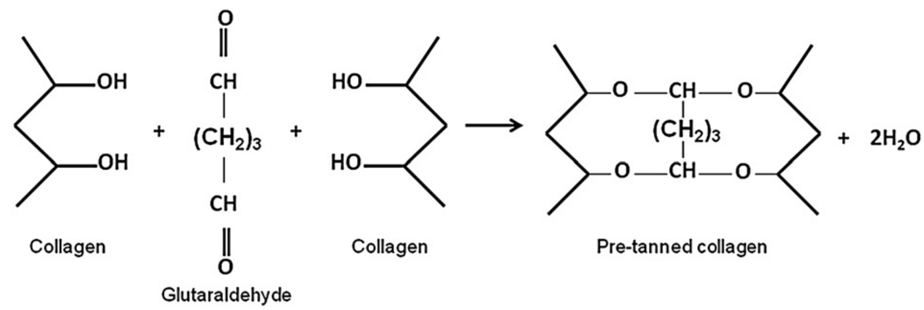

Fig. 2. Schematic representation of reaction between –OH group containing side chain of collagen and glutaraldehyde.

dichloromethane from the flask was subsequently distilled. The extract was dried in the oven for 4 h at 102 °C, cooled in the desiccator and the weight of the flask was recorded. The drying–cooling–weighing cycle was repeated until the difference in the weight due to drying was less than 10 mg. Then final dried weight of the flask was noted (W_2).

Calculation

$$\%\text{Fat content}(\text{as extractable substances with dichloromethane}) = \frac{W_2 - W_1}{W} \times 100$$

The enhancement factor (ε_{us}) due to ultrasound in degreasing process has been calculated using the formula,

$$\varepsilon_{us} = \frac{\%\text{Fat removal in the ultrasound aided process}}{\%\text{Fat removal in the control process}}$$

2.5. Differential scanning calorimetry (DSC)

Differential scanning calorimetric analysis of the pelt samples was performed with a *DuPont DSC 2910* model thermal analyzer system (Delaware, US). The sample was weighed (~10 mg) into a hermetic aluminium pan which then sealed using a sample pan crimper. The thermogram was obtained by heating to 120 °C at the rate of 5 °C min^{-1}. The reference cell used in the analysis was an empty hermetic aluminium pan. The temperature scale was calibrated with standard indium. Shrinkage temperature of the pickled pelt and glutaraldehyde pre-tanned pelt was obtained from the peak temperatures.

3. Results and discussions

3.1. Effect of ultrasound in degreasing process

The average value of fat content of the pelt (with respect to different area of the pelt) before degreasing was found out to be 16.4% (*based on dry pelt weight*) and taken as an initial fat content of the skin. The percentage fat removal with and without ultrasound for various degreasing systems is given in the Table 1. In the trichloroethylene degreasing process at 35 °C, 43.5% fat was removed using ultrasound (US) compared to 19.9% removed without use of ultrasound.

Table 1
Degreasing efficiency of different processes with ultrasound and without ultrasound for 2 h

Process	Temperature (°C)	% Fat removed	Enhancement factor due to US (ε_{us})
TCE degreasing[a] (US)	T_{us}	47.8	2.4
Aq. degreasing[a] (US)	T_{us}	37.6	1.89
TCE degreasing (US)	35	43.5	2.19
Kerosene (US)	T_{us}	54.6	2.74
Control – TCE degreasing (no US)	35	19.9	–

All the values are average of three trials.
[a] Pre-tanned with glutaraldehyde.

3.2. Shrinkage temperature

Thermograms of the pickled and GT pre-tanned skin are shown in Fig. 3a and b, respectively. From the thermograms, it is inferred that the shrinkage temperature of the pickled pelt is 67 °C and that of glutaraldehyde pre-tanned pelt is 78 °C.

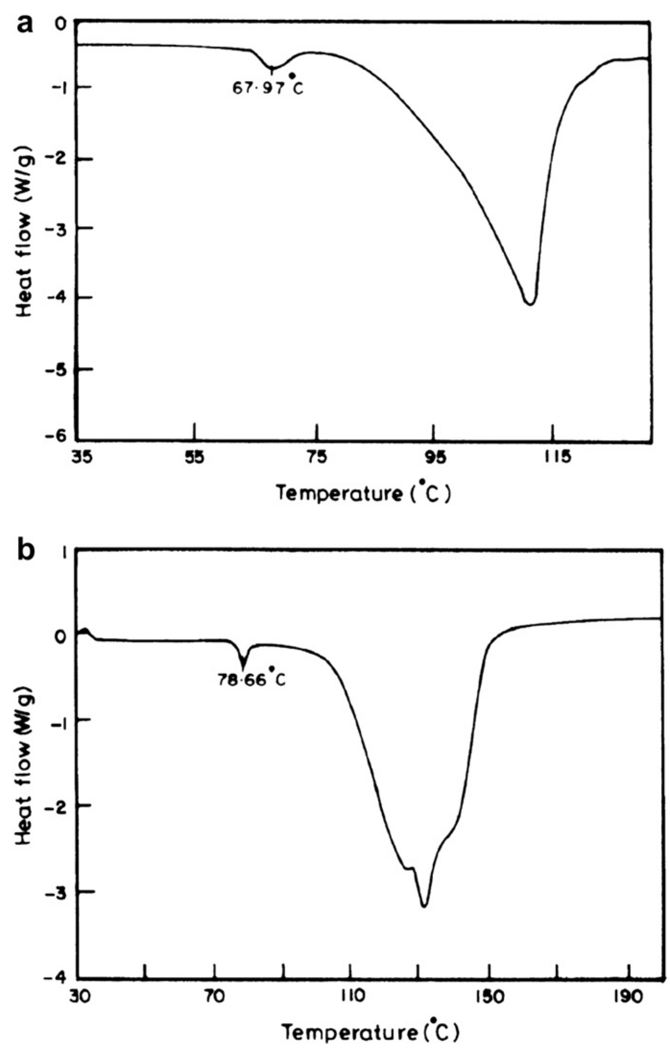

Fig. 3. (a) Thermogram of the pickled pelt before pre-tanning. (b) Thermogram of the glutaraldehyde pre-tanned pelt.

Aqueous degreasing of glutaraldehyde pre-tanned skin with ultrasound gives about 37.6% fat removal. Kerosene process (US) gives about 54.6% degreasing efficiency. There is a twofold increase in the degreasing efficiency due to the use of ultrasound for the solvent process at 35 °C. The increase in the fat removal between the solvent processes carried out at ultrasonic bath temperature and at 35 °C is 21.4%. Therefore, rise in the temperature of the bath during the process helps in improving the fat removal to certain extent. The enhancement factor (ε_{us}) due to the use of ultrasound in different solvent systems in degreasing process is shown in Table 1. Comparing the degreasing efficiencies of the solvent and aqueous based ultrasonic processes about 80% of the solvent degreasing efficiency can be obtained for aqueous degreasing process.

3.3. Mechanisms for enhancement in degreasing with ultrasound

Possible mechanisms for the enhancement in degreasing with ultrasound are as follows:

- Cavitation induced effects of ultrasound are expected to rupture the fat cells which may facilitate the release of fat for its removal.
- Penetrative action of ultrasound such as acoustic streaming through the skin is expected to help in solvent/emulsifier transport to reach the fat site present at the interior of the skin.
- Better emulsification of the fat due to dispersing effect of ultrasound. Schematic representation of aqueous degreasing process in ultrasonic field is shown in Fig. 4.
- Better removal of the emulsified fat from the skin matrix.

4. Conclusions

Use of power ultrasound in degreasing significantly (~2-fold) improves the removal of fat from the skin. Ultrasound also helps to perform aqueous degreasing with minimal use of surfactant. The pre-tannage (with glutaraldehyde) helps to increase the shrinkage temperature of the pelt to be degreased to facilitate the degreasing even at T_{us} ~50 °C without causing any damage to the pelt. The present study offers ultrasound aided degreasing process at ultrasonic bath temperature that could totally eliminate the use of toxic organic solvents and minimise the use of detergents, which could achieve 80% of the TCE solvent degreasing efficiency. The enhancement obtained in degreasing by the use of ultrasound may be due to better emulsification of fat present even in the interior of the skin. Therefore, ultrasound aided eco-friendly degreasing process is a viable option for tanners in future. This novel cleaner degreasing methodology using ultrasound could also be implemented for other industries with suitable modifications.

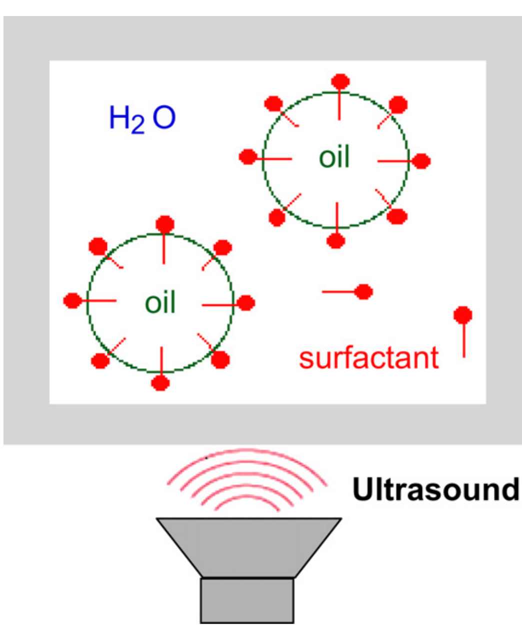

Fig. 4. Schematic representation of aqueous emulsification process under ultrasonic field.

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