SHEEP WOOL CAN BE SCOURED SUFFICIENTLY WITHOUT ANY CHEMICALS

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Abstract: *In our search for an alternative method of scouring sheep wool without using any chemicals, we have tested various methods: a) wool scouring in ultrasonic bath filled with tap water at 40°C under different time modules and, b) simple maceration of wool in unheated tap water. Reference procedure was Soxhlet extraction by dichloromethane. The criteria applied to assess the efficiency of the selected procedures were the mass loss of the scoured sample and the 220 nm absorbance of aqueous extract obtained from the wool after individual scouring steps. Based on the obtained data, it was concluded that the chemical-free water scouring of 20 g wool in ultrasonic bath with the volume of 5 dm^3, at 38 kHz frequency, during 4x10 min and combined with a water exchange every 10 min, provides a very good result. A comparable effect was observed using a simple unheated tap water maceration during 2x7 day intervals with a water exchange after 7 days. Both procedures are more environmentally friendly than the conventional method. Depending on the intended use and required level of wool purity, it is possible to reduce the total time of ultrasonic scouring. While the maceration requires a minimal handling and technical equipment, it is a lengthy process. On the other hand, the scouring with the ultrasonic support takes only few minutes, however, it requires an initial investment, but with a quick economic return. Both methods share a common advantage of the reduced environmental impact.*

Keywords: *sheep wool, ultrasonic scouring, maceration, Soxhlet extraction.*

1 INTRODUCTION

Sheep wool is decreasingly used in the traditional textile production and becomes an unwanted hardly marketable by-product for sheep farmers. In recent years, several studies have appeared focused on examination of this material to be a potential biosorbent [1-3]. Sheep wool belongs to the group of fibrous biosorbents of keratin-type [4, 5] containing a whole range of acidic and basic functional groups that are potentially active sites for binding various substances from the environment [1]. A crude sheep wool contains various types of impurities and grease on the fibre surface and their amount depends on the manner and the region of sheep breeding [6, 7]. Several technological procedures are used to eliminate them. In the textile industry, the sheep wool scouring is usually accomplished in Leviathan, a machine consisting of a series of five tanks. The scouring medium is a slightly alkaline solution of soap or detergent [8, 9]. The laboratory studies describing the removal of greasy impurities from the fibre surface utilize organic solvents, e.g. dichloromethane [2, 10, 11], 1,1,1-trichloroethane and trichlorotrifluoroethane [12], petroleum spirit [13] or carbon tetrachloride [14]. The sheep wool scouring process is accomplished in three steps. First, the fibres are mechanically cleaned, then greasy components are extracted by a solvent and, at the end, washed with water. The solvent is subsequently regenerated by distillation [5]. A newer and cheaper alternative is the utilization of an ultrasonic device which not only reduces the consumption of chemicals, time and energy but, above all prevents felting or knots [15-17]. Although several published articles point to the benefits of the ultrasound utilization [18, 19], so far only few works have been devoted to the study of wool scouring in an ultrasonic bath without the use of any chemicals. Bahtiari and Duran [20] scoured crude sheep wool in five steps consecutively with and without the ultrasound utilization. They found that after the third scouring in an ultrasonic bath, the same results were achieved as by the five-step conventional scouring. The comparison of the ultrasonic scouring efficiency in pure water with the scouring in water containing chemicals showed that the ultrasonic scouring in water at 35°C provided the wool with a good whiteness index value and sufficient impurity removal.

Provided that sheep wool can be a potential sorbent, the application of detergents and other auxiliaries in the bath may have a negative effect on sorption properties of the fibres by occupying the active sites. Regarding the wool potential sorption, our work was focused on the examination of some possibility to remove impurities from the wool without any chemicals including organic solvents.

2 EXPERIMENTAL

2.1 Materials

A sheep wool sample was obtained from a spring cut of the Suffolk-Tsigaya sheep bred in Banská Belá. After the shearing, the wool was cleared of crude impurities (feed, dung, plants) by washing in tepid water until the water was clear. After the pre-cleaning, it was freely dried and stored in a well-ventilated place with minimal access of light and moisture.

2.2 Equipment

The wool samples used for the scouring (à 20 g) were weighed nearest to 0.01 g (scale Kern 440, Germany). The ultrasonic bath with the volume of 5 dm^3 (Kraintek, K5LE, Slovakia, 350 VA, output of 450 W, 38 kHz frequency, tempering from 20 to 80°C, timer from 0 to 90 min, applied intensity level 9) was used for the ultrasonic scouring. The samples were dried in a laboratory oven (Binder ED/FD, Germany). The scoured samples taken for the control of aqueous extracts (à 0.2 g) were weighed on analytical scales with the readability of 0.0001 g (Radwag AS/C/2, Poland) and shaken on a laboratory shaker (Witeg SHR-2D, Germany) at 100 rpm. The corresponding filtrates were centrifuged using a laboratory centrifuge (T23, Czechoslovakia) and the filtrate absorbance was measured by a UV-VIS spectrophotometer (Specord® 50 Plus, Analytikjena, Germany) with a quartz cell of 1 cm path against distilled water as a reference.

2.3 Scouring procedures

The manually pre-cleaned wool of 20 g was taken for each scouring procedure. The following methods were applied to remove the remaining grease from the fibres:

a) Scouring in 40°C warm tap water in an ultrasonic (US) bath in four repeated cycles of various time lengths (US1, US2, US3, US4 see Table 1) and the water exchange after each time interval; the whole procedure was tested thrice.

b) Simple wool maceration in an enclosed container with 5 dm^3 of tap water at room temperature during four consecutive seven-day scouring cycles, with the water exchange every seven days; regarding the minimal mechanical manipulation and the risk of the fibre damage, the experimental deviations were considered as negligible and the experiment was performed in one repetition.

c) Soxhlet extraction with dichloromethane (bp 39°C) used as a comparative method; the sample of 20 g divided into five extraction cartridges and each part extracted separately in 14 overflows (4 h) taken as one cycle.

After every scouring cycle, the samples were washed in 5 dm^3 of distilled water when scoured in water, while twice with 5 dm^3 of distilled water after Soxhlet extraction and evaporation of a residual solvent in a digester. The all washed samples were spread on filter paper and dried freely at room temperature and humidity during 24 h. Then they were post-dried in the oven at 40°C within 24 h and weighed. The applied conditions are summarized in Table 1.

2.4 Scouring process efficiency control

Efficiency of the scouring procedures was checked as follows:

a) directly through the mass loss of the wool. The relative mass loss L_{rel} [%] was calculated using the following equation:

$$L_{rel} = \frac{m_1 - m_2}{m_1}.100 \quad (1)$$

where m_1 and m_2 are the masses of the wool [g] in the dry state before and after the scouring, respectively.

b) indirectly using the measurement absorbance A_{220} nm for the aqueous extracts obtained from the scoured samples after every finished scouring cycle. The aqueous extracts were prepared from 0.2 g of the dried fibres cut into small 3-5 mm pieces, placed in small glass cups and 20 ml of distilled water was added to each sample. The fibres were in contact with water for 24 hours, while during the first 6 hours the cup contents were shaken on a horizontal laboratory shaker (100 rpm) and the rest of the time, they were in static mode. Then, the liquid fraction was decanted and centrifuged (60 seconds, Level 1) to sediment microparticles causing a mild turbidity. The transparent filtrates were used to measure the absorbance at 220 nm against the distilled water as a reference. Data obtained were treated using statistical methods [21].

Table 1 Scouring methods overview

Scouring method identification	T [°C]	Time design of one scouring cycle	Solvent	Number of scouring cycles applied	Water volume used per 1 scouring cycle [litres]
US 1	40	2x10 min	tap water	4	10 TW + 5 DW
US 2	40	3x10 min	tap water	4	15 TW + 5 DW
US 3	40	1x20 min	tap water	4	5 TW + 5 DW
US 4	40	1x30 min	tap water	4	5 TW + 5 DW
Maceration	23	1x7 days	tap water	4	5 TW + 5 DW
Soxhlet extraction	39	240 min	dichloromethane	1	undefined TW to cool extractor + 10 DW

Legend: US – ultrasonic scouring, TW – tap water, DW – distilled water

3 RESULTS AND DISCUSSION

Design of the experiments was based on supposition that the aqueous extracts from the wool scoured by dichloromethane extraction should contain especially low-polar components and, the extracts from the water processes should consist mostly of polar substances. However due to ultrasound, also low-polar substances can be present in the aqueous extracts.

3.1 Effectivity of scouring procedures evaluated by mass loss

The mass loss within the water scouring was assigned to the removed grease and other impurities contained in the wool. After the scouring, a measurable mass loss was recorded only after the first two scouring cycles, while the mass loss was negligible for the following two cycles. The results of the relative mass loss for the individual methods are summarized in Table 2. When measured the mass loss, we did not expect large figures compared to other published works since this depends on level of the wool pre-treatment. Regarding our initial material was pre-treated in the same way; mutual comparison within the used procedures is justified. As could be seen in Table 2, the lowest mass loss was recorded for the seven-day maceration in water (6.2%). The order of the mass loss after the first scouring cycle was as follows: US2 (3x10 min) ~ US4 (1x30 min) > US1 (2x10 min) > US3 (1x20 min) > maceration (7 days). The comparison of the ultrasonic scouring processes showed that the scouring efficiency increased with the duration of ultrasound application. In the second scouring cycle, the measured mass loss in all scouring procedures was almost the same, ranging from 4.8-5.1%. Again, the US2 ultrasonic scouring process (3x10 min) was the most effective.

Regarding the number of scouring cycles, the comparing the dichloromethane Soxhlet extraction with the ultrasonic scouring is debatable. Although the extraction was performed in only one cycle, but with a considerable number of the solvent exchanges for smaller sample portion, the removal of the wool grease itself may be considered as the most efficient. However, from a time, ecological and financial point of view, it is the least effective. In our case, the result of the 10% mass loss after the extraction was a good basis to conclude that a good result may also be achieved by the repeated ultrasonic scouring in water. Even higher mass loss than in the Soxhlet scouring indicates that ultrasound may remove other substances than grease admixtures as well.

3.2 Effectivity of scouring procedures evaluated by aqueous extract absorbance

The using UV-absorbance of aqueous extract from the scoured wool is based on supposition that grease (lanoline) is the only low-molecular component able to pass into solution. While higher grease concentrations in water can be observable as milky emulsion unsuitable to scan transmission spectrum, the scoured wool containing a low remaining amount of the grease, if any, already provides a transparent solution absorbing within UV-spectral region only (Figure 1). The more thoroughly scoured wool, the lower absorbance of the extract. Then absorbance of aqueous extract from the scoured wool can be an indicator of the grease removal rate.

Measured absorbance values for the aqueous extracts from wool scoured in individual procedures are summarized in Table 3.

Table 2 Relative loss of the wool mass during scouring methods

Scouring method	Relative loss of wool mass [%]			
	1st cycle	*2nd cycle*	*3rd and 4th cycles*	*Total loss*
US1 (2x10 min)	6.80 ± 0.07	5.02 ± 0.07	negligible	11.82 ± 0.14
US2 (3x10 min)	7.11 ± 0.07	5.08 ± 0.32	negligible	12.19 ± 0.39
US3 (1x20 min)	6.71 ± 0.02	4.83 ± 0.16	negligible	11.54 ± 0.18
US4 (1x30 min)	7.09 ± 0.07	4.92 ± 0.10	negligible	12.01 ± 0.17
Maceration (7 days)	6.21 ± 0.05	4.85 ± 0.03	negligible	11.06 ± 0.08
Soxhlet extraction	10.00 ± 1.46	-	-	10.00 ± 1.46

Table 3 Absorbance data ($A_{220\ nm}$, 1 cm quartz cell) for aqueous extracts from wool after being scoured; for non-scoured wool $A_{220\ nm}$ = 0.637±0.013

Scouring procedures	Absorbance after repetition of the scouring cycles			
	1st	*2nd*	*3rd*	*4th*
Soxhlet extraction	0.275 ± 0.007	-	-	-
Ultrasonic scouring with 2x10 min cycle (US1)	0.175 ± 0.009	0.115 ± 0.009	0.146 ± 0.048	0.128 ± 0.013
Ultrasonic scouring with 3x10 min cycle (US2)	0.169 ± 0.048	0.124 ± 0,045	0.122 ± 0,002	0.148 ± 0.034
Ultrasonic scouring with 1x20 min cycle (US3)	0.180 ± 0.021	0.174 ± 0.019	0.142 ± 0.004	0.124 ± 0.012
Ultrasonic scouring with 1x30 min cycle (US4)	0.164 ± 0.030	0.147 ± 0.017	0.110 ± 0.080	0.115 ± 0.022
Maceration with 7 days cycle	0.175 ± 0.040	0.106 ± 0.014	0.140 ± 0.015	0.136 ± 0.021

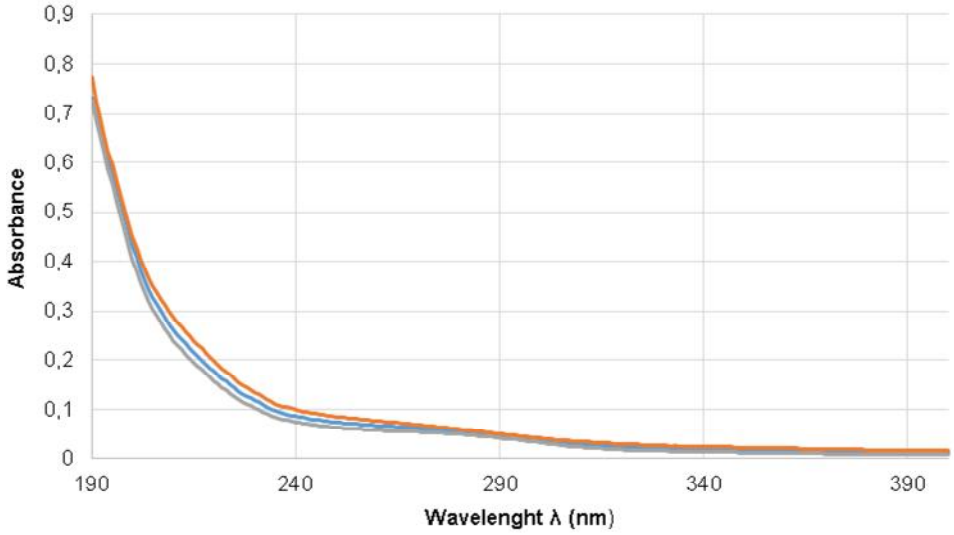

Figure 1 UV spectrum of three parallel aqueous extracts obtained from the scoured wool applying the ultrasonic scouring processes US3 (second cycle)

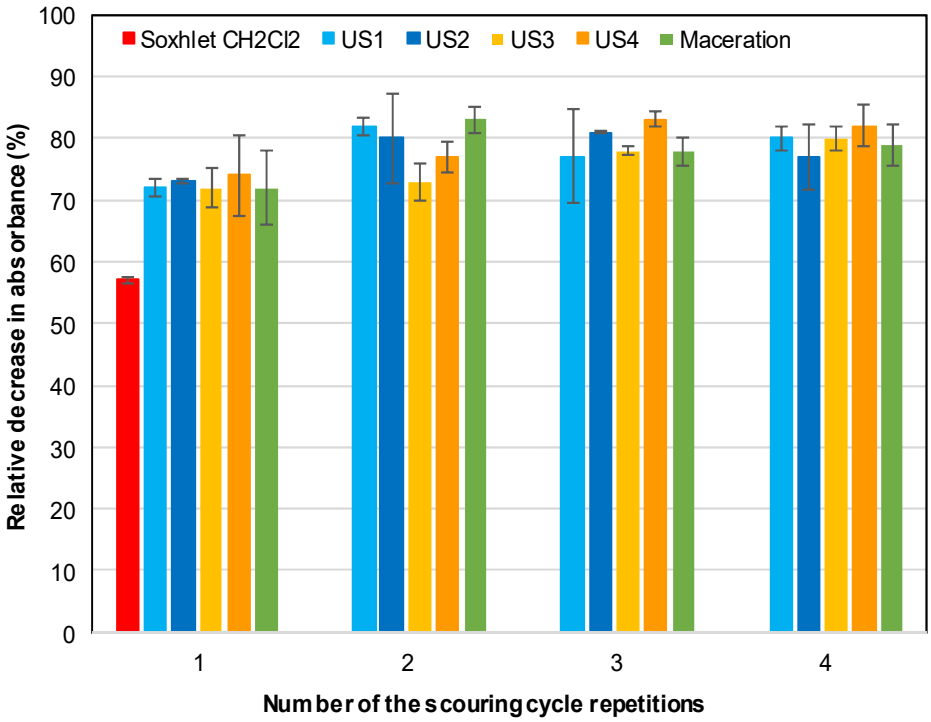

Figure 2 Relative decrease of absorbance $A_{220\ nm}$ for the aqueous extracts from the scoured wool compared with the non-scoured sample after using individual procedures and cycle repetitions. Detailed legend is provided in Tables 1 or 3

Except for the Soxhlet extraction, the absorbance differences between the individual scouring procedures for the first cycle are relatively small in all cases (Table 3). The percentage decrease in the absorbance compared to the non-scoured wool was in the range of 74-71% as displayed in Figure 2.

We expected the lowest absorbance values to be measured for the reference sample. However, the opposite was observed; while the sample after the Soxhlet extraction showed higher mass loss of 10% compared to the first cycle of all water scouring procedures (Table 2), the measured absorbance regarded as a residual grease in the water extracted sample was higher (0.275), even higher than that for the sample macerated (0.175). We have assumed that, while the organic solvent

removed grease admixtures, other constituents more polar than the grease went into the aqueous extract. These are better soluble in water and should correspond to higher absorbance.

Analyzing the absorbance results it was concluded that, the most effective scouring procedure was two repetitions of 2x10 min cycle in US1 mode (i.e. 4x10 min including the water exchange after each 10 min) or two 7-days cycles of the maceration mode (i.e. 2x7 days with the water exchange after 7 days). In the mentioned cases the percentage of the absorbance decrease corresponds to 82-83% (Figure 2) compared with the unscoured wool. After completing the particular second repetitions of the scouring cycles and based on the absorbance decline within the range of 72-83%, the ranking of the method efficiency appears as follows: maceration > US1 > US2 > US4 > US3. It is remarkable that the maceration at room temperature showed the highest decrease in the absorbance overall overpassing the other procedures.

Moderate variations in the absorbance were observed after the third repetitions of the cycles following a mild increase for US1 and the maceration, while US2, US3 and US4 provided lower values. Considering application of the ultrasound we assume a partial damage of the wool fibres and possibly, consequently pass of some micro-fragments into solution. Those despite the centrifuge treatment contributed to higher absorbance. This idea is supported by observation of Li et al. [22] who, using electron microscopy, reported that ultrasonic treatment caused scale cracking/peeling in cuticle on some wool fibres. On the other hand, Kadam et al. [16] did not observe any cracks after ultrasonic scouring however, ultrasound was applied not longer than 15 min. Also Goud et al. [23] did not find any topographic changes or damage when scoured wool ultrasonically during 3 min. Anyway, when the demand on the wool purity is not too high, the total ultrasonic scouring time can be reduced to avoid some damage of the fibre surface.

Different reason for higher absorbance after the third maceration cycle should be considered. Negligible manual manipulation with the fibres compared with the ultrasound action excludes any damage in practice. Even integrity of the fibre surface scoured mechanically is documented in work of Li et al. [22], too. So that the higher absorbance should not be consequence of some micro-fragments in the aqueous extract. But probably, depending on time, progressive dissolution of other components from unimpaired fibre surface increased the absorbance.

As believed the variations of absorbance for the fourth repetitions of the cycles present a mixture several reasons participating at the former steps and it is difficult to differentiate them.

4 CONCLUSION

Looking for a way of sheep wool scouring to avoid any chemicals using, the following procedures were tested: a) scouring in ultrasonic bath filled with tap water at 40°C under different mode and, b) simple maceration of wool in unheated tap water. The efficiency of the tested procedures was assessed by the mass loss as well as by measuring the absorbance at λ=220 nm of the aqueous extract from the scoured sample. The comparison procedure was the grease extraction with dichloromethane in a Soxhlet extractor, considered to be the most effective way to remove grease. As shown by the results of both control methods, the use of water as a scouring medium with ultrasound support can provide good results depending on the choice of scouring-time intervals connected with water exchange. Very good result was achieved after four times 10 min ultrasonic scouring at 40°C with water exchange after every 10 min intervals. Prolonging the effect of ultrasound may lead to partial destruction of the fibres, what indicated increasing absorbance after the eighth 10-minute interval. Comparably satisfactory results were also obtained by the simply maceration of the wool in water for 2x7 days with water exchange after 7 days. The latter procedure is simple with minimal handling and technical equipment, but it is tedious. Despite the assumption, the wool extraction with dichloromethane did not achieve either the highest mass loss or the lowest absorbance of the aqueous extract from the scoured wool. This indicates that except wool grease other impurities are washed up by water, too. If it was applied the wool scouring in water without chemicals on a larger scale and with respect to the required purity degree, optimization will be necessary regarding the ration of wool amount to water volume, ultrasound performance, time-period and number of cycles with water exchange. The presented results of the laboratory testing provide a good starting point for process setup. Waste water from the chemical-free scouring will not need to burden any sewerage plant but, it can serve for agricultural purposes including irrigation of agricultural land and possible additional fertilization.

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5 REFERENCES

1. Balköse D., Baltacioğlu H.: Adsorption of heavy metal cations from aqueous solutions by wool fibers, Journal of Chemical Technology and Biotechnology 54(4), 2007, pp. 393-397, https://doi.org/10.1002/jctb.280540414
2. Hanzlíková Z., Braniša J., Hybler P., Šprinclová I., Jomová K., Porubská M.: Sorption properties of sheep wool irradiated by accelerated electron beam,

Chemical Papers 70(9), 2016, pp. 1299-1308, https://doi.org/10.1515/chempap-2016-0062

3. Hanzlíková Z., Braniša J., Jomová K., Fülöp M., Hybler P., Porubská M.: Electron beam irradiated sheep wool - Prospective sorbent for heavy metals in wastewater, Separation and Purification Technology 193, 2018, pp. 345-350, https://doi.org/10.1016/j.seppur.2017.10.045
4. Ghosh A., Collie S.R.: Keratinous materials as novel absorbent systems for toxic pollutants, Defence Science Journal 64(3), 2014, pp. 209-221, https://doi.org/10.14429/dsj.64.7319
5. Braniša J., Jomová K., Porubská M.: Scouring testing of sheep wool intended for sorption, FIBRES & TEXTILES in Eastern Europe 2019, in press
6. Wang L., Ding X., Wu X.: The Water Footprint of Wool Scouring, Key Engineering Materials 671, 2016, pp. 65-70, https://doi.org/10.4028/www.scientific.net/KEM.671.65
7. Anderson C.A.: Mechanisms of Raw Wool Scouring - The Role of the Protein Contaminant Layer, Textile Research Journal 53(12), 1983, pp. 741-750, https://doi.org/10.1177/004051758305301205
8. Labanda J.,Llorens J.: Wool scouring waste treatment by a combination of coagulation–flocculation process and membrane separation technology, Chemical Engineering and Processing 47(7), 2008, pp. 1061-1068, https://doi.org/10.1016/j.cep.2007.07.010
9. Pospíšil Z. a kol.: Textile Expert's Manual (Príručka textilního odborníka), Vydavateľstvo technickej a ekonomickej literatúry, Bratislava, 1981, pp. 1294, in Slovak
10. Gyepesová, N., Porubská, M. Sheep wool cleaning optimization (Optimalizácia čistenia ovčej vlny), Student Scientific Conference, 2015, pp. 201-204
11. Porubská M., Hanzlíková Z., Braniša J., Kleinová A., Hybler P., Fulop M., Ondruška J., Jomová K.: The effect of electron beam on sheep wool, Polymer Degradation and Stability 111(1), 2015, pp. 151-158, https://doi.org/10.1016/j.polymdegradstab.2014.11.009
12. Wlochowicz A., Ratajska M.: Effects of non toxic organic solvents on the wool fibre structure, Acta Polymerica 31(11), 1980, pp. 713-719, https://doi.org/10.1002/actp.1980.010311110
13. Starovoytova Madara D., Sitati Namango S. Wool Grease Recovery from Scouring Effluent at Textile Mill, Journal of Agriculture, Pure and Applied Science and Technology 10, 2014, pp.1-9
14. Tian C.M., Shi Z.H., Shang H.Y., Xu J.Z., Shi J.R.: Study on the thermal stability of wool treated with flame- retardant reagents, Thermochemica Acta 284(2), 1996, pp.435-439, https://doi.org/10.1016/0040-6031(96)02839-0
15. Czaplicki Z., Ruszkowski K.: Optimization of scouring alpaca wool by ultrasonic technique, Journal of Natural Fibres 11(2), 2014, pp.169-183
16. Kadam V.V., Goud V., Shakyawar D.B.: Ultrasound scouring of wool and its effects on fibre quality, Indian Journal of Fibre and Textile Research 38, 2013, pp. 410-414, http://hdl.handle.net/123456789/24986
17. Hurren Ch., Zhang M., Liu X., Wang X.: A study of ultrasonic scouring of greasy Australian wool, In: Proceedings of 2006 China International Wool Textile Conference & IWTO Wool Forum, Xi'an, China, 2006, Xi'an Polytechnic University, Xi'an, China, pp. 493-497
18. Pan Y., Hurren Ch.J., Li Q.: Effect of sonochemical scouring on the surface morphologies, mechanical properties, and dyeing abilities of wool fibres, Ultrasonics – Sonochemistry 41, 2018, pp. 227-233, https://doi.org/10.1016/j.ultsonch.2017.09.045
19. Li Q., Hurren Ch.J., Wang X.: Ultrasonic assisted industrial wool scouring, Procedia Engineering 200, 2017, pp. 39-44, https://doi.org/10.1016/j.proeng.2017.07.007
20. Bahtivari M.I., Duran K.: A study on the usability of ultrasound in scouring of raw wool, Journal of Cleaner Production 41, 2013, pp. 283-290, https://doi.org/10.1016/j.jclepro.2012.09.009
21. Eckschlager K.: Chyby chemických rozboru (Errors in chemical analyses, in Czech), second ed. SNTL, Praha, 1971. pp.162
22. Li Q., Hurren C.J., Wang L.J., Lin T., Yu H.X., Ding C.L., Wang X.G.: Frequency dependence of ultrasonic wool scouring, Journal of the Textile Institute 102(6), 2011, pp. 505-513, https://doi.org/10.1080/00405000.2010.495858
23. Goud V.S., Honade S.P., Bardhan M.K.,. Rao T.R.: Ultrasound assisted scouring of raw wool, (National Seminar) pages 1-14, Man-Made Textiles in India 2011, 39 (11), pp. 385-390