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STUDY ON MORPHOLOGICAL AND STRUCTURAL CHANGES INDUCED BY ULTRASONIC DEGREASING OF WOOL AND HUMAN HAIR WASTES

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Abstract*. Recovery and reuse of wool and hair waste is a challenge with the ultimate goal environment protection. One of the early stages of the recovery process is the operation of scouring-degreasing wool and human hair waste. In recent decades the use of ultrasound technology has established an important place in different industrial processes and has started to revolutionize environmental protection. The power of ultrasound can enhance a wide variety of chemical and physical processes, mainly due to the phenomenon known as cavitation in a liquid medium. The objective of the present work is to develop eco-friendly effective degreasing system for keratin fiber waste with the aid of ultrasound, using distilled water and also trichlorethylene as a medium of propagation-degreasing, and realized a comparative analysis of efficiency of fat extraction by Soxhlet classical method and via ultrasonication. This work investigate the effect that ultrasonic irradiation has on the structure of wool and hair fibers. Thus were highlighted both morphological and structural changes of treated materials using optical microscopy, and FTIR spectroscopy. By using the unconventional method of cleaning and degreasing with an ultrasonic resonator tube are possible reductions in utility and solvents consumption together with changes in the cuticular layer of wool and hair fibers.*

Key words: *keratin wastes, morphological structure, resonator tube, scouring, spectral analysis*

1. INTRODUCTION

Recycling organic waste from preliminary operations of wool processing industry and human hair from hairdressing salons, aims to use the resulting by-products in areas as diverse as agriculture, cosmetics, building materials, biomaterials, etc [1-3].

For cleaning and removal of fatty substances in the composition of human hair and wool waste the following methods are used [4]:

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

In recent decades the use of ultrasound technology has established an important place in different industrial processes and has started to revolutionize environmental protection.The idea of using ultrasound in textile wet processes is not a new one [5, 6] but the ultrasound-assisted wet wool and hair processes have not been implemented on an industrial scale as yet [7, 8]. In practice, for wool and hair wet processes are reported use of the frequency 20-100 kHz [9].

The power of ultrasound can enhance a wide variety of chemical and physical processes, mainly due to the phenomenon known as cavitation in a liquid medium that is the growth and explosive collapse of microscopic bubbles. Sudden and explosive collapse of these bubbles can

generate ‘‘hot spots’’ i.e., localized high temperature, high pressure, shock waves and severe shear force capable of breaking chemical bonds [10-12].

The objective of the present work is to develop eco-friendly effective degreasing system for keratin fiber waste with the aid of ultrasound using distilled water and also trichlorethylene as a medium of propagation-degreasing, and realized a comparative analysis of efficiency of fat extraction by Soxhlet classical method and via ultrasonication.

This work investigate the effect that ultrasonic irradiation has on the morphological and chemical structure of wool and hair fibers. Thus were highlighted both morphological and structural changes using optical microscopy, and FTIR spectroscopy.

2. APPARATUS AND MATERIALS

For the scouring-degreasing comparative experiments some specific reagents were used such as: trichloroethylene (TCE), distilled water, sodium carbonate, and hydroalcoholic solution.

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. The ultrasonic device worked at the following parameters: power: 750 W; frequency: 25 kHz; duty cycle: 2 s.

3. WORKING METHOD

The washing of wool and hair poses some technical problems, and need to be designed to minimise fiber movement but maximise liquor transfer so as to avoid felting. For the same reason detergents for scouring process need to be in a slightly alkaline range (pH ~ 8.5). Thus, in the first phase, wool and hair samples were cleaned in distilled water at 50^{o}C, and then washed with a solution of 2 g/l Na_2CO_3 and a surfactant solution of 0.5 g/l concentration.

Soxhlet extraction method

The traditional method for determining grease content within wool and hair fiber samples [13] is solvent extraction process in Soxhlet equipment using organic solvents. Thus six parallel hair and wool samples with a weight of 5 g each were extracted individually by Soxhlet equipment with 300 ml of trichloroethylene for 3 h 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^{o}C for 24 hours and conditioned at 20 ^{o}C and 65% humidity for 24 hours.

Ultrasonic extraction

In this experiment six parallel hair and wool samples with a weight of 5 g each were ultrasonicated with a resonator tube for 30 min to 120 min, in 150 ml of distilled water, and trichloroethylene, respectively. The extracted hair and wool 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 DISCUSSION

The measured percent extractables of the hair and wool samples depended upon the method and solvent used as can be seen in figure 1.

These data show that the extracted fat percentages increase in the order: ultrasonic treatment in water bath, Soxhlet extraction, and ultrasonic treatment in TCE bath. However, the extraction by Soxhlet method has a longer duration (3h) comparated with ultrasound extraction (2h), and also uses a two-fold amount of solvent.

The highest percentage of fat is removed for 2h duration of ultrasonic extraction 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.

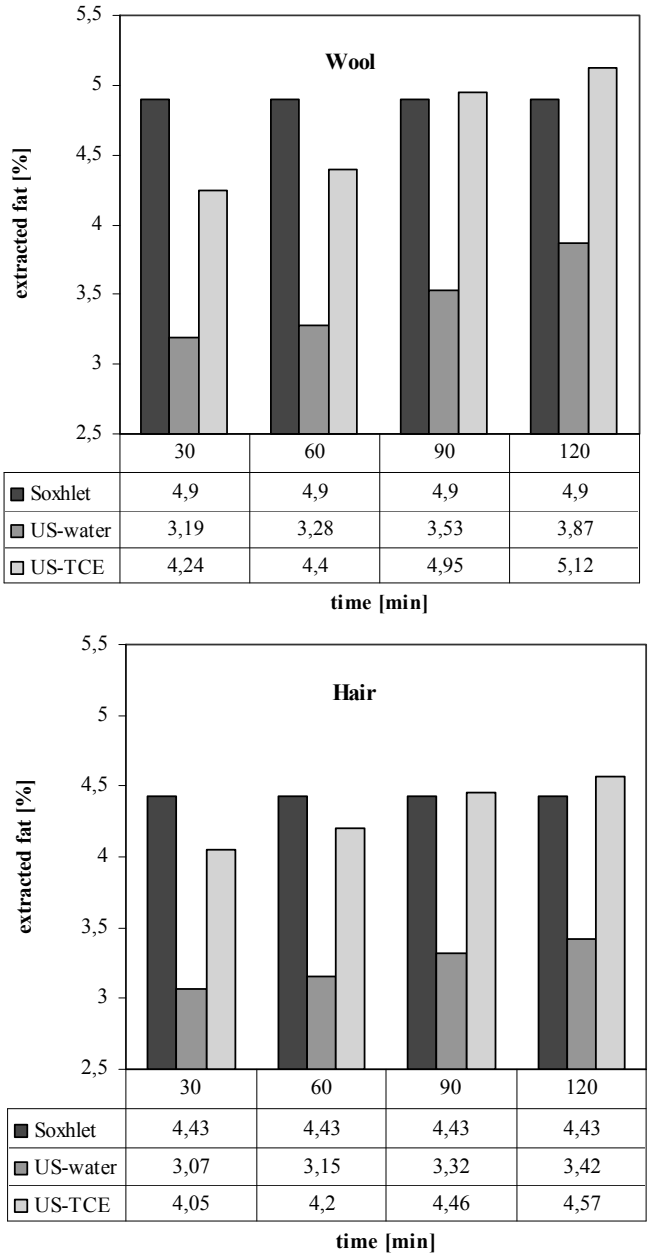


Fig.1. *Percent extractables of wool and hair samples depending on the duration and the method of degreasing.*

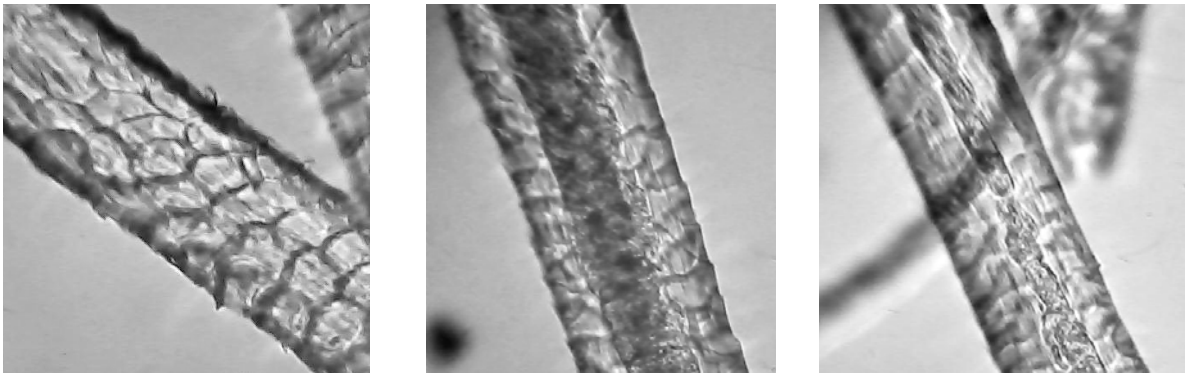
Fibers surface morphology

Microscopic images of initial samples (un-scoured) and after fat extraction by ultrasonic treatment in water and solvent (TCE) respectively, are shown in figure 2 and 3.

Microscopy studies of wool and hair fibres revealed that the ultrasonic waves induced changes in fibre cuticle structure. The defatted fibers have the grease and other surface contaminant removed and show good scale definition and a clean surface.

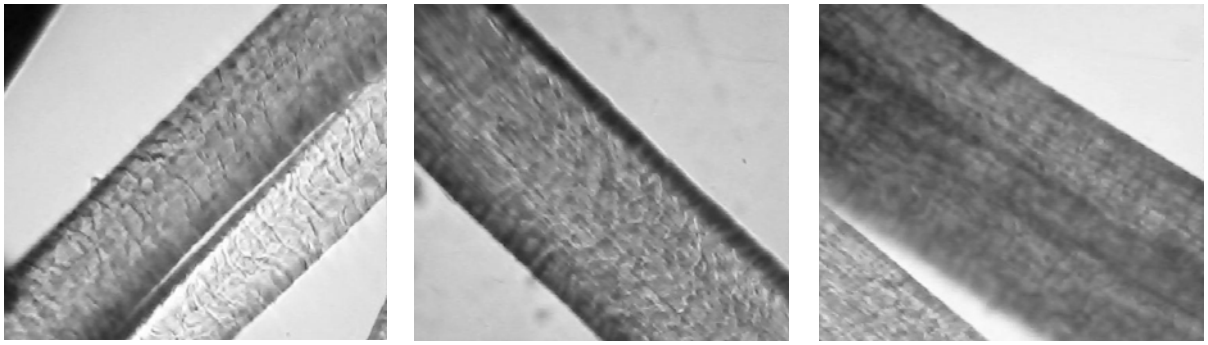
Wool samples (fig. 2c) show a change at the surface of cuticular layer as well as in its depth due to the cavitation effect induced by ultrasonication and further emphasized by the presence of solvent in the treatment bath. Treatment in water only (fig. 2b) left a cushion of air on the surface or within the fibre that limited the impact of cavitation to a mild cracking of the cuticle.

Human hair samples treated with solvent in ultrasonic bath (fig. 3c) reveal also a more affected cuticular layer at the surface and in its depth comparated with the initial sample (fig. 3a) and samples ultrasonicated in distillated water, respectively (fig. 3b). This destruction of the cuticle is more pronounced than for wool samples degreased in the same conditions.



a b c

Fig.2. *Microscopic images of wool samples: a) initial sample; b) ultrasonicated in water for 2h; c) ultrasonicated in TCE for 2h.*



a b c

Fig.3. *Microscopic images of human hair samples: a) initial sample; b) ultrasonicated in water for 2h; c) ultrasonicated in TCE for 2h.*

Spectral analysis

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 and 5.

In the figure 4a and 5a the spectra of both initial samples of hair and wool respectively, showed a band at 3470 cm^{-1} assigned to the H-bonded OH stretch of water residing in keratin. The cuticular layer of hair and wool samples (b) affected by cavitation effect presents a lower signal intensity in this spectral zone, and samples (c), sonicated in TCE bath show a shift of the same band to the left indicating a more tightly bound water structure and possible new intermolecular bonds in different positions in the affected cuticle.

Both initial samples (a) show spectral bands at 3000-2700 cm^{-1} wich are assigned to the stretching modes of the lipid alkyl chains (the methyl CH_3 are observed at 2955 and 2933 cm^{-1}, and CH_2 at 2875 and 2855 cm^{-1}). In the case of ultrasonicated samples signal strength in these areas decreases as well as its response surface, and the hair sample degreased in TCE (fig. 4c) shows the most attenuated signal. This may be due to the degreasing produced by cavitation effect during sonication.

Region between 1700-1500 cm^{-1} contains the most intense features, arising from peptide bond (-CONH-) from protein structures such as amide I and amide II: amide I at 1670-1657 cm^{-1} which is an indicative of alpha-helical structures, is mainly associated with the C=O vibration and is directly related to the backbone conformation; amide II at 1547-1538 cm^{-1} corresponds to N-H bending and C-N vibrations; amide III at 1266-1230 cm^{-1} corresponds to the in-phase combination of C-N stretching and N-H bending, with some contribution from C-C stretching and C=O bending vibrations. The latter is a complex band, and depends on the nature of side chains and hydrogen bonding.

The sonicated hair and wool samples (b and c in figures) shows a lower signal intensity in these spectral zones wich is much more attenuated for the solvent degreased samples; this could be atributted to conformational changes in secondary structure and possible reformation of intramolecular hydrogen bond in the α helical structures and β layers, which can affect also cystine bonds occuring in the near spectral zone.

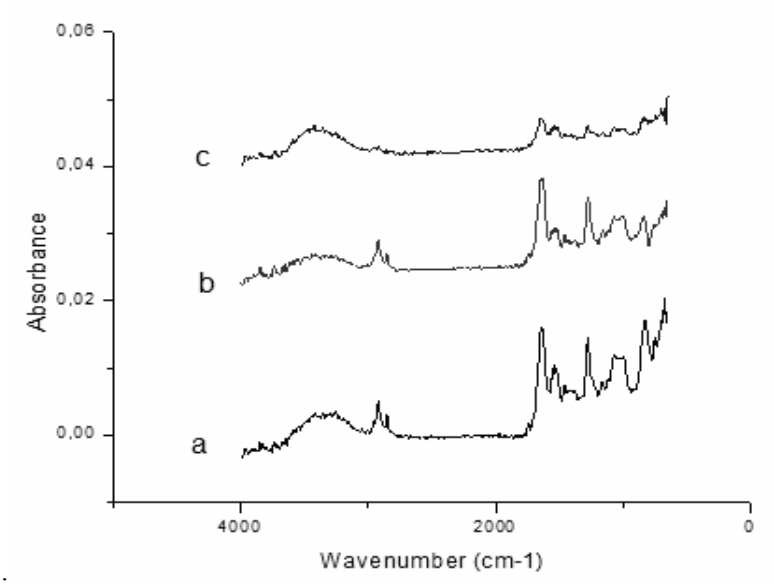


Fig.4. *Human hair IR spectra: a) initial sample, b) ultrasonicated in water for 2h; c) ultrasonicated in TCE for 2h.*

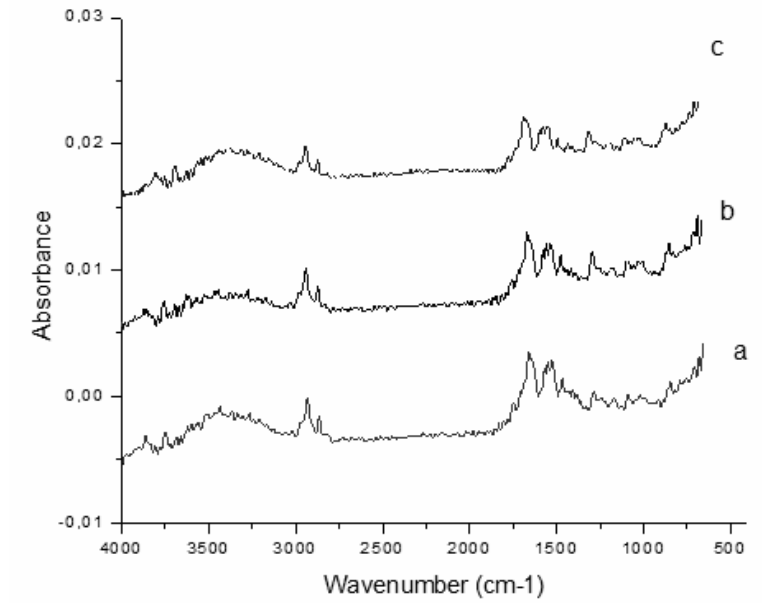


Fig.5. *Wool IR spectra: a) initial sample, b) ultrasonicated in water for 2h; c) ultrasonicated in TCE for 2h.*

5. CONCLUSIONS

1. Concomitant use of sonication and degreasing solvent (TCE) significantly improves the removal of fat from hair and wool fibers.
2. The sonication in solvent bath is superior to the conventional Soxhlet method, at the same time decreasing the amount of solvent used for degreasing and reducing the working time.
3. Ultrasonic extraction in aqueous bath enables also a good removal of fat from the fibers helping to minimize or eliminate the use of detergents and solvents.
4. Human hair treated with solvent in ultrasonic bath reveal a more affected cuticular layer, destruction wich is more pronounced compared with degreased wool samples under the same conditions.
5. IR-ATR highlights the structural changes that occur in both wool and hair after sonication, more pronounced by concomitant use of solvent.

6. The results can be a starting point in finding new ways of extracting components of interest from these sources of waste such as waxes, lanolin, some amino acids, melanin pigments, cholesterol, etc.

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