Scouring Test of Sheep Wool Intended for Sorption

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Abstract
Sheep wool intended for sorption examination was scoured using three procedures consisting of (1) an ultrasonic tempered bath with tap water, (2) the same as (1) but with detergent, and (3) dichloromethane extraction. The loss of wool mass and removal of Cu, Zn and Pb-cations by the scoured wool as a sorbent were tested. While the loss of mass indicated consistency among all procedures, the cation removal was slightly variable. However, the differences are acceptable, concluding that an ultrasonic water bath without any agent is most favoured. The omission of a detergent or carcinogenic solvent can make the scouring process cleaner and environmentally-friendlier.

Key words: sheep wool, scouring, sorption, testing.

Introduction
Several methods aim at the recuperation of technological wastes or elimination of environment contaminators. One of them is the application of various adsorbents by the separation of required or undesirable constituents from mixtures. A whole branch of science deals with research of the preparation and efficiency of sorbents, and it is the topic of an increasing number of studies [1]. Sorbent cost derived from material expenses, technological demands and sorptive efficacy are the determining factors of potential applications. Efforts to reduce costs are reflected in the examination of natural material exploitation, especially when applied to technological by-products or even wastes. The works published focus on the investigation of lignocellulosic biosorbents [2] as well as biopolymers of animal origin, especially of the keratin type [3]. The effort to improve the sorption properties of biopolymers involves chemical or physical modifications with an aim to introduce new active groups into their structure. After being properly modified, sheep wool unusable in the textile industry could be applied as a sorbent as well. However, each modifying procedure requires the wool to be scoured.

The scouring of raw wool fibres is a strenuous task since it contains considerable amounts of impurities. While the authors of studies on wool describe the key modifying procedures used in detail, they refer only briefly – if at all – to the concept of wool scouring before experiments. In the papers previously published, the most frequent methods are degreasing by Soxhlet extraction using organic solvents [4, 5]. Also the application of non-ionic detergent is reported [6].

The results from a few of the works published show an obvious improvement of the scouring effect by the application of ultrasound. Although the principle of the ultrasound cleaning effect has been known for many years, the use of ultrasonic energy for textile washing has not been commercially developed [7]. One advantage of ultrasonic scouring is the avoidance of wool aggressive movement in the cleaning bath provoking the entanglement and felting of wool fibres with hand washing. A possible improvement of ultrasonic scouring using a detergent and higher temperature of the ultrasonic bath was examined by Hurren [8]. He found that both temperature and detergent concentration in the bath can be optimised to maintain cleaning efficiency at an adequate level. The detergent improves the wetting of wool fibres with contaminants and enhances the ultrasonic effect. Ultrasound also increased the rate of dye uptake by the fibres without a significant adverse impact on the fibre mechanical properties. Since wool dyeing is the most frequent issue in the textile industry, there are several papers dealing with this topic in scientific literature e.g. [9].

The results of Hurren [8] and Kadam et al. [10] indicated that a lower power of the ultrasound water bath had no impact on the fibre structure, and at a higher level some transverse cracks were observable on the cuticle. Similarly when distilled water was used with a detergent at low ultrasound power, no visible change in the fibre surface was observed. However, a high power level caused transverse and longitudinal cracks over the fibre surface. Peila et al. [11] examined the ultrasonic effect on washing quality for cotton and wool fabrics using a mixed detergent and temperature of the ultrasonic bath of 25 °C and 60 °C. They found that temperature is a parameter with a high influence on ultrasonic cavitation. Higher temperatures restrain the cavitation, and better results were achieved at a lower temperature and shorter time of 10 min. As observed by Li et al. [12, 13], under certain conditions the application of ultrasound can even improve some wool properties. Compared to classical mechanical washing, ultrasound decreases fibre entanglement due to the reduction of fibre migration in the washing bath [14]. Balhiyari et al. [15] scoured wool fleece successively in five washing steps with and without ultrasound. Comparable results were observed after the third washing step using ultrasound and with the fifth step with no ultrasound. Examination of a bath temperature of 50 °C with ultrasound for 30 min showed as an alternative for non-ultrasonic consecutive scouring. Interesting results were also observed for washing at 35 °C with only water and applying ultrasound. A detailed study on the optimal parameters of ultrasonic scouring using soap and soda is described by Czaplicki and Ruszkowski [16]. Demonstrating on alpaca wool, the work pointed out the benefits of such a procedure, consisting, besides others, especially in the avoidance of entanglement. Kunik et al. [17] combined high-energy discrete processing (HDP), the essence of which is the phenomenon of electric discharge cavitation, with a mixture of detergents and sulfioxide, obtaining a good result.

None of the papers published was devoted to scouring for sorption intention. Currently this aspect has become topical since sheep wool after being irradiated by an accelerated electron beam showed...
interesting sorption properties towards some substances [18, 19].

In the present study, the main purpose was to optimise the scouring of sheep wool before being irradiated and then examined for the sorption/removal of a metal cation from the solution. Since several chemicals with a potential impact on the sorption characteristics of scoured wool, hitherto untried, are used in the industrial procedure, industrial scouring was not taken into consideration as a reference. In addition, scouring using real industrial facility runs with a large wool amount excludes the identification of the origin, breed or age of individual sheep. Therefore even if fibres of the same thickness were selected, they could hardly present material suitable for comparison with an actual laboratory sample. Furthermore an effort to reduce the usage of any chemicals in laboratory scouring could be a suitable contribution to the protection of the environment as well. Therefore the work included scouring in a tap water ultrasonic bath with or without a commercial detergent recommended for wool textile, as well as Soxhlet extraction with dichloromethane, where the primary parameter tested was wool mass loss during the scouring, and the second crucial parameter was the sorption of selected heavy metal cations by the cleaned wool.

### Materials and methods

Experiments were performed with the wool of the Tsigai (meat – dairy breed) and Suffolk (meat breed) crossbreed. The region of fleece sampling from the animal body could not be exactly defined however, and fibres were randomly taken from several parts of the fleece to obtain a representative sample as far as possible. First the sheared wool taken and mixed was manually pre-cleaned from coarse dirt (excrements, dirt, food, etc.) and then rinsed several times in tepid water until it became visually clean. Before the scouring process, the pre-cleaned wool was stored in a dark, dry and airy place. The thickness of the fibre was in the range of 25-33 μm.

All reagents used in the study were of analytical grade purity. Dichloromethane, copper (II) sulfate pentahydrate CuSO₄·5 H₂O, zinc (II) sulfate heptahydrate ZnSO₄·7 H₂O and lead (II) nitrate Pb(NO₃)₂ were supplied by Centralchem, Slovakia. Test solutions of those salts to be applied for the sorption experiments were prepared by diluting the corresponding stock solutions with distilled water to required concentrations.

Standard stock solutions of Cu(II), Zn(II) and Pb(II) for AAS spectrometry, each with a concentration of 1000 mg dm⁻³ in 3 % HNO₃, were supplied by Agilent Technologies, USA. The stock solutions were diluted to required concentrations with distilled water. Nitric acid (67%) was supplied by Analytika, Czech Republic.

The laundry agent Perwoll (Sport & Active) was bought in a retail outlet (Billa, Nitra), with the following declared composition: 5-15% anionic detergents, < 5% non-ionic detergents, soap, phosphonates, enzymes, perfume, and preserving agents.

### Scouring samples

Three different washing methods were applied as follows: (1) ultrasonic washing in tap water, (2) ultrasonic washing in tap water with detergent, and (3) extraction with dichloromethane in Soxhlet apparatus. Each washing experiment was repeated 5 times to minimise the influence of various fibre thicknesses. An amount of 3 g of wool was taken for all parallel experiments.

1. Ultrasonic washing in tap water: A weighed amount of about 3 g of wool was placed in a netted bag and immersed in tap water heated to 40 °C in an ultrasonic bath of 5 dm³ (Krantiek, K5LE, Slovak Republic, power of 350 VA, output of 450 W, frequency of 38 kHz, heating from 20 to 80 °C, timer from 0 to 90 min). A maximal adjustable intensity level of 9 was used. After 10 min washing, the water was changed and the same washing cycle repeated. Then the bag with wool was removed and the sample rinsed with 5 dm³ of distilled water in a vessel. After the washing, the wool was spread on filter paper and free-dried at room temperature and humidity for 24 hours.

2. Ultrasonic washing in tap water with the detergent was performed under the same conditions as the procedure described above for (1). The dosage of the detergent followed the manufacturer’s recommendation, i.e.: 40 cm² of Perwoll per 5 dm³ of water. After each 10-min washing cycle, the sample was rinsed in running water to remove the detergent. After the completion of washing, the sample was washed with 5 dm³ of distilled water, spread on filter paper and free-dried at room temperature and humidity for 24 hours.

3. Soxhlet extraction was carried out with a 3 g wool sample put in a paper thimble. A volume of 250 cm³ of dichloromethane was used, and the extraction ran for 4 hours (14 drain-off cycles). Then the wool sample was removed from the thimble, and the solvent could evaporate freely in a fume hood. Subsequently the sample was washed twice with 5 dm³ of distilled water, spread on filter paper, and dried freely at room temperature and humidity for 24 hours.

After each scouring procedure, the samples were finally dried in an oven (Binder, ED 115, Germany) at 40 °C for 24 hours, and when the temperature dropped to room temperature, the samples were weighed. Before further sorption experiments, the wool samples were stored in zip PE pockets to prevent moisture adsorption from air.

The percentage of the decrease in wool mass (Δm) after the scouring was taken as the criterion of scouring efficiency, calculated using the following Equation (1):

\[
\Delta \text{mass} = \frac{m_0 - m_1}{m_0} \times 100
\]

Where, \( m_0 \) is the mass of the sample taken for scouring in g, and \( m_1 \) – the mass of the sample after scouring in g.

### Sorption experiments

Sorption experiments were carried out with test solutions of Cu²⁺, Zn²⁺ and Pb²⁺ individually with the following concentrations: CuSO₄·5H₂O solutions containing (12.7-50.8) mg Cu/dm³, ZnSO₄·7H₂O solutions containing (6.54-26.16) mg Zn/dm³, and Pb(NO₃)₂ solutions containing (20.7-103.5) mg Pb/dm³. Dry wool fibres (0.2 g) were cut to 3-5 mm and placed in a small 27 cm³ glass cup with a cap. A volume of 12 cm³ of the test solution was added to the wool sample. To ensure a thorough soaking of the wool sample, the fibres were immersed in the solution using a glass rod. The sample was kept in contact with the test solution for 24 hours and shaken for the first 6 hours on a laboratory horizon-
tal shaker (TE, Kavalier, Czech Republic) at room temperature. After 24 h, the remaining solution was filtered through KAS filter paper and used for analysis of the residual amount of the metal cation. Every sorption experiment was repeated 5 times in order to reduce the standard deviation.

**Determination of residual concentration of metal cation**

The test solution concentration in the filtrate was determined by atomic absorption spectrometry (AAS) using a spectrometer – 240 FS AAS (Agilent Technologies, USA). Between measurements the spectrometer was washed with 0.1% HNO₃. The device operative parameters under measurement are given in **Table 1**.

The percentage of ion removal of the scoured sheep wool was calculated from the concentrations measured as the removal efficiency (RE) following the **Equation (2)**:

\[ \text{RE} = \frac{x_0 - x_1}{x_0} \times 100\% \]  

Where, \( x_1 \) is the concentration of relevant added ion in the solution in mg/dm³, and \( x_1 \) is the residual concentration of relevant ion in the solution after contact with the wool sample in mg/dm³.

Every sorption experiment was repeated 5 times.

**Testing of consistency**

Student’s t-criterion was used to test the consistency of results obtained and calculated following the **Equation (3)** [38]:

\[ t_{A-B} = \frac{|x_A - x_B|}{\sqrt{s_A^2 + s_B^2}} \times \sqrt{n - 1} \]  

Where, \( t_{A-B} \) is the t-criterion for statistical sets A and B under comparison, \( s_A, s_B \) are the standard deviations from the arithmetic averages for statistical sets A and B estimated according to Dean-Dixon [20].

**Testing of scouring procedures**

Depending on the breed, age and season, sheep wool contains up to 30% of grease. The wool lipid components are intimately associated with the surface proteins [18] and make the wool hydrophobic. In some processes, such as the sorption of polar substances from the solution, the hydrophobicity obstructs the necessary contact of the sorbent with the sorbate. It is presumable that micro-streaming coming from the cavitation bubble oscillation and following the micro-jetting could erode the surface lipid layer to such a degree that the necessary contact of the polar sorbate with the wool is attained. An ultrasonic bath temperature of 40 °C was selected as it is close to the melting temperature of lanoline – 39.7 °C, as measured by Hanzliková et al. [21], and to the boiling temperature of dichlomethane (39.6 °C). Together with the observation of Peila et al. [11] that higher temperature restricts cavitation and that a time of 10 min showed better results than a longer one, we considered 40 °C temperature and a time of 10 min per 1 cycle as probably optimum. The wool mass reduction for individual scouring procedures was considered as the indicator for cleaning efficacy. Related data are summarised in **Table 2**.

The differences between the scouring effects (**Table 2**) appear relatively large, and the combination of ultrasound with detergent produced the best result. It indicates the support of ultrasound for deeper penetration of the detergent into the wool fibre structure with following solubilisation of lipids in comparison with dichlomethane. From a subjective view, these results should not be identical. Therefore we examined this hypothesis by testing the data using Student’s t-criterion to obtain an objective review. The t-rate estimated was compared to the critical t-value for \( n = 5 \). The results obtained are showed in **Table 3**.

Since the t-criteria do not exceed the critical value of 2.776 in any of the cases, we have to acknowledge that the procedures used are not significantly different and provide consistent results.

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**Table 1. Survey of experimental conditions under AAS measurement.**

| Determined element | Cu | Zn | Pb |
|--------------------|----|----|----|
| Wavelength emitted by lamp, nm | 324.8 | 213.9 | 217.0 |
| Flow acetylene/air, dm³/min | 2.0/13.5 | 2.0/13.5 | 2.0/13.5 |
| Concentration of calibration solutions, mg/dm³ | 2; 4; 10 | 0.3; 0.5; 1; 1.5 | 1; 1.5; 10; 20 |
| Concentration of calibration solutions used to optimise signal for absorbance of 0.2, mg/dm³ | 1.5 | 0.3 | 5 |

**Table 2. Loss of wool mass under scouring.**

| No. | Scouring procedure | Average decrease in mass, % | Standard deviation, % for \( \alpha = 0.05 \) | Relative deviation, % |
|-----|--------------------|----------------------------|--------------------------------|----------------------|
| 1   | Ultrasonic water bath | 5.53 | 0.7136 | 12.9 |
| 2   | Ultrasonic water bath with Perwoll | 11.47 | 0.8598 | 7.50 |
| 3   | Dichloromethane extraction | 9.67 | 1.1478 | 11.79 |

**Table 3. Test consistency of loss in mass under sheep wool scouring for \( \alpha = 0.05 \) level; \( n = 5 \): \( t_{crit.} = 2.776 \).**

| No. | Pair compared for scouring procedure effect | t-criterion calculated | Statement |
|-----|------------------------------------------|----------------------|-----------|
| 1   | Ultrasonic water bath                     | 0.2617               | Consistency |
| 2   | Ultrasonic water bath with Perwoll        |                      |           |
| 3   | Ultrasonic water bath                     | 0.6425               | Consistency |
| 4   | Ultrasonic water bath with Perwoll        |                      |           |
| 5   | Ultrasonic water bath                     | 0.4016               | Consistency |

**Table 4. Efficiency of Cu(II) removal for scoured wool.**

| No. | Scouring medium | Percentage of Cu(II) removal from bath for initial Cu(II) concentration, mg·dm⁻³ |
|-----|----------------|----------------------------------|
|     |                | 12.7 | 19.05 | 25.4 | 31.75 | 38.1 | 44.45 | 50.8 |
| 1   | Ultrasonic water bath | 95.66 | 96.11 | 94.71 | 93.28 | 89.65 | 83.59 | 83.89 |
| 2   | Ultrasonic water bath with Perwoll        | 98.02 | 98.41 | 98.19 | 95.51 | 92.26 | 93.72 | 85.51 |
| 3   | Dichloromethane extraction                | 98.30 | 98.98 | 99.09 | 97.11 | 96.87 | 98.08 | 93.51 |
Testing of sorption

For the intended application, the sorption of the test substances was a coessential criterion. Therefore we examined how the sorption of some cations manifests in the wool scoured by the procedures applied. The range of the test cation concentrations was designed so that the residual concentration falls within the linear section of the relevant AAS calibration curve. From these data, the removal efficiency was calculated. Results for Cu(II) sorption removal are displayed in Table 4. The data in Table 4 underwent testing for consistency, the related results of which are given in Table 5.

The statements in Table 5 show that the pair consisting of an ultrasonic water bath and ultrasonic water bath containing Perwoll (t_{1,2}) gives an indecisive result overall due to the numbers for “consistency” and “inconsistency” being the same and one case being close to inconsistency. On the other hand, the pair involving ultrasonic water and dichloromethane extraction (t_{1,3}) show “inconsistency” for all concentrations applied. The consistency tested for both the ultrasonic water bath containing Perwoll and dichloromethane extraction (t_{1,2}) gives the prevalence of consistency over inconsistency (3:2), with two cases close to inconsistency. Thus an unambiguously different effect can be declared only between the ultrasonic water bath and dichloromethane extraction (t_{1,3}).

The sorption effect of the wool samples on Zn(II) removal is summarised in Table 6. Table 7 shows the tested hypothesis on consistency for relevant Zn(II) removal.

Unlike Cu-sorption by differently scoured wool, the consistency of the scouring procedures under Zn(II) sorption efficiency does not show prevalence in any case. The ultrasonic water bath and ultrasonic water bath containing Perwoll (t_{1,2}) pair is the closest to some kind of balance of consistency to inconsistency, showing a ratio of 3:4. The ultrasonic water bath and dichloromethane extraction (t_{1,3}) pair similarly gives a close prevalence of inconsistency over consistency, while the pair Perwoll ultrasonic water and dichloromethane extraction (t_{1,3}) provides inconsistency for each concentration.

The highest concentrations within AAS analyses could be applied for Pb(II). Data on Pb sorption by the wool samples are

| Initial concentration of Cu(II), mg·dm⁻³ | Pair | t-criterion calculated, t_{crit} for n = 5 = 2.776 | Statement |
|----------------------------------------|------|-----------------------------------------------|-----------|
| 12.7                                   | l₁₂  | 5.339                                         | Inconsistency |
|                                        | l₁₃  | 6.604                                         | Inconsistency |
|                                        | l₂₃  | 0.910                                         | Consistency  |
| 19.05                                  | l₁₂  | 2.604                                         | Close to Inconsistency |
|                                        | l₁₃  | 3.270                                         | Inconsistency |
|                                        | l₂₃  | 4.058                                         | Inconsistency |
| 25.4                                   | l₁₂  | 7.587                                         | Inconsistency |
|                                        | l₁₃  | 14.346                                        | Inconsistency |
|                                        | l₂₃  | 2.605                                         | Close to Inconsistency |
| 31.75                                  | l₁₂  | 2.5183                                        | Consistency  |
|                                        | l₁₃  | 4.296                                         | Inconsistency |
|                                        | l₂₃  | 2.741                                         | Close to Inconsistency |
| 38.1                                   | l₁₂  | 1.058                                         | Consistency  |
|                                        | l₁₃  | 12.492                                        | Inconsistency |
|                                        | l₂₃  | 1.833                                         | Consistency  |
| 44.45                                  | l₁₂  | 3.515                                         | Inconsistency |
|                                        | l₁₃  | 5.028                                         | Inconsistency |
|                                        | l₂₃  | 5.465                                         | Inconsistency |
| 50.8                                   | l₁₂  | 0.3734                                        | Consistency  |
|                                        | l₁₃  | 3.802                                         | Inconsistency |
|                                        | l₂₃  | 1.987                                         | Consistency  |

| Pair | t-criterion calculated, t_{crit} for n = 5 = 2.776 | Statement |
|------|-----------------------------------------------|-----------|
| l₁₂  | 1.694                                         | Consistency |
| l₁₃  | 2.699                                         | Close to Inconsistency |
| l₂₃  | 4.401                                         | Inconsistency |
| l₁₂  | 1.505                                         | Consistency  |
| l₁₃  | 1.548                                         | Consistency  |
| l₂₃  | 3.066                                         | Inconsistency |
| l₁₂  | 3.969                                         | Inconsistency |
| l₁₃  | 1.879                                         | Consistency  |
| l₂₃  | 2.822                                         | Inconsistency |
| l₁₂  | 6.667                                         | Inconsistency |
| l₁₃  | 8.050                                         | Inconsistency |
| l₂₃  | 3.386                                         | Inconsistency |
| l₁₂  | 9.421                                         | Inconsistency |
| l₁₃  | 6.805                                         | Inconsistency |
| l₂₃  | 4.025                                         | Inconsistency |
| l₁₂  | 12.234                                        | Inconsistency |
| l₁₃  | 3.624                                         | Inconsistency |
| l₂₃  | 4.677                                         | Inconsistency |
| l₁₂  | 6.497                                         | Inconsistency |

Table 5. Results of consistency testing for Cu(II) removal efficiency for sheep wool scoured in an ultrasonic water bath (1), ultrasonic water bath containing Perwoll (2) and by dichloromethane Soxhlet extraction (3).

Table 6. Efficiency of Zn(II) removal by scoured sheep wool.

| No.  | Scouring medium       | Percentage of Zn(II) removal from bath for initial Zn(II) concentration, mg·dm⁻³ |
|------|-----------------------|---------------------------------------------------------------------------------|
|      |                       | 6.54                             | 9.81                             | 13.08                            | 16.35                            | 19.62                            | 22.89                            | 26.16                            |
| 1    | Ultrasonic water bath | 95.97                            | 96.13                            | 94.72                            | 93.99                            | 89.87                            | 90.76                            | 85.23                            |
| 2    | Ultrasonic water bath with Perwoll | 95.46                            | 95.31                            | 88.35                            | 93.69                            | 85.12                            | 86.73                            | 83.18                            |
| 3    | Dichloromethane extraction | 96.71                            | 96.86                            | 93.14                            | 96.87                            | 93.62                            | 93.11                            | 91.98                            |

Table 7. Results of consistency testing for Zn(II) removal efficiency of sheep wool scoured in an ultrasonic water bath (1), an ultrasonic water bath containing Perwoll (2) and by dichloromethane Soxhlet extraction (3).
Table 8. Efficiency of Pb(II) removal from scoured sheep wool.

| No. | Scouring medium                          | Percentage of Pb(II) removal from bath for initial Pb(II) concentration, mg·dm⁻³ |
|-----|-----------------------------------------|----------------------------------------------------------------------------------|
|     |                                        | 20.7                               | 41.4                               | 62.1                               | 82.8                               | 103.5                              |
| 1   | Ultrasonic water bath                   | 99.7                               | 99.16                              | 98.59                              | 88.39                              | 77.81                              |
| 2   | Ultrasonic water bath with Perwoll      | 99.59                              | 99.45                              | 98.48                              | 91.35                              | 81.93                              |
| 3   | Dichloromethane extraction              | 99.01                              | 99.07                              | 99.17                              | 97.52                              | 97.37                              |

Table 9. Results of consistency testing for Pb removal efficiency of sheep wool scoured in an ultrasonic water bath (1), an ultrasonic water bath containing Perwoll (2) and by dichloromethane Soxhlet extraction (3).

| Initial concentration of Pb(II), mg·dm⁻³ | Pair | t-coefficient calculated, t (t for n = 5) = 2.776 | Statement |
|-----------------------------------------|------|--------------------------------------------------|-----------|
| 20.7                                    | t₁₂  | 0.5535                                           | Consistency |
|                                         | t₁₃  | 4.4096                                           | Inconsistency |
|                                         | t₁₅  | 3.1978                                           | Inconsistency |
|                                         | t₂₃  | 1.1003                                           | Consistency |
|                                         | t₃₃  | 0.3384                                           | Consistency |
|                                         | t₃₄  | 2.1792                                           | Consistency |
| 41.4                                    | t₁₂  | 0.2266                                           | Consistency |
|                                         | t₁₃  | 1.9480                                           | Consistency |
|                                         | t₁₅  | 1.7479                                           | Consistency |
|                                         | t₂₃  | 0.7347                                           | Consistency |
|                                         | t₃₃  | 2.7807                                           | Inconsistency |
|                                         | t₃₄  | 2.3712                                           | Consistency |
| 62.1                                    | t₁₂  | 0.2266                                           | Consistency |
|                                         | t₁₃  | 1.9480                                           | Consistency |
|                                         | t₁₅  | 1.7479                                           | Consistency |
|                                         | t₂₃  | 0.7347                                           | Consistency |
|                                         | t₃₃  | 2.7807                                           | Inconsistency |
|                                         | t₃₄  | 2.3712                                           | Consistency |
| 82.8                                    | t₁₂  | 2.5341                                           | Consistency |
|                                         | t₁₃  | 12.4069                                          | Inconsistency |
|                                         | t₁₅  | 14.7265                                          | Inconsistency |
| 103.5                                   | t₁₂  | 2.5341                                           | Consistency |
|                                         | t₁₃  | 12.4069                                          | Inconsistency |
|                                         | t₁₅  | 14.7265                                          | Inconsistency |

presented in Table 8, while Table 9 contains results of the consistency testing.

As seen from Table 9, consistency of Pb removal is observed at each Pb-concentration for both the ultrasonic water bath and ultrasonic water bath containing Perwoll (t₁₂). A comparison of the ultrasonic water bath with dichloromethane extraction (t₁₅) gives consistency for only 2 concentrations, while inconsistency is estimated in 3 cases. On the contrary, the ultrasonic water bath containing Perwoll and dichloromethane extraction (t₁₅) shows 3 cases of consistency and 2 cases of inconsistency. It is obvious that under testing, the effect of the scouring procedures on sorption for each of the cations applied provides different results. However, in general, the results indicate that any of the scouring procedures tested based on the loss of mass cannot be rejected due to inconsistency (Table 3). The scatter of results observed under the scouring conditions is not abnormal as it is incidental to fibre thickness. It is well known that a sheep does not have the same wool thickness on the whole body, and it may typically vary from 18 to 40 μm. In the case of the same mass of wool being used in the washing experiment, a thinner fibre means a greater surface, as well as the total amount of potential adhered contaminant (including lanoline) being used as a criterion. Our samples were taken from the raw sheep fleece randomly to imitate the situation in practice. Thus we have to admit considerable variations in the mass loss during the scouring as well as in the sorption efficiency examined in the experiments. A considerable scatter of results for tensile properties due to various fibre thickness was observed also for sheep wool irradiated by an electron beam [22], and such a result scatter can be perceived as a general feature.

Concerning the sorption experiments, except for the concentrations applied, the conditions for Cu(II), Zn(II) and Pb(II) sorption were the same for individual metal cations. Thus only small differences could be expected in the sorption percentage for the comparable experiments, if any. However, this is not so. Results of the cation sorption provide random data with no regularity (Tables 4-9). Considering the number of inconsistent cases from all possible cases (19 in total) following the t₁₂, consistency, 37% of them should be rejected. This portion involves only Cu(II) and Zn(II) almost equally, while Pb(II) shows all results are consistent. Criterion t₁₅ involves most of the inconsistencies, giving about 74%, with the Cu(II) contribution being the largest. In contrast, criterion t₁₃ indicates the least inconsistencies for Cu(II) and Pb(II) and the most for Zn(II).

We consider three possible reasons for the variability. The first is the inhomogeneity in the fibre thickness, since it defines the surface area available for mutual contact. The second reason can be the slightly different surface polarity due to the dissimilar removal of lipids as indicated by the mass lost under scouring. The different sorption properties of the metal cations applied should be considered as the third source of variability. According to several authors [23], an increase in the atomic size means a greater sorption, because a metal with a large ionic radius is readily available for interaction with the sorbent. Some papers [24] confirm such an opinion as well. As Pb has the largest ionic radius among the cations tested, it provides more consistent data than Cu and Zn, which are of comparable ionic radii. Moreover, the cations tested have a different tendency to create complex types with keratin. On the other hand, optimal sorption of metal cation is related to the pH value of the batch and surface charge on sorbent [25, 26]. Regarding the target use of wool as a sorbent potentially subsequently modified by certain procedures, this aspect was not taken into consideration in this study since the factors mentioned can vary sporadically. That is why any adjusting of the pH value in the batch was not carried out in the testing, and only the relative sorption efficiency eliminating other effects was considered. The variability in data consistency observed is most probably a combination of the factors mentioned that may not be comprehensive.

Although the differences in scouring (and partial removal) efficiency are not significant, the sorption efficiency of wool cleaned by dichloromethane seems to be the highest. However, the slightly lower efficiency of the water ultrasonic bath regarding sorption is highly compensated by the omission of the carcinogenic organic solvent under lanoline extraction or of off-loading waste water by detergents. In addition, the waste water without any chemicals can be used for lanoline salting or supplementary fertilising of agricultural land without off-loading it to a sewage treatment plant. It is assumed that relevant life cycle assessment and
economic cost analysis will prove that scouring without chemicals is environmentally friendlier and even cheaper.

## Conclusions

The examination of sheep wool scouring for sorption purposes involved three procedures. The results of scouring using an ultrasonic water bath heated to 40 °C, the same bath with the addition of a commercial detergent, and Soxhlet extraction with dichloromethane were tested for consistency based on mass loss under the scouring. Using the Student’s t-criterion, the scouring effects were considered as mutually consistent. The following targeted testing of Cu(II), Zn(II) and Pb(II) sorption from aqueous solutions by the scoured wool samples provided variable results indicating acceptable consistency of cations removal efficiency for scouring in a heated ultrasonic water bath with or without detergent. Sorption consistency was obtained in less than 50% of cases in dichloromethane extraction and both ultrasonic baths. Any clear coherence was obtained in less than 50% of cases since the slightly lower sorption is compensated by other benefits. The omission of a detergent or carcinogenic solvent makes the ultrasonic process cleaner.

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## References

1. Pietrelli L, Palombo M, Taresco V, Crisante F, Francolini I and Piozzi A, Copper (II) adsorption capacity of a novel hydroxytyrosol-based polyacrylate. Polymer Bulletin 2017; 74: 1175-1191.
2. Abdulali A, Ngo HH, Guo W, et al. A breakthrough biosorbent in removing heavy metals: Equilibrium, kinetic, thermodynamic and mechanism analyses in a lab-scale study. Science of the Total Environment 2016; 542: 603-611.
3. Ghosh A, Collie SR. Keratinous materials as novel absorbent systems for toxic pollutants. Defence Science Journal 2014; 64: 209-221.
4. Aluigi A, Vinea C, Varesano A, Mazzucchetti G, Ferrero F and Tonin C. Structure and properties of keratin/PEO blend nanofibers. European Polymer Journal 2008; 44: 2465-2475.
5. Huson M, Evans D, Church J, Hutchinson S, Maxwell J and Corinno G. New insight into the nature of the wool fibre surface. Journal of Structural Biology 2008; 163: 127-136.
6. Li R, and Wang D. Preparation of regenerated wool keratin films from wool keratin-ionic liquid solutions. Journal of Applied Polymer Science 2013, 127, 2648-2653.
7. Shahidi S, and Wiener J. Radiation effects in textile materials. In Radiation Effects in Materials (ed. Monteiro, W.A.) Rijeka: INTECH; 2016, pp. 309-328.
8. Hurren CJ. A Study into the ultrasonic cleaning of wool. Thesis. Burwood, Australia, Deakin University; 2010.
9. Kamel MM, El Zawahry MM, Ahmed NSE, Abdelghaffar F. Ultrasonic dyeing of cationized cotton fabric with natural dye. Part 1: Cationization of cotton using Softix E. Ultrasonics Sonochemistry 2009; 16: 243-249.
10. Kadam VV, Goud V, Shakaywar DB. Ultrasound scouring of wool and its effects on fibre quality. Indian Journal of Fibre & Textile Research 2013; 38: 410-414.
11. Peila R, Grande GA, Giansetti M, Rehman S, Sicardi S and Rovero G. Washing off intensification of cotton and wool fabrics by ultrasounds. Ultrasonics Sonochemistry 2015; 23: 324-332.
12. Li Q, Hurren CJ, Yu H, Ding C and Wang X. Thermal and mechanical properties of ultrasonically treated wool. Textile Research Journal 2011; 82: 195-202.
13. Li Q, Hurren CJ, Wang X. Changes in wool protein structure and fabric properties with ultrasonic treatment. Smartex Research Journal 2012; 1: 48-55.
14. Li Q, Hurren CJ, Ding C, Wang L, Lin T, and Wang X. Ultrasonic scouring of wool and its effects on fibre breakage during carding. Journal of The Textile Institute 2011; 102: 1059-1064.
15. Bahltyari Mt. and Duran K. A study on the usability of ultrasound in scouring of raw wool. Journal of Cleaner Production 2013; 41: 283-290.
16. Czaplicki Z, and Ruszkowski K. Optimization of Scouring Alpaca Wool by Ultrasonic Technique. Journal of Natural Fibres 2014; 11: 169-183.
17. Kunik A, Semeshko O, Aasayuk T, Sanbyekova Y, and Myasnikov S. Development of a two-step technology of scouring wool by the method of high-energy discrete treatment. Eastern-European Journal of Enterprise Technologies 2016; 4: 36-43.
18. Hanzlikova Z, Braniša J, Hybler P, Šprinclová I, Jomová K, and Porubská M. Sorption properties of sheep wool irradiated by accelerated electron beam. Chemical Papers 2016; 70: 1299-1308.
19. Hanzlikova Z, Braniša J, Jomová K, Fülöp M, Hybler P, Porubská M. Electromagnetic irradiation of wool – Prospective sorbent for heavy metals in wastewaters. Separation and Purification Technology 2018; 193: 345-350.
20. Eckschlager K. Chyby chemických rozboru (Errors in chemical analyses, in Czech). Prague: SNTL; 1971, pp. 17-35.
21. Hanzliková Z, Hybler P, Fülöp M, et al. Irradiated lanoline as a prospective substance for biomedical applications: A spectroscopic and thermal study. Radiation Physics and Chemistry 2015; 113: 41-46.
22. Porubská M, Hanzlíková Z, Braniša J, et al. The effect of electron beam on sheep wool. Polymer Degradation and Stability 2015; 111: 151-158.
23. Kar P, and Misra M. Use of keratin fiber for separation of heavy metals from water. Journal of Chemical Technology and Biotechnology 2004; 79: 1313-1319.
24. Wang F, Lu X, and Li X. Selective removals of heavy metals (Pb 2+, Cu 2+, and Cd 2+) from wastewater by gelatination with alginate for effective metal recovery. Journal of Hazardous Materials 2016; 308: 75-83.
25. Eser A, Triton VN, Aydemir T, Becerik S., and Dinçer A. Removal of nickel(II) ions by histidine modified chitosan beads. Chemical Engineering Journal 2012; 210: 590-596.
26. Genç-Fuhrman H., Mikkelsen PS, and Leckie D. Use of radiated lanolin as a prospective substance for heavy metals: Equilibrium, kinetic, thermodinamic and mechanism analyses in a lab-scale study. Science of the Total Environment 2016; 566-567: 76-85.