

STUDY ON ULTRASONIC DEGREASING OF SHEEPSKIN WASTE

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Abstract: Leather industry is a relatively large source of waste from raw material, so skin waste recovery is a goal of clean technologies. Capitalisation of skin waste aims to obtain: chemical auxiliaries, technical articles, hydrolyzed protein, artificial leather, composite building materials, heat sources and collagen biomaterials with applications in medicine, cosmetics, etc. A first step in the recovery of skin waste is the degreasing operation. Ultrasound is an effective tool to improve the efficiency of the conventional degreasing affecting the chemical substances as well as the treated skin. In addition, the processing time is reduced. Ultrasound is known to enhance the emulsification and dispersion of oils/fat. The usual degreasing methods requires more emulsifier/solvent ratio and process time for emulsification and additional solvent for washing out the emulsified fat. This paper investigates the possibility of recovery through ecological processes of leather waste from finishing operations for further capitalisation. The present study aims emulsification and subsequent removal of the fat present in the chamois powder waste from polishing operation with the aid of ultrasound by an aqueous ecofriendly method. The study also took into account the ultrasonic treatment of the leather waste using trichlorethylene as a medium of propagation-degreasing, and realized a comparative analysis of efficiency of fat extraction by Soxhlet method and via ultrasonication. IR-ATR and optical microscopy highlight both morphological and chemical-structural changes of treated materials by different degreasing methods.

Key words: ultrasonication, cavitation effect, resonator tube, spectral analysis, morphological structure.

1. INTRODUCTION

Green chemistry is an upcoming and emerging field of interest for today's researcher, representing an environmental friendly procedure applicable in leather manufacturing in order to reduce hazardous chemical material output. Innovative methods promote green chemistry of leather making process.

Leather industry is a relatively large source of waste from raw material, so skin waste recovery is a goal of clean technologies, given that only 25% of the raw skin is found in finished products. Worldwide, about 70% of protein waste is recovered, and for the rest is undertaken research in order to find solutions for more efficient use [1]. Capitalisation of skin waste aims to obtain: chemical auxiliaries, technical articles, hydrolyzed protein, artificial leather, composite building materials, heat sources and collagen biomaterials with applications in medicine, cosmetics, etc.

A first step in the recovery of skin waste is the degreasing operation. Organic solvents are currently employed as degreasing agents and grease from sheepskin dry degreasing can be recovered from the organic solvents and sold on the commodity market [2, 3].

The five different methods commonly used for degreasing are [4, 5]:

- degreasing in an aqueous medium with an organic solvent and a non-ionic surfactant;
- degreasing in an aqueous medium with a non-ionic surfactant;
- degreasing in a solvent medium;
- degreasing by pressurized extraction with a fluid;
- degreasing by supercritical extraction with a fluid.

Degreasing process also involves diffusion problem in skin/hide matrix structure having three-dimensional weave of collagen fiber bundles. The diffusion problem includes: (a) transport of degreasing chemicals into the fat site at the interior of skin/hide; (b) emulsification of fat at the interior of the skin/hide and (c) 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 [5, 6]. Hence, large amounts of environmentally sensitive organic solvents (such as white spirit, perchloroethylene or trichloroethylene) surfactants and emulsifiers are used in 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.

Ultrasound is an effective tool to improve the efficiency of the degreasing process using a frequency higher than 20 kHz which affect the chemical substances as well as the treated skin. In addition, the processing time is reduced. It has been reported that the ultrasonic field affects the particle size and particle distribution of the used chemicals. Enhanced penetration through the pores of the leather matrix is achieved by a decrease in particle size and a uniform distribution of the particles. Ultrasound is known to enhance the emulsification and dispersion of oils/fat [3].

The usual degreasing methods 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. Some physico-chemical principles of water-based degreasing process have also been described recently [6]. 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. Dry cleaning of finished leather with solvent was studied earlier with 22 and 44 kHz ultrasonic waves for 8 min to remove the oily dirt adhered with the leather [7]. 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 [8, 9]. The application of ultrasound in leather processing has been studied elsewhere [10, 11]. The uses of ultrasound in soaking [12], liming [13], dyeing [14], tanning [15] and fatliquoring [16] have been reported.

This paper investigates the possibility of recovery through ecological processes of chamois leather waste from finishing operations for further capitalisation. In the present work, the influence of ultrasound in fat removal has been studied. The research objective is to develop eco-friendly effective degreasing system for chamois powder waste from polishing operation using ultrasound at low intensity at specified frequency range without necessitating temperature control. The study also took into account the ultrasonic treatment of the chamois powder waste using trichloroethylene as a medium of propagation-degreasing, and realized a comparative analysis of efficiency of fat extraction by Soxhlet method and via ultrasonication.

2. APPARATUS AND MATERIALS

For the comparative degreasing experiments were used: specific reagents such as: trichloroethylene (TCE), distilled water, and hydroalcoholic solution; chamois powder waste resulting from polishing operation, provided from sheep skin finishing company.

The analysis techniques were: IR-ATR spectroscopy using a DIGILAB – SCIMITAR Series FTS 2000 spectrometer with ZnSe crystal, 750 - 4000 cm^{-1} range, 4 cm^{-1} resolution, and optical microscopy using an Optical Microscope EUROMEX ME 2665(Holland) with video digital camera.

For degreasing a classic Soxhlet installation and an ultrasonic device Sonic Vibrocell type with resonator tube were used (figure 1).

3. WORKING METHOD

Effectiveness of degreasing by ultrasonic method was compared with the classical Soxhlet method of degreasing.

Soxhlet extraction [17-19]

Six parallel sheepskin powder samples with a weight of 5 g each were extracted individually with 300ml of trichloroethylene solvent. Each Soxhlet apparatus worked continuously for 3h with approximately three extractions performed per hour. After fat extraction sample cartridges were subjected to washing with 50% alcohol solution, and then dried at 50°C for 24 hours and conditioned at 20°C and 65% humidity for 24 hours.

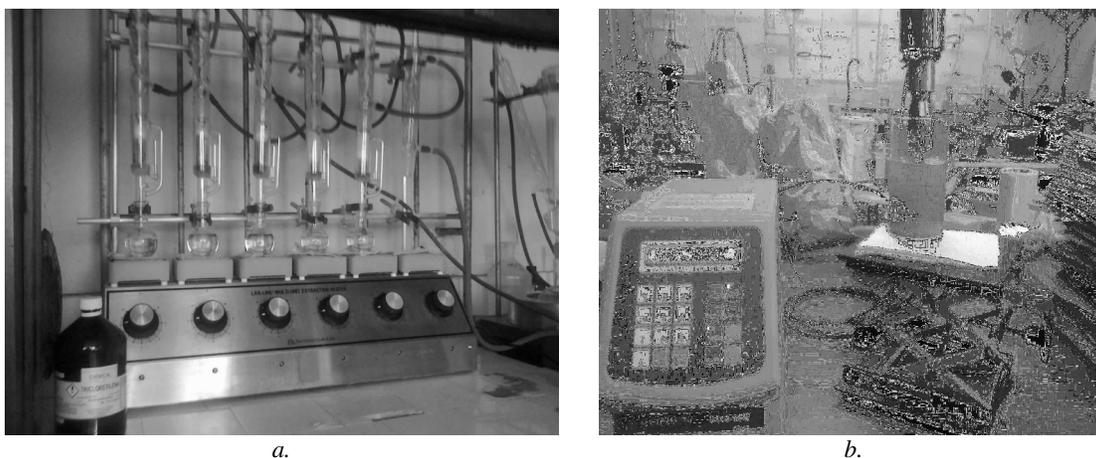


Fig. 1: a) Soxhlet installation; b) Ultrasonic device with resonator tube

Ultrasonic extraction

Six parallel samples with a weight of 5g each were ultrasonicated in 150 ml of distilled water, and other six samples of the same weight in 150 ml of trichloroethylene.

The ultrasonic device worked at the following parameters: power actually dissipated to the system: 70 W; frequency: 25 kHz; duty cycle: 2 s; time: 30 min ÷ 2h. In order to find out the influence of ultrasound effects, ultrasonic experiments were carried out without external cooling or heating of ultrasonic bath; in these conditions the ultrasonic bath temperature does not exceed 50 °C in 2h process time. The extracted samples were then washed with 50% hydroalcoholic solution to recover any remaining organic residue and then dried in the same conditions as above.

4. RESULTS AND DISSCUTION

The results for fat extraction with Soxhlet apparatus in comparison with ultrasonic degreasing in water and TEC are shown in figure 2.

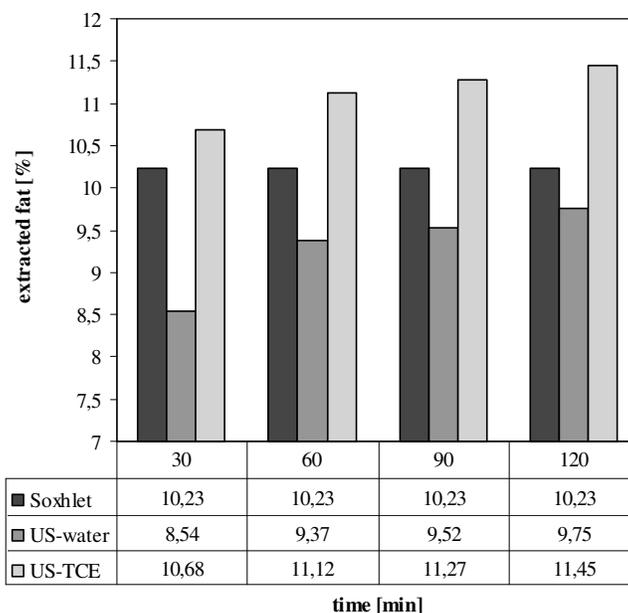


Fig.2. Extracted fat percentages depending on the duration and method of degreasing

As can be seen in figure 2 the use of the ultrasonic tube enhances the fat removal processes from samples. Thus, the highest yields are observed at the combined use of sonication with degreasing

agent (TCE) for a period of 120 min; the percentage of fat removed is superior to the Soxhlet method. The highest percentage of fat is removed for 2h process time regardless whether the sample is degreased by ultrasonication in distilled water or in solvent bath. Concomitant use of sonication and degreasing solvent enhances the cavitation effect, enabling a more rapid removal of fat. Ultrasound also helps to perform an aqueous degreasing and to obtain a good removal of fat from the skin.

The enhancement in degreasing with ultrasound is due to possible mechanisms as follows:

- fat cells undergo breaking processes due cavitation which facilitates the release of fat and its subsequent removal;
- the action of ultrasound helps the solvent/emulsifier to penetrate the fat site from the interior of the skin;
- the dispersing effect of ultrasound facilitates better emulsification of the fat from the skin;
- the removal of the emulsified fat from the skin matrix is improved.

Microscopic images of an initial sample (greasy skin powder) and of the skin after fat extraction by the methods described above are shown in Figure 3. Thus, we can observe the surface changes of the samples subjected to degreasing by various methods; the sample sonicated in a solvent shows a more pronounced loosening of the constituent fibers as compared with the samples degreased by Soxhlet method, and by sonication in distilled water, respectively. The initial sample of greasy skin shows a pronounced agglomeration of fibrous component due to the presence of fatty substances on the surface and within the material.

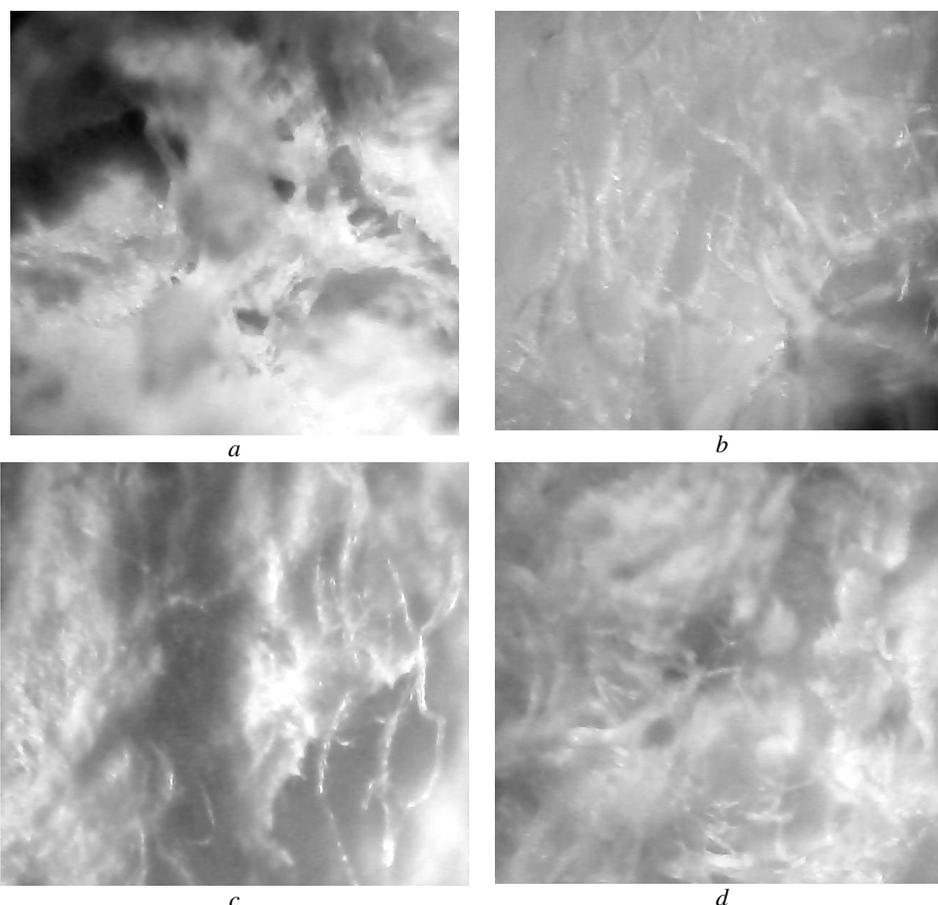


Fig. 3. Aspects of skin powder treated in different conditions obtained by optical microscopy: *a)* initial sample; *b)* extracted in Soxhlet; *c)* ultrasonicated in water for 2h; *d)* ultrasonicated in TCE for 2h.

IR-ATR spectra of the initial sample and of the samples degreased via sonication in water and TCE for 2 h are presented in figure 4.

The spectra in the figure 4 show a shift of the characteristic peaks in the range $3450\text{-}3300\text{ cm}^{-1}$ (of NH + OH groups) and of 3200 cm^{-1} spectral band (of free OH groups) of the initial sample to 3100 cm^{-1} , and 3000 cm^{-1} bands respectively, which could indicate possible new intermolecular interactions through Hydrogen bonds.

It can be also seen a decrease in signal intensity of spectral bands characteristic of CO groups from amide I located between 1650-1650 cm^{-1} , of NH groups from amide II located between 1555 - 1545 cm^{-1} , and of NH +CH groups from amide III located between 1240-1230 cm^{-1} , for the sonicated samples (b) and (c) compared to the control sample (a). Decreasing of signal strength and response surface of spectral bands might be due to the cavitation effect which causes possible breaks of physical bonds and new intermolecular bonds formation.

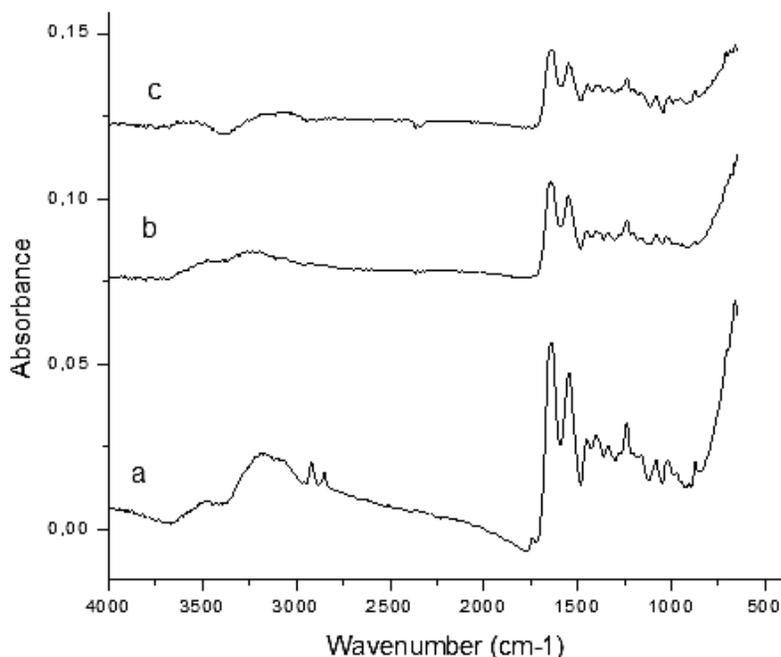


Fig. 4. IR spectra of sheepskin waste powder: a) initial sample; b) ultrasonicated in water for 2h; c) ultrasonicated in TCE for 2h.

5. CONCLUSIONS

1. The use of ultrasound in degreasing improves significantly the removal of fat from the skin powder waste.
2. Concomitant use of sonication and degreasing solvent (TCE) enhances the cavitation effect, enabling a more rapid fat removal; the highest yields are observed for a sonication period of 120 min.
3. The percentage of fat removed by sonication with solvent is superior to the Soxhlet method, at the same time decreasing the amount of solvent used for degreasing and reducing the working time.
4. Ultrasound also helps to perform an aqueous degreasing and to obtain a good removal of fat from the skin powder waste helping to minimize or eliminate the use of detergents and solvents.
5. IR-ATR and optical microscopy highlight both morphological and chemical-structural changes of treated materials by different degreasing methods.
6. The results can be a starting point in finding new ways of extracting components of interest from these sources of waste such as chemical auxiliaries, hydrolyzed protein, artificial leather, composite building materials, and collagen biomaterials, etc.

REFERENCES

- [1] G. Lofrano, S. Meric, G. Emel Zengin, D. Orhon, "Chemical and biological treatment technologies for leather tannery chemicals and wastewaters: A review", *Science of the Total Environment*, vol. 461, pp., 265–281, 2013.

- [2] A. Cassano, A. Molinari, M. Romano, and E. Drioli, “*Treatment of aqueous effluents of the leather industry by membrane processes. A review*”, *Journal of Membrane Science* vol. 181, pp. 111–126, 2001.
- [3] V. Sivakumar, F. Chandrasekaran, G. Swaminathan, P.G. Rao, “*Towards cleaner degreasing method in industries: ultrasound-assisted aqueous degreasing process in leather making*”, *Journal of Cleaner Production* vol., 17, pp., 101–104, 2009.
- [4] J. Dyer and A. Grosvenor, “*Protein Fibre Surface Modification*”, in *Natural Dyes*, E. Akcakoca Kumbasar Publisher Intech., 2011, chap.7, pp. 111- 124.
- [5] D. Bienkiewicz, “*Physical Chemistry of Leather Making*”, Robert E. Krieger Publishing Company, New York, 1993.
- [6] G.R. Pabst, P. Lamalle, R. Boehn, G. Oetter, R. Erhardt, “*Physico-chemical principles of water-based degreasing of animal skins*”, *J. Am. Leather. Chem. Assoc.*, vol. 99, pp. 151–156, 2004.
- [7] H. Herfeld, “*About the use of ultrasonics in chemicals cleaning of leather and for the acceleration of wet processing in leather production*”, *Leder und Haute Markt*, vol. 30, pp.232–237, 1978.
- [8] P. Gourlay, “*Emulsification and dispersion by using ultrasonics*”, *Rev. Tech. Ind. Cuir*, vol. 51(11), pp. 240–243, 1959.
- [9] V. Sivakumar, R. Poorna Prakash, P.G. Rao, B.V. Ramabrahman, G. Swaminathan, “*Power ultrasound in fatliquor preparation based on vegetable oil for leather application*”, *J. Cleaner Prod.*, vol. 16(4), pp. 549–553, 2008.
- [10] A. Shoh, “*Industrial applications of ultrasound – a review I*”, *High-power ultrasound. IEEE Trans. Sonics Ultrason*, vol. 22(2), pp. 60–71, 1975.
- [11] V. Sivakumar, P.G. Rao, “*Application of power ultrasound in leather processing: an eco-friendly approach*”, *J Cleaner Prod*, vol. 9(1), pp. 25–33, 2001.
- [12] V. Sivakumar, G. Swaminathan, P.G. Rao, “*Use of ultrasound In soaking for improved efficiency*”, *J. Soc. Leather Technol. Chem.*, vol. 88(6), pp. 249–251, 2004.
- [13] Alpa SpA., “*Reducing the load: ultrasound in liming and unhairing*”, *World Leather*, vol. 8(7), pp. 89–91, Italy, 1996.
- [14] V. Sivakumar, P.G. Rao, “*Studies on the use of power ultrasound in leather dyeing*”, *Ultrason Sonochem.*, vol. 10(2), pp. 85–94, 2003.
- [15] R. L Ernst, F. Gutmann, “*Ultrasonically assisted tanning*”, *J. Soc. Leather Technol. Chem.*, vol. 34, pp. 454–459, 1950.
- [16] T.C. Thorstensen, “*Practical Leather Technology, Fatliquoring*”, Fourth Edition, Krieger Publishing Company, Malabar, Florida, pp. 202 – 221, 1993.
- [17] SLTC (Society of Leather Technologists and Chemists), IULTCS, Official methods, UK, 1996.
- [18] ISO 2419, *Leather -Physical and mechanical tests - Sample preparation and conditioning*, 2006.
- [19] ISO 4048, *Leather-Chemical Tests- Determination of matter soluble in dichloromethane and free fatty acid content*, 2008.